Series: **Sustainable Water Developments** 1

Membrane Technologies for Water Treatment

Removal of Toxic Trace Elements with Emphasis on Arsenic, Fluoride and Uranium

Editors: Alberto Figoli, Jan Hoinkis & Jochen Bundschuh

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MEMBRANE TECHNOLOGIES FOR WATER TREATMENT: REMOVAL OF TOXIC TRACE ELEMENTS WITH EMPHASIS ON ARSENIC, FLUORIDE AND URANIUM

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Sustainable Water Developments
Resources, Management, Treatment, Efficiency and Reuse

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Volume 1

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Membrane Technologies for Water Treatment: Removal of Toxic Trace Elements with Emphasis on Arsenic, Fluoride and Uranium

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Cover photo
The upper photo shows one of the largest reverse osmosis plants in South America, which treats arsenic-laden water coming from the boreholes in Virrey Del Pino in La Matanza, Buenos Aires, Argentina by means of the reverse osmosis system. It produces 47,040 m^3 of drinking water per day for 400,000 inhabitants.

The other photo shows the tap of an autonomous desalination plant Mörk Desalin^{TM} for drinking water production in developing countries which has been put on the market by the German company Mörk Water Solutions, Leonberg.

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About the book series

Augmentation of freshwater supply and better sanitation are two of the world's most pressing challenges. However, such improvements must be done economically in an environmentally and societally sustainable way.

Increasingly, groundwater – the source that is much larger than surface water and which provides a stable supply through all the seasons – is used for freshwater supply, which is exploited from ever-deeper groundwater resources. However, the availability of groundwater in sufficient quantity and good quality is severely impacted by the increased water demand for industrial production, cooling in energy production, public water supply and in particular agricultural use, which at present consumes on a global scale about 70% of the exploited freshwater resources. In addition, climate change may have a positive or negative impact on freshwater availability, but which one is presently unknown. These developments result in a continuously increasing water stress, as has already been observed in several world regions and which has adverse implications for the security of food, water and energy supplies, the severity of which will further increase in future. This demands case-specific mitigation and adaptation pathways, which require a better assessment and understanding of surface water and groundwater systems and how they interact with a view to improve their protection and their effective and sustainable management.

With the current and anticipated increased future freshwater demand, it is increasingly difficult to sustain freshwater supply security without producing freshwater from contaminated, brackish or saline water and reusing agricultural, industrial, and municipal wastewater after adequate treatment, which extends the life cycle of water and is beneficial not only to the environment but also leads to cost reduction. Water treatment, particularly desalination, requires large amounts of energy, making energy-efficient options and use of renewable energies important. The technologies, which can either be sophisticated or simple, use physical, chemical and biological processes for water and wastewater treatment, to produce freshwater of a desired quality. Both industrial-scale approaches and smaller-scale applications are important but need a different technological approach. In particular, low-tech, cost-effective, but at the same time sustainable water and wastewater treatment systems, such as artificial wetlands or wastewater gardens, are options suitable for many small-scale applications. Technological improvements and finding new approaches to conventional technologies (e.g. those of seawater desalination), and development of innovative processes, approaches, and methods to improve water and wastewater treatment and sanitation are needed. Improving economic, environmental and societal sustainability needs research and development to improve process design, operation, performance, automation and management of water and wastewater systems considering aims, and local conditions.

In all freshwater consuming sectors, the increasing water scarcity and correspondingly increasing costs of freshwater, calls for a shift towards more water efficiency and water savings. In the industrial and agricultural sector, it also includes the development of technologies that reduce contamination of freshwater resources, e.g. through development of a chemical-free agriculture. In the domestic sector, there are plenty of options for freshwater saving and improving efficiency such as water-efficient toilets, water-free toilets, or on-site recycling for uses such as toilet flushing, which alone could provide an estimated 30% reduction in water use for the average household. As already mentioned, in all water-consuming sectors, the recycling and reuse of the respective wastewater can provide an important freshwater source. However, the rate at which these water efficient technologies and water-saving applications are developed and adopted depends on the behavior of individual consumers and requires favorable political, policy and financial conditions.

Due to the interdependency of water and energy (water-energy nexus); i.e. water production needs energy (e.g. for groundwater pumping) and energy generation needs water (e.g. for cooling), the management of both commodities should be more coordinated. This requires integrated energy and water planning, i.e. management of both commodities in a well-coordinated form rather than managing water and energy separately as is routine at present. Only such integrated management allows reducing trade-offs between water and energy use.

However, water is not just linked to energy, but must be considered within the whole of the water-energy-food-ecosystem-climate nexus. This requires consideration of what a planned water development requires from the other sectors or how it affects – positively or negatively – the other sectors. Such integrated management of water and the other interlinked resources can implement synergies, reduce trade-offs, optimize resources use and management efficiency, all in all improving security of water, energy, and food security and contributing to protection of ecosystems and climate. Corresponding actions, policies and regulations that support such integral approaches, as well as corresponding research, training and teaching are necessary for their implementation.

The fact that in many developing and transition countries women are disproportionately disadvantaged by water and sanitation limitation requires special attention to this aspect in these countries. Women (including schoolgirls) often spend several hours a day fetching water. This time could be much better used for attending school or working to improve knowledge and skills as well as to generate income and so to reduce gender inequality and poverty. Absence of in-door sanitary facilities exposes women to potential harassment. Moreover, missing single-sex sanitation facilities in schools and absence of clean water contributes to diseases. This is why women and girls are a critical factor in solving water and sanitation problems in these countries and necessitates that men and women work side by side to address the water and wastewater related operations for improvement of economic, social and sustainable freshwater provision and sanitation.

Individual volumes published in the series span the wide spectrum between research, development and practice in the topic of freshwater and related areas such as gender and social aspects as well as policy, regulatory, legal and economic aspects of water. The series covers all fields and facets in optimal approaches to the:

- Assessment, protection, development and sustainable management of groundwater and surface water resources thereby optimizing their use.
- Improvement of human access to water resources in adequate quantity and good quality.
- Meeting of the increasing demand for drinking water, and irrigation water needed for food and energy security, protection of ecosystems and climate and contribution to a socially and economically sound human development.
- Treatment of water and wastewater also including its reuse.
- Implementation of water efficient technologies and water saving measures.

A key goal of the series is to include all countries of the globe in jointly addressing the challenges of water security and sanitation. Therefore, we aim for a balanced selection of authors and editors originating from developing and developed countries as well as for gender equality. This will help society to provide access to freshwater resources in adequate quantity and of good quality, meeting the increasing demand for drinking water, domestic water and irrigation water needed for food security while contributing to socially and economically sound development.

This book series aims to become a state-of-the-art resource for a broad group of readers including professionals, academics and students dealing with ground and surface water resources, their assessment, exploitation and management as well as the water and wastewater industry. This comprises especially hydrogeologists, hydrologists, water resources engineers, wastewater engineers, chemical engineers and environmental engineers and scientists.

The book series provides a source of valuable information on surface water but especially on aquifers and groundwater resources in all their facets. As such, it covers not only the scientific and technical aspects but also environmental, legal, policy, economic, social, and gender aspects of groundwater resources management. Without departing from the larger framework of integrated groundwater resources management, the topics are centered on water, solute and heat transport in aquifers, hydrogeochemical processes in aquifers, contamination, protection, resources assessment and use.

The book series constitutes an information source and facilitator for the transfer of knowledge, both for small communities with decentralized water supply and sanitation as well as large industries that employ hundreds or thousands of professionals in countries worldwide, working in the different fields of freshwater production, wastewater treatment and water reuse as well as those concerned with water efficient technologies and water saving measures. In contrast to many other industries, suffering from the global economic downturn, water and wastewater industries are rapidly growing sectors providing significant opportunities for investments. This applies especially to those using sustainable water and wastewater technologies, which are increasingly favored. The series is also aimed at communities, manufacturers and consultants as well as a range of stakeholders and professionals from governmental and non-governmental organizations, international funding agencies, public health, policy, regulating and other relevant institutions, and the broader public. It is designed to increase awareness of water resources protection and understanding of sustainable water and wastewater solutions including the promotion of water and wastewater reuse and water savings.

By consolidating international research and technical results, the objective of this book series is to focus on practical solutions in better understanding groundwater and surface water systems, the implementation of sustainable water and wastewater treatment and water reuse and the implementation of water efficient technologies and water saving measures. Failing to improve and move forward would have serious social, environmental and economic impacts on a global scale.

The book series includes books authored and edited by world-renowned scientists and engineers and by leading authorities in economics and politics. Women are particularly encouraged to contribute, either as author or editor.

Jochen Bundschuh
(Series Editor)

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Taffa Tulu (watershed hydrology; watershed management; water resources engineering; irrigation engineering; water harvesting), Center of Environment and Development, College of Development Studies, Addis Ababa University (AAU), Addis Ababa

FEDERATED STATES OF MICRONESIA

Leerenson Lee Airens (water supply for Small Islands Development States (SIDS)), GEF IWRM Focal Point; Manager, Water Works, Pohnpei Utilities Corporation (PUC), Pohnpei State

FIJI

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FINLAND

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FRANCE

Catherine Faur (water treatment involving fluid-solid interactions; engineering of polymer membranes by twin product – processes approaches), Department Engineering of Membrane Processes, University of Montpellier (UM), Montpellier

GEORGIA

Givi Gavardashvili (water management; erosion-debris flow processes; floods), Ts. Mirstkhulava Water Management Institute, Georgian Technical University (GTU), Tbilisi

GERMANY

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Jan Hoinkis (membrane technologies; membrane bioreactor technology; water and wastewater treatment; water reuse; sensor and control systems in water treatment), Institute of Applied Research, Karlsruhe University of Applied Sciences (HsKA), Karlsruhe

Heidrun Steinmetz (resource oriented sanitation (nutrient recovery, energy efficiency); biological and advanced wastewater treatment; water quality management), Chair of Sanitary Engineering and Water Recycling, University of Stuttgart, Stuttgart

GREECE

Maria Mimikou (hydrology; water resources management; hydro-energy engineering; climate change), School of Civil Engineering, National Technical University of Athens (NTUA), Athens

Anastasios Zouboulis (water and wastewater treatment; biotechnological applications), School of Chemistry, Aristotle University of Thessaloniki (AUTH), Thessaloniki

HAITI

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HONDURAS

Sadia Iraisis Lanza (water resources and climate change; physical hydrogeology; hydrology; water quality), Physics Department, National Autonomous University of Honduras (UNAH), San Pedro Sula, Cortés

HONG KONG

Jiu Jimmy Jiao (hydrogeology; influence of groundwater and rainfall on landslides; impact of human activities on groundwater regimes; dewatering system design; contaminant fate and transport modeling and groundwater remediation design; global optimization approaches for parameter identification in flow and transport modeling; parameter sensitivity analysis and its influence on parameter estimation), Editor Hydrogeology Journal; Department of Earth Sciences, The University of Hong Kong (HKU), Hong Kong

HUNGARY

László Somlyódy (wastewater treatment; environmental engineering), past President of the International Water Association (IWA), Head, Department of Sanitary and Environmental Engineering, Faculty of Engineering, Budapest University of Technology and Economics (BME), Budapest

INDIA

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Arun Kumar (environmental management of water bodies), Alternate Hydro Energy Centre, Indian Institute of Technology – Roorkee (IITR), Roorkee, Uttarakhand

Rakesh Kumar (urban hydrology; hydrological modeling; watershed management; drought mitigation and management; flood estimation, routing, management and socio-economic aspects; impact of climate change on water resources), Head, Surface Water Hydrology Division, National Institute of Hydrology (NIH), Roorkee, Uttarakhand

Abhijit Mukherjee (physical, chemical and isotope hydrogeology; modeling of groundwater flow and solute transport; hydrostratigraphy; contaminant fate and transport; surface water-seawater-groundwater interactions; effect of climate change on water resources; mine-site hydrology; environmental geochemistry), Department of Geology and Geophysics, Indian Institute of Technology – Kharagpur (IIT Kgp), Kharagpur, West Bengal

INDONESIA

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IRAN

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ISRAEL

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Michael Zilberbrand (groundwater resources; hydrogeochemical processes and hydrogeological and hydrogeochemical modeling in aquifers and in the unsaturated zone), Israeli Water Authority, Hydrological Service, Jerusalem

ITALY

Alessandra Criscuoli (membrane science and technology; membrane distillation and membrane contactors; integrated membrane processes; water and wastewater treatment; desalination of brackish water and seawater), Institute on Membrane Technology, ITM-CNR, Rende (CS)

Enrico Drioli (membrane science and engineering; membrane preparation and transport phenomena in membranes; desalination of brackish and saline water; integrated membrane processes; membrane distillation and membrane contactors; catalytic membrane and catalytic membrane reactors; salinity gradient energy fuel cells), Institute on Membrane Technology, ITM-CNR, Rende (CS)

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Marco Petitta (groundwater pollution, management, and protection), President IAH Chapter Italy; Department of Earth Sciences, Sapienza University of Rome, Rome

Ludovico Spinosa (sludge management), (retired) National Research Council (CNR); Consultant at Governmental Commissariat Environmental Emergencies in Region Puglia; Convenor at ISO/TC275/WG6 (Thickening and Dewatering) and CEN/TC308/WG1 (Process Control Methods) on sludge standardization

JAMAICA

Arpita Mandal (hydrology; hydrogeology; water resources and impacts of climate change; water supply; climate variability; flood risk and control; hydrochemistry of groundwater; saline water intrusion), Department of Geography and Geology, University of the West Indies (UWI), Mona Campus, Mona, Kingston

JAPAN

Hiroaki Furumai (build-up and wash-off of micropollutants in urban areas; characterization of DOM/NOM in lakes and reservoirs for drinking water sources; fate and behavior of DOM in flocculation and advanced oxidation processes; biological nutrient removal from wastewater; modeling activated sludge in aerobic/anaerobic SBR; characterization of domestic sewage from the viewpoint of nutrient removal), Board of Directors, IWA; Department of Urban Engineering, The University of Tokyo (Todai), Tokyo

Makoto Nishigaki (modeling groundwater and multiphase flow and solute transport in porous media; modeling seepage in the saturated-unsaturated zone; development of methods of measuring hydraulic properties in rock mass), Department of Environmental and Civil Design, Faculty of Environmental Science and Technology, Okayama University, Okayama

Taikan Oki (global water balance and world water resources; climatic variation and the Asian monsoon; land-atmosphere interaction and its modeling; remote sensing in hydrology; temporal and spatial distribution of rainfall), Institute of Industrial Science, The University of Tokyo, Komaba, Tokyo

Yuichi Onda (hillslope hydrology; hydro-geomorphology; radionuclide transfer; forest hydrology), Center for Research in Isotopes and Environmental Dynamics, University of Tsukuba, Tsukuba, Ibaraki

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JORDAN

Fawzi A. Banat (desalination), Department of Chemical Engineering, Jordan University of Science and Technology (JUST), Irbid

Samer Talozi (irrigation and water resources engineering, planning and policy), Civil Engineering Department, Jordan University of Science and Technology (JUST), Irbid

KENYA

Daniel Olago (environmental geology; surface and sub-surface water chemistry and dynamics; water-energy and related nexuses; human impact on the environment, global change processes, vulnerability and adaptation to climate change: past and present; environmental policies, laws and regulations and capacity development in global environmental change), Chairman, Network of African Science Academies (NASAC) Water Program; Member, International Lake Environment Committee; Member and focal point for water, Kenya National Academy of Sciences (KNAS); Institute for Climate Change and Adaptation (ICCA) & Department of Geology, University of Nairobi, Nairobi

Mwakio Tole (water and geothermal energy resources; waste disposal; environmental impact assessment), School of Environmental and Earth Sciences, Department of Environmental Sciences, Pwani University, Kilifi

KOREA

Jaeweon Cho (water reuse; membrane filtration; ecological engineering (treatment wetland); desalination), School of Urban and Environmental Engineering, Ulsan Institute of Science and Technology (UNIST), Ulsan

KYRGYZSTAN

Bolot Moldobekov (hydrogeology; engineering geology; geographic information systems – GIS; geoinformatics; interdisciplinary geosciences; natural hazards), Co-Director, Central-Asian Institute for Applied Geosciences (CAIAG), Bishkek

LATVIA

Māris Kļaviņš (aquatic chemistry; geochemical analysis; environmental pollution and its chemical analysis; environmental education, including also political and social sciences), Head, Department of Environmental Science, University of Latvia (LU), Riga

LITHUANIA

Robert Mokrik (groundwater resources, flow and transport modeling; hydrogeochemistry and groundwater isotopes; palaeohydrogeology), Department of Hydrogeology and Engineering Geology, Faculty of Natural Sciences, Vilnius University, Vilnius

LUXEMBOURG

Joachim Hansen (wastewater treatment; micropollutants; wastewater reuse; water-energy nexus), Engineering Science – Hydraulic Engineering, Faculty of Science, Technology and Communication, University of Luxembourg – Campus Kirchberg, Luxembourg

MADAGASCAR

Désiré Rakotondravaly (hydrology; hydrogeology; hydraulics; geology; rural water supply; vulnerability mapping; water and sanitation; GIS; project management; capacity building; community development; conservation; development cooperation), Ministry of Mines, Antananarivo

MALAWI

Victor Chipofya (urban water utility operation and management; groundwater development, monitoring and management; groundwater quality; rural water supply; water and sanitation in peri-urban and rural areas; water reuse; hygiene promotion), Executive Director, Institute of Water and Environmental Sanitation (IWES); National Coordinator of the Malawi Water Partnership (MWP); Steering Committee Member: Water Supply and Sanitation Collaborative Council (WSSCC) for Eastern and Southern Africa, Blantyre

MALAYSIA

Mohamed Kheireddine Aroua (separation processes; water and wastewater treatment), Director, Centre for Separation Science & Technology (CSST), Department of Chemical Engineering, Faculty of Engineering, University of Malaya (UM), Kuala Lumpur

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Ali Hashim (separation processes – flotation; liquid-liquid extraction; water and wastewater treatment; ionic liquids – synthesis and applications), Department of Chemical Engineering, Faculty of Engineering, University of Malaya (UM), Kuala Lumpur

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Hilmi Mukhtar (membrane development; membrane modeling; membrane applications including wastewater treatment engineering and natural gas separation), Department of Chemical Engineering, Faculty of Engineering, Petronas University of Technology (UTP), Bandar Seri Iskandar, Perak

Mohd Razman Bin Salim (water and wastewater treatment), Deputy Director, Centre for Environmental Sustainability and Water Security (IPASA), Faculty of Civil Engineering, University of Technology Malaysia (UTM), Johor Bahru, Johor

Saim Suratman (hydrogeology; groundwater management), Deputy Director General, National Hydraulics Research Institute of Malaysia (NAHRIM), Seri Kembangan Selangor Darul Ehsan, Malaysia

Wan Azlina Wan Ab Karim Ghani (chemical and environmental engineering; biochar and composites for water, wastewater and soil treatment; biomass conversion; biomass energy), Research Coordinator, Department of Chemical & Environmental Engineering, Faculty of Engineering, Putra University Malaysia (UPM), Serdang

MALTA

Kevin Gatt (governance, policy and planning issues related to water resources; waste management and sustainable development), Faculty for the Built Environment, University of Malta (UoM), Tal-Qroqq, Msida

MAURITIUS

Arvinda Kumar Ragen (wastewater engineering; constructed wetlands for household greywater; water pollution control in sugar factories; environmental impact assessment), Department of Chemical & Environmental Engineering, Faculty of Engineering, University of Mauritius (UoM), Le Reduit, Moka.

MEXICO

Ma. Teresa Alarcón Herrera (water resources; water treatment using artificial wetlands), Director, Durango Unit of the Advanced Materials Research Center (CIMAV), Durango, Dgo.

Maria Aurora Armienta (hydrogeology; trace element contaminants; water treatment using geological materials), Institute of Geophysics, National Autonomous University of Mexico (UNAM), Ciudad Universitaria, Mexico City, D.F.

Sofia Garrido Hoyos (drinking water; collection and treatment of rainwater; biological wastewater treatment; treatment and/or utilization of sludge and biosolids), Mexican Institute of Water Technology (IMTA), Jiutepec, Mor.

Luz Olivia Leal Quezada (environmental engineering; environmental chemistry; automation of chemical analysis techniques for environmental monitoring, particularly for the determination and speciation of trace elements; techniques for determining water quality and chemical aspects of their treatment), Advanced Materials Research Center (CIMAV), Environment and Energy Department, Chihuahua, Chih.

MOROCCO

Lhoussaine Bouchaou (hydrology; water quality; aquatic ecosystems; environmental impact assessment; climatology; climate change), President IAH Chapter Morocco; Applied Geology and Geo-Environment Laboratory, Faculty of Sciences, University Ibn Zohr (UIZ), Agadir

MOZAMBIQUE

Catine Chimene (municipal water and infrastructure; water supply engineering; agricultural water; rural development), Higher School of Rural Development (ESUDER), Eduardo Mondlane University (UEM), Inhambane, Vilankulo

MYANMAR

Khin-Ni-Ni Thein (hydroinformatics, integrated water resources management, river basin management, coastal-zone management, sustainable hydropower assessment, disaster risk reduction, climate change; sustainability; capacity building; community development; water and environmental policy; public policy analysis; green economy and green growth), Secretary, Advisory Group, Member, National Water Resources Committee; Advisory Group Member, National Disaster Management Committee; Founder and President, Water, Research and Training Centre (WRTC); Visiting Senior Professor, Yangon Technological University (YTU), Yangon, Myanmar; Regional Water Expert for Green Growth, UNESCAP

NAMIBIA

Benjamin Mapani (groundwater recharge and vulnerability mapping; groundwater development, management, monitoring and modeling; environmental hydrogeology; climate change), Board of Trustees, WaterNet; Department of Geology, University of Namibia (UNAM), Windhoek

NEPAL

Bandana K. Pradhan (environment and public health), Department of Community Medicine and Public Health, Institute of Medicine, Tribhuvan University (TU), Maharajgunj

NEW ZEALAND

David Hamilton (modeling of water quality in lakes and reservoirs; sediment-water interactions in lakes; boom-forming algae, particularly cyanobacteria; ice cover in lakes), Environmental Research Institute (ERI), University of Waikato, Waikato

NICARAGUA

Andrew Longley (hydrogeology; groundwater engineering; catchment studies and groundwater modeling; international development: projects in the water, geothermal, agriculture, environment and health sectors; rural water supply; arsenic contamination: mapping, hydrogeology, epidemiology; bridging the gap between academia, industry, public and charity sectors), Director, Nuevas Esperanzas UK, León

Katherine Vammen (aquatic microbiology; climate change and water resources; water supply and sanitation for the poor; urban waters), Co-Chair of the Water Programme of the Interamerican Network of the Academies of Science; Nicaraguan focal point for water programme in the InterAmerican Network of Academies of Sciences (IANAS); Central American University, Managua

NIGERIA

Peter Cookey (sustainable water and wastewater management in developing countries), Rivers State College of Health Science and Technology, Port Harcourt, Nigeria and Earthwatch Research Institute (EWRI), Port Harcourt

NORWAY

Torleiv Bilstad (water, oil and gas separation; environmental science and engineering), Former President of EWA-Norway; Department of Mathematics and Natural Sciences, University of Stavanger (UiS), Stavanger

Hallvard Ødegaard (water and wastewater treatment; innovative solutions for integrated approaches to urban water management), Department of Hydraulic and Environmental Engineering, Norwegian University of Science and Technology (NTNU), Trondheim

OMAN

Mohammed Zahir Al-Abri (thermal desalination; water and wastewater treatment; nanotechnology), Petroleum and Chemical Engineering Department, Sultan Qaboos University (SQU), Al Khoudh, Muscat

PAKISTAN

Ghani Akbar (agricultural engineering; integrated water management; soil and water conservation and climate-smart agricultural practices), Program Leader, Integrated Watershed Management Program (IWMP), Climate Change, Alternate Energy and Water Resources Institute (CAEWRI), National Agricultural Research Centre (NARC), Chak Shahzad, Islamabad

PALESTINIAN AUTONOMOUS AREAS

Marwan Haddad (interdisciplinary approaches to water resources and quality management; renewable energy; recycling), Director, Water and Environmental Studies Institute, An Najah National University, Nabus

PANAMA

José R. Fábrega (sustainable water and wastewater management; environmental fate of chemicals in water and soil systems), Panamanian focal point for water in the InterAmerican Network of Academies of Sciences (IANAS); Hydraulic and

Hydrotechnical Research Center (CIHH), Technological University of Panama (UTP), Panama City

PARAGUAY

Alicia Eisenkölbl (environmental management; environmental impact assessment; trans-boundary aquifers; rural development), Faculty of Agricultural Sciences Hohenau, Catholic University Our Lady of the Assumption (UCA), Campus Itapúa, Encarnación

PERU

Nicole Bernex Weiss de Falen (integrated water resources management; human sustainable development; climate change adaptation; integrated ecosystemic services, water management and risks (droughts and floods) with land planning at a water basin, regional and national level), Peruvian focal point for water in the InterAmerican Network of Academies of Sciences (IANAS); member of the technical Committee of Global Water Partnership GWP; LAC Chair in the CST of the UNCCD; Center of Research in Applied Geography (CIGA), Pontifical Catholic University of Peru (PUCP), Lima

PHILIPPINES

Victor Ella (surface and groundwater hydrology; irrigation and drainage engineering; water quality; simulation modeling; wastewater engineering; contaminant transport in soils; geostatistics; hydraulic engineering), Land and Water Resources Division, Institute of Agricultural Engineering, College of Engineering and Agro-Industrial Technology, University of the Philippines Los Baños (UPLB), College, Laguna

POLAND

Marek Bryjak (adsorption based water treatment), Department Polymer & Carbon Materials, Wrocław University of Technology, Wrocław

Wieslaw Bujakowski (geothermics), Mineral and Energy Economy Research Institute, Polish Academy of Sciences (PAS), Kraków

Jacek Makinia (wastewater treatment; nutrient removal and recovery from wastewater), Faculty of Hydro and Environmental Engineering, Vice-Rector for Cooperation and Innovation, Gdańsk University of Technology (GUT), Gdańsk

Barbara Tomaszewska (monitoring of the aquatic environments; geothermics; scaling of geothermal systems; membrane technologies for geothermal water treatment for water resource purposes), AGH University of Science and Technology; Mineral and Energy Economy Research Institute, Polish Academy of Sciences (PAS MEER), Kraków

PORTUGAL

Maria do Céu Almeida (sewer processes and networks), National Laboratory of Civil Engineering (LNEC), Lisbon

Helena Marecos (water reuse), Civil Engineering Department, Lisbon Engineering Superior Institute (ISEL), Lisbon

Helena Ramos (water-energy nexus; energy efficiency and renewable energies; hydraulics; hydrotransients; hydropower; pumping systems; leakage control; water supply; water vulnerability), Department of Civil Engineering, University of Lisbon (ULisboa), Lisbon

QATAR

Farid Benyahia (immobilized nitrifiers in wastewater treatment; membrane distillation desalination; water quality and energy efficiency analysis; airlift bioreactors; low-grade heat in membrane distillation for freshwater production; bioremediation of oil spills; development, design and evaluation of advanced refinery wastewater treatment processes), College of Engineering, Department of Chemical Engineering, Qatar University (QU), Doha

Patrick Linke (design, engineering and optimization of efficient processes, integrated systems and associated infrastructures; efficient utilization of natural resources (energy, water and raw materials); water-energy-food nexus), Chair, Chemical Engineering Program, Texas A&M University at Qatar (TAMUQ), Managing Director of the Qatar Sustainable Water and Energy Utilization Initiative (QWE) at TAMUQ, Qatar Environment and Energy Research Institute (QEERI), Doha

REPUBLIC OF GUINEA

Hafiziou Barry (integrated water resources management), Polytechnic Institute, University Gamal Abdel Nasser, Conakry

ROMANIA

Anton Anton (pumping stations; municipal water networks), Hydraulics and Environmental Protection Department, Technical University of Civil Engineering (UTCB), Bucharest

RUSSIAN FEDERATION

Sergey Pozdniakov (water resources; water quality; hydrogeology; contaminant transport; geostatistics; water balance; climate change), Faculty of Geology, Moscow State University (MSU), Moscow

RWANDA

Omar Munyaneza (hydrology; climate change and water resources management), College of Science and Technology, Department of Civil Engineering, University of Rwanda (UR), Kigali

SAUDI ARABIA

Noreddine Ghaffour (renewable energy for desalination and water treatment), Water Desalination and Reuse Research Center, King Abdullah University of Science and Technology (KAUST), Thuwal

Mattheus Goosen (renewable energy for desalination and water treatment; membranes), Office of Research and Graduate Studies, Alfaisal University, Riyadh

SENEGAL

Alioune Kane (water quality; hydraulics; water-poverty relationships; climate variability and water availability), Director of the Master Programme GIDEL (Integrated Management and Sustainable Development of Coastal West Africa); Coordinator of WANWATCE (Centres Network of Excellence for Science and Water Techniques NEPAD), Department of Geography, Cheikh Anta Diop University (UCAD), Dakar

SERBIA

Petar Milanović (karst hydrogeology; theory and engineering practice in karst), President IAH Chapter Serbia and Montenegro, Belgrade

SINGAPORE

Vladan Babovic (hydroinformatics; data assimilation; data mining), Department of Civil and Environmental Engineering, National University of Singapore (NUS), Singapore

Jiangyong Hu (water treatment technology; water quality; water reuse; health impacts), Department of Civil and Environmental Engineering & Co-Director, Centre for Water Research, National University of Singapore (NUS), Singapore

SLOVAKIA

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SLOVENIA

Boris Kompare (wastewater treatment; modeling), Past President EWA-Slovenia; Faculty of Civil Engineering and Geodesy, University of Ljubljana (UL), Ljubljana

SOMALIA

Abdullahi Mohumed Abdinasir (water resources management; groundwater governance; water supply), Ministry of Water, Petroleum, Energy and Mineral Resources, Mogadishu

SOUTH AFRICA

Tamiru A. Abiye (community water supply problems; water quality assessment and monitoring; hydrochemical modeling; groundwater flow and solute transport; trace metals in groundwater; surface and groundwater interactions; climate change impact on groundwater; spatial and temporal variability of groundwater recharge), School of Geosciences, Faculty of Science (East Campus), University of the Witwatersrand (Wits University), Johannesburg

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Sabelo Mhlanga (water-energy nexus; nano-structured materials for water purification and recovery; energy-efficient and antifouling membrane filtration technologies for water treatment; community involvement in water related problems in rural communities; green chemistry), Deputy Director, Nanotechnology and Water Sustainability (NanoWS) Research Unit, College of Science Engineering and Technology, University of South Africa (Unisa), Johannesburg

Anthony Turton (water-energy-food nexus; hydropolitical risk model; mine water management; mine closure planning and strategies; groundwater governance; wastewater reuse), Director, Environmental Engineering Institute of Africa; Centre for Environmental Management, University of Free State (UFS), Bloemfontein; professor at UNESCO Chair in Groundwater, Department of Earth Sciences, University of Western Cape (UWC)

SPAIN

José Ignacio Calvo (membrane technologies; modifications of structure and surface properties of membranes to increase selectivity), School of Agriculture, Food Technology and Forestry, ETSIIAA, University of Valladolid (UVa), Palencia

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Elena Giménez-Forcada (hydrogeology; hydrogeochemistry; water quality; groundwater contamination; trace elements), Geological Survey of Spain (IGME), Salamanca

J. Jaime Gómez-Hernández (stochastic hydrogeology; geostatistics; inverse modeling; nuclear waste disposal), Head of the Group of Hydrogeology, Research Institute of Water and Environmental Engineering, UPV, Valencia

Aurora Seco Torrecillas (nutrient removal and recovery from wastewater; anaerobic membrane bioreactor for wastewater treatment (WWT); microalgae cultivation for WWT), Chemical Engineering Department, University of Valencia (UV), Valencia

Guillermo Zaragoza (solar energy for desalination; thermal and membrane technologies for water treatment), Solar Platform of Almería (PSA-CIEMAT), Almería

SRI LANKA

Nadeeka S. Miguntanna (urban stormwater quality and monitoring; surrogate water quality parameters; urban water pollution; rainwater harvesting), Environmental Engineering Laboratory, Department of Civil and Environmental Engineering, Faculty of Engineering, University of Ruhuna (UOR), Hapugala, Galle

Meththika Suharshini Vithanage (water quality; water chemistry; impact of tsunamis on aquifers; groundwater modeling; soil and water monitoring for pollution; mechanistic modeling of biochar and nano materials for water and soil remediation (landfill leachates, nutrients and toxic metal(loid)s)), Group Leader – Chemical and Environmental Systems Modeling Research Group, National Institute of Fundamental Studies (NIFS), Kandy

SUDAN (REPUBLIC OF)

Abdin Mohamed Ali Salih (environmental sciences with emphasis on water resources management in arid and semi-arid zones), Board Member at UNESCO-IHE; Civil Engineering Department, Faculty of Engineering, The University of Khartoum (UofK), Khartoum

SURINAME

Sieuwnath Naipal (hydrology; climate change impact on climate variability; marine and coastal engineering), Anton De Kom University of Suriname (AdeKUS), Tammenga

SWAZILAND

Absalom M. Manyatsi (land and water resources management; environmental impact assessment; remote sensing; GIS and spatial climate change impacts; climate change adaptation and mitigation; climate smart agriculture; climate change and climate variability impacts on water resources and agriculture), Head of Department, Agricultural and Biosystems Engineering Department, University of Swaziland (UNISWA), Luyengo

SWEDEN

Prosun Bhattacharya (groundwater resources; hydrogeochemistry; arsenic), Coordinator, KTH-International Groundwater Arsenic Research Group, Department of Sustainable Development, Environmental Science and Engineering, Royal Institute of Technology (KTH), Stockholm

Joydeep Dutta (application of nanotechnology for water treatment; water-environment-energy nexus; photocatalytic materials, electrocatalysis and capacitive desalination of water, plasmon resonance sensors for heavy metal ion detection), Chair, Functional Materials Division, Materials- and Nano Physics Department, ICT School, Kista, Stockholm

Gunnar Jacks (hydrology; hydrogeology; hydrochemistry; groundwater chemistry; groundwater arsenic and fluoride; acidification of soil and groundwater; artificial groundwater recharge; water supply and sanitation in suburban areas), (retired) Department of Sustainable Development, Environmental Science and Engineering, Royal Institute of Technology (KTH), Stockholm

Erik Kärrman (sustainable wastewater management; decision support and multi-criteria analysis of municipal and local water and wastewater systems), Director of Research and Development, Urban Water & Royal Institute of Technology (KTH), Stockholm

Andrew Martin (membrane distillation for desalination and water purification; biomass and municipal solid waste; polygeneration), Department of Energy Technology, Royal Institute of Technology (KTH), Stockholm

Aapo Sääsk (development of polygeneration and zero liquid discharge), CEO, Scarab Development AB, Stockholm

Nury Simfors (geothermal exploration, geogenic trace contaminants, GIS and hazard mitigation), MVI/MTA, Swedish National Defence University (FHS), Stockholm

SWITZERLAND

Annette Johnson (geochemistry of inorganic contaminants in surface- and groundwater; chemistry of the mineral-water interface; geogenic contamination of groundwater and drinking water; waste management), Leader, Department of Water Resources and Drinking Water, Swiss Federal Institute of Aquatic Science and Technology (Eawag), Düebendorf

Eberhard Morgenroth (biological wastewater treatment using activated sludge, granular biomass, or biofilm based systems; biological drinking water treatment; mixed culture environmental biotechnology for bioenergy production; mathematical modeling; sustainable development of urban water management), Chair of Process Engineering in Urban Water Management, ETH Zurich & Swiss Federal Institute of Aquatic Science and Technology (Eawag), Dübendorf

Thomas Wintgens (water reuse), Institute for Ecopreneurship, School for Life Sciences, University of Applied Sciences and Arts Northwestern Switzerland (FHNW), Muttenz

TAIWAN

How-Ran Guo (epidemiology; environmental health and medicine; health impacts of water contaminants; cancers and chronic diseases in endemic areas of arsenic intoxication; epidemiologic characteristics of diseases associated with arsenic), Department of Environmental and Occupational Health, College of Medicine, National Cheng-Kung University (NCKU), Tainan

Tsair-Fuh Lin (analysis and monitoring of algae, cyanobacteria and metabolites; water treatment; site remediation; adsorption technology), Director, Global Water Quality Research Center, Department of Environmental Engineering, National Cheng-Kung University (NCKU), Tainan

Jyoti Prakash Maity (water and wastewater treatment with microbes and algae), Department of Earth and Environmental Sciences, National Chung Cheng University (CCU), Ming-Shung, Chiayi County

TANZANIA

Jamidu H.Y. Katima (sustainable wastewater management), College of Engineering and Technology, University of Dar es Salaam (UDSM), Dar es Salaam

THAILAND

Nathaporn Areerachakul (rainwater utilization; photocatalytic hybrid systems), Graduate School, Suan Sunandha Rajhabhat University (SSRU), Dusit, Bangkok

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Foreword by Subhas K. Sikdar

Commercial applications of semipermeable membranes started with the invention, in the nineteen sixties, of an asymmetric reverse osmosis membrane for the purpose of producing potable water by desalination. Since then much research gave rise to developing newer and newer membranes. Development of various methods and techniques then led to a multitude of industrial and domestic applications. The objective of membrane methods has mostly been to separate water in some pure form from offending agents, be they particulates, ions, or dissolved or suspended organic chemicals. However, some of the most successful applications have been in separating gases, for instance, nitrogen from air by hollow fibers. The traditional membrane applications rely on the ability of membranes to act as barriers, allowing passage through the membranes based on size of the transferred entities, such as particulates or dissolved ions. In this sense, membranes can be looked upon as an option for separating unwanted materials that span the entire size spectrum from molecular dimension, measured in Angstrom, to particulates, in millimeters. The corresponding membrane methods based on this principle are reverse osmosis, nanofiltration, ultrafiltration, microfiltration and the like.

Barrier technique, however, has not been sufficient to achieve many significant needs. Thus, in parallel, researchers have attempted to exploit membrane affinity as a property to impart a gatekeeping role to membranes. When the membrane affinity is for the desired entity, such as water or nitrogen, the membrane has to offer high flux because the permeating species is dominant in quantity. The separation factor of the permeating species with respect to the undesirable species has to be satisfactory also. Reverse osmosis for desalination, and the famed Monsanto Prism membrane for air separation, are examples of these features. On the other hand, when the permeating species are the minor constituents, such as an organic solvent in aqueous medium worthy of recovery, separation factor will be the dominant criterion for the economy of the process. Examples are pervaporation of organic chemicals from contaminated water, or liquid membranes for heavy metal recovery, the latter exploiting chelating ability of membranes.

A very promising approach has recently emerged by combining adsorption with membranes for organic or metallic species. In this contraption, membranes are endowed with functionalities that bind the target species by physical or chemical bonds preventing them to transgress through the membrane. Unlike a typical barrier process, the success of this operation depends critically on the capacity of the membrane for the target species, and also on the fouling of the active sites by competing species that are invariably present. These membranes need to be regenerated after the sites are saturated. The result of this type of membrane process is the creation of a concentrated stream containing the targeted species which need to be either recovered in case they are valuable or treated when they are undesirable. There is one exception to this regeneration requirement. Sometimes the physical adsorption is taken advantage of to increase the species concentration inside the membrane such that the permeating species experience a larger driving gradient between the membrane and the receiving medium. An example will be pervaporation of volatile organic compounds (VOCs) from a liquid stream to a condensed phase across the membrane. In physical adsorption, the principle of reversible equilibrium adsorption-desorption principle holds, which means the capacity depends on the strength of the incoming stream. The realizable capacity of these adsorptive membranes will be low for low concentration streams and high for high concentration streams. The adsorption isotherms for physical adsorption suggest what can be achieved, not what will be achieved. Too frequent regeneration can be expensive and unaffordable, thus the realizable equilibrium needs to be considerable. Chemisorption provides an escape from this dilemma. Since the bonds that hold the target species to the membrane are chemical, the same reversible equilibrium principle does not apply. High capacity requirement is still a necessity, as it is directly relevant to cost of operation. Microfiltration membranes offer the best potential for this adsorption-membrane combined technique because the affinity ligands can be deposited inside the pores of the membranes, largely increasing the capacity of capture and allowing higher flux of the effluent.

This book is focused on removing trace elements from wastewater or from water that would be used for potable purposes. Arsenic, uranium, and fluorides are especially examined with various membrane methods, including some adsorptive techniques. Arsenic, typically appearing in water as anionic species, became first a local concern in the nineteen nineties when naturally occurring arsenic in groundwater, used for domestic needs, revealed severe health impacts in Bangladesh and parts of Eastern India. Gradually it became a worldwide concern. In the United States, the Environmental Protection Agency ran a demonstration program in which many technologies from all parts of the world were tested for their efficacy in removing arsenic from ground water. Almost without exception the tested technologies, some of which are already deployed, are adsorption-based. They typically exploit chemical reactions to change the valence of the existing arsenic species before adsorptive removal. Several chapters in the book are devoted to sorption of arsenic, including biosorption in membranes. Arsenic is highly toxic, hence a disposal method is always required after its removal. Like arsenic, fluorides also are naturally occurring in groundwater, and when fluorides are present in excessive amounts in potable water, consumption can lead to dental fluorosis and other bone loss diseases. However, fluoride in tiny amounts also fight dental cavities. In the 1984 World Health Organization guideline, fluoride was recommended to be added to drinking water supplies. In many countries, it is also added to tooth pastes. To avoid fluorosis in many countries, the Governments have banned its presence in drinking water. Thus a robust controversy exists on what to do about fluorides. Several authors in the book offer research results on membrane removal of fluorides from water. Uranium, a radioactive metal, also is found in some groundwater which can, if not removed, be a human health concern. Uranium is mostly not absorbed by the human body, but a part stay in the body and can cause kidney problems because of chemical reactions, not because of radioactivity. Uranium is consumed mostly through foods, not water. Being a very heavy metal, it is amenable to be removed by barrier techniques such as reverse osmosis, or by chemical affinity such as ion exchange. Half a dozen chapters in this book deal with uranium removal by several membrane techniques. Like Fluoride, it is not certain what to do about Uranium on the regulatory front. Research results that are presented in the book on removal from water of both elements will prove to be a resource for researchers if their removal from water resources were mandated by the authorities. This book is not meant to be a general purpose treatise on membranes. Its value is in the specialized knowledge of the applicability of membrane methods to remove arsenic, fluorides and uranium from water.

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Editors' foreword

Uraniun, arsenic and fluoride are found in many regions around the world, where they make freshwater sources unsuitable for drinking or irrigation without prior treatment. The origin of these contaminants can be natural being released from geogenic sources by their mobilization through natural physico-chemical processes affecting, in particular, groundwater resources often on a regional scale and, most importantly, often co-occuring. Since groundwater is increasingly used for freshwater supply, its treatment to an adequate standard is becoming increasingly important. Uraniun, arsenic and fluoride can also be mobilized from geogenic sources through mining into freshwater resources or can be of purely anthropogenic origin resulting from industrial processes. The possibility of finding appropriate technologies to treat freshwater resources contaminated by uraniun, arsenic and fluoride and to reuse treated industrial and other wastewater for reuse for industrial or agricultural or drinking water purposes is one of the major global challenges of the present century.

This book addresses conventional and novel membrane technologies and their application for removing toxic metal(loid)s and halogens from water, with particular attention devoted to the removal of uranium (U), arsenic (As), and fluoride (F^-). All of these compounds exist in the earth's crust at average levels of between two and five thousands micrograms per kg (parts per million) and all are considered highly toxic to humans with exposure primarily through air, food and water. In order to comply with new maximum contaminant levels, numerous studies have been undertaken to improve established treatments or to develop novel treatment technologies for removing toxic metal(loid)s and fluoride from contaminated surface and groundwaters. Among the available technologies applicable for water treatment, membrane technology has been identified as a promising approach for the removal of such toxic contaminants from water. Therefore, this book is devoted to describing both pressure driven traditional methods (Nanofiltration, Reverse Osmosis, Ultrafiltration, etc.) and more advanced and novel membrane processes (such as Forward Osmosis, Membrane Distillation and Membrane Bioreactors) employed in the removal of uranium, arsenic and fluoride.

One key goal of this book is to provide information both on membrane technologies and on the results obtained in their application. All the authors involved in the writing of the chapters are experts in the specific membrane technology described and this makes the book really unique. The information provided should facilitate the choice of process suitable for a specific application and also show the potential of these innovative membrane processes. The different chapters each cover a specific membrane process, allowing the possibility of describing the technology in detail and evaluating its potentiality.

This book is divided in three parts: Part I contains the introductory Chapter 1 which provides an overview of the chemistry and human concerns of the toxic contaminants (U, As, and F^-) to be removed from water by membrane technologies. Part II contains five chapters dealing with the use of different conventional membranes while Part III gives detailed insights into new trends in materials and membrane process development to be applied for the target contaminants from water. Within Part II, Chapter 2 provides details on the basic principles of microfiltration (MF) and ultrafiltration (UF) processes and selected applications in the treatment of drinking water specifically with respect to arsenic removal. It also illustrates and highlights the significant advantages which can be achieved through the integration of these membrane technologies with adsorption and coagulation/flocculation technologies. These principles can be generally extended to the removal of fluoride and uranium from drinking water. Chapter 3 reports the successful application of nanofiltration in the removal of fluoride and uranium from groundwater in order to meet WHO regulations. Chapter 4 focuses on the reverse osmosis (RO) process and the removal of As, F^- and U by reverse osmosis (RO) using different types of membrane modules. Chapter 5 presents the most relevant electromembrane processes for treating water containing traces of toxic contaminants and addressing the removal of As, F^- and U. Two case-studies are reported and discussed in order to illustrate the possible successful application of Donnan dialysis, applied either as a single treatment or part of an integrated approach for the removal of arsenate and ionic mercury from contaminated water sources. Chapter 6 reports the removal of the three target contaminants from water and wastewater using adsorbent materials (including mixed matrix membrane) and integrated membrane systems. In Chapter 7, the application and comparison of liquid membrane techniques for the removal of U from lean solutions is extensively evaluated and discussed. Chapter 8 reports the main theoretical aspects of transport in supported liquid membranes (SLMs) and their potential applications in the removal and recovery of toxic ions from water with a specific study on arsenic removal. Chapter 9 describes the Polymer Inclusion Membranes (PIMs) process and explores progress made on the development of PIMs for the separation of U and As from aqueous solutions. The separation of U and As illustrates the applicability of PIM-based technology, which is considered to be a relatively novel type of self-supporting liquid membrane with low energy requirements, to industrial separation and environmental remediation. In Chapter 10, the removal of arsenic by means of nanofiltration (NF) membranes is discussed. The aim of this chapter is to give a comprehensive overview of the use of NF membrane-based processes for As removal, providing not only a critical analysis of the current treatment status of using membrane based processes, but also pointing out new development directions for arsenic removal in a more energy efficient manner and reporting a specific case study on the preparation of high performance NF membranes. Chapter 11 reports the positive effect of the coupling of biochemical processes with membranes in membrane bioreactors (MBR). The MBR process is described in detail and its potential for use in water treatment and removal of toxic compounds is also reported. The basic principles of membrane distillation and the application of this membrane process to treat polluted water, in terms of permeate flux and contaminant rejection, are reviewed and discussed in depth in Chapter 12. Finally, in Chapter 13, the potential of Forward Osmosis (FO), considered an emerging membrane technology, for the removal of contaminants (both organics and inorganics), particularly As, from impaired water is discussed.

The book is a "first of its kind"; as there are no other contemporary publications on this topic available and we believe that this book will provide the readers with a thorough understanding of the different available membrane technologies for the removal of traces of toxic compounds such as uranium, arsenic, and fluoride from water.

We hope that this book will help all readers, professionals, academics and non-specialists, as well as key institutions that are working on membrane technology and water treatment projects. It will be useful for leading decision and policy makers, water sector representatives and administrators, policy makers from government, business leaders, companies involved in water treatment, and engineers/scientists from both industrialized and developing countries. It is expected that this book will become a standard, used by educational institutions and Research and Development establishments involved in the respective issues.

Alberto Figoli
Jan Hoinkis
Jochen Bundschuh
(editors)
November 2015

About the editors

Alberto Figoli (1970, Italy) got his PhD degree at Membrane Technology Group, Twente University (NL) in 2001. He is Senior Researcher at the Institute on Membrane Technology (ITM-CNR) in Rende (CS), Italy, since 2001.

Alberto Figoli is expert in the field of membrane technology, particularly in *membrane preparation and characterisation* and *application in water treatment.*

In 1996, he obtained his Master Degree in Food Science and Technology, at the Agriculture University of Milan. Then, he worked for about 1 year at Quest International Nederland B.V. (ICI), Naarden (The Netherlands) at the Process Research Group, on a pilot plant for aromatic compounds extraction using the pervaporation membrane technology. He has been granted twice by National Research Council of Italy (CNR) to the Short Term Mobility Programme, as visiting researcher of the Environmental Protection Agency of United States (USEPA) at the Sustainable Technology Division in Cincinnati (USA). The research was devoted to pervaporation studies in the environmental field.

In recent years, he has been involved in several European and National projects (as scientist responsible or principal investigator for ITM-CNR) in the field of Membrane Technology. In particular, he has been the scientific coordinator of several National projects with Industries and a Marie Curie EU Project. He is the author of more than 80 scientific peer-review papers and chapters published in international journals and books. He is the editor of one book and author of two patents on membrane technology.

In 2015, he was elected as Council Member of the European Membrane Society, EMS, for the period 2015–2019. He is responsible for the Awards and Summer Schools.

Jan Hoinkis (1957, Germany) conducted a doctorate in thermodynamics at the University of Karlsruhe, Germany (now Karlsruhe Institute of Technology). After completion of his thesis he moved to the Swiss company Ciba-Geigy, where he was working as head of an R&D group on process development in the field of fine chemicals production with focus on environmentally friendly technologies. He has been working since 1996 as a professor at the Karlsruhe University of Applied Sciences giving lectures in chemistry, thermodynamics as well as environmental process engineering. His R&D work is focused on water treatment and water reuse with special attention on sensor-based membrane technologies. He was involved in several national and international R&D projects. In 2008 he was appointed Scientific Director of the Institute of Applied Research, which is the central research facility at the Karlsruhe University of Applied Sciences.

Jochen Bundschuh (1960, Germany), finished his PhD on numerical modeling of heat transport in aquifers in Tübingen in 1990. He is working in geothermics, subsurface and surface hydrology and integrated water resources management, and connected disciplines. From 1993 to1999, he served as an expert for the German Agency of Technical Cooperation (GTZ – now GIZ) and as a long-term professor for the DAAD (German Academic Exchange Service) in Argentina. From 2001 to 2008 he worked within the framework of the German governmental cooperation (Integrated Expert Program of CIM; GTZ/BA) as adviser in mission to Costa Rica at the Instituto Costarricense de Electricidad (ICE). Here, he assisted the country in evaluation and development of its huge low-enthalpy geothermal resources for power generation. Since 2005, he has been an affiliate professor of the Royal Institute of Technology, Stockholm, Sweden. In 2006, he was elected Vice-President of the International Society of Groundwater for Sustainable Development ISGSD. From 2009–2011 he was visiting professor at the Department of Earth Sciences at the National Cheng Kung University, Tainan, Taiwan.

Since 2012, Dr. Bundschuh has been professor in hydrogeology at the University of Southern Queensland, Toowoomba, Australia where he is working in the wide field of water resources and low/middle enthalpy geothermal resources, water and wastewater treatment and sustainable and renewable energy resources. In November 2012, Prof. Bundschuh was appointed as president of the newly established Australian Chapter of the International Medical Geology Association (IMGA).

Dr. Bundschuh is author of the books “Low-Enthalpy Geothermal Resources for Power Generation” (2008) (Taylor & Francis/CRC Press) and “Introduction to the Numerical Modeling of Groundwater and Geothermal Systems: Fundamentals of Mass, Energy and Solute Transport in Poroelastic Rocks”. He is editor of 16 books and editor of the book series “Multiphysics Modeling”, “Arsenic in the Environment”, “Sustainable Energy Developments” and the recently established series “Sustainable Water Developments” (all CRC Press/Taylor & Francis). Since 2015, he has been editor in chief of the Elsevier journal “Groundwater for Sustainable Development”.

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Part I
Generality on arsenic, fluoride and uranium

CHAPTER 1

Fluoride, uranium and arsenic: occurrence, mobility, chemistry, human health impacts and concerns

Alberto Figoli, Jochen Bundschuh & Jan Hoinkis

1.1 INTRODUCTION

Mainly due to global population growth the demand for potable water is continuously rising. According to the United Nations, world population is projected to reach 9.6 billion by 2050 with most growth in developing regions, especially in Africa (UN, 2013). During the same period, the population of developed regions will remain largely unchanged at around 1.3 billion people (UN, 2013). This forecast highlights well the need for safe drinking water especially in less developed regions, where the population is expected to grow significantly. About 97% of the freshwater reserve is stored in aquifers, which makes the groundwater the largest global freshwater resource. That resource caters to the need of a population of over 1.5 billion (Jacks and Battacharya, 2009). When comparing this freshwater to surface water quality many advantages turn out. Groundwater is generally free from pathogenic bacteria and viruses and has far lower concentrations of organic matter. However, a variety of organic and inorganic contaminants have been identified in groundwater that are potentially toxic to humans or animals (Hoinkis *et al.*, 2011). The origin of these contaminants is on the one hand naturally occurring through mobilization from the rocks and minerals through physical, chemical, and microbiological processes into the groundwater while on the other hand uniquely human sources like pesticides, fertilizers or industrial and mine waste discharge are other sources.

Rapid and intensive industrialization has generated large volumes of aqueous wastes containing dangerous materials, such as heavy metals and metalloids. Water contamination by heavy metals, metalloids and other minor and trace elements such as fluoride constitute a big global health hazard (An *et al.*, 2001; Mulligan *et al.*, 2001) as they can be toxic and carcinogenic even at very low concentrations, and, hence, usually pose a serious threat to the environmental and public health (Liu *et al.*, 2008; Vilar *et al.*, 2007). During traditional wastewater treatment, most heavy metals (e.g., lead, chromium and cadmium) and metalloids (e.g., arsenic (As)) pass unhindered through the treatment process, which is mainly due to their occurrence in trace amounts. In fact, little to no attention has historically been given to metals and metalloids in wastewater treatment plants.

Natural sources (volcanic emission, weathering of rocks and microbiological activity), release of geogenic contaminants through mining and anthropogenic sources (e.g., burning of fossil fuels, use of arsenical pesticides and herbicides, etc.) are responsible for high As concentrations in water in many parts of the world (ATSDR, 2007). In the affected areas, As concentrations in groundwater are generally found in the range of 100–2000 $\mu g\,L^{-1}$ On the other hand, the potential sources for high concentration of F^- in water are dissolution of F^- bearing rocks under favorable natural conditions and/or discharge of F^- contaminated wastes from the industry (Mohapatra *et al.*, 2009). Moreover, like As and F, U is also distributed in the environment due to natural (weathering of rock) and anthropogenic (mining, nuclear power production and phosphate fertilization) sources and leaves a very high impact on the environment, which is a latent risk factor for both human and animals (Langmuir, 1997; Oliver *et al.*, 2008).

As a result of the high concentration of these chemical species in groundwater, an adequate treatment is required for removal of these contaminants before supplying it for human consumption.

Various chemical treatment technologies have been applied to remove these ions from drinking water sources, including ion exchange, metal oxide based adsorption and coagulation. However, these methods alone are insufficient to remove the contaminants below the Maximum Contaminant Limit (MCL) and therefore are better to be used as a pretreatment step (Favre-Réguillon *et al.*, 2005; Mondal *et al.*, 2013).

In fact, the presence of such inorganic arsenic (As(V/III)), fluoride (F^-) and uranium (U(VI)) species (mostly ions) in groundwater (and to less extent in surface water) is a critical global issue, and has created severe health impacts for decades. Bioaccumulation and adverse effects on human health by intake of these ions via drinking water have been well documented (e.g., Fawell *et al.*, 2006; Orloff *et al.*, 2004; Smedley and Kinniburgh, 2002).

The aim of this book is to describe, analyze and bring to the attention the existence of different types of membrane processes, which could be successfully applied for the removal of toxic metals from water. In particular, the removal of As, U and F^- fluoride will be taken into consideration as specific cases.

This introductory chapter for this volume provides basic information on the occurrence and chemical species of As, U and F^- in freshwater resources (predominantly groundwater), their release from rocks and sediments and mobility as well as the principal health impacts, which occur due to human uptake through drinking water or through the human food chain. The chapter provides only simplified insight into these topics as far as this knowledge is needed for selecting the most appropriate technology and design for removal of these trace contaminants from drinking and irrigation water and provide the reader with knowledge of the global importance of contamination of freshwater resources with these geogenic and, of minor importance anthropogenic, trace elements and related potential health impacts, which clearly demonstrate the importance of their removal through adequate treatment.

1.2 FLUORIDE

Fluorine is the lightest, reactive and most electronegative element in the halogen group of the periodic system and has a strong tendency to acquire a negative charge. Thus, it remains as a negative ion (F^-) in solution (Fawell *et al.*, 2006) and forms negative and positive complexes (e.g., dissolved $[MgF]^+$ complexes). Soluble fluoride complexes with Al^{3+}, Fe^{3+} and Si^{4+} have high equilibrium constants ranging from 10^6 to 10^5, but the amount of Al^{3+}, Fe^{3+} and Si^{4+} ions is below $1\,mg\,L^{-1}$ in most natural waters (pH 5 to 8, $Eh = -200$ to $+200\,mV$) (Baas Becking *et al.*, 1960). Graham *et al.* (1975) and Roberson and Barnes (1978) state that fluoride complexes with Al^{3+}, Fe^{3+} and Si^{4+} must therefore only be considered at rather low pH-values. In areas where high fluoride concentrations are correlated with arsenic like in Arizona (Robertson, 1984) and especially in the Argentine Pampa and Chaco plains, additionally the fluoride complexes of As must be considered (e.g., $HAsO_3F^- + H_2O = F^- + H^+ + H_2AsO_4^-$, $pK = -46.112$ and $AsO_3F^{2-} + H_2O = F^- + H_2AsO_4^-$, $pK = -40.245$) (Bundschuh *et al.*, 2000; 2004). However, ionized and non-ionized organic and inorganic F occur in the environment.

1.2.1 *Sources, release and mobility*

In many regions, fluorine is a widely distributed constituent found in sedimentary porous aquifers, in porous aquifers formed by the overburdens of hard bedrock aquifers and in hard rock aquifers in concentrations beyond the WHO guideline value of $1.5\,mg\,L^{-1}$ (Fawell *et al.*, 2006).

The presence of F^- in the environment occurs not only naturally through its presence in the earth's crust but also due to industrial activities, such as electroplating, semiconductor manufacturing, glass making, steel production and fertilizer industries (Sujana *et al.*, 1998; Toyoda and

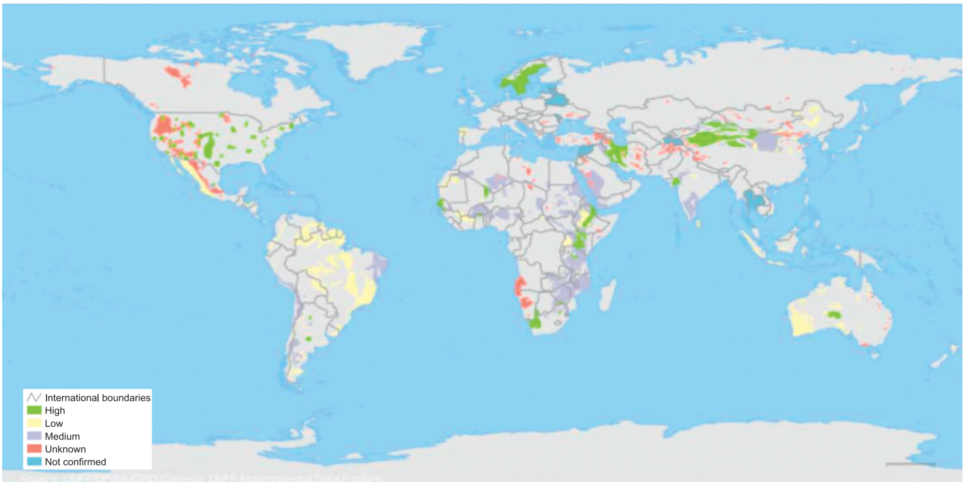

Figure 1.1. Fluoride in groundwater – Probability of occurrence (IGRAC, 2014 Environmental Data Explorer, compiled from IGRAC: Internet Site: http://geodata.grid.unep.ch/options.php?selectedID=2241&selectedDatasettype=16 (accessed on 05 February 2014).

Taira, 2000). The release of wastewater from these industries leads to the F^- pollution of surface and groundwater. The US Environmental Protection Agency (USEPA) established the effluent discharge standard of 4 mg L^{-1} for F^- from a wastewater treatment plant (Khatibikamala *et al.*, 2010; Shen *et al.*, 2003). The breakdown of rocks and soils or weathering and deposition of atmospheric volcanic particles are the biggest source of F^- found in the groundwater. Because they often contain abundant F^--bearing minerals crystalline rocks, especially granites, are particularly susceptible to F^- build-up. Concentrations of F^- in groundwater can range from below 1 mg L^{-1} to more than 50 mg L^{-1}.

Figure 1.1 provides an overview over the probability of occurrence of the F^- distribution worldwide. The known hotspots of F^- with high concentrations in groundwater are found to be in Scandinavia, China, Western India, East Africa North America and South America. Despite this forecast a variety of different publications showed several other spots of high F^- concentrations in groundwater. In Pakistan, Thailand, China, Sri Lanka, eastern and southern Africa high groundwater F^- concentrations associated with igneous and metamorphic rocks such as gneisses and granites have been reported (Fawell *et al.*, 2006). About half of the states and territories in India reported to have naturally high concentrations of F^- in water (UNICEF, 1999). In Sri Lanka, concentrations up to 10 mg L^{-1} have been reported and in China fluorosis has been reported to be widely spread (Fawell *et al.*, 2006). Since millions of people worldwide are exposed to high F^- concentrations this poses a serious global health threat to the consumers.

The northern Tanzania region is known for being among the most F^- affected areas worldwide. Already in the early 1980s, Nanyaro *et al.* (1984) reported high F^- contents in some rivers, springs, alkaline ponds and lakes in northern areas of Tanzania. The F^- contents found have been 12–26 mg L^{-1} for rivers, 15–63 mg L^{-1} for springs and even mg 60–690 L^{-1} for alkaline ponds and lakes. Also Bugaisa (1971) identified particular F^- problems in groundwater of Tanzania. The concentrations found vary between 4 and 330 mg L^{-1}. Such concentrations are extremely high compared to other F^- contaminated groundwater sources. In the East-African Rift zone lavas (intrusions and ashes) and other volcanic rocks with fluorine-rich minerals are found in much higher concentrations than in similar rock types elsewhere in the world (Kilham and Hecky, 1973). Hot springs are also an important source for high F^- concentrations in the groundwater. In addition, in extreme cases of evaporation of lakes coexisting with infiltration of lake water to the shallow aquifers, F^- contamination of the aquifer might occur.

1.2.2 *Human health effects*

Fluoride toxicity can happen by a number of ways. Bhatnagar *et al.* (2011) noted that the impact of F^- in drinking water can be beneficial or detrimental to human well-being. Small amounts in consumed water, for example, are usually considered to have a beneficial effect by reducing the rate of occurrence of dental cavities, predominantly amongst children (Mahramanlioglu *et al.*, 2002). In contrast, consumption of large amounts of F^- has been shown to lead to diseases such as osteoporosis, arthritis, cancer, infertility, brain damage, Alzheimer syndrome, and thyroid disorder (Chinoy, 1991; Harrison, 2005). In addition, F^- has been shown to poison kidney function at high doses over short-term exposures in both animals and humans (http://www.fluoridealert.org/studies/kidney01/). Fluoride exposure has also been linked to bladder cancer particularly among workers exposed to excess F^- in the workplace (Bhatnagar *et al.*, 2011; Chinoy, 1991). Thyroid activity is also known to be influenced by F^- (Harrison, 2005). There is therefore an urgent need to find out effective and robust technologies for the removal of excess F^- from drinking water.

1.3 URANIUM

Due to growing global energy demands, nuclear power appears to be a long term prospect as an alternative to fossil fuel based power sources. At this moment, most of the nuclear plants operate on enriched uranium (U) based fuels, thus making U one of the most precious elements.

1.3.1 *Sources, release and mobility*

The sources of U are commonly known minerals such as uraninite (UO_2) and pitch blend (U_3O_8); though other minerals such as carnotite, autunite, uranophane, torbernite, and coffinite also contain U. Secondary sources of U include phosphatic rocks and minerals such as lignite and monazite. Estimated U deposit in phosphatic rocks (world average U content in phosphate rock is estimated at 50–200 $mg\,kg^{-1}$) is about 9 million tons (http://www.wise-uranium.org/uod.html). The U recovery from the minerals involves acid (using dilute sulfuric acid) or alkaline (using sodium carbonate) leaching followed by solvent extraction methods using D2EHPA (di-2-ethylhexylphosphoric acid) and tri-alkyl amines which are well known as the DAPEX (dialkylphosphoric acid extraction) and AMEX (amine extraction) processes, respectively. Uranium produced through these processes is further purified to obtain nuclear-grade U by a solvent extraction method from a nitric acid medium using TBP (tri-*n*-butyl phosphate) in kerosene as the extractant.

The metal can also occur in the environment as a result of nuclear industry activities, mill tailings and fuels combustion. Its chemical toxicity is even greater than its radioactivity (Grenthe *et al.*, 1992; Sheppard *et al.*, 2005). The maximum admissible concentration (MAC) of U for drinking water according to the USEPA is $30\,\mu g\,L^{-1}$. The the World Health Organization (WHO) which introduced in 1998 the health-based drinking-water guideline for U of $2\,\mu g\,L^{-1}$ but increased to a $30\,\mu g\,L^{-1}$ in 2011 (WHO, 2004; Reimann and Banks, 2004). Figure 1.2 shows the U reserves in the world (OECD, 2010).

The map of Figure 1.2 highlights where the known natural sources of the metal are significant or low. Uranium is found in ground- and surface waters due to its natural occurrence in geological formations. Countries like Australia and Kazakhstan appear to be U-rich (with reserves of about 1,673,000 and 480,300 metric tons, respectively) and relatively high concentrations of U in groundwater are expected in these cases. Elevated levels of U in water can be also found outside the areas shown in the world map, however. The presence of U in groundwater has been reported, for instance, also in Europe (Scandinavia, Sweden, Finland, Spain, Portugal, France, the Czech Republic and Ukraine) (Raff and Wilken, 1999). The formation of U deposits is essentially a normal geological process leading to its presence in granite and sedimentary rocks. Naturally occurring U is located only in minor amounts on dry land, though. In fact, the estimated quantity

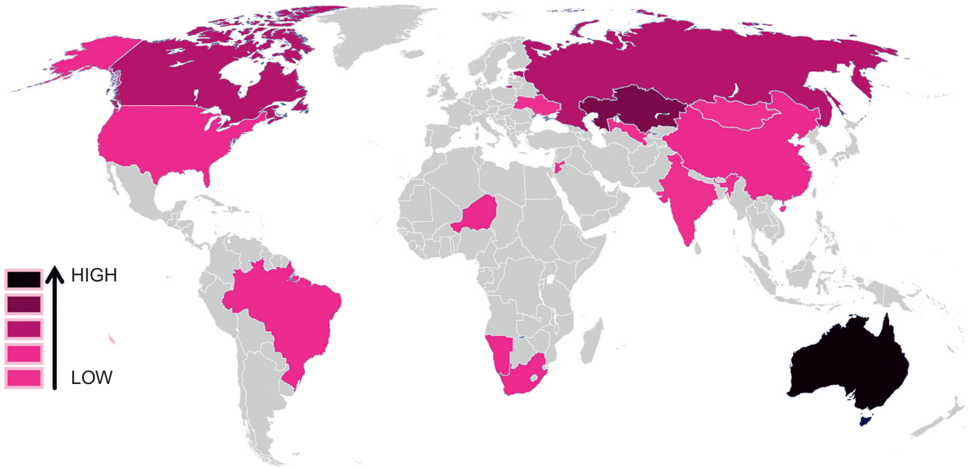

Figure 1.2. Uranium reserves in the world (OECD, 2010).

of dissolved U (3–4 $\mu g\,L^{-1}$) in seawater is ~4.5 billion metric tons, which is approximately 1000 times greater than that of U resources available in different known rock formations suitable for U exploitation (OECD, 2000). In view of this, seawater is being considered as a potential source of U. However, the process should be effective and economical for the selective concentration of uranyl ions. Japan has carried out extensive efforts for the recovery of U from seawater and several materials/processes have been developed and proposed toward the achievement of this goal (Kanno, 1984; Kawai *et al.*, 2008; Kobuke *et al.*, 1988; Schwochau, 1984).

1.3.2 *Human health effects*

Uranium occurs naturally in variable concentrations in all soils, minerals, rocks and waters. It can also be derived from several anthropogenic sources. Uranium is weakly radioactive and human exposure to the element has long been considered to pose a radiological as well as toxic hazard (WHO, 2004; 2008; Smedley *et al.*, 2006). This dissolved toxic radioactive metal may poison drinking water sources and the food chain via contaminated surfaces and groundwater. In recent years, there has been increasing concern that the chemical effects of uranium may also pose a potential hazard to exposed populations. However, there are few if any epidemiological studies that have been able to demonstrate any resultant harm, even in occupational contexts (The Royal Society, 2001).

The primary non-carcinogenic toxic effect of uranium is on the kidneys. Published studies in rats, rabbits, and humans show effects of chronic uranium exposure at low levels in drinking water. Effects seen in rats, at the lowest average dose of $0.06\,mg\,U\,kg^{-1}\,day^{-1}$, including histopathological lesions of the kidney tubules, glomeruli and interstitium are considered clearly adverse effects albeit not severe (OEHHA, 2001).

However, little information is available on the chronic health effects of exposure to environmental uranium in humans which makes it difficult to establish adequate guideline and regulatory limits for uranium in drinking water. Human risk from drinking water is significantly higher due to chemical exposure compared to radiation; the last would only be significant if uranium concentrations exceed $100\,\mu g\,L^{-1}$ (WHO, 2004).

In drinking water, histopathological effects were also seen at the same exposure level in the liver including nuclear anisokaryosis and vesiculation. Effects on biochemical indicators of kidney function were seen in the urine of humans exposed to low levels of uranium in drinking water for periods up to 33 years. Uranium is an emitter of ionizing radiation, and ionizing radiation

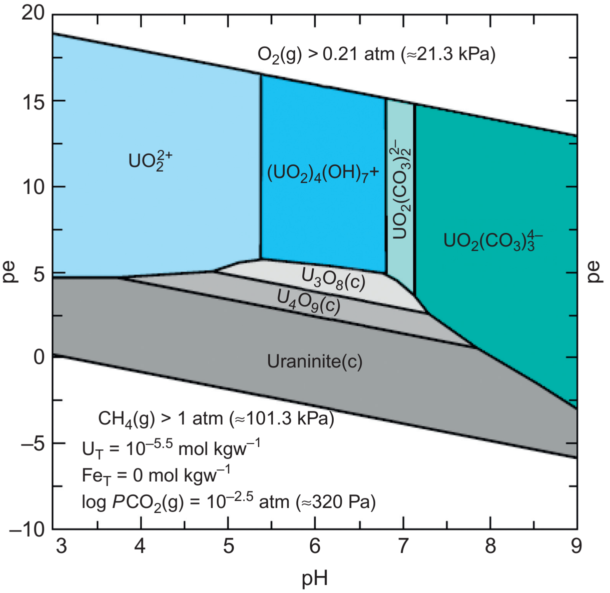

Figure 1.3. pe/pH predominance diagrams at 10°C for uranium (adpated from The Royal Society, 2001). (kgw: kg water).

is carcinogenic, mutagenic and teratogenic. A level of 0.5 $\mu g\,L^{-1}$ (0.43 pCi L^{-1}) is considered protective for both carcinogenicity and kidney toxicity (OEHHA, 2001).

1.3.3 *Uranium species*

The mobility of U in water is controlled by a number of factors, among the most important being pH, redox status and concentrations of coexisting dissolved ions. Uranium occurs in the environment in several oxidation states (+2, +3, +4, +5 and +6), but U(IV) (uranous) and U(VI) (uranyl) are most common in the natural environment. In oxic groundwater with low pH, UO_2^{2+} is predominant (Langmuir, 1997), whereas U(IV) is mainly present in reducing groundwater environment and in solid phase (Fig. 1.3) (Rossiter *et al.*, 2010). Complexes of UO_2^{2+} with carbonate, oxalate, and hydroxide are formed in the aqueous medium (Favre-Reguillon *et al.*, 2003). In addition, the UO_2^{2+} cation gets easily sorbed on different surfaces with the aid of dissolved organic matter or by complexation/precipitation with several anions such as hydroxide, silicates, phosphates etc. Uranyl ions are readily soluble and are easily transportable via forming complexes with carbonate (Zhou and Gu, 2005), phosphate (Cheng *et al.*, 2004), hydroxides and organic matters and these complexes are redundant in groundwater with basic pH (Rossiter *et al.*, 2010). The pE (potential)/pH diagram illustrates the different U species in groundwater.

1.4 ARSENIC

Arsenic (As) is a naturally occurring element present in food, water, and air. This element has been known for centuries to be an effective poison. Arsenic, a semi-metal element in the periodic table, is odorless and tasteless. It enters drinking water supplies from natural deposits in the earth or from agricultural and industrial practices. Since groundwater contamination by geogenic arsenic is known from over 70 countries (Fig. 1.4) and because As-associated human health problems have now been recognized in many parts of the world, mainly in developing countries, it is a problem and challenge of global concern.

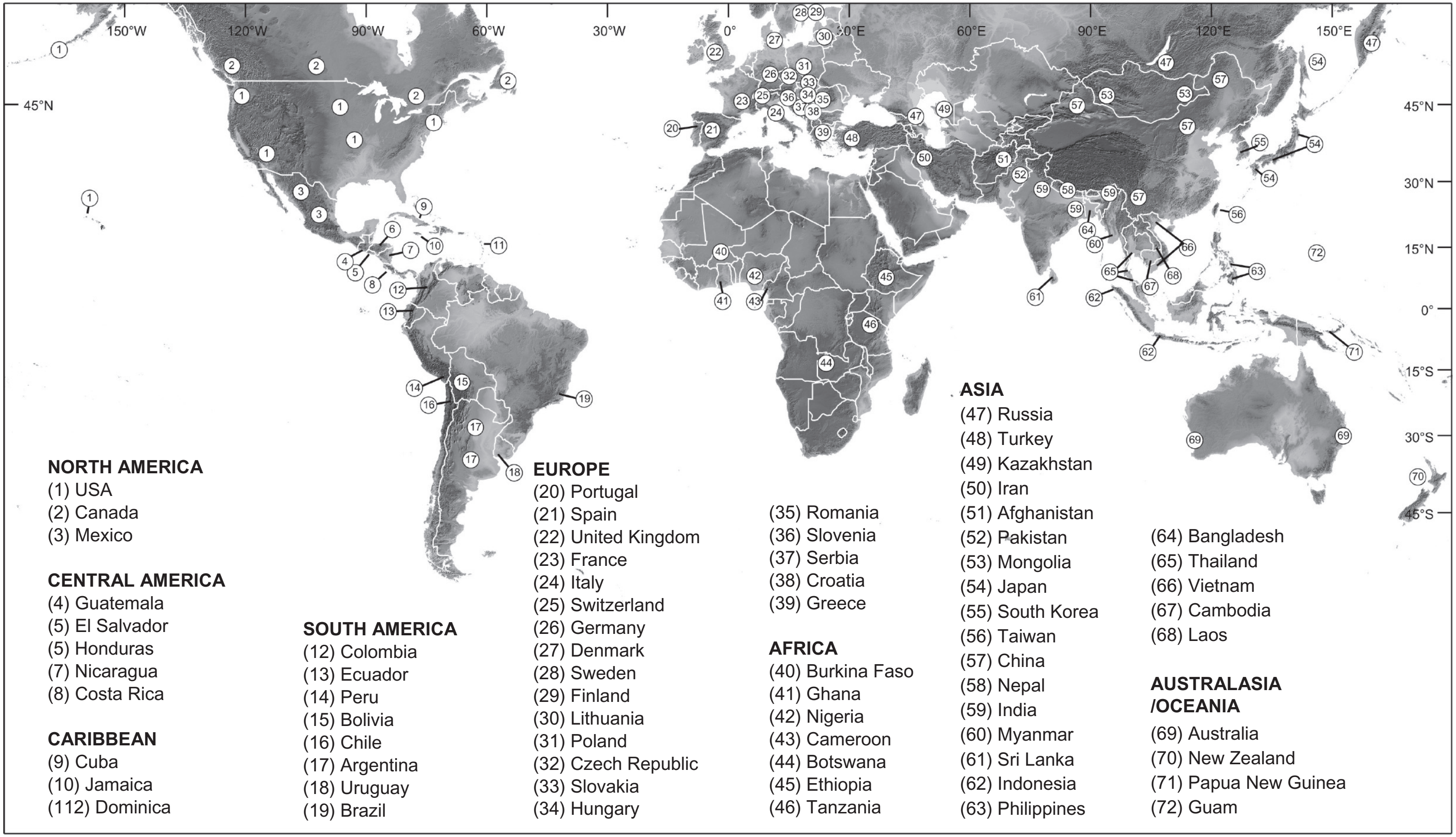

Figure 1.4. Countries with aquifers and surface water bodies with high concentrations of dissolved As as known today. Where space permitted individual arsenic-affected areas are shown within the individual countries. Adapted from Bundschuh and Litter (2010) based on compilations and data from: Bundschuh *et al.*, 2008a; Chandrasekharam and Bundschuh, 2008; Ravenscroft, 2007; Smedley, 2006; Welch *et al.*, 2000; 2009a, and from unpublished information of the authors.

In order to understand the global importance of the problem of high arsenic (As) concentrations in water used for drinking and irrigation water supplies, and the required mitigation needs, in the following sections a short global overview of the occurrence of geogenic As in water resources and a characterization of the conditions under which As is released from the solid aquifer material of from sediments into groundwater and surface water bodies, which is helpful for the formulation of sustainable mitigation solutions, such as As removal from drinking water or zero-treatment options (Section 1.4.1). To show the importance of As removal from water, in the following section (1.4.2) a short overview on human health effects due to exposure to As from water sources is provided. A last section provides information of arsenic species as the species in specific types of groundwater is essential for the selection and design of the As removal technology.

1.4.1 *Groundwater arsenic: sources, release and mobility*

Toxic As concentrations in groundwater and to lesser extent in surface water mostly result from physical or chemical abiotic and biotic weathering of primary or secondary As-containing minerals. Therefore, aquifers with elevated levels of groundwater As derived from natural sources can be classified according to the origin of the As and the mobilization mechanism into the water:

- In reduced alluvial aquifers, the As is predominantly released from iron oxyhydroxides: principle examples are the flood and delta plains of the Himalayan rivers, i.e., the Ganges-Brahmaputra-Meghna plain/deltas in India and Bangladesh (Bhattacharya *et al.*, 2002a; 2002b; 2007a; 2007b; Bhowmick *et al.*, 2013; Prakash Maity *et al.*, 2011a; Reza *et al.*, 2011a), the Indus plain in Pakistan (Nickson *et al.*, 2005), the Irrawady delta in Myanmar (WRUD 2001), the Red River delta in Vietnam (Berg *et al.*, 2001), and the Mekong river delta in Cambodia and Laos (Feldman and Rosenboom, 2001).
- In oxidized, mostly sedimentary, aquifers (normal pH range, $5 < \text{pH} < 10$) where desorption of As from Fe, Al, and Mn oxyhydroxides occurs at high pH (8–9.5). This is the principal mechanism responsible for the high As concentration of geogenic As in the groundwater of extended areas of the Argentine Chaco-Pampean plain and its continuation into the neighboring countries Uruguay, Paraguay and Bolivia (Bhattacharya *et al.*, 2006; Bundschuh *et al.*, 2004; 2008a; 2009a; 2009b; 2009c; 2012a; Chatterjee *et al.*, 2010; Nicolli *et al.*, 2010; 2012; Raychowdhury *et al.*, 2013; Smedley *et al.*, 2005; 2009), the Appalachian Highlands, NE Ohio (Matisoff *et al.*, 1982); the Interior Plains, S. Dakota, (Carter *et al.*, 1998); the Carson Desert, Nevada, (Welch and Lico, 1998); the Pacific Mountain System, NW Washington (Davies *et al.*, 1991; Ficklin *et al.*, 1989) and Arizona (Goldblatt *et al.*, 1963; Nadakavukaren *et al.*, 1984). In the groundwater of dry regions, As is often positively correlated to fluoride (Alarcon-Herrera *et al.*, 2013).
- In oxidized environments, at very low pH ($\text{pH} < 4$), the geogenic As is released by sulfide oxidation. This process is found in many areas with deposits of sulfide mineral ores. Examples include the mineral deposits in the Andes and Andean highlands (Ormachea Muñoz *et al.*, 2013; 2015; Ramos Ramos *et al.*, 2012; 2014), the Middle and North American cordillera, the Transmexican volcanic belt, the Appalachian belts from Massachusetts to Maine (Ayotte *et al.*, 1998; Boudette *et al.*, 1985; Peters, 2008; Peters *et al.*, 1999; Zuena and Keane, 1985), the Interior Plains of E. Michigan, (Westjohn *et al.*, 1998), the Variscian mountains in Europe, the Central Balkan peninsula in Siberia (Dangic and Dangic, 2007), Albania (Lazo *et al.*, 2007), Ghana (Smedley, 1996), Nigeria (Gbadebo, 2005), and many mining sites all around the world. Gold mining forms another geogenic source for contamination of water resources by arsenic as observed e.g. in Brazil (Ono *et al.*, 2012) and Cuba (Toujaguez *et al.*, 2013)

Other mechanisms, which can play a role in controlling As mobilization are the site-specific geomorphological, geological and hydrogeological conditions as well as climate, land use patterns, and groundwater exploitation (Bundschuh *et al.*, 2010; Hasan *et al.*, 2007; Mukherjee *et al.*, 2007) and the inflow of As-rich geothermal water into freshwater sources (Birkle *et al.*, 2010; Bundschuh and Prakash Maity, 2015; Bundschuh *et al.*, 2013; López *et al.*, 2012) or from release of mud volcano fluids mixing with surface water (Jean *et al*., 2010; Liu *et al*., 2011; 2013; Prakash Maity *et al*., 2011b), and the presence and contents and species of organic matter (Jean *et al*., 2010; Liu *et al*., 2013; Reza *et al*., 2011b). Arid and semiarid climate can be a principal or an additional control and, due to evaporative concentration increases, contribute to the genesis of As-rich groundwater and surface water. Examples where climate contributes to increased As concentrations in groundwater and surface waters include the Atacama desert in N Chile (Borgoño and Greiber, 1971; Bundschuh, 2008a; 2008b; 2008c; 2009a; 2009b), aquifers in the Chaco-Pampean plain in Argentina (Bhattacharya *et al*., 2006; Bundschuh *et al*., 2000; 2004; 2008a; 2008b; 2008c; 2009b; 2009c; 2012a; Chatterjee *et al*., 2010; Nicolli *et al*., 2010; 2012; Raychowdhury *et al*., 2013), shallow aquifers of the Carson desert in Nevada (Fontaine, 1994; Welch and Lico, 1998) and shallow aquifers in the southern San Joaquin valley in California (Fujii and Swain, 1995; Swartz, 1995; Swartz *et al*., 1996).

1.4.2 *Human health effects related to arsenic exposure*

Inorganic As is a Class 1, non-threshold, carcinogen, and chronic exposure also causes a range of ailments such as skin lesions (hyperkeratosis, melanosis), nervous system impairment, irritation of respiratory organs and the gastrointestinal tract, anemia, liver disorders, vascular illnesses and even diabetes mellitus, skin, lung and bladder cancer (Albores *et al*., 2001; Bates *et al*., 1992; Cullen *et al*., 1989; Del Razo *et al*., 2000; 2005; Endo *et al*., 2003; Kirk and Sarfaraz, 2003; McClintock *et al*., 2012; Oremland *et al*., 2003; Rossman, 2003). Chronic As exposure can also affect the intellectual development of children (Borja *et al*., 2001; Wasserman *et al*., 2004).

Ground and surface water sources with As concentrations at toxic level, used for drinking and irrigation, poses a direct threat to human health and environmental sustainability. When considering human exposure to inorganic As, besides direct ingestion from drinking water, other exposure pathways include water used in food preparation (such as rice cooking), direct contamination of food sources through the use of groundwater in agricultural irrigation or aquaculture, and the indirect contamination of food sources, such as feeding straw elevated in As to livestock (e.g., Bundschuh *et al*., 2012b and references therein).

At present, it is not possible to precisely assess the number of persons potentially exposed worldwide to elevated inorganic As from groundwater and surface water exposure routes at levels that constitute a health threat. However, some regional or countrywide estimates for drinking water exposure exist. In the Bengal delta, 31 million people are exposed to water with $>50\,\mu g\,L^{-1}$ and 50 million to $>10\,\mu g\,L^{-1}$ of As (Chakraborti *et al*., 2002), which is the WHO, EU and USA limit.

Regulatory agencies have published the MCL for As in drinking water to protect human health. According to the WHO and USEPA guidelines the current recommended limit of As in drinking-water is $10\,\mu g\,L^{-1}$, although this value is designated as provisional because of measurement difficulties and the practical difficulties in removing As from drinking water (USEPA, 2001; WHO, 2001).

1.4.3 *Arsenic species*

Arsenic can be found in two primary forms; organic and inorganic. Organic species of As are mainly found in food, such as shellfish, and include forms as monomethyl arsenic acid (MMAA), dimethyl arsenic acid (DMAA) and arseno-sugars. Inorganic Arsenic occurs in several oxidation states (−3, 0, +3, +5), although in a natural aquatic environment, the existence of As (0) and As (−3) are scarce (Oremland and Stolz, 2003). Groundwater is enriched with inorganic As species where As(V) is the dominant form under oxidizing conditions and exists as $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-} and H_3AsO_4. As(III) is dominant under reducing conditions and exists as $H_2AsO_3^-$ and H_3AsO_3 species (Ng *et al*., 2004). As(III) is several times more toxic than As(V) (Jain and Ali, 2000) and the concentrations of these species in groundwater are varied depending on the redox conditions of the aquifer organoarsenic compounds are commonly found in surface water that is affected by industrial pollution (Smedley and Kinniburgh, 2002). As(V) is a soft acid and easily

Table 1.1. Aqueous forms of arsenic (adapted from USEPA, 2003).

Arsenite As(III)	H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$, AsO_3^{3-}
Arsenate As(V)	H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}

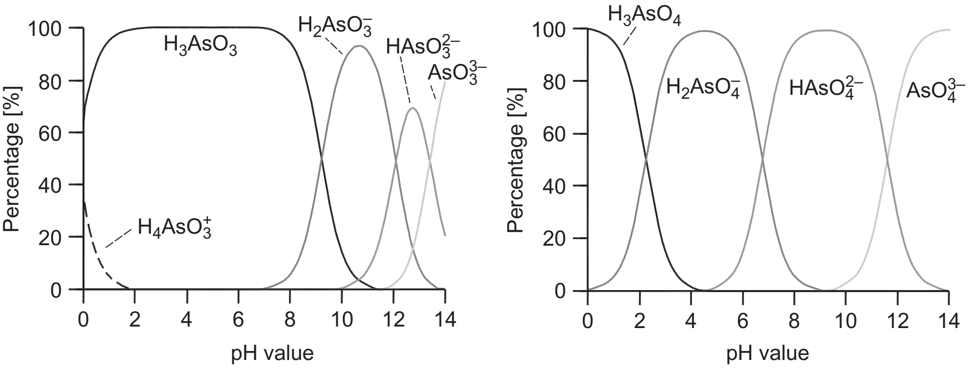

Figure 1.5. Speciation of As(III), (left), and As(V), (right). Total As concentration: 100 $\mu g\,L^{-1}$ (adapted from Höll, 2009).

forms complexes with soft bases like sulfide whereas As(III) is a hard acid and prefers to bind with hard bases (e.g., oxides and nitrogen) (Bodek *et al.*, 1998). While As(V) is negatively charged, As(III) is neutral below pH 9 (Smedley and Kinniburgh, 2002) and thus is very difficult to remove from water by conventional technologies.

The formation and concentration change with solution pH of As(III) and As(V) as illustrated in Figure 1.5.

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Part II
Traditional membrane processes

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CHAPTER 2

Arsenic removal by low pressure-driven membrane operations

Alfredo Cassano

2.1 INTRODUCTION

Water sources are often contaminated by micro-pollutants coming from rainfall, sewage, landfill leachate and industrial wastewaters. These micro-pollutants include micro-organisms, dispersed substances, organic compounds, such as natural organic matter (NOM), and inorganic substances. Among different inorganic compounds arsenic (As), uranium (U) and fluoride (F^-) have been found in natural water sources and wastewaters at concentrations potentially dangerous for human health (Bodzek *et al.*, 2011).

In this chapter basic principles of microfiltration (MF) and ultrafiltration (UF) processes and selected applications within the treatment of drinking water for As removal are illustrated and discussed highlighting significant advantages which can be achieved through their integration with adsorption and coagulation/flocculation technologies. These principles can be extended in good approximation to the removal of F^- and U from drinking water.

Conventional methods of As removal from drinking water include oxidation/precipitation, coagulation/flocculation, adsorption, ion-exchange and membrane technologies. Similar approaches can be used also for defluoridation (Meenakshi and Maheshwari, 2006) and removal of U from drinking water (Katsoyiannis and Zouboulis, 2013) although some of these methods have been tested at laboratory or pilot scale only.

Oxidation methods are relatively simple and assure oxidation of other impurities and microbial degradation with minimum residual mass; as drawbacks they mainly remove As(V) and require an efficient control of pH (Zaw and Emett, 2002).

Coagulation/flocculation methodologies are based on the use of commercially available chemicals such as aluminum, ferric sulfate, ferric chloride, slaked or hydrated lime, ferric hydroxide and polyaluminum chloride (Meng *et al.*, 2001; Ng *et al.*, 2004). They are effective over a wider range of pH, simple in operation and characterized by low capital costs. Some disadvantages are in terms of the production of toxic sludge, low removal of As, release of taste and odor compounds due to chlorination, floc disposal and post-treatment (Song *et al.*, 2006; Wickramasinghe *et al.*, 2004).

Adsorption methods based on the use of activated carbon, activated alumina and ion exchanger resins are promising processes for As removal because of the low cost, high efficiency, removal capability of both As(III) and As(V), independence on pH (Kim and Benjamin, 2004; Mohan and Pittman, 2007). The main disadvantages of adsorption methods are the requirement for multiple chemical treatments, high running/capital costs, pre- and/or post-treatments of drinking water, disposal of both spent media and wastewaters produced during regeneration/cleaning of columns.

The use of pressure-driven membrane processes, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO), for the removal of As from drinking water has been reviewed by Shih (2005) and Uddin *et al.* (2007a). These processes are characterized by low consumption of energy, no requirement for chemical substances to be added, an easy way to increase the capacity (modular system), separation in the continuous mode, the possibility of integration with other unit processes (hybrid processes), and separation carried out in mild environment conditions (Drioli *et al.*, 1999). In particular, the use of NF and RO membranes for the removal of As from drinking water has been largely investigated (Cakmakci *et al.*, 2009;

Figoli *et al.*, 2010; Geucke *et al.*, 2006; Johnston *et al.*, 2001; Kang *et al.*, 2000; Kim *et al.*, 2006; Košutić *et al.*, 2005; Ning, 2002; Oh *et al.*, 2000; Saitúa *et al.*, 2005; Sato *et al.*, 2002; Uddin *et al.*, 2007b; Urase *et al.*, 1998; Vrijenhoek and Waypa, 2000). These processes allow efficient reduction of the As concentration at values lower than 10 $\mu g\,L^{-1}$ and do not produce toxic solid wastes. However, a high fouling potential of these membranes may hinder full scale applications.

Since As(V) can be adsorbed more strongly onto adsorbents than As(III), the oxidation of As(III) can be exploited and integrated with UF and MF systems at low pressure and adsorption/coagulation media for effective and low cost As removal.

2.2 MICROFILTRATION AND ULTRAFILTRATION

2.2.1 *General properties*

2.2.1.1 *Terminology*

Microfiltration (MF) and ultrafiltration (MF) are typical low-driven pressure membrane processes widely applied in various chemical and biochemical processes thanks to their advantages over traditional filtration methods. They are generally a thermal and simple in concept and operation and do not involve phase changes or chemical additives. Additionally, they are modular, easy to scale-up and characterized by low energy consumptions (Mulder, 1998).

In these processes fluids and solutes are selectively transported through a permselective barrier (membrane) under a hydrostatic pressure applied across it. As a result the feed solution is converted into two different streams: a solution containing all components which have permeated the membrane (permeate) and the remaining one containing all compounds rejected by the membrane (retentate) (Fig. 2.1). In most cases the feed flows tangentially to the membrane surface and the term ‘cross-flow filtration’ is used to describe such applications.

The separation mechanism in both MF and UF process is based on a sieving effect and particles are separated according to their dimensions although the separation is influenced by the interactions between the membrane itself and the particles being filtered. MF membranes generally have a symmetric structure and pores with diameter from 0.1 to 10 μm. Such membranes retain dispersed particles such as colloids, fat globules or cells: these particles are generally larger than those separated by UF and RO. Consequently, the osmotic pressure for MF is negligible and hydrostatic pressure differences used in MF are relatively small (in the range of 0.05–0.2 MPa).

The term UF is used when dissolved molecules or small particles with diameter not larger than 0.1 μm are separated from a solvent or other low molecular weight compounds. Most UF membranes are asymmetric in structure with a dense active layer of 0.5–1 μm in thickness supported by a more porous support layer of greater thickness. Pore sizes in the skin layer are in the range 2–10 nm. Performance data of UF membranes are generally presented by membrane manufacturers in terms of molecular weight cut-off (MWCO), defined as the equivalent molecular weight of the smallest species that exhibit 90% rejection. The MWCO for UF membranes ranges between 2 and 300 kD (kilo Dalton).

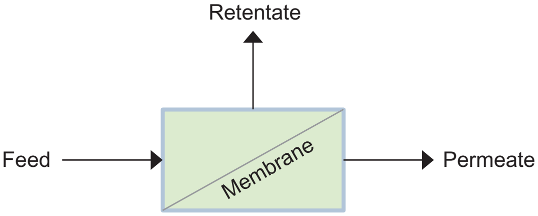

Figure 2.1. Schematic representation of a membrane process.

Typical rejected species include biomolecules, polymers and colloidal particles, as well as emulsions and micelles. Hydrostatic pressures are required to decrease with increasing MWCO and are generally between 0.1 and 0.5 MPa. In both MF and UF processes the filtration rate can be expressed by:

$$J = L_\mathrm{v}\frac{\Delta p}{l} \tag{2.1}$$

where J is the permeate flux across the membrane, Δp the pressure difference between the feed and the permeate solution, l the membrane thickness and L_v is the hydrodynamic permeability of the membrane.

The separation characteristics of MF and UF membranes can be expressed in terms of membrane rejection or retention (R):

$$R = \left(1 - \frac{C_\mathrm{p}}{C_\mathrm{f}}\right) \cdot 100 \tag{2.2}$$

where C_p is the solute concentration in the permeate and C_f the solute concentration in the feed. Rejection values are between 0% (for solutes having the highest probability to pass through the membrane) and 100% (when solutes are completely retained by the membrane).

The volume reduction factor (VRF) in UF and MF processes is defined as the ratio between the initial feed volume and the volume of the resulting retentate given by:

$$VRF = \frac{V_\mathrm{f}}{V_\mathrm{r}} \tag{2.3}$$

where V_f and V_r are the volume of feed and retentate, respectively.

2.2.1.2 *Mode of operation*

MF and UF processes can be operated either in dead-end or in cross-flow configurations. Dead-end UF (Fig. 2.2a) is used on small-scale and laboratory applications: the feed flow is forced perpendicularly through the membrane causing a build-up of retained particles at the membrane surface and the formation of a cake layer. The thickness of the cake layer increases with the filtration time; therefore, the permeation rate decreases by increasing the cake layer thickness. The cross-flow mode (Fig. 2.2b) is largely used on medium- and large-scale processes. In this approach the fluid to be filtered flows tangentially to the membrane surface and permeates through the membrane due to the imposed transmembrane pressure (TMP) difference. This configuration allows minimizing the accumulation of solute and particles near the membrane surface. In addition, the recirculation of the retentate stream to the feed tank is facilitated and can be applied to mixing with fresh feed.

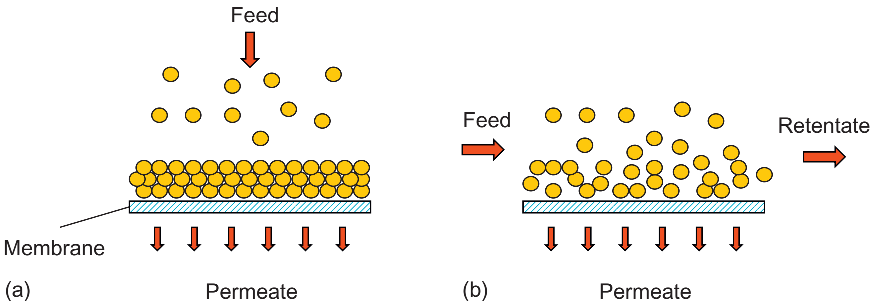

Figure 2.2. Mechanism of dead-end (a) and cross-flow (b) filtration.

Cross-flow MF and UF can be operated in different configurations, depending on the requirements of the process. Commonly used modes of operation are total recycle, batch concentration, feed-and-bleed and diafiltration (Cheryan, 1998; Ho and Sirkar, 1992).

In the total recycle configuration both permeate and retentate streams are recycled in the feed tank. This configuration is mainly used in research to measure the permeate flux at different operating conditions. In the batch mode, the retentate is recycled back to the feed tank while the permeate is collected separately. As a result, the concentration of particles increases with time. This configuration is usually restricted to small-scale operations. The feed-and-bleed configuration is commonly used at industrial level to obtain high concentration factors. The permeate is collected separately and the retentate is removed from the system when its final concentration is reached. Most of the retentate is recycled to maintain high tangential velocities through the membrane.

In the diafiltration operation the retentate is recycled in the feed tank and the fresh solvent (generally water) is added to the feed tank simultaneously with filtration. This configuration is typically used to improve the removal of dissolved solute species through the membrane system.

2.2.1.3 *Membranes and membrane modules*

MF and UF membranes can be polymeric or inorganic. Membrane materials must be chemical resistant to both feed and cleaning solutions, mechanically and thermally stable, and characterized by high selectivity and permeability. Polysulfone (PS), polyethersulfone (PES), polyamide (PA), cellulose acetate (CA), polyacrylonitrile (PAN), polytetrafluoroethylene (PTFE), poly(vinylidene F^-) (PVDF) and polypropylene (PP) are typical materials commonly used to cast the membrane. Alumina, zirconia and ceramic materials are usually used as inorganic materials.

Polymeric membranes, even if largely used in different industrial sectors, can operate in limited conditions of pH and temperature. Ceramic membranes offer a greater chemical, mechanical and thermal stability; on the other hand, the available pore size range is more limited.

The separation process in UF and MF systems is realized in proper devices known as membrane modules. A membrane module must be able to support the membrane, to minimize the concentration polarization phenomenon and to provide a large surface area in a compact volume.

The most common configurations of cross-flow modules are the plate-and-frame, spiral-wound, tubular and hollow-fiber types (Fig. 2.3).

Flat-sheet membranes are normally assembled in plate-and-frame devices together with porous support plates and spacers forming the feed flow channels. The feed solution is pressurized in the housing and forced across the membrane (Fig. 2.3a). The support plate provides a flow channel for the permeate that is collected from a tube on the side of the plate. Feed channel heights vary from 0.3 to 0.75 mm depending on the viscosity of the feed solution to be filtered.

In the spiral-wound configuration membranes are sandwiched together with feed flow channel spacers and the porous membrane support around a central permeate collecting tube (Fig. 2.3b). Commercial systems are about 1 meter long with diameters between 10 and 60 cm. Membrane areas can be in the range of 3–60 m^2. Spiral-wound membranes offer a good membrane surface/volume and low capital/operating cost ratios. Nevertheless, they cannot be mechanically cleaned and a feed pretreatment is required.

In tubular membrane modules membranes are cast on a relatively thick and mechanically strong porous support material. Tube diameters are typically in the range of 10–25 mm. The feed solution is fed through the tubular bundle while the permeate is collected on the shell side of the module (Fig. 2.3c). These systems allow an efficient control of the concentration polarization and membrane fouling phenomena and are easy to clean. However, as the tube diameter increases, they occupy a larger space and require high pumping costs.

Hollow fiber membrane modules (Fig. 2.3d), consisting of fibers with diameters of 0.001–1.2 mm, offer the highest packing density of all modules available on the market and can withstand relatively high pressures. However, the control of concentration polarization and membrane fouling is difficult and an extensive pretreatment of the feed solution is required in order to remove particles, macromolecules or other materials which can precipitate at the membrane surface.

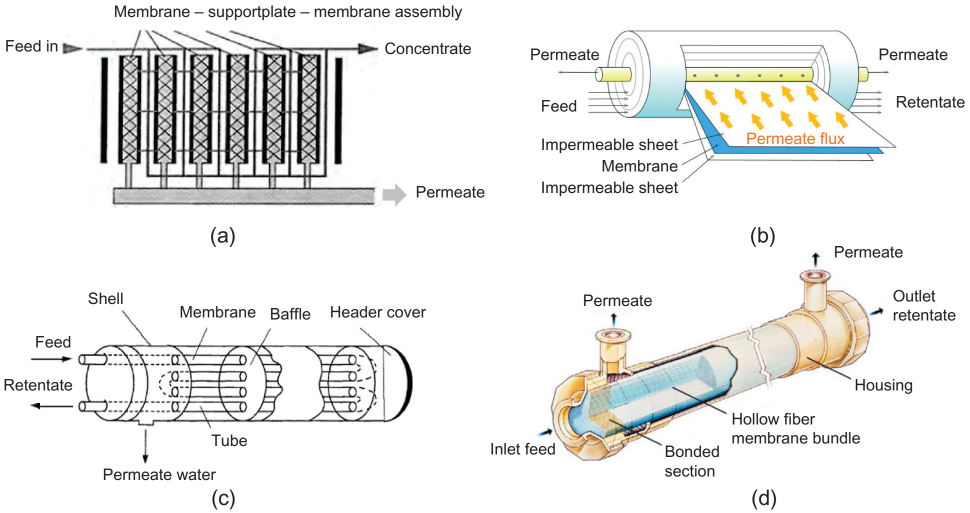

Figure 2.3. Schematic representation of plate-and-frame (a), spiral-wound (b), tubular (c) and follow-fiber (d) membrane modules.

2.2.1.4 *Concentration polarization and membrane fouling*

In both MF and UF processes the accumulation of rejected particles over the membrane surface under a given pressure leads to a development of a thin boundary layer adjacent to the membrane surface. This phenomenon, depicted in Figure 2.4, is known as concentration polarization (Fane, 1984; Rautenbach and Albrecht, 1986). The increased concentration of rejected solutes at the membrane surface leads to a reduction of the permeate flux, a modification of the rejection characteristics of the membrane, a decline in the driving force (as the osmotic pressure at the membrane-solution interface increases with concentration) and, often, the formation of a gel type layer over the membrane surface due to the precipitation of rejected solutes on the membrane.

The flux decay due to concentration polarization has been attributed to the hydrodynamic resistance to the solvent flow, in addition to the membrane resistance, generated by the accumulated solute on the membrane surface. Generally, small particles tend to form a dense particle cake layer, while large macromolecules provide a "gel" layer. According to another view the accumulation of solutes on the membrane surface results in a higher osmotic pressure with a decrease in the driving force (Cheryan, 1998).

The film theory assumes that the concentration gradient generated by the convective transport of solute to the membrane surface causes a diffusive transport of solute back into the bulk of the solution. At steady state the convective transport is counterbalanced by the diffusive flux. This is described mathematically by:

$$-D\frac{dC}{dx} = JC_{\mathrm{B}} \tag{2.4}$$

where D is the diffusion coefficient, dC/dx the concentration gradient over a differential element in the boundary layer, C_{B} the bulk concentration of rejected solute and J the permeate flux.

If D is assumed constant, this expression may be integrated to the boundary conditions to give:

$$J = \frac{D}{\delta}\ln\frac{C_{\mathrm{G}}}{C_{\mathrm{B}}} = k\ln\frac{C_{\mathrm{G}}}{C_{\mathrm{B}}} \tag{2.5}$$

where C_{G} is the gel concentration, δ the thickness of the boundary layer and $k = D/\delta$ is the mass transfer coefficient.

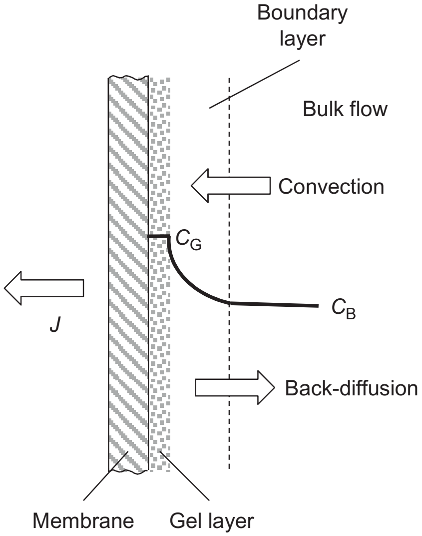

Figure 2.4. Schematic of concentration polarization (C_G = gel concentration; C_B = bulk concentration; J = permeate flux).

According to this model the permeate flux at steady-state is independent of the imposed pressure drop and it is controlled by the concentration polarization boundary layer. The increasing pressure drop results in a thicker solute layer until convection and diffusion in the boundary layer will balance again.

A more simple approach to describe the membrane flux in case of a gel or a cake layer formation is based on the use of the "resistance-in-series" concept. According to this model, the osmotic pressure of the feed solution can be neglected and the permeate flux can be expressed as:

$$J = \frac{\Delta p}{\mu(R_m + R_f + R_p)} \tag{2.6}$$

where μ is the viscosity of the solvent, Δp the transmembrane pressure, R_m the membrane resistance, R_f the fouling layer resistance and R_p the polarization layer resistance (Fane, 1983).

Concentration polarization phenomena in MF and UF processes can be minimized by using different approaches including increasing the cross flow velocity, insertion of turbulence promoters, chemical modification of the membrane surface, application of electrical fields influencing the charge on macromolecules, use of ultrasonics inducing cavitation at the surface and inert gas inducing turbulence.

The term *membrane fouling* is used to describe a long term flux decline caused by the interactions between retained particles and the membrane surface and/or membrane pores. It may occur due to a concentration polarization layer development over the membrane surface, the formation of a cake layer and/or a blockage of the membrane pores.

Solute properties (conformation, hydrophobic interactions, charge, etc.), operating conditions (cross-flow velocity, pressure and temperature) and membrane material are all factors which affect membrane fouling.

The consequences of membrane fouling are in terms of higher capital costs due to the lower average permeate flux, reduction of operating life of the membrane due to the use of cleaning agents to restore membrane flux, change of the effective sieving and transport properties of the membranes (Cheryan, 1998).

Methods and strategies to reduce membrane fouling include feed pretreatment systems, selection of appropriate membranes and membrane modules, change of membrane properties, selection of proper operating conditions and membrane cleaning.

Although the flux decline is a typical aspect involved in concentration polarization and membrane fouling, there are some substantial differences between these phenomena. Concentration polarization is a reversible process which takes place over a few seconds. It can be easily controlled by decreasing the TMP, lowering the feed concentration or increasing the cross-flow velocity. In membrane fouling, the flux decline is irreversible and takes place over many minutes, hours or days. It is more difficult to describe and to control experimentally. In addition, a continuous flux decline can often be observed.

2.3 ARSENIC REMOVAL BY USING MICROFILTRATION

MF membranes can remove only particulate forms of As in water since their pore size is too large to remove dissolved or colloidal species of As (Amy *et al.*, 2000). Unfortunately, the content of As as a particulate in water is very low. Coagulation and flocculation processes prior to MF can increase the particle size of As bearing species and, consequently, improve the As removal efficiency.

2.3.1 *Combined process coagulation/MF*

A combined coagulation/MF system to remove As from groundwater in Albuquerque (New Mexico) was investigated by Ghurye *et al.* (2004). In this approach an iron-based coagulant, such as ferric chloride, is added in water to form a $Fe(OH)_3$ precipitate with a net positive charge on the surface. At pH values between 4 and 10 arsenite is neutral in charge, while arsenate is negatively charged: therefore it can be adsorbed onto the positively charged precipitate by surface complexation. A MF membrane with a nominal pore size of 0.2 μm is used in the following step to remove the adsorbed As. The process allows production of treated water containing less than 2 μg As L^{-1} (starting from a feedwater with 40 μg As L^{-1}) using either 7 mg L^{-1} of ferric chloride, without a pH reduction, or a smaller dose of 1.9 mg L^{-1} Fe after the addition of sulfuric acid to reduce the pH value at 6.4. No increase in TMP was observed on a pilot-scale process after five days of continuous operation as a consequence of a low fouling index of the membrane.

When compared with ion exchange and activated alumina adsorption, the combined coagulation/MF system presents lower capital and maintenance costs. The principal differences are related to the large salt requirement for the ion exchange process and to the necessity of reducing the pH to 6 for activated alumina adsorption, followed by base addition to stabilize water (Chwirka *et al.*, 2000).

The combined coagulation/NF has been recognized by the USEPA as an emerging technology for the removal of As from drinking water. A summary of the process concepts, chemistry and design considerations for the use of this technology is reviewed by Chwirka *et al.* (2004).

The removal efficiency for arsenite is poor if compared to that for arsenate since arsenite exists as a neutral species and the coagulation processes rely upon ionic interactions. Consequently, a complete oxidation of arsenite to arsenate is needed.

According to the results of Brandhuber and Amy (1998) the most important variables controlling As removal are pH and concentration of ferric chloride. In particular, the As removal increases by increasing the coagulant dose, while the percentage of As removal decreases by increasing the pH value in the range from 6 to 9. The apparent size of the As bearing floc remains in the submicron range for coagulant doses (as mg L^{-1} $FeCl_3$) between 5 and 20 mg L^{-1}. For coagulant doses of 25 mg L^{-1} most As is removed as flocs of apparent size greater than 1 μm. For a MF membrane with a pore size of 0.2 μm the following equation was found to describe empirically the hyperbolic relationship between dose and As removal:

$$\%\ \text{As removal} = 100 \cdot \frac{k \cdot \text{Dose}}{1 + k \cdot \text{Dose}} \tag{2.7}$$

where $k = 0.332\ \text{L mg}^{-1}$ and Dose is the $FeCl_3$ dose in mg L^{-1}.

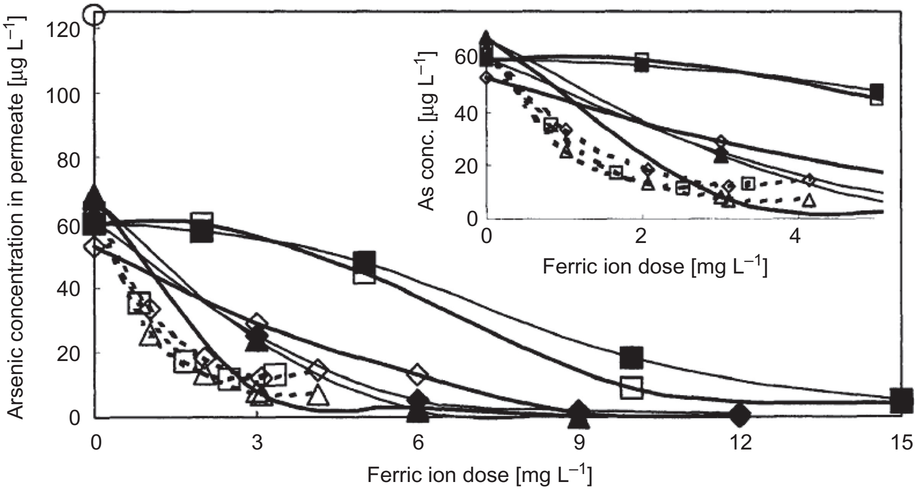

Figure 2.5. Effect of raw water pH on the variation of residual arsenic concentration with ferric ion dose. After coagulation, the suspension was vacuum filtered using 0.22 μm pore size membrane disk. ■ + thin solid line: US water, pH 8.7, $Fe_2(SO_4)_3$ as coagulant; ◆ + thin solid line: US water, pH 6.8, $Fe_2(SO_4)_3$ as coagulant; ▲ + thin solid line: US water, pH 6.2, $Fe_2(SO_4)_3$ as coagulant; □ + thick solid line: US water, pH 8.7, $FeCl_3$ as coagulant; ◇ + thick solid line: US water, pH 6.8, $FeCl_3$ as coagulant; △ + thick solid line: US water, pH 6.2, $FeCl_3$ as coagulant; ○ unfiltered Bangladesh water, pH 7.5; ◇ + dashed line: Bangladesh water, pH 6.8, $Fe_2(SO_4)_3$ as coagulant; △ + dashed line: Bangladesh water, pH 6.2, $Fe_2(SO_4)_3$ as coagulant; □ + dashed line: Bangladesh water, pH 6.8, $FeCl_3$ as coagulant (Wickramasinghe *et al.*, 2004, with permission from Elsevier).

A similar relationship, but with a *k* value of 0.496, was found by Brandhuber and Amy (1998) in pilot tests performed by using a Memcor 4M1W 0.2 μm MF unit and coagulant doses of $FeCl_3$ from 2 to 10 mg L^{-1}. A dose of 7.0 mg L^{-1} as $FeCl_3$, a permeate flux of about 170 L m^{-2} h^{-1} and a 90% recovery were identified as optimum operating conditions for the pilot plant. In these conditions, an average As rejection and turbidity reduction of 84% and 64%, respectively, were obtained. Membrane fouling was successfully controlled by air backwashes of the membrane at 15 minute intervals.

Wickramasinghe *et al.* (2004) evaluated the removal of As from USA and Bangladesh groundwater by using a combined approach coagulation/MF. Ferric chloride or ferric sulfate was used as coagulant. In addition, a cationic polyelectrolyte (CY 2461, Cytec Industries, Stamford, CT) was also tested as a coagulant aid (doses were of 0.02 and 0.3 mg L^{-1}). MF was performed by using hollow-fiber membranes from A/G Technology (Needham, MA) with nominal pore size of 0.1 μm. Results of bench-scale experiments indicated that the As removal is highly dependent on the raw water quality and the used coagulants gave efficient results; however, the use of ferric sulfate led to a lower residual turbidity in the treated water. The addition of polyelectrolyte as a coagulant aid improved the permeate flux but had no effect on the As residual concentration. In a pH range of 6.2–8.7 the As removal was improved by decreasing the pH value (Fig. 2.5). This result can be explained assuming that when pH is lowered, the As adsorption is increased leading to an increased particle size (Jain and Loeppert, 2000; Meng *et al.*, 2000). Consequently, also the membrane rejection towards precipitate particles at a given ferric ion dose is increased by decreasing pH. Therefore, pH adjustment may be necessary in order to reduce the ferric ion dose required.

Similar results were obtained by Han *et al.* (2002) in a combined system flocculation/MF in which ferric chloride and ferric sulfate were used as flocculants and mixed esters of cellulose acetate and cellulose nitrate with pore sizes of 0.22 and 1.2 μm as MF membranes. Flocculation prior to MF led to significant As removal in the permeate with a consequent reduction of its turbidity.

Recently the combination of the electrocoagulation (EC) process and MF was found to be effective in removal 98.9% of As from a feed solution containing 200 μg As L^{-1} in presence of fluoride and iron contaminant (Ghosh *et al.*, 2011).

MF processes are characterized by lower energy requirement and higher fluxes when compared with NF and RO. Consequently, the combination of flocculation with MF represents a cost effective method to reduce the As content of drinking water.

2.4 ARSENIC REMOVAL BY USING ULTRAFILTRATION

UF membranes, similarly to MF membranes, are not able to remove dissolved or colloidal species of As in water due to their large pore size. However, significant removal efficiencies can be achieved by using UF membranes negatively charged, colloid-enhanced UF (CEUF) and electro-ultrafiltration (EUF).

2.4.1 *Negatively charged UF membranes*

UF membranes with electric repulsion show a better As removal efficiency when compared to UF membranes with only pore-size dependent sieving. The influence of membrane charge on the As removal efficiency was investigated in bench-scale tests by Amy *et al.* (1998). Negatively charged GM2540F UF membranes (supplied by GE Osmonics, Minnetonka, MN) gave a 63% rejection of As(V) at neutral pH but a very low rejection at acidic pH. A poor rejection for both As(III) and As(V) species was observed by using an uncharged UF membrane (FV2540). So the high removal rate of As(V) was attributed to the electrostatic interaction between As ions and the negatively charged membrane surface. Pilot-scale studies showed As removal of about 70% in groundwater with high dissolved organic compounds and lower rejections (about 30%) in those with low dissolved organic compounds. This behavior was attributed to the adsorption of natural organic matter which reduces the membrane surface charge increasing the repulsion towards negatively charged As.

The influence of operating conditions and water quality on the As rejection of negatively charged UF membranes was evaluated by Brandhuber and Amy (2001). Bench-scale experiments were carried out by using a flat-sheet cross flow cell equipped with a thin film composite sulfonated polysulfone membrane having a MWCO of 8 kDa (GE Osmonics, GM). The observed trends of As(V) rejection were in agreement with the Donnan exclusion mechanism. In particular, a reduction of As(V) rejection was observed by increasing the bulk As(V) concentration and the ionic strength of the feed solution. The presence of co-occurring divalent ions, such as Ca^{2+} and Mg^{2+} reduced also the As(V) rejection. This phenomenon was attributed to the formation of ion pairs between counter ions and the fixed charged group in the membrane matrix, which locally neutralizes the membrane charges. According to the Donnan equilibrium, the As(V) rejection slightly increased with increasing flux at constant recovery (Bhattacharyya and Grieves, 1978). An increasing recovery at constant permeate flux produced a substantial decrease in apparent As rejection due to a decrease in membrane cross-flow velocity. According to the concentration polarization phenomenon, a decrease in cross-flow velocity results in a thicker boundary layer, decreased solute back transport and a greater concentration of As at the membrane surface. A slight reduction of As rejection by increasing the temperature in the range 20–40°C was attributed to the increased diffusivity of As with temperature which in turn increases the diffusive transport of As across the membrane. The presence of natural organic matter (NOM) improved the As(V) rejection in presence of divalent cations. This phenomenon can be attributed to the complexation capacity of divalent ions, such as Ca^{2+} and Mg^{2+}, with organic matter (Mathuthu and Ephraim, 1993) with a consequent modification of free ion distribution at the membrane surface. This leads to a reduction of the equilibrium partitioning of As ions into the membrane reducing their transport through the membrane and, consequently, the As rejection. In addition, the adsorption of organic matter onto the membrane surface leads to a formation of a negatively charged layer in the adjacent membrane layer increasing the rejection of negatively charged As species.

The applicability of polyacrylonitrile (PAN)-based negatively charged UF membrane for As removal was demonstrated for the first time by Lohokare *et al.* (2008). The surface of flat-sheet PAN-based UF membranes was hydrolyzed by using NaOH in cross-flow mode: this approach led to the reduction in pore size (as demonstrated by the reduction in water flux and the increased rejection towards proteins and polyethylene glycol) due to the formation of carboxylate ($-COO^-$) groups on both membrane and pore wall surfaces and an increased membrane hydrophilicity. The MWCO after the NaOH treatment was found to be of about 6 kDa. These modified membranes showed excellent As(V) rejections (close to 100%) when simulated solutions containing 50 $\mu g\,L^{-1}$ of As in pure water were used as feed samples. For these samples the rejection coefficient was independent of cross-flow velocity and TMP. For feed samples containing 1000 $mg\,L^{-1}$ of As the rejection was between 40 and 65% depending on the cross-flow velocity and TMP and, consequently, on concentration polarization phenomena.

The effect of foulants, such as ovalbumin, humic acid and egg white, on the As(V) rejection of modified PAN UF membranes has been recently investigated (Agarwal *et al.*, 2013). Results indicate a decreasing in As(V) rejection with increasing concentration of proteins and humic acid. In addition the As(V) rejection was affected by the total quantity of proteins and not by the variety of proteins in the feed solution.

2.4.2 *Colloid-enhanced ultrafiltration (CEUF)*

Colloid-enhanced ultrafiltration (CEUF) is a separation technique based on the use of colloids able to bind multivalent metal ions by electrostatic interactions. The colloidal solution is then filtered under pressure through a UF membrane with a pore size smaller than the size of the colloid, producing a purified water stream (permeate) and a concentrated stream containing almost all of the colloid and metal ions (retentate) (Dunn *et al.*, 1989). CEUF can be distinguished in micellar-enhanced ultrafiltration (MEUF), if the colloidal species is a micelle-forming surfactant, and in polyelectrolyte-enhanced ultrafiltration (PEUF) when the colloidal species is a polyelecrolyte.

2.4.2.1 *Micellar-enhanced ultrafiltration (MEUF)*

Micellar-enhanced UF (MEUF) is a technology that employs surfactant micelles to solubilize inorganic and organic pollutants from effluent streams (De and Mondal, 2012). It is particularly effective for removal of metal ions (Juang *et al.*, 2003; Liu and Li, 2005; Rahmanian *et al.*, 2010), small amounts of organic substances (Adamczak *et al.*, 1999; Dunn *et al.*, 1985; Sabatè *et al.*, 2002) and anionic pollutants such as chromate, nitrate and phosphate (Baek and Yang, 2004; Morel *et al.*, 1997).

Surfactants are usually organic compounds containing both hydrophobic groups acting as their *tails* and hydrophilic groups acting as their *heads*. Typically, the tail consists of a hydrocarbon chain which can be branch, linear or aromatic. In the bulk aqueous phase, surfactants form micelles where the hydrophobic tails form the core of the aggregate and the hydrophilic heads are in contact with the surrounding liquid (Fig. 2.6).

Other types of aggregates such as spherical or cylindrical micelles or bilayers can be formed depending on the balance of the sizes of the hydrophobic tail and the hydrophilic head.

Surfactants are generally classified according to the polar head group as: non-ionics (if they have no charge groups in their head), anionics (if the head carries a negative net charge), cationics (if the head carries a positive net charge) and zwitterionics (if the head contains two oppositely charged groups).

When a cationic surfactant is added to contaminated water above its critical micelle concentration (CMC), it forms micelles positively charged on the surface which can adsorb anionic As

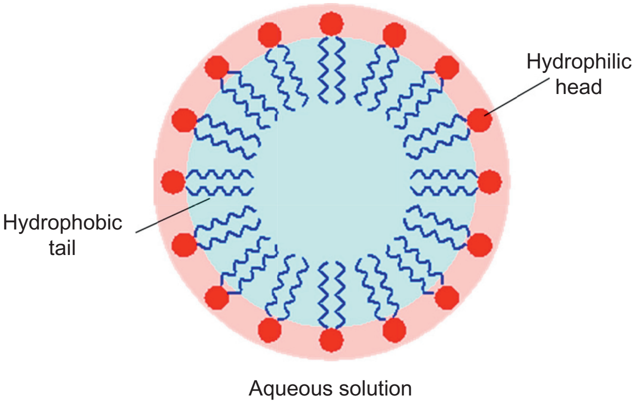

Figure 2.6. Schematic representation of spherical micelles.

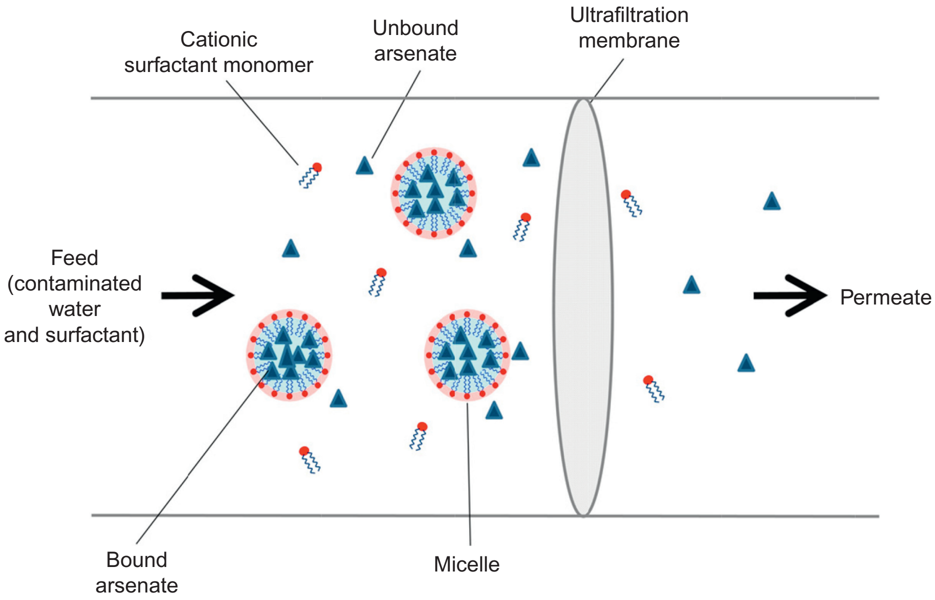

Figure 2.7. Schematic of As removal process by MEUF.

species (arsenite or arsenate) by electrostatic interaction. These micelles can be efficiently separated from aqueous streams by using UF membranes whose pores are too small to allow their permeation (Fig. 2.7).

Gecol *et al.* (2004) investigated the removal of As(V) from water by using flat sheet UF membranes and cetylpyridinium chloride (CPC) as cationic surfactant. In particular, regenerated cellulose (RC) membranes with a MWCO of 10 kDa and polyethersulfone (PES) membranes with MWCO of 5 and 10 kDa were used. When membranes were used without surfactant micelles PES membranes exhibited a lower As removal than RC membranes. This was attributed to the negatively charged surface of RC membranes and, consequently, to a Donnan exclusion mechanism. However, in both cases the As concentration in the permeate stream was higher than the MCL of $10\,\mu g\,L^{-1}$. The addition of CPC (10 mM) reduced the As concentration in the permeate of all tested membranes well below the MCL.

Both As removal and permeate fluxes were influenced by membrane materials, MWCO and pH. The maximum As removal was obtained with 5 kDa PES membranes at pH 5.5 and 10 kDa RC membranes at pH 8.

The presence of co-occurring inorganic solutes, such as HCO_3^-, HPO_4^{2-}, H_4SiO_4 and SO_4^{2-} species, did not affect the As(V) removal efficiency when a PES 5 kDa membrane was used in combination with CPC (Ergican *et al.*, 2005). Permeate fluxes decreased by increasing the As concentration of the feed water and the co-occurring inorganic solute concentration.

CPC exhibited the highest As removal efficiency (96%) when used in combination with RC membranes of 3 and 10 kDa (YM3 and YM10, Amicon, USA). The removal of arsenate with hexadecyltrimethylammonium bromide (CTAB), benzalkonium chloride (BC) and octadecylamine acetate (ODA) at a surfactant concentration of 10 mM was of 94, 81 and 55%, respectively (Iqbal *et al.*, 2007).

2.4.2.2 *Polyelectrolyte-enhanced ultrafiltration (PEUF)*

Water soluble polymers with ion exchange properties can be efficiently used to remove ions from aqueous medium. For example, polymeric electrolytes containing quaternary ammonium groups, as ion-exchanged cationic groups, have been extensively investigated for their metal ion binding properties (Rivas *et al.*, 2006a; 2006b). The arsenate retention with two cationic water-soluble polymers containing tetra alkylammonium groups (poly[2-(acryloyloxy)ethyl]trimethylammonium chloride and poly[2-(acryloyloxy)ethyl]trimethylammonium methyl sulphate) was investigated by Rivas *et al.* (2007) by using the liquid-phase polymer-based retention (LPR) technique. Results demonstrated a greater retention property for the cationic soluble polymer containing chloride counteranions at pH 8.

The addition of water-soluble polymers followed by ultrafiltration, named as polyelectrolyte-enhanced ultrafiltration (PEUF), can be efficiently exploited to remove ionic species from aqueous solutions. This process is based on the use of a polyelectrolyte having an opposite charge to that of the target ions and the formation of macromolecular complexes between pollutant ions and polymer due to electrostatic attractions. These complexes are too large to pass through a UF membrane so they are retained in the retentate streams. Examples of separation of both cationic and anionic metal ions by PEUF have been extensively reported (Christian *et al.*, 1995; Tabatabai *et al.*, 1995a; Tangvijitsri *et al.*, 2002).

The use of PEUF for the removal of As anions from water has been investigated by Pookrod *et al.* (2004). In this approach, a cationic polyelectrolyte, poly(diallyldimethyl ammonium chloride) (poly-DADMAC), was used to bind anionic As species in order to form macrocomplexes which can be retained by a UF membrane (10 kDa RC acetate membrane, Millipore, Bedford, MA). The repeating unit of the polymer is $(H_2CCHCH_2)_2N(CH_3)_2Cl$. A schematic diagram of the process is depicted in Figure 2.8.

An increasing of the [poly-DADMAC]/[As] ratio produced an increasing of the number of positively charged sites on the polymer per unit volume and, consequently, of the fraction of bound As anions. Therefore, the As rejection is enhanced by increasing the polymer concentration.

The As rejection decreased by increasing the feed salt concentration and the valence of the added anion. This phenomenon can be attributed to the competition between arsenate and other anions (such as phosphate, silicalite, carbonate commonly present in water) for binding sites on the polymer. A similar behavior has been also observed in the As removal by using ion-exchange resins containing ammonium groups (Berdal *et al.*, 2000).

The As rejection increased by increasing the pH. In particular, an increase in pH from 6.5 to 8.5 produced an increase in As rejection from 99.06 to 99.95% due to an increasing of the ratio $HAsO_4^{2-}/H_2AsO^{4-}$ in the feed solution so improving the As binding capacity to the polymer.

The polymer concentration at which the permeate flux is zero, defined as gel point concentration, was found to be 655–665 mM (approximately 5.98–6.07 wt%). These values allow high water recoveries (higher than 99%) to be obtained. An advantage of the PEUF system in the

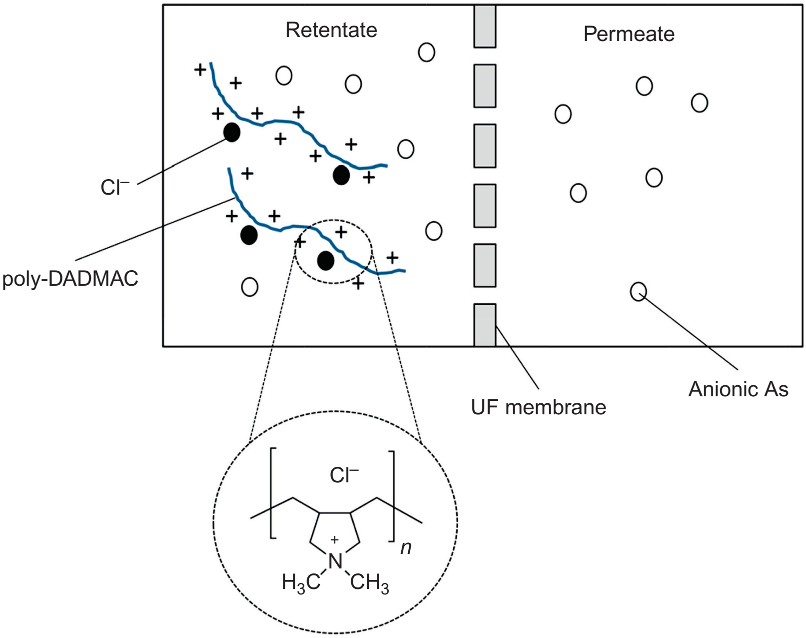

Figure 2.8. Schematic diagram of PEUF to remove anionic arsenic from water.

removal of As, if compared with other pollutants, is that the As feed concentration is often very low (lower than 100 $\mu g\,L^{-1}$).

Pookrod *et al.* (2004) estimated that for a [poly-DADMAC]/[As] ratio of 100 and an As feed concentration of 100 $\mu g\,L^{-1}$ the retentate could be concentrated by a factor of 547 (up to 72.9 mM), when the relative flux is reduced to 0.4, with a permeate/feed volume of 0.998.

PEUF shows a greater potential when compared with a combination of ion exchange and UF for the removal of hardness ions as well as viruses, bacteria and pyrogen (Tabatabai *et al.*, 1995b). The formation of polarized layers due to the presence of polyelectrolites is one of the disadvantages of the PEUF process since it has a detrimental effect on permeate fluxes and total costs. The combination of colloids as well as the development of improved turbulence promoters has been suggested as a source of further sustainable growth of the PEUF process.

2.4.3 *Electro-ultrafiltration (EUF)*

As previously reported, the pore size of MF and UF membranes is too small to remove arsenite and arsenate species whose molecular weights are 126 and 142 $g\,mol^{-1}$, respectively. Typical As(III) and As(V) rejections of UF membranes (Brandhuber and Amy, 1998) are 5 and 40%, respectively. NF and RO processes, based on the use of dense membranes, allow obtaining higher separation efficiencies. The different charge characteristics of As(III) and As(V) species are very important factors that should be carefully considered when these membrane technologies are employed for As removal. At neutral pH the predominant species for As(V) are $H_2AsO_4^-$ and $HAsO_4^{2-}$ which means that As(V) exists as an anion at a typical pH in natural water (pH 5–8), whereas in this range of pH As(III) is mainly present as uncharged species (H_3AsO_3) and, therefore, is less efficiently rejected by RO or NF membranes (Amy *et al.*, 1998; Brandhuber and Amy, 2001; Geucke *et al.*, 2009; Uddin *et al.*, 2007a).

The role of Donnan exclusion in the As removal from water by using loose NF membranes was investigated by Seidel *et al.* (2001): they found that the removal of As(V) increased from

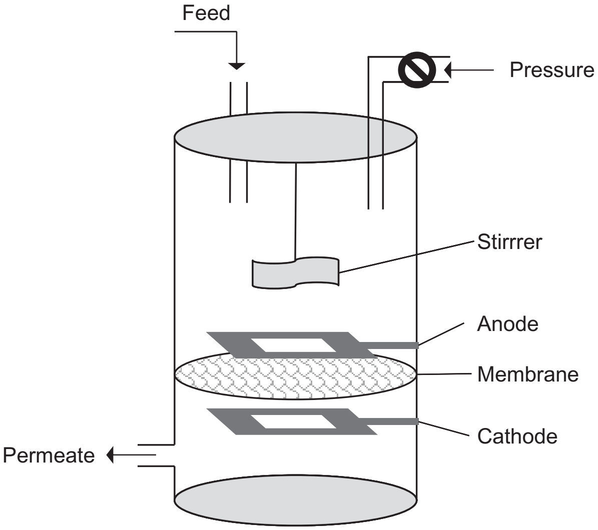

Figure 2.9. Schematic diagram of electro-ultrafiltration (adapted from Saxena *et al.*, 2007).

60 to 90% as the As feed water concentration was increased from 10 to 316 μg L^{-1}; in a similar range of feed concentration the rejection of As(III) decreased from 28 to 5%.

According to these results, the performance of UF membranes in the removal of As from water can be enhanced through the application of an electric field across the membrane in order to attract the As charged species. In this process, called electro-ultrafiltration (EUF), the electric field acts as an additional driving force to the TMP (Charcosset, 2012; Huotari *et al.*, 1999; Saxena *et al.*, 2009). The electric gradient is generally applied by two parallel electrodes positioned on either side to the UF membrane. In most cases platinum electrodes are inserted into the feed and permeate channels (Saxena and Shahi, 2007). When an electric field is applied to the system a displacement of charged species towards the electrode with the opposite sign occurs (Fig. 2.9).

EUF has been largely investigated for separation or concentration of protein solutions (Sung *et al.*, 2007; Zhou *et al.*, 1995). In addition, it is an effective method to decrease the gel layer formation on the membrane surface and to increase the filtration flux due to electrokinetic phenomena such electrophoresis and electroosmosis (Weber and Stahl, 2003).

The removal of As and humic substances (HSs) from water by using EUF was investigated by Weng *et al.* (2005). The laboratory scale EUF system was equipped with a polyacrylonitrile (PAN) UF membrane with a MWCO of 100 kDa (GE Osmonics). Results indicated that the As(V) rejection in presence of humic acid increased from 30% to more than 90% when an electric voltage was applied. On the other hand, the As(III) rejection was lower than 20%, independently on the presence of humic substances, even with the addition of electrical voltages (Fig. 2.10).

Since As(III) is non-ionic at a neutral pH it is not influenced by the electrical field. However, the removal of As(III) can be enhanced through the oxidation of As(III) to As(V) (Bissen and Frimmel, 2003) or by increasing the pH of water thus leaving As(III) negatively charged (Kang *et al.*, 2000).

The EUF system was also tested on two groundwater samples coming from the I-Ian County in the northeastern part of Taiwan (Chaung-Hsieh *et al.*, 2008). The removal of As in absence of an electrical voltage was in the range of 1–14%. The application of an electrical voltage of 25 V to the UF system reduced the total As concentration in both groundwater samples by over 79%. The association between As(III) species and dissolved organic matter was suggested as a possible factor enhancing the As removal.

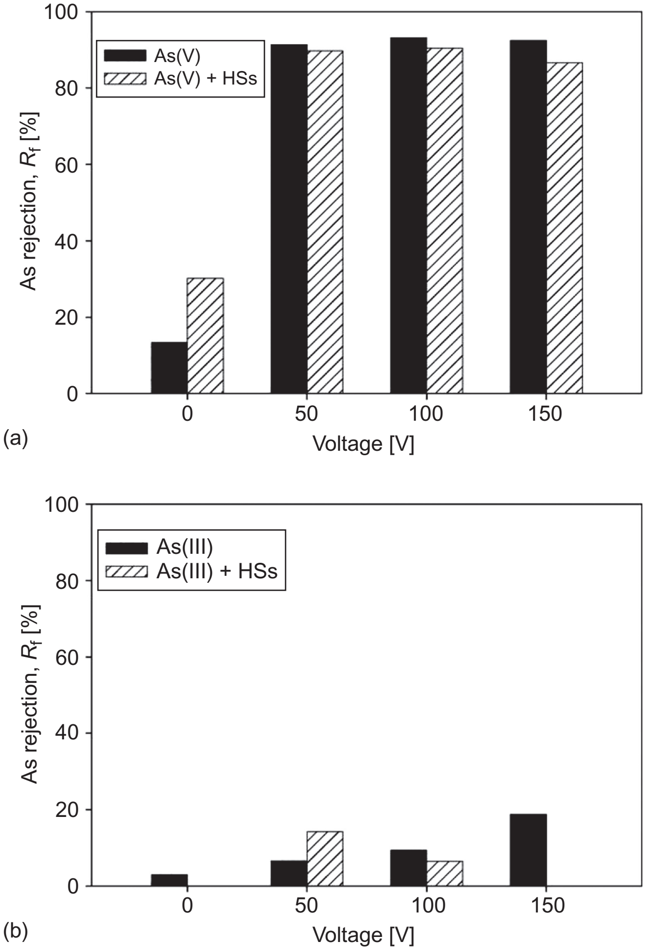

Figure 2.10. Removal of synthetic (a) As(V) and (b) As(III) from water by EUF at different voltages (pH = 6) (Weng *et al.*, 2005, with permission from Elsevier).

2.5 CONCLUSIONS

Low pressure membrane technologies, such as MF and UF, have been demonstrated to be effective in the removal of As from water when combined with coagulation/flocculation methodologies or colloidal species such as micelle-forming surfactants and polyelectrolytes.

The removal of As by MEUF depends on the As concentration and surfactants, solution pH, ionic strength, and parameters related to membrane operation. The surfactant may account for a large portion of operating costs: therefore, the recovery and reuse of the surfactant is a key factor to make the process economically feasible and to avoid secondary pollution. However, the combination of high MWCO membranes and low surfactant concentrations can benefit the overall process economics for the lower membrane area requirement (due to greater flux) and the reduced surfactant consumption.

The use of negatively charged membranes and the application of an electric field acting as an additional driving force to the transmembrane pressure across UF membranes have been also successfully explored for the removal of As from water sources. In these approaches the removal efficiency of As(V) is higher if compared with the removal of As(III). Therefore, the use of oxidizing agents (i.e., $KMnO_4$, NaClO and ozone) improves the As removal in raw waters where As(III) is predominant. Since oxidizing agents can damage MF and UF membranes, research efforts can be addressed to explore the integration of microorganisms able to transform arsenate to arsenite (biooxidation) with MF or UF membranes.

Membrane properties and operating conditions (pH, temperature, pressure) affect the As removal efficiency and the operating costs. Therefore, they should be carefully selected and optimized for each water source.

Complexing agents have been proven to achieve selective separation of As with low energy requirements. The main parameters affecting PEUF are the polymer type, the ratio of As to polymer, pH and existence of other metal ions in the solution. Advantages of PEUF include high removal efficiency and high binding selectivity.

The combination of colloids as well as the development of improved turbulence promoters appears as an attractive way to improve the performance of the PEUF process.

NOMENCLATURE

C	concentration [$\mathrm{mol\,m^{-3}}$, $\mathrm{mol\,L^{-1}}$]
D	diffusion coefficient [$\mathrm{m^2\,s^{-1}}$]
J	permeate flux [$\mathrm{m\,s^{-1}}$]
k	mass transfer coefficient [$\mathrm{m\,s^{-1}}$]
l	membrane thickness [m]
L_v	hydrodynamic permeability [$\mathrm{m^2\,Pa^{-1}\,s^{-1}}$]
p	pressure [Pa]
R	rejection [–]
R_m	membrane resistance [$\mathrm{m^{-1}}$]
R_f	fouling resistance [$\mathrm{m^{-1}}$]
R_p	polarization layer resistance [$\mathrm{m^{-1}}$]
V	volume [$\mathrm{m^3}$]
VRF	volume reduction factor [–]
x	directional co-ordinate [m]

Greek letters

δ	boundary layer thickness [m]
Δ	difference [–]
μ	viscosity [Pa s]

Subscripts

B	bulk
f	feed
G	membrane wall (gel)
p	permeate
r	retentate

Abbreviations

As	arsenic
CA	cellulose acetate
MF	microfiltration
MWCO	molecular weight cut-off
NF	nanofiltration

PA	polyamide
PAN	polyacrylonitrile
PES	polyethersulfone
PP	polypropylene
PS	polysulfone
PTFE	polytetrafluoroethylene
PVDF	poly(vinylidene fluoride)
RO	reverse osmosis
TMP	transmembrane pressure
UF	ultrafiltration
USEPA	US Environmental Protection Agency

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CHAPTER 3

Fluoride and uranium removal by nanofiltration

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3.1 INTRODUCTION

Membrane separation processes have been extensively used for the fractionation/concentration of suspended particles and dissolved substances in different streams. In this context, nanofiltration (NF) appears attractive and has shown potential for the treatment of wastewaters. Reverse osmosis (RO), currently in widespread use to produce drinking or irrigation water from briny waters or seawater (Hassan *et al.*, 1998) seriously challenges the distillation process, whereas ultrafiltration (UF) constitutes a valuable aid for the fractionation and concentration of colloidal substances contained in seawater (Teuler *et al.*, 1999). Based on both the size of separated species and pressures involved, NF is in between the UF and RO and it has been more recently developed than the other two processes. The NF process is characterized by low energy consumption, and is usually applied to separate multivalent ions from monovalent ones, and also for separation between ions with the same valence. NF membranes are designed as "loose" or "low pressure" RO membranes; these terms define a first clear objective to NF membranes: partial rejection of salts (Forare, 2009). The main application of NF is in the wastewater treatment, water softening, desalination of brackish water and removal of several compounds, such as pollutants, pesticides, dyes, and organic solvents, from effluents. NF is a transition zone, also in terms of physicochemical interactions and transport mechanisms (solution-diffusion mechanism), with features between UF and RO (Li *et al.*, 2008). The membranes for NF have slightly larger pore size than RO membranes. In fact, NF membranes have a molecular weight cutoff (MWCO) to dissolved organic solutes of 200–1000 Dalton; while, for RO membranes, the molecular weight cut-off is less than 50 Dalton. NF membrane pore size is in the order of nanometers, particularly ≤ 2 nm, and the driving force used is a pressure in the range of 1.0–2.5 MPa (Sheppard *et al.*, 2005). These membranes are usually asymmetric, with negative surface charge at neutral and alkaline drinking water pH; which explains higher rejection of cations and anions. For this reason, the rejection (or permeation) of salts depends not only on the membrane characteristic and molecular size, but also Donnan exclusion effects. These characteristics lead to having similar ion separation degrees to RO membranes but with higher water fluxes (Forare, 2009). The most important works, dealing with the removal of uranium (U) and fluoride (F^-) by NF mainly from water, are discussed and reported in this section.

3.2 COMMON REMOVAL TECHNOLOGIES

3.2.1 *Fluoride*

Different water defluorination methods have been investigated: adsorption (Ben Nasr *et al.*, 2011; Fan *et al.*, 2003), ion exchange (Meenakshi *et al.*, 2007; Solangi *et al.*, 2009), chemicals addition to cause precipitation (Nath *et al.*, 2010; Turner *et al.*, 2005) and membrane processes such as RO, electrodialysis (ED) and NF (Amor *et al.*, 2001; Ben Nasr *et al.*, 2011; Tahaikt *et al.*, 2007). RO, activated alumina and ED are the most common F^- removal technologies (Adhikary *et al.*, 1989; Amor *et al.*, 2001; Min *et al.*, 1984; Cohen *et al.*, 1998; WHO, 2006). Activated alumina is one of a variety of precipitation and adsorption materials. Adsorption materials are widely used for F^- treatment in groundwater due to their simple handling and low costs. In Senegal, Diawara *et al.* (2011) described charcoals and clays as being efficient in F^- removal. The performance of clay in absorbing fluorine ions is strongly bounded to its specific area, the quality of the raw water, (physically and chemically) and the geometry of the filtration module. Gumbo *et al.* (1995) reported findings of a pilot defluorination plant installed in Tanzania. They described the investigations of the efficiency for the Magnesite and Nalgonda technique. For the Nalgonda technique high concentrations of aluminum and lime are used, while for the Magnesite technique, magnesia obtained by calcination of Magnesite, have been investigated. A ratio of $800\,\mathrm{mg\,L^{-1}}$ alum and $80\,\mathrm{mg\,L^{-1}}$ lime reduced the F^- concentration in average from 22 to $3.5\,\mathrm{mg\,L^{-1}}$. After passing a filter-bed filled with calcinated magnesite the F^- concentration decreased by another $1\,\mathrm{mg\,L^{-1}}$ but the pH raised to around 10 and required further treatment (Gumbo *et al.*, 1995). As another adsorbent, developed by Chen *et al.* (2012), Fe-Ti has been tested and considered as efficient and economical in terms of F^- removal from drinking water. It has been reported that this adsorbent is much cheaper and has a higher adsorption capacity (about $47\,\mathrm{mg\,g^{-1}}$) than other adsorbing materials, like zirconium oxide and rare earth metal oxides. Vaishali *et al.* (2013) described the adsorption capacity of *Citrus limonum* leaf. His group found a maximum defluoridation capacity of 70% of $2\,\mathrm{mg\,L^{-1}}$ F^- ion. The capacity was found to be dependent on the pH, adsorbent dose, contact time and initial F^- concentrations.

Despite its simplicity, the use of adsorption media has major drawbacks in particular for application in remote rural areas which is of high importance for worldwide groundwater treatment: (i) supply of adsorption media needs to be ensured, (ii) safe disposal of exhausted media or regeneration, (iii) adsorption capacity largely depends on the particular feed water quality such as e.g. presence co-ions, pH, hence in many cases safe compliance with MCL cannot be ensured.

3.2.2 *Uranium*

Solid phase/solvent extraction and membrane separation are efficient technologies for the removal of U from water (Tang *et al.*, 2003). Solid phase extraction is a highly efficient methodology for the preconcentration and purification of U traces from water (Kantipuly *et al.*, 1990). This technique is based on the use of chelating resin materials, such as modified cellulose/silica, activated carbon/alumina and polymeric resins (Hancock and Martell, 1989; Helfferich, 1962; Mahmoud and Al Saadi, 2001; Schmitt and Pietrzyk, 1985; Yaman and Gucer, 1995; Yamini *et al.*, 2002) featuring anionic functional groups (e.g., strong acid-SO_3H; weak acid-COOH; strong base-NR_3Cl; weak base-NH_2RCl) able to bind U to the resins (Kabay and Egawa, 1993; Rivas *et al.*, 2003). Fibrous polymeric adsorbents, containing amidoxime groups, have shown a growing attention in view of their several advantages, such as, i.e., high adsorption ability and selectivity for the uranyl ions uptake and easy handling and eco-compatibility (Abbasi and Streat, 1994). Chattanathan *et al.* (2013), investigated the effect of hydroxyapatite prepared from catfish bones in the removal of U from wastewater, achieving promising results in terms of adsorption efficiency. Qadeer and Hanif (1994) studied the influence of kinetic factors on the U ions adsorption on activated charcoal from aqueous solutions. Kutahyali and Eral (2004) reported U adsorption experiments on chemically activated carbon. Solvent extraction is generally based on the use of a pregnant leach solution which provides the chelation or ion-association of U and the subsequent extraction of uraniferous ions in a suitable solvent (Khopkar and Charmers, 1970; Ritcey and Ashbrook, 1984). In the leaching step, uranyl sulfates or carbonates are formed and can be efficiently extracted in anionic solvents. Di-2-ethylhexyl phosphoric acid/trioctylphosphine oxide is a good mixture for the extraction of U from phosphoric acid solutions (Mohsen *et al.*, 2013). Koban and Bernhard (2004) proposed the use of glycerol-1-phosphate for the formation of U^{6+} complexes. Singh *et al.* (2001) studied the extraction power of the system di-nonyl phenyl phosphoric acid, with di-butyl butyl phosphonate in an aliphatic diluent, obtaining promising results for the U stripping from concentrated phosphoric acid solutions. Kulkarni (2003) used trioctylphosphine oxide in paraffin oil and sodium carbonate as carrier and stripping agent, respectively for the purification of acidic wastes. One of the most promising technologies for water treatment is membrane separation. Villalobos-Rodriguez *et al.* (2012) investigated the UF removal of U using composite activated carbon cellulose triacetate membranes. The permeation based on the molecular sieving mechanism coupled with the adsorption of the cationic species by the carbon particles improved the U rejection from the aqueous medium.

3.3 REMOVAL OF DISSOLVED FLUORIDE AND URANIUM BY NF

3.3.1 *Fluoride*

NF offers selective desalination and is generally used to remove divalent ions such as sulfate and calcium ions and also to separate ions of the same valency (Ben Nasr *et al.*, 2011; van der Bruggen *et al.*, 2004). Therefore NF is typically not applied for removal of monovalent ions such as F^-. However, in the case of F^- due to its small ionic radius compared to e.g. chloride, and a consequently larger hydrate shell, the NF can offer a viable option. Hence, the smaller the ionic radii, the higher the hydration numbers; the larger the hydrated radii, the more difficult its transfer across the membrane will be (Paugham *et al.*, 2004). The NF operates under significantly lower pressure. As the treatment of F^- contaminated groundwater by NF requires only a comparably low pressure of about 0.5–1.0 MPa, this technique is a very energy efficient solution in comparison to RO. It can be easily operated by renewable energies like photovoltaic or wind turbines and therefore has a great potential to lower capital and operating costs. In fact, for applications in rural areas of less developed countries, the basic requirements are: low cost, very simple to operate and easy to maintain water treatment. Additionally, water remineralization with NF is not needed (Ben Nasr *et al.*, 2011). However, up to now, studies on F^- removal using NF membranes are limited to laboratory or small pilot trials. Table 3.1 gives an overview of different rejection rates for F^- removal. As shown in this table, NF membranes can remove up to 99% of F^- from water. Lhassani *et al.* (2001) studied defluorination of brackish water model solutions with halides such as Cl^- and I^- by use of the Dow NF 70. It has been shown that since F^- ions are more solvated than chloride and iodide ions, the small F^- ions can be better retained than the bigger halides. Under reduced pressure, this effect is even higher when selectivity is the most. By adjusting the operating conditions, the ions of same valency can be removed selectively. Hence, Diawara *et al.* (2003) also analyzed the F^- removal from brackish water model solutions by use of a spiral wound NF 45-2540. The focus of this work was to test the rejection of fluoride co-existing with other sodium and lithium halides. It has been shown that a selective defluorination can be achieved by the use of this membrane. The NF 70 membranes, that have been investigated by Pontie *et al.* (2002), showed an increasing retention $F^- > Cl^- > Br^-$ at low pressure following the increasing hydrated ionic radius. Choi *et al.* (2001) have investigated two commercial NF membranes from Nitto Denko Corporation regarding the influence of the co-existing ions on the F^- rejection. The average F^- rejection found to be between 70–72%. The performance of three thin-film composite NF membranes have been studied with model solutions, for the F^- removal, under different operating conditions, concentration up to 1000 mg L^{-1} at costant pressure of about 1.37 MPa (Chakrabortty *et al.*, 2013). Additionally, in this study a mathematical model has been used to interpret the performance of the NF membranes at different F^- contents. By using this model, the membrane performance has been calculated based on three membrane parameters. In some cases, the F^- rejection was higher than 80%. The F^- removal by NF on F^--spiked groundwater in Morocco has been studied by Tahaikt *et al.* (2007; 2008). Four different spiral-wound NF 4040 membranes have been tested.

By using F^--spiked groundwater (1.8–22 mg L^{-1}) the F^- rejection of the NF 90 was highest (96–99%) and having the best performance among the tested membranes. As the retention of the NF 270, NF 400 and TR 60 was in a similar range (about 50–88%) they might be applied in treating groundwater with lower initial F^- content. Hoinkis *et al.* (2011) showed that the fluoride level in permeate was below the MCL up to 10 mg L^{-1} in feed for the NF 270 and

Table 3.1. NF membranes rejection [%] for fluoride removal.

Membrane and manufacturer	Water origin	Rejection [%]	Permeate flux [L h^{-1} m^{-2}]	Reference
NTR 7250, Nitto Denko Corporation	Model solutions with Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-	70	–	Choi *et al.* (2001)
NTR 7450, Nitto Denko Corporation		72		
NF 70-2540 spiral wound, Dow/Filmtec	Model solutions with Na^+, Cl^-, I^-	Single solute >90 at low recovery	20–25 (at 1.0 MPa)	Lhassani *et al.* (2001)
NF 55, Dow Filmtec	Model solutions with K^+, F^-, Cl^- and Br^-	95	–	Pontie *et al.* (2002)
NF 70, Dow Filmtec		55		
NF 90, Dow Filmtec		n/a		
NF 45-2540 spiral wound, Dow Filmtec	Model solutions with Na^+ and Li^+, Cl^-, I^-	NaF: 91–96 LiF: 88–93	–	Diawara *et al.* (2003)
SR-1, Koch	Model solutions with Na^+	0–70	60–80	Hu *et al.* (2006)
DS-5-DL, Osmonics		10–80	50–65	
HS-51-HL, Osmonics		20–95	58–80	
NF 90-4040 spiral wound, Dow Filmtec	Fluoride spiked natural groundwater	96–99	46 (at 1.0 MPa)	Tahaikt *et al.* (2007)
NF 400-4040 spiral wound, Dow Filmtec		50–86	49 (at 1.0 MPa)	
NF 90-4040, Dow Filmtec	Fluoride spiked natural groundwater	NF 90: 98–90	59 (at 1.2 MPa)* 64 (at 0.9 MPa)*	Tahaikt *et al.* (2008)
NF 270-4040, Dow Filmtec		83–88	61 (at 0.5 MPa)*	
TR60-4040, Toray		74–86	64 (at 0.9 MPa)*	
NF 270, Dow Filmtec	Fluorine brackish groundwater	63.3–71	78 (at 0.79–0.89 MPa)	Diawara *et al.* (2011)
NF 270, Dow Filmtec	Model fluoride water (20 mg/L, 25°C, pH 7)	87–88	60 (at 0.5 MPa), 112 (at 1 MPa) 142 (at 1.5 MPa)	Hoinkis *et al.*. (2011)
NF 90, Dow Filmtec		98–98.6	30 (at 0.5 MPa), 62 (at 1 MPa), 88 (at 1.5 MPa), 116 (at 2 MPa)	
NF 5 Applied Membranes Inc.	Groundwater	57	120 (at 1.0 MPa, 25°C)	Ben Nasr *et al.* (2013)
NF 9 Applied Membranes Inc.		88	85 (at 10 MPa, 25°C)	
NF-1 Sepro Membranes Inc. (USA)	Fluorine brackish groundwater from Asanjola village, West Bengal, India	98.5	158 (at 1.373 MPa)	Chakrabortty *et al.* (2013)
NF-2 Sepro Membranes Inc. (USA)		91	214 (at 1.373 MPa)	
NF-20 Sepro Membranes Inc. (USA)		n/a	365 (at 1.373 MPa)	

up to 20 mg L^{-1} for the NF 90, respectively. In addition, they could show no significant influence of HCO_3^- to the fluoride rejection, whereas at the pH of 5 the fluoride rejection was noticeably lower. Diawara *et al.* (2011) published their outcomes of a pilot unit installed in Senegal for the treatment of fluorine rich brackish water. The module of the pilot unit is composed of 169 circular flat membranes with a total area of 7.605 m^2. The permeate flow of 10 L min^{-1} has been kept constant by adjusting the feed pressure between 0.79 and 0.89 MPa. However, after 300 hours of running, a chemical cleaning was necessary due to fouling on the membrane surface. Ben Nasr *et al.* (2013) conducted the F^- removal of two commercial NF membranes NF5 and NF9. After tests with model water a pilot unit with underground water was studied. The difference in both membranes lies mainly in different salt rejection rates. Beside the initial F^- content, the effect of chloride, sulfate and calcium were analyzed since these ions usually co-exist in groundwater. It has been shown that the NF membranes reject divalent anions very strongly and in addition, the smaller the monovalent ion the better it is retained. They described that the reason for that is derived from the solvation energy of the ions by water. Since chloride ions are less solvated they are lower retained than F^- ions (Ben Nasr *et al.*, 2013). Chakrabortty *et al.* (2013) measured an increase in flux by rising transmembrane pressure. This effect is well reported in literature (e.g., Tahaikt *et al.*, 2007). By comparing the transmembrane pressure with the volumetric flux an optimum pressure of 14 kg cm^{-2} (1.373 MPa) was considered because beyond that no further improvement in F^- rejection was measured. An increase in flux came along with the increase of the cross flow rate and indicated a strong correlation between both parameters. An economic evaluation for a plant of a capacity of 10 m^3 d^{-1} indicated costs of 1.17 US$ m^{-3} including capital costs and operating costs (Chakrabortty *et al.*, 2013).

3.3.2 *Uranium*

The removal of U from drinking water was evaluated by Raff *et al.* (2009). These authors studied the influence of the pH on the membrane uranyl rejection in deionized water. In particular, the performance of five types of NF membranes, of which three purchased from the Companies Osmonics Desal (Desal 5DK, Desal 5DL and Desal 51HL) and two from Dow (NF90 and NF45), were investigated. In each case, the U rejection was between 81 and 99%. The best results were observed using the membranes Desal 5DK (96–99%) and Desal 5DL (94–98%). These promising results indicated that the rejection of two negatively charged uranyl carbonate complexes $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ was 94% or greater. Frave-Reguillon *et al.* (2003) investigated the removal of U dissolved in seawater. A simulated seawater was prepared by mixing uranyl nitrate $UO_2(NO_3)_2$, distilled water, Na_2CO_3 and different ions such as Na^+, K^+, Ca^{2+} and Mg^{2+}. For this study, four different NF flat sheet membranes purchased from Osmonics and having different molecular weight cut off (G50:8000 Da, G20:3500 Da, G10:2500 Da and 5DL:150–300 Da), were used. When the pH of the aqueous solution was 8.3, $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ were the most abundant species. Initially, these authors studied the U retention using a feed solution containing U carbonate with sodium chloride. The U rejection decreased with the increasing of NaCl concentration. Only for the G50 membrane was a rapid decrease at already low concentrations of NaCl (1 g L^{-1}) observed. The other three membranes (5DL, G10 and G20) showed a retention coefficient greater than 70%. The tests carried out with the simulated seawater, the U^{6+} retention coefficient (R) decreased to 50% for the G20 membranes. The retention coefficient (R%) is defined as $[(1 - C_p/C_f) \times 100]$, where C_p and C_f are concentrations in mol L^{-1} of the metal ions in permeate and the feed solutions, respectively. For G10 and 5DL there was no significant decrease in terms of U^{6+} retention, but for 5DL the selectivity for U^{6+}/Ca^{++} was dramatically low. Only the G10 membrane showed a high retention coefficient for U^{6+} and a low retention coefficient for sodium and calcium, leading to high U^{6+}/Ca^{++} and U^{6+}/Na^+ selectivities. The best efficiency was obtained using the G10 membrane, which evidenced the possibility to selectively filter U. The removal of U^{6+}, dissolved in drinking water, was also investigated by Favre-Reguillon *et al.* (2008). These authors demonstrated that NF membranes were able to reject U^{6+} from mineral water with a relatively high selectivity, despite a high concentration of alkaline and alkaline-earth cations. They studied the performance of three different commercial polyamides supported on a polysulfone NF membranes (Osmonics). These membranes presented different MWCO and isoelectric point (pI). G10 (2500 Da, 3.7 pI), DL (150–300 Da, –), DK (150–300 Da, 4.0 pI). They studied the solutions deriving from the addition of uranyl nitrate ($UO_2(NO_3)_2 \cdot 6H_2O$) to three different commercial mineral waters. The rejection of U^{6+} was 40%, 95% and 99% for the G10, DL and DK membranes, respectively; the highest cut-off membrane exhibited the lowest solute rejection for the same water composition. The rejection of alkaline and alkaline-earth ions marked the same trend for all the tested membranes. A positive trend was observed for the DL membrane. In fact, in all cases U^{6+} rejection was high (95%), whereas that for the monovalent and divalent ions was low. On the contrary, the DK membrane demonstrated the ability to highly reject not only the U^{6+}, but also the monovalent and divalent ions. Moreover, the U^{6+} rejection obtained using the G10 membrane was the lowest. Kryvoruchko *et al.* (2013) and Yurlova (2010) studied the purification of U-containing water by NF using the OPMN-P, a polyamide commercial membrane (Vladipor Company). The innovation of this work resides in the simultaneous use of modified montmorillonite (Cherkassy Deposit) with polyethyleneimine (MW, 2000), in NF process. This study demonstrated the possibility to couple the use of montmorrillonite as a sorbent for water purification from U^{6+} and the NF separation process. The application of modified montmorillonite in NF process allowed to achieve U retention coefficients as high as 0.999. In another study, U^{6+} removal by micellar-enhanced ultra- and nano- filtration was investigated to study the influence of the concentration and the steric structure of the surfactants (sodium dodecyl sulfate and sodium dodecyl benzene sulfonate), and the pH. The steric hindrance of the examined surfactants affected the efficiency of treatment of U-contaminated waters. Interestingly, water decontamination from U^{6+} was the most efficient when the surfactants were added in concentrations close to their critical micelle concentrations. Richards *et al.* (2011) evaluated the effects of fluctuating energy and pH on the retention of dissolved contaminants from real Australian groundwaters, using a solar (photovoltaic) powered UF-NF/RO system using four NF/RO membranes (BW30, ESPA4, NF90, and TFC-S). Whereas the fluctuations in energy affected pressure and flow, the solar irradiance levels influenced the retention of fluoride, magnesium, nitrate, potassium, and sodium. On the other hand, the retention of calcium, strontium, and U was found to be very high and independent of the solar irradiance, which was a combined effect of size and charge exclusion. The groundwater characteristics also affected the retention and, therefore, solutes were categorized into two groups according to their retention behavior as a function of pH: (1) pH-independent retention (arsenic, calcium, chloride, nitrate, potassium, selenium, sodium, strontium, and sulfate) and (2) pH-dependent retention (copper, magnesium, manganese, molybdenum, nickel, uranium, vanadium and zinc). The retention of Group 1 solutes was typically high and attributed to steric effects. Group 2 solutes had dominant, insoluble species under specific conditions which led to deposition on the membrane surface (and thus varying apparent retention). However, the renewable energy membrane system was effective in removing a large number of groundwater solutes for a range of real energy and pH conditions. Oliveira *et al.* (2012; 2013) evaluated the performance of a NF membrane for treatment of a low-level radioactive liquid waste (carbonated water during conversion of UF_6 to UO_2) through static and dynamic tests. Membrane hydraulic permeability, permeate flow and selectivity were measured before and after its immersion in the liquid waste (static tests). In the dynamic tests, to determine the performance of NF membranes for U removal, the waste was permeated through the membrane at 0.5 MPa. The surface layer of the membrane was characterized by zeta potential, field emission microscopy, atomic force spectroscopy and infrared spectroscopy. The static test showed that the membrane surface charge was not significantly changed; the U rejection after the dynamic test was 99%. Prabhakar *et al.* (1996) compared the performance of cellulose acetate (CA) and polyamide (PA) membranes for the removal of radioactive species from ammonium diuranate filtrate effluents (ADUF). Even though the CA based membrane was promising in terms of very good decontamination factors (DF) and volume reduction factors (VRF). However, it was associated with the limitation of short membrane life which put was against its large scale application for the intended purpose. Therefore, PA based RO, NF, and UF membranes were tested on real effluents corresponding to specific activity levels of microcuries/liter containing ~4% ammonium nitrate. These treatments yielded decontaminated streams containing nanocurie/liter levels of radiocontaminants both for RO and NF membranes. In addition, the NF membranes showed the potential to achieve very high VRF and better decontamination factors owing to their poor ammonium nitrate rejection characteristics and the consequent maintenance of permeate fluxes. The studies indicate the viability of the NF process for the treatment of ammonium diuranate filtrate effluents in large scale. NF has the advantage of very low solute rejection for monovalent species, probably due to their very small sizes (hydrated radii), and higher rejection for multivalent species which are large enough (i.e., more than the critical pore diameter) for rejections based on physicochemical interactions. Therefore, solute rejection of ammonium nitrate was very low and the DF values were very high. Rana *et al.* (2013) have recently reviewed the efficacy of radioactive decontamination by membrane processes. These authors have classified the membrane technology into different processes and, for each process, stated progresses made since the onset of this millennium in the radioactive decontamination of water. The new directions are shown considering the growth made in membrane manufacturing and membrane processes. The combined efforts of researchers engaged in membrane and membrane process design with those engaged in nuclear waste treatment near the plant sites were highlighted. Table 3.2 summarizes the experimental results reported in the previously presented

Table 3.2. NF membranes rejection [%] for uranium removal.

Membrane and manufacturer	Water origin	Rejection [%]	Permeate flux [$L\,h^{-1}\,m^{-2}$]	Reference
Desal 5 DK, Osmonics Desa Companies	Model solutions with $NaHCO_3$ (pH 7.3–8.3)	96–99	3.5–7 (at 0.8 MPa)	Raff *et al.* (1999)
Desal 5 DL, Osmonics Desa Companies	Model solutions with $NaHCO_3$	94–98	n/a	
Desal 51 HL, Osmonics Desa Companies	De-ionized water at pH 6.7	88	n/a	
NF 90, Dow Chemical	De-ionized water at pH 6.7	82	n/a	
NF 45, Dow Chemical	De-ionized water with $NaHCO_3$ at pH 5.9	81	n/a	
G50, Osmonics	Model seawater solution	n/a	n/a	Frave-Reguillon *et al.* (2003)
G20, Osmonics	Model seawater solution	~50	n/a	
G10, Osmonics	Model seawater solution	~83	n/a	
5DL, Osmonics	Model seawater solution	~95	n/a	
G10, Osmonics	Commercial mineral water	40	n/a	Frave-Reguillon *et al.* (2008)
DL, Osmonics	Commercial mineral water	95	n/a	
DK, Osmonics	Commercial mineral water	99	n/a	
OPMN_P, Vladipor Company	Distilled water	99	n/a	Yurlova *et al.* (2010)
BW30, Koch	Groundwater	~100	n/a	Richards *et al.* (2011)
SW-0, DOW	Radioactive waste solution at pH 9.4	94	2.4	Oliveria *et al.* (2013)
Cellulose acetate membrane, HMIL	Ammonium diuranate filtrate effluents (ADUF)	n/a	n/a	Prabhakar *et al.* (1996)
Polyamide membrane, HMIL	Ammonium diuranate filtrate effluents (ADUF)	n/a	n/a	

works. As evidenced by the rejection results, NF membranes represent a very efficient system to remove the dissolved U.

3.4 CONCLUSIONS AND OUTLOOK

NF membrane separation offers the possibility to replace the common water treatment processes by a single-step procedure with low operating and energy costs. Several successful works on the removal of dissolved F^- and U from water by NF have demonstrated the opportunity to meet regulations for their lowered content in groundwater. In particular, it has been shown that even at elevated influent levels, NF membranes have the ability to reject F^- below the maximum contaminant level (MCL) of $1.5\,mg\,L^{-1}$ recommended by WHO (WHO, 2014). Also for the U removal, it has been evidenced as commercial NF membranes are able to reject U^{6+} from mineral water with high selectivity (Frave-Reguillon *et al.*, 2008), making this process suitable in the reduction of U content in drinking water to less than the WHO maximum admissible concentration ($0.002\,mg\,L^{-1}$). Nevertheless, some drawbacks, such as the fouling, the cost and the maintenance of the membranes, still limit the use of NF separation processes on an industrial scale. Pre-treatment processes may be suitable to largely eliminate pollutants from groundwaters such as viruses and bacteria and to prevent the membrane fouling. In this context, implementing a hybrid system, e.g. coupling NF with adsorption, RO or UF, may greatly enhance the efficiency of the removal process. Based on present investigation, it can be concluded that further studies on the concentration fraction is the key parameter to improve F^- and U removal by NF.

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CHAPTER 4

The use of reverse osmosis (RO) for removal of arsenic, fluoride and uranium from drinking water

Priyanka Mondal, Anh Thi Kim Tran & Bart Van der Bruggen

4.1 REVERSE OSMOSIS: BACKGROUND AND TRANSPORT MECHANISM

RO was used for removal of salts from water and was first patented on 1931 by Horvath. In this process a fluid is passed through a semi permeable membrane from a higher solute concentration compartment to lower solute concentration compartment by applying pressure. In 1959, a remarkable improvement of this process was established by Reid and Breton as they achieved 98% of salt rejection by applying a cellulose acetate membrane. However, due to the large thickness of the membrane (5–20 μm) the resultant flux was not high. The use of anisotropic cellulose acetate membranes (Loeb and Sourirajan, 1963) increased the applicability of RO in the desalination industry due to its improved performance. Improved composite membranes (made by interfacial polymerization) (Cadotte, 1977) also made a large breakthrough for economical application of RO membrane in drinking water industry. The RO membranes are also able to exclude lower molar mass species (salt ions, organics etc.) due to their non-porous structure. Some membranes have a performance between ultrafiltration and RO due to their porous structure; these are known as "loose RO membranes". However, the pore size of those membranes is very small (in the order of 10 Å or less) (Baker, 2004). Nowadays, several improvements are being implemented on conventional RO membranes (detailed discussion in Section 4.2) and also in RO plants, to make the system more sustainable. Although at present, RO is used mainly in desalination, further improvements are still required for broader applications of this technique.

RO membranes consist of two layers, (i) a thin dense top polymer layer and (ii) a porous sublayer, which gives support to the top layer and increases the mechanical stability of the membrane. These membranes have been effectively used for water desalination with a very high rejection (sometimes over 99%) of the low molecular mass compounds (inorganic salts or small organic molecules) (Velizarov *et al.*, 2004). However, there are some drawbacks for RO treatment, which include (i) lack of dissolved minerals in the treated water, (ii) low rejection of neutral molecules and (iii) high energy consumption (Mondal *et al.*, 2013).

The transport of salts and water through RO membrane is controlled by the solution-diffusion mechanism and the flux of water (J) is calculated as:

$$J = A(\Delta p - \Delta\pi) \tag{4.1}$$

where A is a constant, Δp is difference across the membrane and $\Delta\pi$ is osmotic pressure difference across the membrane. Equation (4.1) explains three phenomenon; (i) when $\Delta\pi > \Delta p$, osmosis takes place, which implies that water flows from the dilute side to the concentrated side, (ii) $\Delta p = \Delta\pi$, in this case flux of water is not possible, and (iii) $\Delta\pi < \Delta p$, this condition implies that water flows from the higher concentration compartment to the lower concentration compartment, through a semi permeable membrane. Thus, the water flux is proportional to the applied pressure. However, the salt flux is independent of pressure. These three conditions are schematically represented in Figure 4.1. The overall rejection (R) of the salts is given by:

$$R = [1 - (C_{\text{permeate}}/C_{\text{feed}})] \tag{4.2}$$

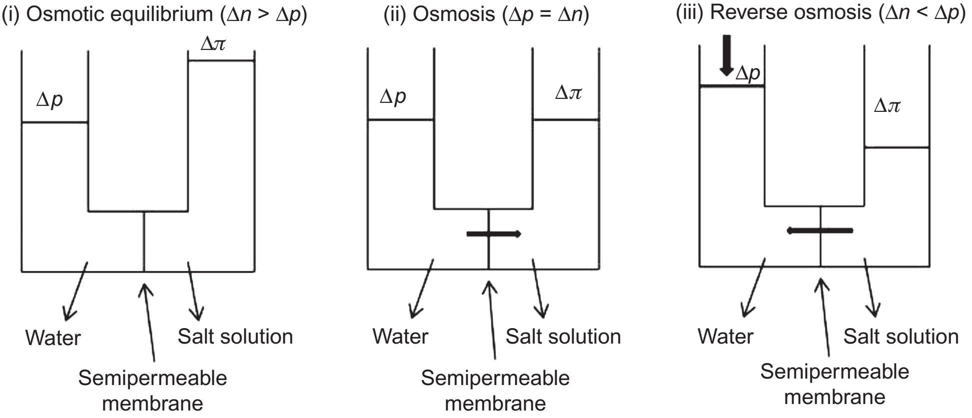

Figure 4.1. A schematic representation of (i) osmotic equilibrium, (ii) osmosis and (iii) reverse osmosis.

where C_{permeate} is the concentrations of salts at the permeate side and C_{feed} is the concentration of salts at the feed side of the membrane. However, there are several physical parameters that affect the salt rejection such as, concentration of salts in the feed chamber, feed water temperature, operating pressure and pH of the feed solution.

4.2 TYPES OF RO MEMBRANES

RO membranes are divided into three categories, i.e., cellulose acetate based membranes, polyamide based membranes and composite membranes. All of these three kinds of membranes are discussed below.

4.2.1 *Cellulose acetate membranes*

Cellulose acetate was the first material used to make RO membranes. This kind of material was first used by Loeb and Sourirajan in 1963. Nowadays the use of these membranes is limited due to their lower performance than composite membranes. Cellulose acetate membranes are inexpensive, very easy to prepare, resistant against oxidants and mechanically tough in nature. The membrane has an asymmetric or an anisotropic structure and consists of a thin active layer on a coarse supportive layer. However, this kind of membrane is very sensitive towards the pH and temperature of the feed water. Thus, it is better to maintain the feed water pH between 4 and 6 because the membranes are slowly hydrolyzed with time and above 35°C, the properties of the membrane change (Vos *et al.*, 1966). Moreover, these types of membranes are very susceptible to biological attack.

4.2.2 *Aromatic polyamide membranes*

Aromatic polyamide membranes are also known as non-cellulosic polyamide membranes. Several polymer materials were proposed to overcome the problems related to cellulose acetate membranes but only the use of polyamide proved successful (Wang *et al.*, 2011). Due to the lower rejection and relatively lower flux, aliphatic polyamide membranes are ruled out by aromatic polyamide membranes, which have a significantly higher rejection and are successfully produced commercially (Endoh *et al.*, 1977; McKinney and Rhodes, 1971; Strathmann, 1990). These membranes are asymmetric in nature and have very high salt rejections.

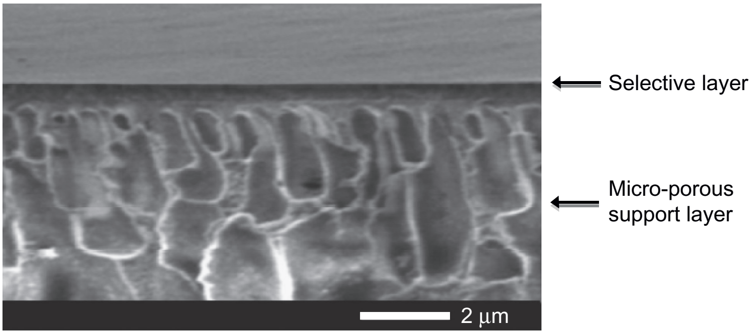

Figure 4.2. Scanning electron microscopic image of composite membrane (adapted from Perera *et al.*, 2014).

4.2.3 *Composite membranes*

Composite membranes are made of two or more polymeric materials. These types of membranes are prepared by coating microporous support layers with two or more active dense very thin ($\leq 0.1\ \mu m$) polymer layers (Fig. 4.2). The first composite membrane for RO was invented and patented by Cadotte in 1981. These membranes have a very high flux, high salt rejection, and are resistant over a broad range of pH (4–11) and can be operated above 35°C. However, the chlorine resistance of these membranes is very poor, which decreases the selectivity of membranes and makes them very difficult to use with chlorine contaminated (few $\mu g\,L^{-1}$) feed water (Baker, 2004).

4.3 MEMBRANE MODULES AND THEIR APPLICATION

A filtration device consists of a filtrate outlet structure and a membrane unit in which a specific membrane surface area is housed, the membrane module. There are four types of membrane modules that are used for RO: plate and frame, tubular, spiral wound and hollow fiber. A brief description about these membrane modules and their functions is given in the following sub sections. Several advantages and disadvantages of all these membrane modules are also discussed in Table 4.1.

4.3.1 *Plate and frame modules*

This type of module consists of a membrane, which is placed between the feed spacer and product spacer and then the system is attached to both sides of a rigid plane or end plate (Fig. 4.3). The plates are made of different materials, e.g., porous fiberglass, solid plastic with grooved channels on the surface, reinforced porous paper, etc. The membrane unit is placed in a pressurized vessel. Feed water is forced to pass across the surface of the membrane for filtration. Permeates are collected in product manifold after passing through the membrane and brine solution is collected from porous media. However, this membrane module is not used in large scale applications because of the complexity and cost of operation.

4.3.2 *Tubular modules*

In tubular modules, a number of tubes are arranged in series (Fig. 4.4). The tubes are made with porous paper or fiberglass support and the membranes are installed inside the tubes. The water is circulated through the tube under pressure and the filtered water is collected from collecting tube installed inside the system. Although the system can operate in extreme turbid feed water

Table 4.1. Advantages and disadvantages of several membrane modules.

Membrane modules	Advantages	Disadvantages
Plate and frame	(i) Applicable for high viscous liquid and can be operated at high pressure (ii) Easy to replace and clean the membrane	(i) Membrane working area is very small
Tubular	(i) Good resistivity with fouling (ii) Comparatively easy to clean	(i) Packing density is very low (ii) Energy consumption is highest with respect to other modules
Spiral wound	(i) Packing density is high (ii) Cost is relatively low (iii) Easy to adjust with hydrodynamics by changing the spacer thickness and can avoid the risk of fouling	(i) Difficult to clean (ii) Pressure drop is large
Hollow fiber	(i) Very high packing density (surface area to volume ratio) (ii) Energy consumption relatively low	(i) Very high capital cost (ii) Fouling resistivity is poor (iii) Difficult to clean and change the membrane

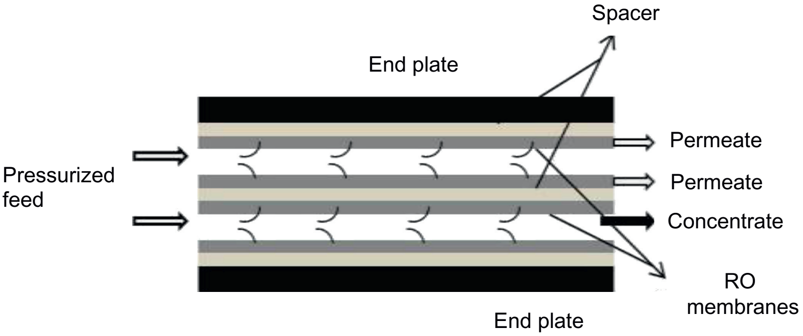

Figure 4.3. Schematic diagram for plate and frame module used in RO system.

and is easy to clean (mechanically or hydraulically), it is not the best option for RO due to its high capital cost.

4.3.3 *Spiral wound modules*

Spiral wound membrane modules are well-known in water desalination and are better than plate frame and tubular modules due to their high water flux, lower salt permeability and lower operational cost. Several membrane elements are connected with each other in a spiral mode and wrapped around a centrally installed permeate tube (Fig. 4.5). The whole setup is placed inside a pressurized tubular vessel where the feed water passes through the membranes axially down the module.

4.3.4 *Hollow fiber module*

Hollow fiber membrane modules consist of large number of hollow fibers that are asymmetric in nature (Fig. 4.6). Usually hollow fiber membrane modules are formed in two geometries, (i) a small diameter and thick wall fiber bundle (internal diameter 50 μm and outer diameter 100 to

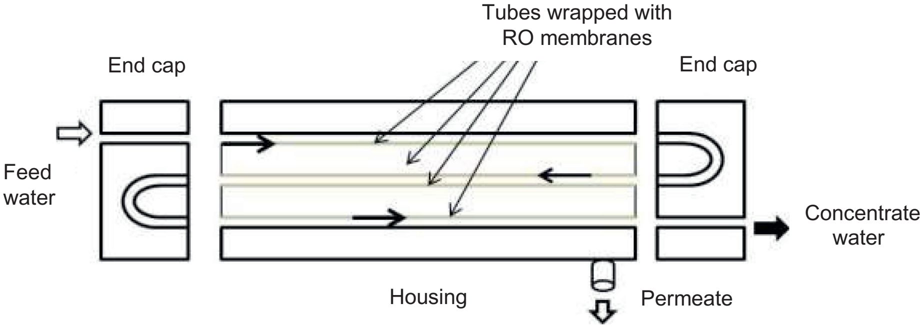

Figure 4.4. Schematic representation of tubular RO membrane module.

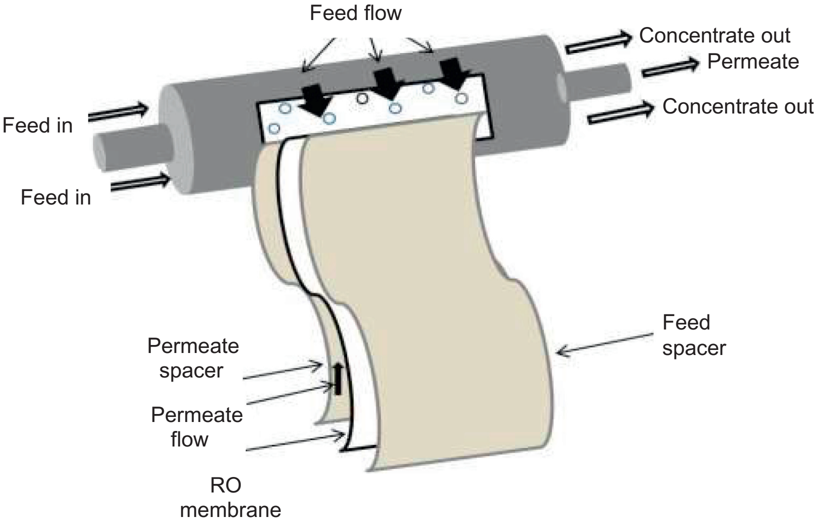

Figure 4.5. Schematic representation of spiral wound RO membrane module.

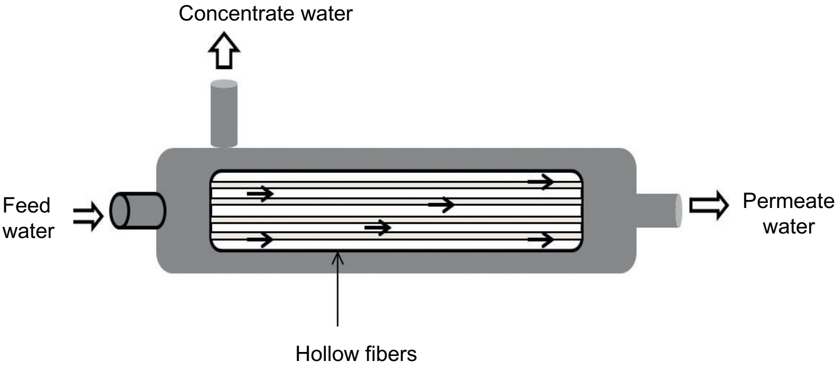

Figure 4.6. Schematic representation of hollow fiber RO membrane module.

200 μm) contained in a vessel where the feed water passes through the fiber wall and permeates are collected through open fiber end, and (ii) feed water passes through the bore of the fiber, which is open at both ends (known as bore side feed type hollow fiber membrane) (Baker, 2004). The pressurized feed water flows radially over the fiber bundle and the permeate is collected outside of the fiber bundle into the hollow fiber bore. This module serves a very large surface area for polluted water purification. However, this module is very susceptible to fouling due to its compact structure.

4.4 REVERSE OSMOSIS FOR ARSENIC, FLUORIDE AND URANIUM REMOVAL FROM WATER

RO is a well-established technology that has been used successfully to remove As, F and U from contaminated water for many years. As and F generally occur as an anionic species in experimental pH conditions. Similarly, zeta potential values of the applied RO membranes are also negative within the studied pH range. Therefore, better rejection was observed due to charge exclusion (Donna exclusion). However, not only charge exclusion, size exclusion (especially for U) and diffusion coefficients play an important role for the removal of these contaminants. A brief summary of the removal efficiency and experimental details of these contaminants by using RO membranes are elaborated in the following sections.

4.4.1 *RO for removal of arsenic from water*

Several studies have been performed on removal of As from water by RO. These are summarized in Table 4.2.

Yoon *et al.* (2009) used a bench-scale cross-flow flat-sheet filtration system with an LFC-1 (Hydranautics), polyamide TFC RO membrane to remove As(III) and As(V) from model and natural waters. They found a high removal of As(V) and the rejection enhanced (90–99%) with increasing pH (from 4–10) due to the higher degree of dissociation of fixed ionizable functional groups on the membrane. Moreover, they also found that the rejection of As(III) by the same RO membranes was constant (92–96%) and the change in pH did not affect the rejection due to dominance of steric exclusion over charge repulsion. Teychene *et al.* (2013) observed that the SW membrane has better removal efficiency for As(III) than the BW membrane. They concluded that the rejection of the metalloid depends on the applied transmembrane pressure, characteristics of the membrane and the pH of the solution. A similar conclusion was also suggested by Akin *et al.* (2011). Low pressure polyamide RO membranes were used by Deowan *et al.* (2008). They found that the rejection of As(V) (over 98%) was higher than that of As(III) (60–80%) from As spiked local tap water. The rejection of As(V) by the LE membrane was high and reached below the MCL up to a feed concentration of 2000 $\mu g\,L^{-1}$. For the XLE membrane, the maximum feed concentration was 800 $\mu g\ L^{-1}$ of As(V) above which the permeate concentration exceeded the MCL. On the other hand, the rejection of As(III) below the MCL was possible if the initial feed concentration was up to 50 $\mu g\,L^{-1}$. In another study, a small scale RO unit for the removal of both As(V) and As(III) using spiked local tap water was studied by Geucke *et al.* (2009). In conventional RO systems, the energy from the rejected water is usually wasted, but the RO pump (Fig. 4.7) used in this study could reuse the energy of the rejected water and thus, reduced the expenses by 50–90%. However, they also observed that in case of As(III), the permeate concentrations reached below the MCL only when the feed concentration was below 350 $\mu g\,L^{-1}$ for As(III), whereas for As(V), the limit was up to 2400 $\mu g\,L^{-1}$. Thus, these studies suggest a better removal efficiency of As(V) than As(III) in RO systems mainly due to electrostatic repulsion between RO membranes and As(V) species. The rejection of As(III) is low because of its neutral characteristics.

Floch *et al.* (2004) studied the removal of As in a pilot plant using a polyvinylidene fluoride RO membrane (ZW-1000; ZENON Environmental Inc. Canada), after several pretreatment

Table 4.2. Arsenic removal by RO.

Type of RO membrane and manufacturer	Origin of water	Rejection [%]		Operating pH	Flux [m^3 m^{-2} h^{-1}]
		As(V)	As(III)		
SW30HR (DOW, FilmTec)	Synthetic brackish water (Teychene *et al.*, 2013)	–	>99	7.6	18.72 (at 2.4 MPa)
SCW5 (Hydranautics)		–	>99	7.6	27.84 (at 2.4 MPa)
BW30LE (DOW, FilmTec)		–	99	9.6	85.6 (at 4.0 MPa)
ESPAB (Hydranautics)		–	99	9.6	102.8 (at 4.0 MPa)
ESPA2 (Hydranautics)		–	99	9.6	118.4 (at 4.0 MPa)
XLE-2521 (DOW, FilmTec)	As spiked local tap water (Geuke *et al.*, 2009)	96.1–>99	73.2–97	7.2	28.3 (at 0.45 MPa)
TW30-2521 (DOW, FilmTec)					26.7 (at 0.96 MPa)
SW30-2521 (DOW, FilmTec)					25.8 (at 1.52 MPa)
ZW 1000 (Zenon)	Well water (Floch *et al.*, 2004)	Total As rejection 97–>99		–	–
SWHR (DOW, FilmTec)	Spiked water and Natural groundwater sample (Akin *et al.*, 2011)	96	83	2.4–10.4	11.60 and 7.07 (at 1.0–3.5 MPa) for As(V) and As(III), respectively
BW-30 (DOW, FilmTec)		78	68		0.70 and 0.28 (at 1.0–3.5 MPa) for As(V) and As(III), respectively
LE (DOW water)	Arsenic spiked local tap water (Deowan *et al.*, 2008)	>95	60–80	5–9	40–60
XLE (DOW water)		>95	60–80		40–60
BW30 (DOW, FilmTec)	Australian groundwater (Richards *et al.*, 2009)	Total As removal 79		3–11	22.5
ESPA4		Total As removal 75			

processes such as oxidation with potassium permanganate and coagulation with ferrous sulfate. The pretreatment units were separated into three parts prior to the application of membrane filtration, and the As concentration in the permeate was below the MCL. However, the As contaminated pretreatment waste may be a greater concern for the environment.

A photovoltaic-powered RO desalination system combined with a two-staged membrane system (UF and RO) was studied by Richards *et al.* (2009). They used two RO membranes for removal of As from Australian groundwater and obtained a high rejection of total As. The flux during the operation decreased from 24.2 to 22.5 L m^{-2} h^{-1} due to precipitation on the surface of the membrane. Their study suggested that a proper understanding of the dominant aqueous species, along with the proper choice of membranes and the use of renewable energy sources can resolve the problem of water scarcity in many parts of the world.

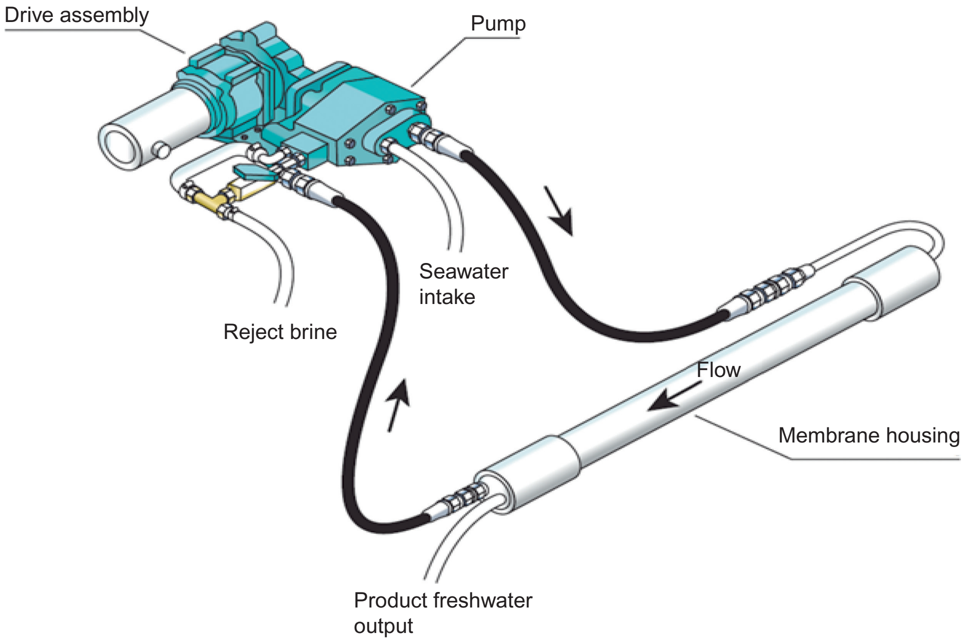

Figure 4.7. RO pump used by Geuke *et al.* (2009) (adapted from Bhattacharya *et al.*, 2009) (Katadyn Power Survivor, 160E, 2009).

All the studies related to removal of As from aqueous solution are summarized in Table 4.2. These studies prove that although RO can remove As(V) below the MCL, limitations are related to the occurrence of As(III) at nearly neutral pH.

4.4.2 *Fluoride removal from water by RO*

Reported studies on F^- removal from aqueous solution by RO are summarized in Table 4.3.

The pH is an important parameter for the removal of F^- by RO. Richards *et al.* (2010) studied the dependence of F^- retention on pH with two RO membranes, BW30 (RO, Dow, FilmTec), UTC-80A (RO, Toray). The results demonstrate that at acidic pH, the retention of F^- was low due to the dominance of HF, and is much different among the 6 tested membranes. On the contrary, at $pH > 7$, with Cl^-, HCO_3^- and Na^+ as co-existing ions, the rejection was more than 90% for both the RO membranes.

In a different study, Dolar *et al.* (2011) studied the F^- removal efficiency with three RO membranes to treat fertilizer wastewater. With RO membranes LFC-1 (assumed pore size 0.75 nm), XLE (0.62 nm) and ULP (0.73 nm), the efficiency was above 96%.

Apart from studies on a laboratory scale, F^- removal was also successfully applied on a pilot scale. Sehn (2008) used a pilot plant with a RO membrane (capacity of $6000\,m^3\,d^{-1}$) and demonstrated that RO can remove F^- from groundwater below $0.03\,mg\,L^{-1}$ (the rejection was 98.4%). The rejection remained unchanged after 3 years of operation. Similarly, Diawara *et al.* (2011) investigated F^- removal from brackish ground water for the 2000 inhabitants of the rural community of Ndiaffate (Kaolack, Senegal). The pilot plant low pressure reverse osmosis (LPRO) from Dow Company was designed with a feed flow rate of $900\,L\,h^{-1}$ and a conversion rate of 66%. With the LPRO, the rejection was higher, i.e., between 97 and 98.9%. Thus, LPRO appeared to be an effective method to treat the water to meet drinking water standards.

Table 4.3. Fluoride removal by RO.

Membrane manufacturer	Water origin	Rejection [%]	Flux [$L\,m^{-2}\,h^{-1}$]
XLE (Dow/Filmtec) (Sehn, 2008)	Groundwater	98.4	n/a (at 0.6–1.1 MPa)
BW30 (RO, Dow, FilmTec) (Richard *et al.*, 2010)	Water spiked with NaF, NaCl and $NaHCO_3$	90–95 (pH > 7)	12.1 (at 0.5 MPa)
UTC-80A (RO, Toray) (Richard *et al.*, 2010)		90–95 (pH > 7)	15.4 (at 0.5 MPa)
LFC-1 (RO, Hydranautics) (Dolar *et al.*, 2011)	Real wastewater from fertilizer factory	96.8	25.57 (at 2.5 MPa)
XLE (RO, Dow, FilmTec) (Dolar *et al.*, 2011)		96	26.96 (at 2.5 MPa)
ULP (RO, Koch Membrane) (Dolar *et al.*, 2011)		96.6	30.51 (at 2.5 MPa)
LPRO (Dow Chemical) (Diawara *et al.*, 2011)	Brackish groundwater	97–98.9	79 ($Y = 66\%$) (Y is the conversion rate)

4.4.3 *RO for uranium removal from water*

Several water treatment technologies have been used for removal of U below the MCL including activated carbon (Coleman *et al.*, 2003), coagulation-flocculation (Gafvert *et al.*, 2002), ion exchange (Barton *et al.*, 2004), adsorption (Shuibo *et al.*, 2009) and ultrafiltration with precomplexation (Kryvoruchko *et al.*, 2004). However, very few studies focused on removal of U from contaminated water by using RO.

Removal of U from brackish groundwater of Australia using direct solar powered ultrafiltration-nanofiltration/reverse osmosis membrane system was studied by Rossiter *et al.* (2010) (Fig. 4.8). The feed pressure and feed flow were 0.9 MPa and 400 $L\,h^{-1}$, respectively. They found that U was strongly adsorbed to membranes at pH 4–7 but retained by the membranes over the pH range of 3–11. The retention of U including other divalent cations was >99% for batch experiments and 95–98% for continuous experiments. However, during the solar energy experiments, they observed a decreased retention of U (above WHO limit), which was because of precipitation of U on the membrane. In another study by Montaña *et al.* (2013) more than 90% U removal from contaminated river water was obtained by using an RO pilot plant. They also found that the heavy molecular weight U complexes were rejected by dense RO membranes *via* molecular filtration. RO can remove 99% U with higher water desalination and therefore is a better option than other technologies (Gamal Khedr, 2013).

4.5 EXPERIMENTAL STUDY FOR REMOVAL OF ARSENIC AND FLUORIDE FROM WATER BY RO AND LOOSE RO MEMBRANES

4.5.1 *Materials and methods*

4.5.1.1 *Membranes*

RO experiments with low pressure and high pressure membranes were performed by using four types of commercial membranes supplied by Dow-FilmTec with flat sheet configuration having an active surface area of 59 cm^2. For high pressure RO experiments SWHR and BW-30 flat sheet membranes were used. Similarly, NF90 and NF 270, two dense nanofiltration membranes were used for low pressure RO experiments.

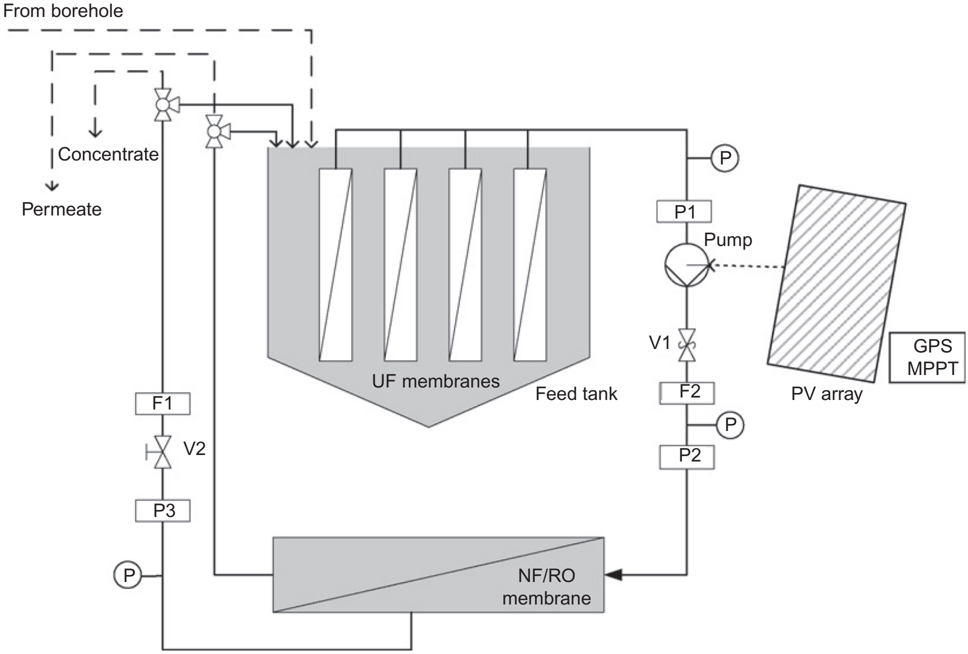

Figure 4.8. Solar powered membrane filtration system for uranium removal (adapted from Rossiter *et al.*, 2010) where P = pressure gauges; P1–3 = pressure transducers; F1–2 = flow sensors; V1 = pressure relief valve; V2 = pressure control valve; GPS = solar tracker guided by global positioning system and MPPT = maximum power point tracker.

4.5.1.2 *Reagents and chemicals*

The solution of pentavalent arsenic and monovalent fluorine was prepared by dissolving analytical grade $Na_2HAsO_4{\cdot}7H_2O$ (RPL, Belgium) and NaF (Riedel-deHaën) in distilled water. Arsenic and F^- standard solutions, with concentration ranging 50–300 $\mu g\,L^{-1}$ and 2.5–15 $mg\,L^{-1}$ respectively were prepared by dilution, immediately before starting the experiment. All stock solutions were prepared using deionized (DI) water (18.2 $m\Omega\,cm^{-1}$) from a Mili-Q water system. The pH of the solution (7 ± 0.2) was adjusted by either HNO_3 or NaOH.

4.5.1.3 *Groundwater characteristics*

The synthetic groundwater was prepared by following the northeastern India groundwater composition mentioned in Singh *et al.* (2008). In brief, synthetic groundwater was prepared by adding $NaNO_3$ (Riedel-deHaën), Na_2SO_4 (Acros), $MgCO_3$ (Sigma-Alrrich) and $CaSO_4{\cdot}2H_2O$ (Riedel-deHaën) into deionized water. Arsenic and F^- solutions were spiked from a 1000 $mg\,L^{-1}$ stock solution. The initial concentrations of the ions in the synthetic groundwater were as following: Ca^{2+}: 180 $mg\,L^{-1}$, Mg^{2+}: 62 $mg\,L^{-1}$, Na^+: 140 $mg\,L^{-1}$, SO_4^{2-}: 385 $mg\,L^{-1}$, As(V): 0.2 $mg\,L^{-1}$, F^-: 10 $mg\,L^{-1}$ and NO_3^-: 220 $mg\,L^{-1}$.

4.5.1.4 *Membrane performance*

All the experiments for the removal of As(V) and F^- were carried out for 6 hours and each time a new membrane was used in each experiment. The rejections of all the ions were calculated according to the following equation:

$$\text{Rejection } [\%] = (1 - (C_{\text{permeate}}/C_{\text{feed}})) \times 100 \tag{4.3}$$

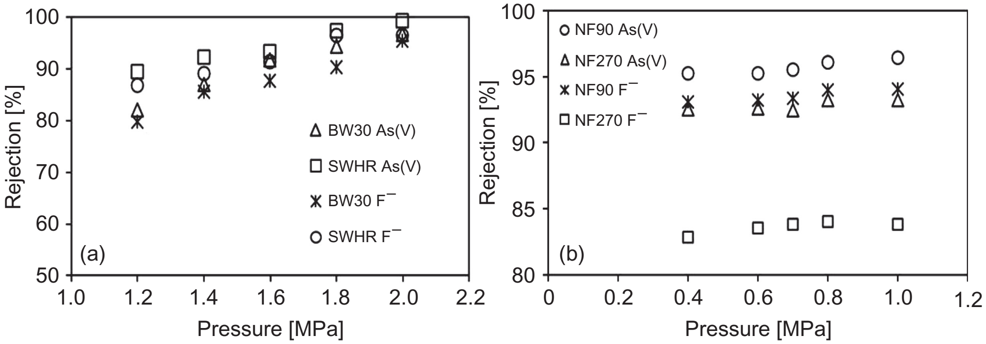

Figure 4.9. The rejection of As(V) and F^- as a function of pressure for (a) RO and (b) NF. Operational conditions: As(V) = 150 μg L^{-1}, $F^- = 7.5$ mg L^{-1}, pH = 7 ± 0.2, Temperature = 20°C).

where C_{permeate} and C_{feed} are the concentration of the ions [mg L^{-1}] in permeate and feed, respectively.

4.5.1.5 *Analytical methods*

Samples of the feed and permeate from the membrane system were taken at 30 min intervals and made ready for analysis. The concentrations of cations (As^{+5}, Ca^{2+}, Mg^{2+} and Na^+) were determined by ICP-MS (Thermo Electron Corporation X series ICP-MS) and anions (F^-, NO_3^-, SO_4^{2-}) were determined by IC-DIONEX (ICS 2000). The pH was fixed at 7 ± 2 for all the experiments and measured by an Orion pH meter (USA).

4.5.2 *Results and discussion*

4.5.2.1 *Effect of operating pressure*

Figure 4.9 shows that the removal of both As(V) and F^- in RO increases with increasing operating pressure. With RO, the rejection of As(V) increased from 82.1 to 96.7% and from 89.4 to 99.4% when using the BW30 and SWHR membranes, respectively, whereas for F^- the rejection increased from 79.7 to 95.4% and from 86.8 to 96.5% for the BW30 and SWHR membranes, respectively, by increasing the pressure from 1.2 to 2.0 MPa. For all operating pressure conditions, SWHR membranes provided higher As(V) and F^- rejections (with a large difference) and thus, in comparison with BW30 membranes, SWHR membranes were shown to have higher rejection efficiencies for both As(V) and F^- (Fig. 4.9). Similar results were obtained by Akin *et al.* (2011) and Gholami *et al.* (2006) for As(V). However, the F^- rejection obtained with the BW membrane was lower than reported in the literature (98.4%) (Sehn, 2008). Since As(V) was present in the solution as divalent $HAsO_4^{2-}$, which is strongly repulsed by the membranes and increased the ionic strength, the divalent $HAsO_4^{2-}$ forces F^- to pass through the membranes to maintain the electroneutrality and ultimately decreases the rejection (Choi *et al.*, 2001).

Similarly, the rejection of both As(V) and F^- by NF90 was higher than that of NF270 over the investigated pressure range (Fig. 4.9). The removal of As and F with the NF90 membrane was higher than 96% and 94%, while for the NF270 membrane the rejection was higher (than 93% and 84%, respectively). The lower molecular weight cutoff of the loose NF270 membrane (300 Da) in comparison with the more dense NF90 membrane (200 Da) (Hoinkis *et al.*, 2011) causes a lower rejection of NF270. The increase in operating pressure did not improve the As rejection significantly, which was similar to the findings of Saitua *et al.* (2011) and Figoli *et al.* (2010). The rejection of F^- decreases with increasing pore size of the membrane (Fig. 4.9) from NF 90 (~93%) (pore size 0.68 nm) (Nghiem and Hawkes, 2001) to NF 270 (~83%) (pore size ~0.84 nm) (Nghiem and Hawkes, 2007) because the looser membrane (NF 270) has a lower rejection than

Table 4.4. Ions and their respective diffusion coefficient and hydrated radii.

Ions	Diffusion coefficient [10^{-5} cm^2 s^{-1}]	Hydrated radii [Å]
Na^+	1.33 (Linde and Jönson, 1995)	3.58 (Nightingale Jr, 1959)
Mg^{2+}	0.71 (Linde and Jönson, 1995)	4.28 (Nightingale Jr, 1959)
Ca^{2+}	0.92 (Vrijenhoek and Waypa, 2000)	4.12 (Nightingale Jr, 1959)
NO_3^-	1.902 (Wang *et al.*, 2005)	3.35 (Nightingale Jr, 1959)
F^-	1.45 (Atkins, 1998)	3.52 (Nightingale Jr, 1959)
$HAsO_4^{2-}$	0.323 (Vrijenhoek and Waypa, 2000)	>2.0–2.2 (Robinson and Stokes, 1965)
SO_4^{2-}	1.065 (Vrijenhoek and Waypa, 2000)	3.79 (Nightingale Jr, 1959)

the tight membrane (NF 90). Dolar *et al.* (2011) found asimilar rejection of F^- by the tight NF90 membrane (98.9%) and the loose TFC membrane (75.4%). The removal of divalent $H_2AsO_4^{2-}$ was always higher than that of monovalent F^- for balancing the electroneutrality. This is also related to the low diffusion coefficient of $H_2AsO_4^{2-}$ compared to F^- (Table 4.4). However, the As and F^- concentration in the permeate of both membranes was always below the MCL.

4.5.2.2 *Effect of feed water concentration*

The rejection of As(V) and F^- as a function of feed water concentration is shown in Figure 4.10. The experiments were performed at 0.8 and 1.8 MPa for low pressure RO and high pressure RO membranes, respectively, and at a temperature of 20°C. There was no significant change observed for As(V) rejection with change of the concentrations (96.1–96.4% for BW30 and 97.8–98.6% for SWHR). Because of the increase of the feed water concentration, the concentration in permeate also increased. Thus, the permeate concentration of As remained nearly constant. The rejection of As(V) by the SWHR membrane was always higher than that of the BW30 membrane (Fig. 4.10a). This result is in agreement with what has been reported by Gholami *et al.* (2006) and Akin *et al.* (2011). However, a slight decrease of rejection with increasing concentrations was observed for F^- with both membranes (88.6–87.1% for BW30 and 92.1–91.2% for SWHR) due to the high ionic concentration (Fig. 4.10b). The concentration of F^- was below the detection limit (BDL) with an initial concentration of 2.5 mg L^{-1} and 5 mg L^{-1}, and remained below the MCL for all the other concentrations. Dolar *et al.* (2011) also reported similar results for F^- removal using the BW membrane.

Figures 4.10c and 4.10d show the effect of As(V) and F feed concentrations for both low pressure RO membranes at an operating pressure of 0.8 MPa and a temperature of 20°C. The NF90 membrane (over 96%) showed a higher As rejection than the NF270 membrane (over 92%), in the investigated As feed concentration range. The rejection of As(V) by both membranes decreased slightly (NF90 99–96% and NF270 95–92%) with increasing concentration from 50 μg L^{-1} to 300 μg L^{-1} (Fig. 4.10c). This is in agreement with Akbari *et al.* (2011), who found a decrease of the As rejection with the NF90 membrane from 98.3 to 96.6%, by increasing the feed concentration. Furthermore, the rejection of F^- by the NF90 membrane (over 95%) was higher than for the NF 270 membrane (over 84%), and the rejection was decreased with increasing feed concentration (95–92% NF90 and 84–84.2% NF270) (Fig. 4.10d).

4.5.2.3 *Removal of As and F from synthetic groundwater*

Figure 4.11 shows the total rejection of several ions including As(V) and F^- by two low pressure RO membranes and two high pressure RO membranes. The rejection for As(V) ranged between 96.1 and 98.6% and for F^- between 84.4 and 97.2%. For all four membranes, the rejection sequence of cations was $Ca^{2+} \geq Mg^{2+} > Na^+$ and for the anions $SO_4^{2-} > HAsO_4^{2-} > F^- > NO_3^-$. For cations, the higher rejection of divalent cations (Ca^{2+} and Mg^{2+}) compared to monovalent

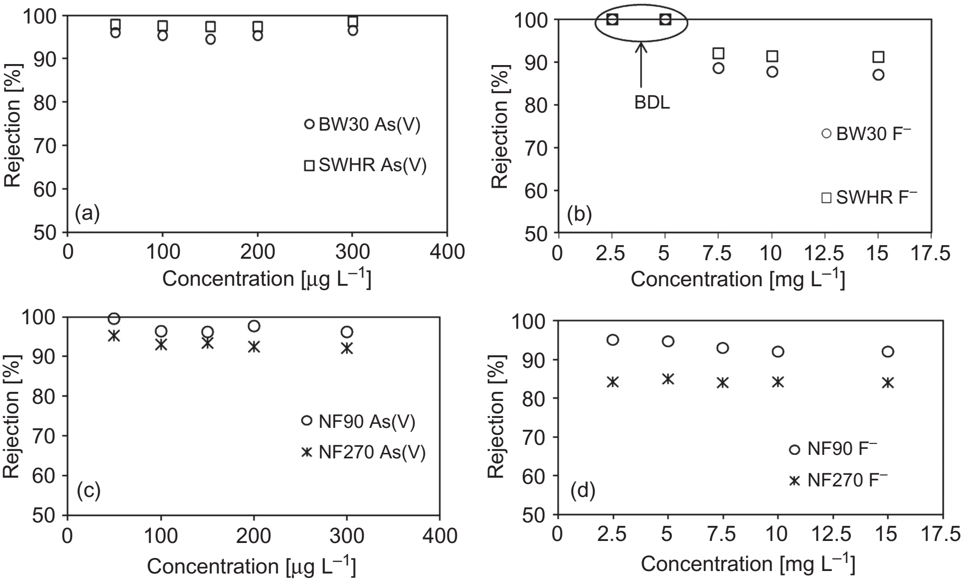

Figure 4.10. Rejection of (a) As(V) and (b) F^- of RO and rejection of (c) As(V) and (d) F^- for NF as a function of concentration. (Operational conditions: pressure 1.8 MPa, $pH = 7 \pm 0.2$, temperature = 20°C).

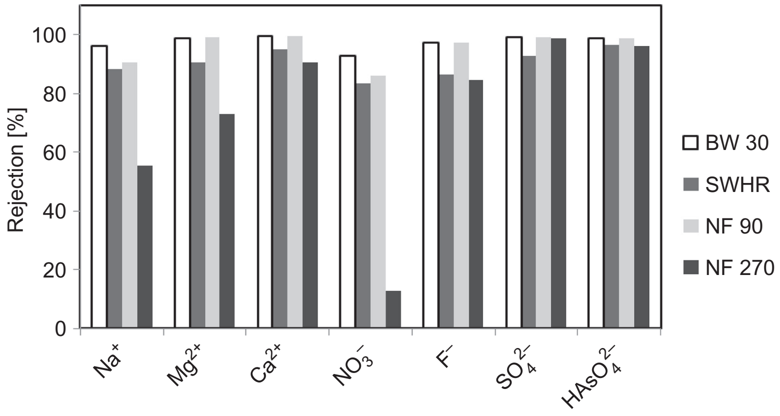

Figure 4.11. Removal of individual ions by BW30, SWHR, NF90, and NF270 membranes (Ca^{2+}: 180 mg L^{-1}, Mg^{2+}: 62 mg L^{-1}, Na^+: 140 mg L^{-1}, SO_4^{2-}: 385 mg L^{-1}, $HAsO_4^{2-}$: 0.2 mg L^{-1}, F^-: 10 mg L^{-1} and NO_3^-: 220 mg L^{-1}; Pressure, NF = 0.8 MPa, RO = 1.8 MPa; pH 7; Temperature 20°C).

cations (Na^+) was observed due to their larger hydrated radii (steric effect) (Table 4.4). Similarly, a higher rejection of divalent anions ($HAsO_4^{2-}$ and SO_4^{2-}) was obtained due to combined steric effects and electrostatical effects (Table 4.4). SO_4^{2-} ions have the largest hydrated radii, thus, the rejection was highest among all anions. Althoughthe hydrated radius of $HAsO_4^{2-}$ is smaller than that of F^- and NO_3^-, the rejection was high due to the low diffusion coefficient and high charge density (Akin *et al.*, 2011; Hoinkis *et al.*, 2011).

For nanofiltration, the rejection of ions with NF 270 was the lowest (55.4% Na^+, 72.9% Mg^{2+}, 90.4% Ca^{2+}, 13.0% NO_3^-, 84.5% F^-, 98.8% SO_4^{2-} and 96.1% $HAsO_4^{2-}$). This can be explained by the large pore size of NF 270 (~0.84 nm) (Nghiem and Hawkes, 2001) compared to NF90 (0.68 nm) (Nghiem and Hawkes, 2007). The metal ions shielded the negative charge of the membrane, which simultaneously decreased the charge of the membrane, especially when high concentrations of divalent cations were present in the solution (Choi *et al.*, 2001) and thus, the anions easily passed through the larger pore size membrane and the rejection decreased. Moreover, it was observed that the rejection of monovalent anions (NO_3^-, F^-) was lower than for divalent anions (SO_4^{2-}, $HAsO_4^{2-}$). In addition, NO_3^- ions have a lower hydrated radius and can pass through the membrane more easily than F^- (Fig. 4.11). Although the divalent cations Ca^{2+} and Mg^{2+} were highly rejected by negatively charged membranes, a small amount of divalent cations could still pass to the permeate stream, which made the monovalent anions (NO_3^-, F^-) and a small amount of $HAsO_4^{2-}$ forced to pass through the membrane for balancing the electroneutrality. Thus, a lower rejection of monovalent anions was obtained (Choi *et al.*, 2001).

Previous studies (Akin *et al.*, 2011; Teychene *et al.*, 2013) have shown a higher rejection of F^- by SWHR than by BW 30. However, in our study we found that the removal of all the ions was higher in case of BW 30 rather than SWHR. This can be explained due to the higher negative zeta potential (ZP) of the BW 30 membrane (−13 mV, pH 7) (Ishida *et al.*, 2005) than that of SWHR (−5 mV, pH 7) (Lee *et al.*, 2010) and as a result, the separation increases due to greater electrostatic repulsion between the anions and the membrane.

In summary, from the above experiments, it can be concluded that the BW30 membrane has a higher rejection of both As and F from synthetic groundwater solution (>90%) than all other membranes tested. NF90, NF270 and SWHR membranes can also be used potentially for removal of both As and F^- and other ions (except nitrate for NF270).

4.6 CONCLUSION

Several remediation technologies have been considered for removal of As, F and U from water. RO appears to be the most effective processes to remove these contaminants from aqueous solution. Thus, an application of this technique is reviewed in this chapter along with experimental observations to support the reported performances.

It is clear from the literature review that the rejection efficiency for As(V) is remarkably higher than As(III) by both high pressure and low pressure RO membranes due to electrostatic repulsion and size exclusion. Therefore, oxidation from As(III) to As(V) becomes a very important pretreatment step for removing total As below the MCL. Removal of fluoride by both high pressure and low pressure RO technologies is also very effective and are sufficient to reduce the permeate concentration below the MCL. Although there are very few studies that have evaluated removal of U from drinking water by RO membranes the removal efficiency of U have showed successful application of the technique in the drinking water industry.

Many researchers have used RO for desalination and production of potable water but there are some drawbacks, which need to be considered. Fouling on the semi-permeable RO membrane is one of the important drawbacks. In this case cleaning or replacement of the membrane or an increase in operating pressure is necessary to avoid the problem, which simultaneously increases the cost of operation. Moreover, this technology is not sufficient to lower the contaminant concentration below the MCL especially when the contaminated water has a high concentration of the inorganic pollutant and application of integrated/hybrid technology could be a better option. Additionally the removal efficiency of these toxic inorganic ions by RO depends on some important parameters, such as the source of water, pH of the solution, membrane materials and the conditions applied during the removal process. Therefore, all of these facts need to be considered and the development of better quality membranes (with higher-fouling resistance, rejection efficiency and water flux) is necessary before the application of RO in both developed as well as newly industrialized developing countries for potable water production.

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CHAPTER 5

Electro-membrane processes for the removal of trace toxic metal ions from water

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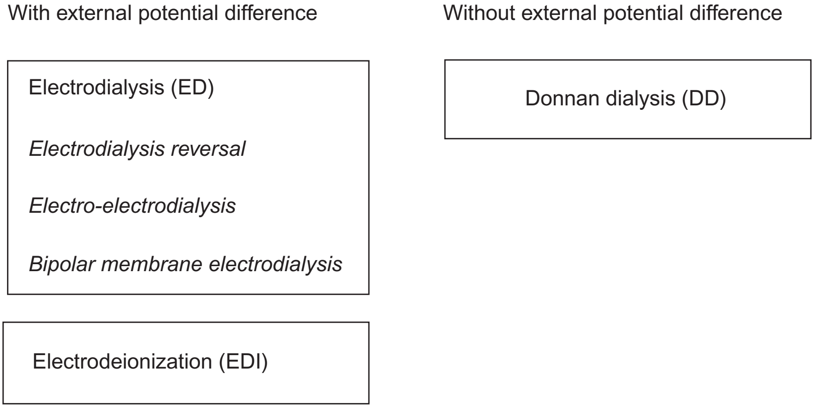
5.1 INTRODUCTION

The contamination of water sources with toxic metals and semi-metallic elements, including arsenic (As) and selenium (Se), is a matter of great concern worldwide, because of their potential negative impact on the ecosystems. While in very small amounts, many of these metals are necessary to support life, in larger amounts, they can become extremely toxic. Their bioaccumulation in animals and human bodies may lead to long-term negative health effects and chronic diseases (Richardson, 2003; Smith *et al.*, 2002). Aqueous streams, containing toxic metals (Cd, Ni, Hg, Pb, Co, Cu, Zn, Al, Sb, Mo, Sn, V, U, etc.) are produced in many industrial processes, such as metal-finishing applications (e.g., electroplating), production of accumulators and batteries, fuel, paints, pesticides and cellulose acetate manufacturing, etc. Due to intensive mining activities, the water in the vicinity of such places can become severely polluted. Therefore, the maximum allowed concentrations of such compounds are generally set by the drinking water quality regulatory standards in the relatively low $\mu g\,L^{-1}$ to $mg\,L^{-1}$ range, therefore, the majority of them can be referred to as trace metal pollutants or micropollutants. Since, usually there are no detectable organoleptic changes in drinking water in the presence of toxic metal ions in trace levels, it is rather possible that some of them may easily remain undetected, thus additionally increasing the possible health risks. Therefore, environmental sustainability requires a complete removal of these contaminants from the water cycle.

Membrane separation processes, if properly selected, offer the advantage of producing high quality drinking water. In many cases, one membrane process can be followed by another or applied in combination of physical, chemical and/or biological processing, to produce water of even higher quality. In these processes, the membrane can be viewed as a barrier between contaminated and purified water streams. This physical phase separation of the two streams often allows for operation with no or minimal chemical water pre-treatment, which otherwise forms deleterious by-products (Bergman *et al.*, 1995; Jacangelo *et al.*, 1997). Pressure-driven membrane processes such as reverse osmosis (RO) and nanofiltration (NF) are well-developed and widely used technologies for water treatment (Shih, 2005; Van der Bruggen *et al.*, 2008). However, they are wasteful because they require most of the water to be permeated through the membrane and all or most solutes are retained instead of only the target trace contaminant(s).

Since most metal-containing species in water are either positively (cations) or negatively (anions) charged, the use of electro-membrane processing for their removal appears as a natural choice. Therefore it is not surprising that the scientific and patent literature devoted to possible applications of electro-membrane processing for removal of trace toxic metal ions from water is abundant. Therefore this chapter does not pretend to be exhaustive and covers mainly some recently published studies, focusing on hybrid processes, which are gaining increasing attention. Older studies that have explored possible applications of electromembrane processes in water treatment have been discussed elsewhere (e.g., Banasiak, 2009; Davis *et al.*, 2000; Grimm *et al.*, 1998; Strathmann, 2004; Koter and Warszawski, 2000; Strathmann, 2010; Velizarov *et al.*, 2004). After briefly presenting the most relevant electromembrane processes for treating waters, containing traces of toxic metal ions, and addressing the removal of arsenic (As), fluoride (F^-) and



Scheme 5.1. Electro-membrane processes for separation of metal ions from water.

uranium (U), we have selected and discussed two case-studies developed in our recent research, in order to illustrate possible successful application of Donnan dialysis, applied as a single or part of an integrated treatment for the removal of arsenate and ionic mercury from contaminated water sources. They are based on a novel water treatment concept, combining a continuous membrane transport of an ionic pollutant with its simultaneous chemical or biological treatment (referred to as ion-exchange membrane reactor (IEMR) or ion-exchange membrane bioreactor (IEMB), respectively) (Velizarov *et al.*, 2011).

Membrane processes that use ion-exchange membranes and electric potential difference as the driving force for ionic species transport are referred to as electromembrane processes (Strathmann, 2004). The following electro-membrane separation processes (Scheme 5.1) can be distinguished: electrodialysis (ED), including variations such as electrodialysis reversal, electro-electrodialysis and bipolar membrane electrodialysis, electrodeionization (EDI), and Donnan dialysis (DD).

Although the driving force in Donnan dialysis is not an external electric potential difference but a concentration difference, the latter leads to the establishment of an internal electric (Donnan) potential difference, which can be utilized for transport and separation of target ionic species. Moreover, as will be discussed in more detail later, this process is especially appropriate for removing trace target ions from low salinity waters. The Donnan dialysis type of operation requires the presence in the stripping solution of a so-called “driving” counter-ion, which is transported across the membrane in a direction opposite to that of the target counter-ion(s) in order to maintain overall electroneutrality in the system. From the operational, economic and environmental points of view, chloride has been generally considered as a suitable driving counter-ion when anionic pollutants have to be removed from contaminated drinking water supplies (Velizarov *et al.*, 2004). In the case of cationic pollutants, sodium, potassium or hydrogen ions appear to be the best possible choices.

In ED, the transport of ions present in contaminated water is accelerated due to an electric potential difference applied externally by means of electrodes (anode and cathode). In this process, anion-exchange membranes and cation-exchange membranes are applied in order to transport anions and cations to the anode or cathode, respectively. Process deterioration due to membrane scaling is a frequently observed problem; therefore, the ED systems are usually operated in the so-called electrodialysis reversal mode, in which the polarity of the electrodes is reversed several times per hour to change the direction of ion movement (Strathmann, 2004). The external electric potential driving force allows higher ionic fluxes to be obtained than those achievable in DD, but a different degree of demineralization (desired anions and/or cations are also removed from the water) depending on the voltage and type of the membranes used is obtained.

Electrodeionization (EDI) is a hybrid process combining ion-exchange with electrodialysis by introducing ion-exchange resins into the electrodialysis chambers. The combination allows for treating very dilute electrolyte solutions, while the ion-exchange resin beads inside the chambers are continuously regenerated *in-situ* by hydrogen and hydroxide ions produced by water electrolysis occurring in the two external electrode compartments (Monzie *et al.*, 2005). Therefore, the EDI process has received increasing attention in the purification of solutions containing toxic metal ions (Dzyako and Belyakov, 2004; Grebenyuk *et al.*, 1998; Mahmoud and Hoadley, 2012; Spoor *et al.*, 2002a; 2002b).

One of the major possible drawbacks is that EDI is susceptible to precipitation of bivalent metal hydroxides as a result of metal ions reacting with hydroxide ions generated within the EDI apparatus. The implementation of EDI in water treatment has been greatly limited by this drawback (Feng *et al.*, 2007). Therefore, possible integrations of ED with other processes (other than EDI) are emerging (Abou-Shady *et al.*, 2012; Nataraj *et al.*, 2007; Tran *et al.*, 2012).

When the purpose is toxic metal(s) removal, reduction in water hardness could be a desired side effect in some cases but in others may cause too "deep" softening (as in RO treatment), therefore the applicability of ED and EDI depends strongly on the polluted water ionic composition (Velizarov *et al.*, 2004).

In summary, electromembrane processes, especially when used as part of hybrid treatment schemes, can provide an efficient removal of toxic metal ions from water. When a target metal exists in water as a mono-valent species, the use of mono-valent (cation- and/or anion-permselective membranes) is especially attractive. Situations, in which ED appears to be less applicable are for waters of very low salinity (conductivity of less than $0.5\ \mathrm{mS\ cm^{-1}}$), for which EDI or DD can be better choices, and, in cases when besides ions, removal of low molecular mass non-charged compounds from the water is desired. In the latter case, pressure-driven membrane processes such as RO or NF may be preferable.

5.1.1 *Removal of uranium fluoride and arsenic by electro-membrane processes*

Uranium is a very toxic and radioactive heavy metal found in nuclear effluents also naturally and in uranium, coal, hydrocarbon exploitation and associated activities. It is therefore not surprising that it was the first to be historically considered for electro-membrane treatment (Davis *et al.*, 1971; Wallace, 1967).

The feasibility of applying electro-membrane processes as DD, ED and EDI has been evaluated. Since concentration ratios determine the Donnan equilibrium, not concentration differences, DD allows for transport of a target counter-ion against its own concentration gradient, it is a convenient method for treating water containing only trace levels of toxic ions. Furthermore, the hydraulic residence time can be independently adjusted in the two compartments (feed and stripping), thus allowing the degree of extraction of the target toxic pollutant to be optimized. Due to these characteristics, the removal of U (in the form of uranuyl ions $(UO_2)^{2+}$) from water streams by Donnan dialysis has received a lot of attention.

Cation-exchange membranes were assembled in a plate-and-frame Donnan dialyzer with solution compartments arranged so that the feed and stripping streams flow in a countercurrent mode of operation. This apparatus was used to recover $UO_2(NO_3)_2$ from a 0.01 M feed to a final content of 0.28 M with 2 M HNO_3 as the stripping electrolyte and to 0.46 M with 2 M H_2SO_4 as the stripping electrolyte (Wallace, 1967).

Although DD allows for achieving very high degrees of separation and concentration of target counter-ions, its possible limitation is the relatively slow transport kinetics because of the absence of externally applied electric potential difference. Therefore ED has been also studied for $(UO_2)^{2+}$ removal (Zaki, 2002). Indeed, applying a potential difference of 30 V across the used Nafion membranes, and by using Na_2CO_3 as the stripping electrolyte solution, the membrane flux of $(UO_2)^{2+}$ was increased by two orders of magnitude. However, this was at the price of a very significant electroosmotic water transport, which can be considered as an undesirable side effect.

More recently, ED and EDI have been applied for treatment of dilute U-containing synthetic aqueous streams. The use of ED was found to be effective, but the presence of magnesium ions in the feed solution caused a decrease in U removal by the subsequent "polishing" EDI process (Zaheri *et al.*, 2010).

Besides treatment of nuclear plant effluents, a more recent trend in the field of membrane-assisted U removal is the treatment of water streams possessing natural radioactivity. A pilot ED plant has been built to test the possibility to improve the quality of the water supplied to the Barcelona metropolitan area from the Llobregat River through reducing its natural radioactivity. The results obtained revealed a significant improvement in the radiological water quality provided by ED with removal rates higher than 60% for gross alpha, gross beta or U activities (Montana *et al.*, 2013).

In the 1990s, the F^- drinking water sources contamination problem, which is especially important in some African countries, stimulated research on possible ways of its removal to the desired low concentration. It is important to note that, contrary to the cases of U and As, low levels ($\sim 1\,\mathrm{mg\,L^{-1}}$) of F^- in the drinking water are health beneficial.

Fluoride removal by Donnan dialysis was investigated and mathematically modeled for a bi-ionic system (NaF as the feed and NaCl as the strip) by Dieye *et al.* (1998) and later on tested in synthetic drinking waters with compositions close to those found in some natural waters in Africa (Hichour *et al.*, 2000). An F^- concentration in agreement with the norm ($<1.5\,\mathrm{mg\,L^{-1}}$) was reached in the later study and the addition of a complex-forming ion such as Al^{3+} (to obtain F^- complexes, which are not able to cross the membrane) to the strip solution allowed a low free F^- concentration in the strip and a reasonably high process driving force to be maintained. A pilot-scale plate-and-frame DD module, consisting of eleven cells (five feed and six strip cells) separated by DSV anion-exchange membranes (Asahi Glass was tested and the maximum treated water production rate reached $2.5\,\mathrm{L\,m^{-2}\,h^{-1}}$); however, the treated water salinity was increased by about 25% due to electrolyte leakage from the strip to the feed solution. It may be concluded that the Donnan co-ion exclusion provided by this type of membrane was not sufficiently high.

The use of a Neosepta ACS membrane (Tokuyama) was able to solve this problem in a subsequent study by Garmes *et al.* (2002), who also investigated a combination of a Donnan dialytic transport of F^- with its adsorption on Al_2O_3 or ZrO_2, added to the stripping solution.

ED has been also extensively studied as a possible way for removing F^- from water. Using model NaF salt solutions, it has been reported that ED is most effective only if F^- is either the single anionic specie in the water or is present in great excess (Kabay *et al.*, 2008). This situation is, however, rather unlikely to occur in natural waters, which as a rule contain various ionic species at higher levels than the F^- level. Especially problematic is chloride, because due to the anion-exchange membrane resin preference for Cl^- over F^-, any presence of chloride would reduce the ED process efficiency for F^- removal from water streams.

Brackish water, containing $3000\,\mathrm{mg\,L^{-1}}$ of TDS and $3\,\mathrm{mg\,L^{-1}}$ of F^-, was tested by Amor *et al.* (2001). The use of a mono-anion permselective membrane (Neosepta ACS) allowed for maintaining the water sulfate concentration close to its original value (only 5% was removed). The membrane transported the anions in the following order: $Cl^- > F^- > HCO_3^- > SO_4^{2-}$.

Using the same Neosepta ACS and a Neosepta CMX as the cation-exchange membrane, an ED process for testing the feasibility for removing F^- from natural groundwater in Morocco has been also tested. It was found that the required F^- drinking water content ($<1.5\,\mathrm{mg\,L^{-1}}$) can be obtained, but at a very high overall water demineralization rate of 80% (Sahli *et al.*, 2007).

Therefore it can be concluded that ED treatment of multi-ionic water with a relatively high F^- concentration for defluoridation appears to be not feasible, because it would require a very high amount of energy. Moreover, concentration polarization problems at the membrane surfaces can occur in both dilute and concentrate compartments.

Arsenic (As) removal from drinking water supplies by electro-membrane processes until recently has been rarely reported. The latter may stem from the fact that the required target As value in the treated water must be extremely low ($10\,\mu\mathrm{g\,L^{-1}}$ as As). Therefore it could be anticipated that the accompanying anions competition and water demineralization problems, especially in the case of ED, would be much more severe compared to the case of F^- removal (required to the very low F^- $\mathrm{mg\,L^{-1}}$ instead of $\mu\mathrm{g\,L^{-1}}$ range). In any case, during the last few years, there is an obvious increasing interest in this topic, which has led to gaining a much better insight into the mechanisms of arsenate/arsenite transport across anion-exchange membranes (Guell *et al.*, 2011; Velizarov *et al.*, 2005; 2013; Zhao *et al.*, 2010) as well as to testing a DD-based pilot plant (Zhao *et al.*, 2012).

Since it is widely distributed throughout the earth's crust, As represents one of the most serious environmental concerns worldwide. Although organic forms of As are possible in water, only the inorganic arsenite (As(III)) and arsenate (As(V)) forms have been found to be significant in groundwater (Henke *et al.*, 2009). The maximum allowed concentration of this element in drinking water is set to $10\,\mu g\,L^{-1}$ (USEPA, 2001; WHO, 2008). In Portugal, recent findings have shown high levels in numerous locations (located far from centralized drinking water facilities and serving populations in remote rural locations), in some cases exceeding the recommended limit by more than fifty times (Garcia, 2006).

While arsenate removal by conventional anion-exchange has been extensively explored, only a few studies have been reported on the separation of As-containing ions by Donnan dialysis (Guell *et al.*, 2011; Velizarov *et al.*, 2005; 2013; Zhao *et al.*, 2010; 2012). Unlike conventional ion-exchange, involving resin loading and regeneration steps, Donnan dialysis is an ion-exchange membrane based separation process that can be performed under either batch or continuous operation conditions (Davis, 2000). Another potential advantage of applying Donnan dialysis instead of conventional ion-exchange, is that the degree of removal of a target charged pollutant can be optimized through independently adjusting the hydraulic residence times in the feed (contaminated water) and stripping compartments that are separated by the ion-exchange membrane.

Zhao *et al.* (2010) performed batch Donnan dialysis studies at different pH values using two types of anion-exchange membranes, one homogeneous and another heterogeneous. They reported that the arsenate removal efficiency was higher for the case of the homogenous membrane. Furthermore, it has been recently revealed that the use of membranes with mono-anion-permselective properties such as Neosepta ACS is not recommended because of slow transport of arsenate and its significant retention in the membrane phase (Velizarov, 2013).

5.1.2 *The ion-exchange membrane bioreactor concept*

A novel hybrid process concept, referred to as ion-exchange membrane bioreactor (IEMB) for the transport of ionic pollutants present in water through an ion-exchange membrane and their simultaneous biotransformation to harmless products, has been proposed by Crespo and Reis (2001). More recently, this concept was tested for the simultaneous transport and chemical precipitation of arsenate and the designation of the process was modified to ion-exchange membrane reactor (IEMR) in order to highlight the absence of biological treatment in the latter case (Oehmen *et al.*, 2011).

The IEMB concept integrates the transport of target ionic pollutants from an aqueous stream, through a dense ion-exchange membrane, to a stripping compartment where these ionic compounds are biologically reduced to harmless products (see Fig. 5.1). In order to enhance the transport of the target ionic pollutants, an appropriate counter ion is added to the stripping compartment at sufficiently high concentration. This procedure makes it possible to transport the target pollutant, even against its own concentration gradient. Once the ionic pollutant reaches the stripping compartment, it is converted by an appropriate microbial culture, which is able to reduce it under anoxic conditions. A non-charged and non-fermenting carbon source (used as electron donor, e.g., ethanol) is fed to the stripping biological compartment in enough amounts, in order to assure the complete biological reduction of the transported ionic solutes.

This concept is rather simple but it presents a series of relevant features, which answer to problems previously encountered in physical/chemical and biological treatment of charged pollutants:

- The microbial culture able to reduce the target pollutant(s) is physically separated from the water stream by a dense, non-porous membrane, thus assuring that the treated water is never in contact with the microorganisms responsible for the bioconversion.

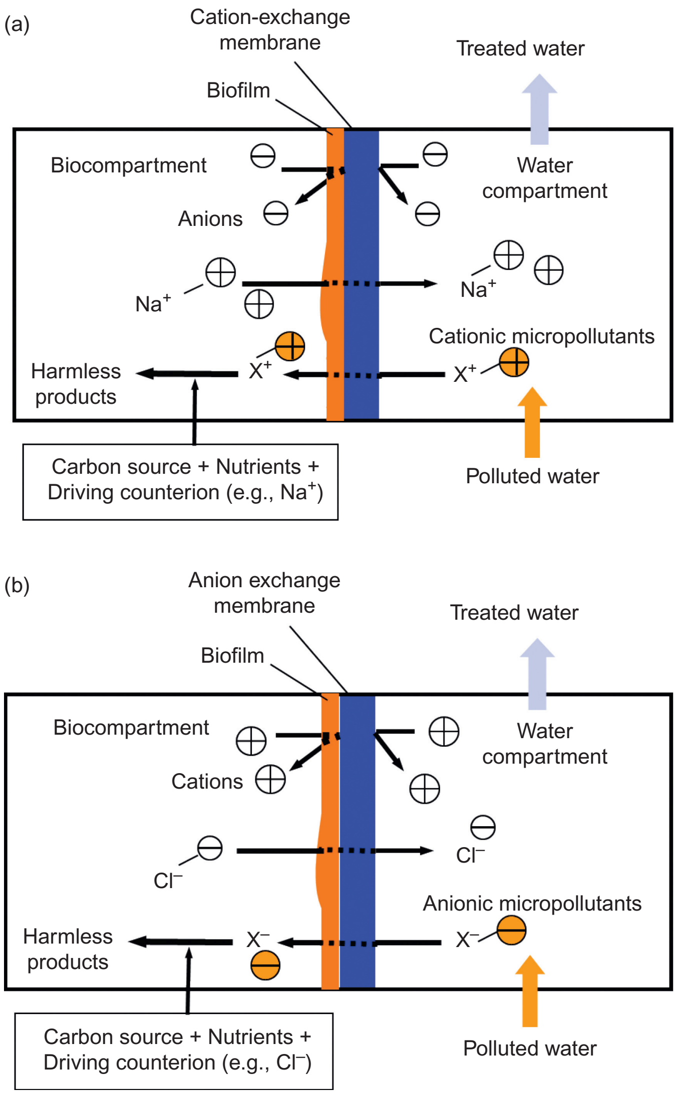


Figure 5.1. Schematic diagram of the ion transport mechanism in the ion-exchange membrane bioreactor (IEMB). (a): for removal of cationic and (b): anionic micropolutants.

- As the membrane selected is charged (fixed charge opposite to the charge of the solutes aimed to be transported) and non-porous, it is possible to assure that transport of non-charged metabolic by-products is extremely reduced; if they present a charge identical to that of the membrane fixed functional sites, their transport may be completely avoided.
- Naturally, a biofilm develops on the membrane surface contacting the biological compartment. This biofilm acts as an active reaction zone, where most of the aimed reaction process takes place, also providing an additional barrier to the transport of excess carbon source, used as electron donor, from the biomedium to the treated water. These three features assure that secondary contamination of treated water by microorganisms, metabolic by-products and excess carbon source can be avoided if an appropriate membrane and operating conditions are selected. Also, strict control of the rate of addition of carbon source, aiming to avoid a situation of excess or deprivation, is not required.

- As the microbial culture can be selected by using appropriate selective pressure conditions, only target ionic pollutants are converted. As a consequence, the driving force for transport of ionic compounds from the water stream is only kept high for compounds that are biologically converted. This feature assures that the water stream is not unspecifically depleted of ions which may be important to maintain an adequate water composition balance (in opposition to some physical water treatment processes, such as reverse osmosis).
- As anoxic conditions are used in the biological compartment, the yield (and rate) of cell mass production is much lower than the one typical for aerobic membrane bioreactors, where biofilm development represents a significant problem in terms of resistance to mass transfer and membrane clogging and fouling. In the IEMB system, the biofilms that develop naturally at the membrane surface are rather thin, having a positive impact as an active reaction zone and barrier to carbon source loss through the membrane. Also, as the membrane is non-porous, clogging problems are not an issue. The IEMB system proved that it can be operated during long periods of time without flux decline or need for membrane cleaning (tests with an extension of 4 months have been accomplished).
- The concentration of driving counter-ion (e.g., Cl^-) may be adjusted in order to assure a high transport rate of the target polluting ion, even against its own concentration gradient. This feature is also particularly interesting if (e.g., due to some operating problem) the target ion accumulates in the biocompartment.
- As the target ionic pollutants are converted to harmless products (e.g., N_2, Cl^-) and not just transferred and concentrated in a stripping compartment/stream, as happens in physical processes for water treatment, brine solutions are not produced, thus avoiding the need of their treatment and disposal.
- The hydraulic residence time (HRT) can be adjusted independently in both water and biological compartments. Typically, very large residence times may be used in the biological compartment (the biological reaction takes mostly place within the biofilm at the surface of the membrane), originating a waste stream with an extremely reduced volume when compared with the volume of treated water.

The treated water throughput of the IEMB system depends strongly from the driving force for transport of the target polluting anion. For relatively low, but common, levels of contamination the IEMB system allows the micropollutant concentration in the treated water to be reduced to target values, at a throughput of 30–10 L/(m^2 of membrane × h). This throughput is rather competitive, even when compared with common throughputs obtained by nanofiltration and/or reverse osmosis. Additionally, as mentioned before, the IEMB presents the advantages of leading to a well-balanced treated water (in terms of its ionic composition) and not forming a brine stream that requires further disposal/treatment (which may be costly, according to local dispositions).

The IEMB process has shown excellent performance for the case of removal of monovalent anions, such as bromate (Matos *et al.*, 2008) as well as nitrate and perchlorate (Ricardo *et al.*, 2012). On the other hand, while the removal of some ions (nitrate, nitrite, perchlorate, and bromate) is relatively easier, further research is needed to extend this approach to the more challenging cases of metal-containing ions such as arsenate, chromate, ionic mercury, etc. These situations are more complex due to the strong pH dependence of their speciation in water, affecting their charge, solubility and complex-forming behavior (DeZuane, 1997).

5.2 CASE STUDIES

5.2.1 *Arsenic removal from groundwater by a hybrid DD-coagulation process*

Contrary to the cases of nitrate, perchlorate and bromate, neither the biologically catalyzed reduction of arsenate to arsenite nor the oxidation of arsenite to arsenate are beneficial since they do not result in the formation of innocuous products. Since the As-related toxicity is due to the metal itself and not due to the oxy-anionic form in which it is present, biotransformation

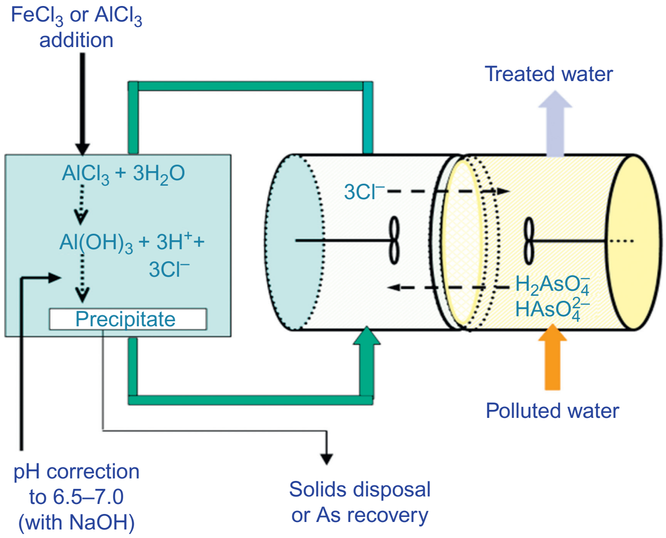


Figure 5.2. Schematic representation of the integrated concept for combined transport and treatment of arsenic species (right: polluted water entrance and outlet of treated water; left: a re-circulation vessel to which $FeCl_3$ or $AlCl_3$ is periodically added for arsenic precipitation).

is ineffective in this case. Therefore, a modified integrated process was developed (Oehmen *et al.*, 2011) through replacing the application of a mixed microbial culture in the stripping compartment by co-precipitation with iron or aluminum as a way of achieving As removal in the stripping compartment solution (Fig. 5.2). Therefore, the process was referred to as an IEMR, instead of IEMB in order to more correctly represent its features.

The approach is based on the isolation of the contaminated drinking water stream by an anion-exchange membrane barrier, through which arsenate diffuses to a stripping compartment, operated as a closed vessel with re-circulation, to which a coagulant ($FeCl_3$ or $AlCl_3$) and, if necessary, pH-controlling reagents can be periodically added to guarantee the most appropriate conditions for As precipitation. The membrane excludes the transport of cations (including Fe^{3+}, Al^{3+}) while permitting the flow of anions.

The transport of arsenate to the stripping compartment is therefore stimulated by the excess of Cl^- available for arsenate counter transport through the membrane, according to Donnan dialysis principles. The chemical precipitation additionally keeps the arsenate concentration in the stripping compartment at low levels, thus ensuring high driving force for its transport. Thus, the chemical coagulant ($FeCl_3/AlCl_3$) is completely utilized as a chemical precipitant (i.e., Fe^{3+} or Al^{3+}) and as a source of counter-ions for arsenate transport (i.e., Cl^-), simultaneously achieving both purposes with the addition of only one chemical. For very dilute electrolyte solutions, the counter-ion flux through ion-exchange membranes is diffusion boundary layer controlled, since it is directly proportional to the counter-ion concentration in water (Velizarov, 2003) An increase in the F/A ratio led to a proportional increase in the transport driving force for arsenate, and subsequently, its flux through the membrane. At high water throughputs, the arsenate residence time in the water compartment becomes very short (in the range of few minutes), which probably introduces an additional resistance to its transport due to the kinetics of the required anion-exchange reaction at the membrane – water interface, thus diminishing the arsenate flux and increasing the As concentrations in the treated water (Fig. 5.3).

The R204-UZRA membrane was selected amongst a number of anion-exchange membranes tested (Zhao *et al.*, 2011) as the most suitable membrane for the As removal process, due to the comparatively high flux of arsenate, good mechanical properties and more affordable cost. Next,

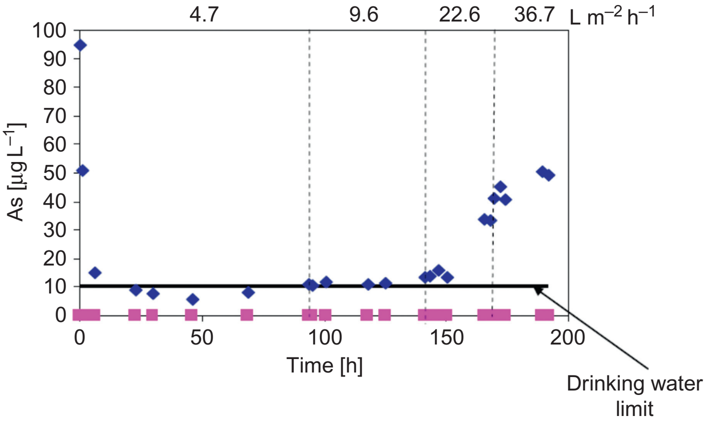


Figure 5.3. Arsenic concentration in treated water (arsenic concentration in the polluted water = 100 µg L^{-1}). $FeCl_3$ was used as the coagulant. The system was operated at different feed water flow rate (F) to membrane area (A) ratios (F/A = from 4.7 to 36.7 L m^{-2} h^{-1}) corresponding to the time intervals marked by dotted lines.

the optimal membrane to reactor volume ratios and reactor operation regimes were identified. $FeCl_3$ presented the best coagulant behavior under low flow to membrane area (F/A) ratios. When iron was added to the stripping compartment, the As concentration was maintained below the detection limit (<0.5 µg L^{-1}) throughout the entire experiment, The As concentration in the treated water for different polluted water flow rates was analyzed through ICP measurements and the results obtained are presented in Figure 5.3.

The results obtained showed that this integrated process can remove efficiently arsenate present in drinking water supplies, at a water treatment rate per square meter of membrane as high as 10 L m^{-2} h^{-1}. If higher throughputs are needed, the treated water obtained can be further blended with water from an As-free source (if available) in order to be conform with the current maximum contaminant limit of 10 µg L^{-1} of As in drinking water. Such treatment rates are common for nanofiltration and demonstrate that they can be achieved also in a process that does not utilize pressure as a driving force. However, it has to be pointed out that the process was effective in avoiding secondary contamination of the treated water by the undesirable presence of coagulants, even at very high dosage levels. The latter translates into extremely high drinking water quality, which is the principal advantage of the hybrid process compared to the traditional coagulation/precipitation process.

5.2.2 *Mercury removal via the ion-exchange membrane bioreactor (IEMB)*

Mercury (Hg) is the most toxic heavy metal, and offers no beneficial biological function in any of its forms (Nies, 1999). Mercury pollution in the environment has previously triggered disasters on numerous occasions, such as the poisoning of large populations from Minnamata, Japan or in other countries such as Iraq, Brazil, Indonesia, the USA and China (Jiang, 2006). Industrial activities including mining and the chlor-alkali process have been linked with mercury contaminated water supplies, although on occasion natural sources have been responsible for high mercury levels (Lisha *et al.*, 2009). The drinking water limit for Hg recommended by the World Health Organization is 1 µg L^{-1}, and the by the USEPA is 2 µg L^{-1}. Hg levels above these limits have been previously observed in drinking water supplies (Barringer *et al.*, 2006) and reservoirs that could otherwise be used as drinking water sources (Heaven *et al.*, 2000; Liu *et al.*, 2012; Yan *et al.*, 2009) in many countries worldwide.

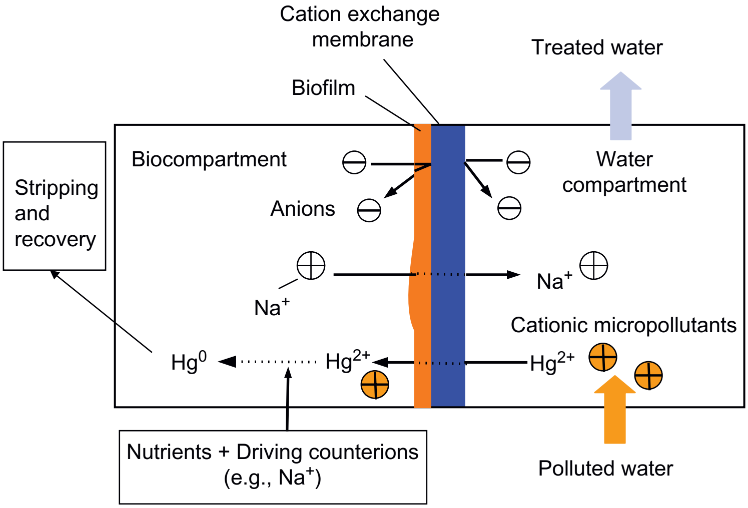


Figure 5.4. Ion-exchange membrane bioreactor (IEMB) schematic for mercury removal.

The advantages of Donnan dialysis-based processes for mercury removal from drinking water are similar to the case of As, where continuous operation without regeneration can be employed and the hydraulic retention times in both the feed and stripping compartments can be independently adjusted. Unlike the case of As, Hg(II), the most common form of Hg in water supplies, can be biologically reduced to Hg(0), which has a very low solubility in water. Therefore, mercury can be selectively removed and recovered from the water phase through the ion-exchange membrane bioreactor (IEMB) process, illustrated in Figure 5.4 (Oehmen *et al.*, 2006). The negatively charged cation-exchange membrane excludes the transport of similarly charged anions, permitting the flow of cations (e.g., Na^+) for counter transport, according to Donnan dialysis principles. The bioreduction of Hg(II) to Hg(0) in the biocompartment keeps its concentration at low levels, ensuring an adequate driving force for transport. The Hg(0) that is produced is then stripped from solution through the aeration gas and selectively recovered through sorption onto various materials, e.g., activated carbon.

The main concern of applying biological processes for drinking water treatment purposes in most cases is the risk of secondary pollution by cells and the accumulation of incompletely degraded nutrients and metabolic by-products, which can promote microbial growth in water distribution systems. The integration of bioremediation with Donnan dialysis in the IEMB prevents these undesirable attributes associated with biological processes for drinking water treatment, and provides an environmentally friendly means of removing and recovering this toxic heavy metal.

The choice of cation-exchange membrane to be employed in the IEMB process was based on a series of batch experiments operated under Donnan dialysis conditions in a stirred diffusion cell. The initial flux of Hg(II) through 11 commercially available cation-exchange membranes was assessed, and the results are shown in Figure 5.5. While some membranes, such as the Nafion, PCA and two Fumatech membranes, exhibited a substantial Hg flux to the stripping compartment, a very low rate of Hg transport was observed through the other membranes tested. A substantial portion of Hg(II) was likely retained in the membrane in these latter cases. The explanation for this result likely relates to the membrane properties, where comparatively thicker membranes ($>200\,\mu m$ – i.e., Ionics, Neosepta and Fumatech FTCM) require longer time to reach steady-state conditions.

The transport mechanism of Hg(II) through the membranes also depends on the speciation of Hg(II), which is pH dependent. In water at near-neutral pH, Hg(II) is largely present in the form of

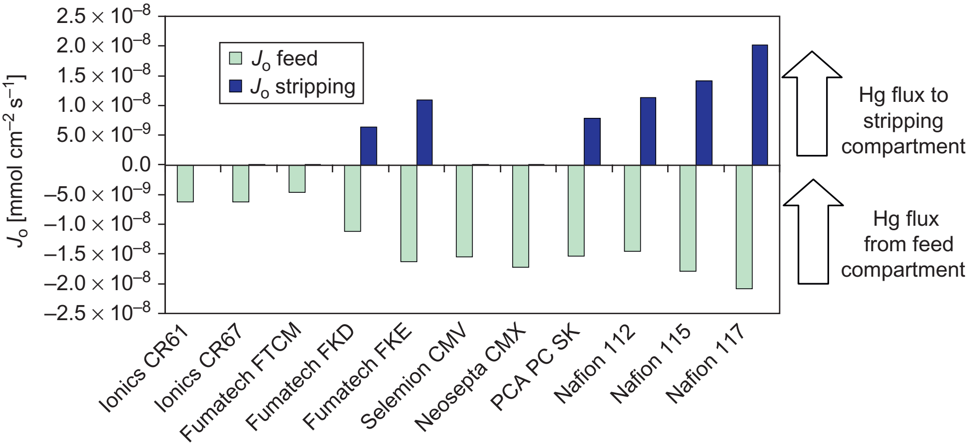


Figure 5.5. Hg(II) transport through cation-exchange membranes through Donnan dialysis (0.01 mM of $HgCl_2$ was initially present in the "feed" water compartment).

Table 5.1. Hg removal from drinking water through Donnan dialysis at a water throughput (i.e., flow rate per membrane area) of 3.1 L m^{-2} h^{-1}.

	Contaminated water	Treated water	Stripping solution
Hg [µg L^{-1}]	12.0 ± 1.6	0.6 ± 0.2	<0.2

$HgCl_2$ and $Hg(OH)_2$, where a comparatively smaller fraction exists as Hg^{2+}, $Hg(OH)^+$ and $HgCl^+$. Nevertheless, the continuous transport of the positively charged components shifts the chemical equilibrium towards the formation of additional charged compound that is then transported across the membrane. Moreover, the negatively-charged cation-exchange membranes possess a lower pH than the aqueous solutions, further accelerating the shift in chemical equilibrium of the mercuric compounds within the membrane towards the cationic form. It should also be noted that a fraction of the Hg(II) can also be transported through molecular diffusion, in addition to the Donnan counter-ion based exchange mechanism.

In order to minimize the time required to achieve steady-state flux conditions, the Fumatech FKE membrane was selected for further study via the IEMB system, considering also the comparatively low cost of this membrane as compared to e.g., Nafion membranes. Further tests were performed at lower initial Hg concentrations in order to assess the suitability of the process for achieving Hg removal from contaminated drinking water. It was found that Hg removal to levels below the 1 µg L^{-1} limit could be readily achieved (Table 5.1), although Hg was not detected in the stripping compartment, even before inoculation with Hg(II) reducing biomass.

The reason for this is likely due to the extended time required with relatively dilute solutions to equilibrate the membrane and achieve steady-state conditions. One potential alternative could be to pre-treat the membrane with a $HgCl_2$ solution in order to accelerate this process.

In cases where steady-state conditions are achieved, Donnan dialysis can be effectively integrated with Hg(II) bioreduction to Hg(0) using mixed microbial cultures. While many organisms have been shown to perform Hg(II) bioreduction in pure culture, mixed microbial cultures offer the advantage of not requiring aseptic operational conditions, and can thus be much more readily integrated with the IEMB process, where aseptic conditions would involve additional operational costs and complicate the process unnecessarily. Efficient Hg(II) bioreducing mixed cultures have been previously developed (Oehmen *et al.*, 2009) and permit the selective recovery of Hg(0) in the off-gas. This allows for simultaneous treatment of the drinking water and brine solutions, thereby minimizing the quantity of contaminated waste that is generated through the IEMB process and reducing its environmental impact.

5.3 CONCLUDING REMARKS AND FUTURE NEEDS

- As it was shown in this chapter, electromembrane processes can be successfully used for the removal of trace toxic metals from water. While laboratory bench-scale processes have been used for process development and optimization, the next steps are the validation of this process at the pilot-scale before implementation of large-scale units in the drinking water industry.
- Uranium in the form of uranyl cations, fluorine as fluoride ion and arsenic in form of arsenate can be efficiently removed by electro-membrane processes. The use of DD appears to be more indicated than that of ED, especially in the case of treating drinking water supplies, since in the latter case, high water demineralization rates, electroosmosis, and membrane scaling related issues can emerge. Moreover, although in general allowing for higher target ion fluxes than DD the elevated energy costs for ED can become an important issue in case of presence of high levels of accompanying ions in the water to be treated. This can significantly limit the ED feasibility as a process of choice. As a general rule, the lower the target toxic ion concentration in the treated water, and the higher the amounts of accompanying ions in the feed water, the less indicated becomes the application of an ED process. Special care must be also taken to possible anion-exchange competitions (higher selectivies of strong anion-exchange resin-based membranes for chloride over fluoride and for sulfate and arsenate) when the objective is fluoride or arsenate removal from water, respectively.
- Nowadays, the relatively high cost of ion-exchange membranes is one of the main limitations towards wider use of electromembrane processes in practice. Since these membranes are industrially produced almost exclusively with a flat geometry (for electrodialysis process applications), the membrane to volume ratio (compactness) of the apparatuses and the control of the hydrodynamic conditions in the chambers are limited. On the other hand, for Donnan dialysis applications, hollow fiber membrane modules seem to be more suitable since no electrodes are required for process operation. Therefore, the development of appropriate ion-exchange membranes with hollow fiber geometry would make possible the design of more compact Donnan dialysis systems, which would permit operation under more efficient water fluid dynamic conditions, by circulating the stream containing trace toxic metal(s) inside the lumen of the fibers.
- In the absence of suitable hollow fiber anion-exchange membranes, plate-and-frame configurations have to be used. The most significant aspect that has to be taken into consideration is the design of the flow channels in both the biological and water stream sides, in order to avoid clogging in the biological channel and provide adequate fluid dynamic conditions in the water channel. The design of dedicated and appropriate spacers to be introduced in the water channel, assuring reduced mass transfer resistance, low pressure drop and reduced energy input, is of major importance.
- The route towards sustainable water treatment raises new challenges to electromembrane processes. From a life cycle analysis viewpoint, sustainability has to take into account the various process stages – including the manufacturing of ion-exchange membranes, which have to respect the principles of "Green Chemistry", and the process material and energy demands, where the fate of the waste streams, such as the brine solutions, must be treated and/or disposed. The latter applies also to the "end of life" of these very membranes. The main challenges involve sustainable development and manufacturing of ion-exchange membranes with improved properties in terms of their exchange capacity, selectivity and operational stability, while reducing the environmental impact associated with their production and use in electromembrane processing. Furthermore, ion-exchange membranes, which have been used to remove toxic metals,

may slowly release them, if they are still attached to the membrane polymeric matrixes. Burning ion-exchange membranes, if not incinerated properly, may release toxic and odorous fumes.

- In what concerns the treatment/disposal of brine solutions, future approaches are expected to increasingly involve the development of integrated (hybrid) processes aiming at minimization of the volume and ecotoxicity of the brine streams, either through combining the electromembrane transport of a toxic metal with its simultaneous coagulation, adsorption, electrochemical oxidation/reduction at appropriate electrodes in a separate compartment or by volatilization (see the case of mercury removal through the IEMB concept described in this chapter).

The overall process sustainability has to be evaluated in terms of a life-cycle analysis perspective, where treatment schemes involving electromembrane processing for the removal of toxic metals from water must be benchmarked against other alternative routes.

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CHAPTER 6

Fluoride, arsenic and uranium removal from water using adsorbent materials and integrated membrane systems

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6.1 INTRODUCTION

Depending on the region and the geology, untreated water may contain, naturally occurring toxic elements, such as arsenic (As), uranium (U) and fluoride (F^-). These elements, which are considered as extremely poisonous, are directly transmitted to people when the untreated water is used for drinking, food preparation, recreation, or for various domestic purposes (Bhatnagar *et al.*, 2011; Iakovleva and Sillanpää, 2013; Nordstrom, 2002). As a result millions of people around the world are threatened by F^-, As and U contamination. There is, thus, a need for low-cost and proven technologies that can effectively treat polluted water especially in developing countries. In this chapter, novel and conventional techniques are critically reviewed for the removal of these toxic contaminants from groundwater and wastewater.

6.2 FLUORIDE

6.2.1 *Introduction*

A comprehensive review on defluoridation of drinking water with an emphasis on the use of sustainable technologies was written by Ayoob *et al.* (2008). The authors critically compared different processes. It was concluded by them that while traditional coagulation methods have generally been found to be effective in defluoridation, they were unsuccessful in reducing F^- concentrations to desired low levels. Furthermore, they maintained that while newer technologies such as membrane processes do not require additives, the technology is relatively expensive to install and operate and the membranes are prone to fouling, scaling, or degradation.

6.2.2 *An overview of technologies for fluoride removal from water*

In a recent review containing over 200 references, Bhatnagar *et al.* (2011) reported on traditional adsorption methods for removing F^- from drinking water including liming (i.e., addition of calcium hydroxide) and the accompanying precipitation of fluorite, the precipitation and coagulation processes with iron (III), activated alumina, alum sludge and calcium, and ion exchange (Table 6.1). The authors argued that shortcomings of most of these methods included high operating and upkeep costs, secondary contamination such as production of a toxic sludge by-product, and complex treatment processes.

Ayoob *et al.* (2008) highlighted the basic principles and procedures involved in current F^- elimination technologies. They reported that defluoridation techniques can be generally grouped into coagulation, adsorption and/or ion exchange, electrochemical, and membrane processes. The coagulation technique involves precipitation or coprecipitation of F^- by using suitable reagents like lime, calcium and magnesium salts, polyaluminum chloride, and alum. Adsorption is another important technique most widely used for excess F^- removal from aqueous solution. In this process a packed bed of adsorbent in fixed columns is continuously used for cyclic sorption and/or desorption of pollutants by effectively utilizing the capacity of the bed. The adsorbents

Table 6.1. Adsorption techniques for fluoride removal from water (adapted from Bhatnagar *et al.*, 2011).

Adsorbent	Examples
Alumina & aluminum based adsorbents	Fluoride (F^-) binds to $Al(OH)_3$ and Al_2O_3
Calcium-based sorbents	Affinity of calcium (Ca^{2+}) for fluoride anion
Iron-based sorbents	Granular ferric hydroxide $Fe(OH)^3$ binds F^-
Metal oxides/hydroxides	Cerium-based adsorbent
Carbon-based adsorbents	Small grain sizes for better F^- adsorption
Natural materials as sorbents	Fluoride binds to bituminous coal & clay
Biosorbents	Chitosan with NH_3^+ & OH^- binds fluoride
Agricultural wastes	Corn cob powder for fluoride adsorption
Industrial wastes as sorbents	Carbon slurry from fertilizer industry
Hydroxyapatite	Highly porous for large adsorption surface
Nano-sorbents	Carbon nanotubes with large surface area

generally used include bone char, activated alumina, activated carbon, activated bauxite, ion-exchange resins, fly ash, super phosphate and tricalcium phosphate, clays and soils, synthetic zeolites, and other minerals.

Electrochemical techniques include electrocoagulation and involve the use of aluminum electrodes that release Al^{3+} ions by an anodic reaction, and the ions then react with F^- ions that are found in excess near the anode. Here, precipitation and thereby removal of F^- occurs at the electrode/electrolyte interface. In addition, membrane techniques include reverse osmosis, nano-/ultrafiltration, and electrodialysis. Defluoridation based on a combination of two or more of these processes have also been reported (Hu *et al.*, 2003; Mjengera and Mkongo, 2003; Velizarov *et al.*, 2004). Mjengera and Mkongo (2003) for example determined that the bone char method was appropriate for use in rural areas of Tanzania suffering from excessive F^- in their water sources due to its simplicity, local availability of materials and the possibility of processing the material locally (Fig. 6.1a). The authors also reported on an institution level defluoridation plant based on the alum and lime method (Fig. 6.1b). While effective it can be argued that such a complex system would not be feasible for poor rural areas.

6.2.3 *Fluoride removal from drinking water by adsorption on naturally occurring biopolymers*

Kamble *et al.* (2007) reported on the applicability of chitin, chitosan and chemically modified chitosan (20%-lanthanum chitosan) as adsorbents for the removal of excess F^- from drinking water. Chitosan which is derived from chitin is one of the main components of crustacean shells of prawn, crab, shrimp or lobster, has the ability to coordinate metal ions because of its high concentration of amine functional groups (Li *et al.*, 1992). It is also a non-toxic, biodegradable and biocompatible material. Furthermore, the effects of various physico-chemical parameters such as pH, adsorbent dose, initial F^- concentration and the presence of interfering ions on adsorption of F^- were assessed by Kamble *et al.* (2007). The authors concluded that lanthanum chitosan adsorbents were better at removal of F^- from water than plain chitosan and chitin (Fig. 6.2).

The adsorption of F^- on the surface of the adsorbent was found to depend mainly on the pH of the solution as well as the concentration and type of co-anions (Fig. 6.3). Kamble *et al.* (2007) also established that the presence of anions has a deleterious effect on the adsorption of F^-, particularly carbonate and bicarbonate anions. The mechanism of adsorption of F^- on lanthanum (La) modified chitosan was explained in terms of the ligand exchange mechanism between F^- ion and hydroxide ion coordinated to La(III) ion immobilized on the chitosan.

The percentage removal of F^- in distilled water was also observed to be higher than ground water; this may have been due to the fact that the latter contains different types of ions. No significant leaching of lanthanum was observed from the adsorbent. It was also possible to regenerate the material, which is important for sustainability.

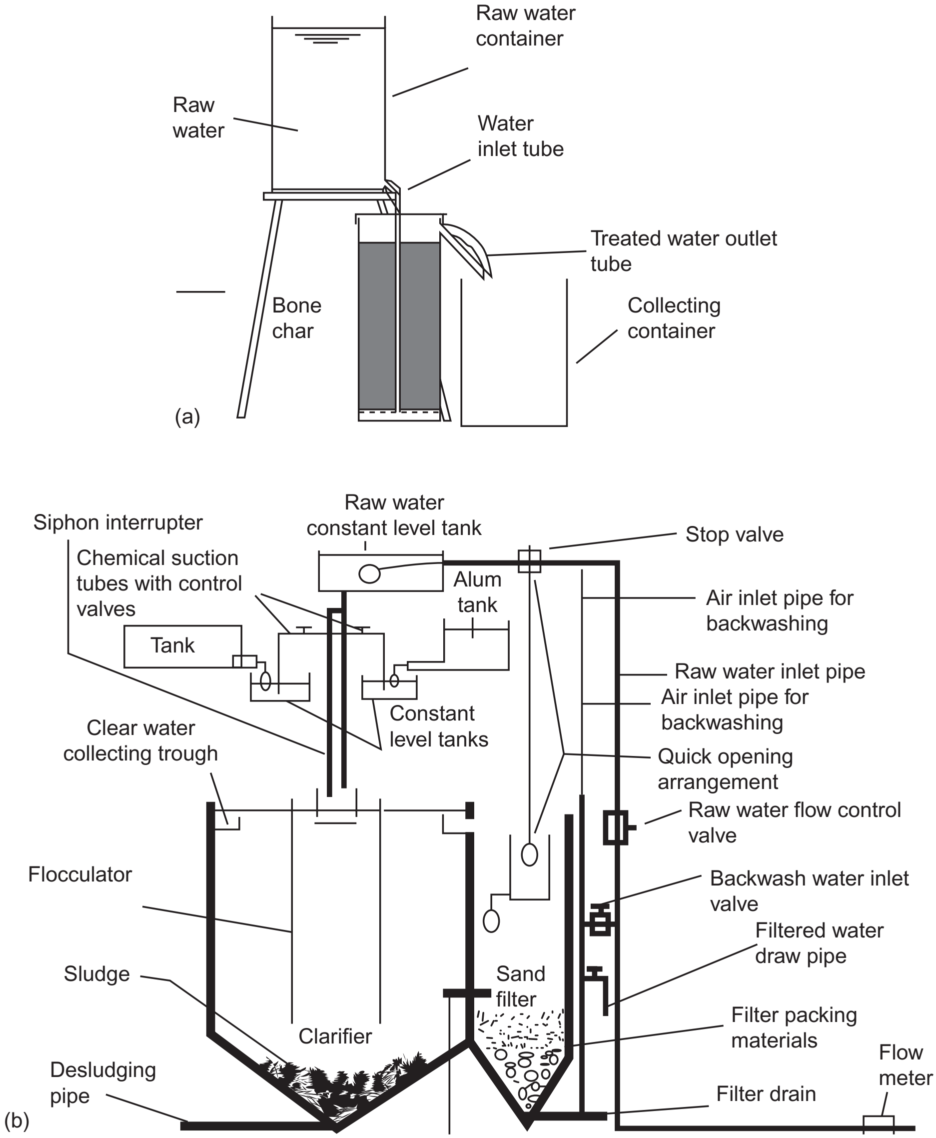

Figure 6.1. (a) Arrangement of household bone char filter column defluoridation unit; (b) an institution level defluoridation plant based on alum and lime method (adapted from Mjengera and Mkongo, 2003).

In a related study, a biomass material, bone char was investigated by Ma *et al.* (2008) for its feasibility as a cost-effective biosorbent for F^- removal from drinking water. The amorphous biosorbent powder, which is composed mainly of calcium phosphate and a small amount of carbon, was prepared by heating bone-biomass. The adsorption capacity of the bone char was shown to be better than that of activated aluminum and tourmaline (i.e., crystal boron silicate mineral compounded with elements such as aluminum, iron, magnesium, sodium, lithium, or potassium). Removal of F^- was attributed to the processes of ion binding and ion exchange between bone char and F^-. The authors developed static and kinetic models which provided a satisfactory prediction of F^- concentration after adsorption. Experiments with fixed-bed columns

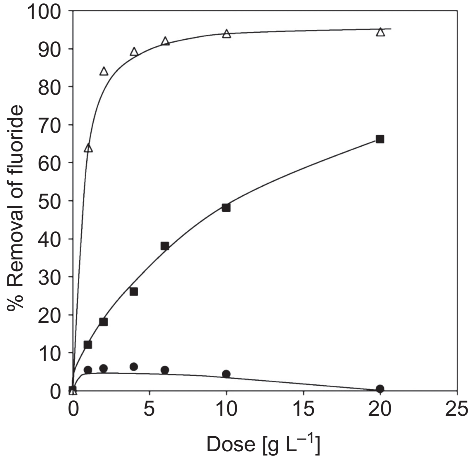

Figure 6.2. Comparison of chitin, chitosan and 20% La-chitosan for fluoride removal (pH 6.7, contact time = 24 h). (●) Chitin; (■) chitosan; (△) 20% La-chitosan (Kamble *et al.*, 2007).

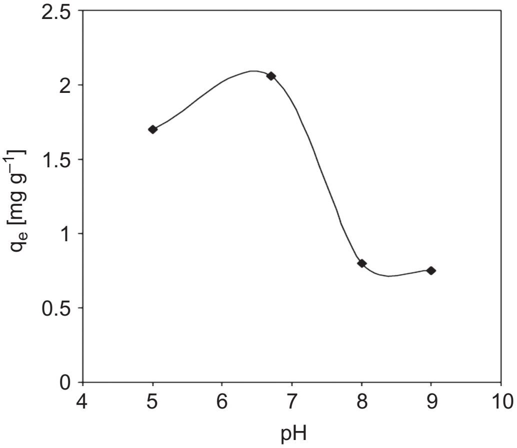

Figure 6.3. Effect of pH on adsorption of fluoride (initial concentration = 5 mg L^{-1}; optimum dose = 2 g L^{-1}; contact time = 24 h) (Kamble *et al.*, 2007).

indicated that adsorption capacity depends strongly on the water flow rate, inlet F^- concentration, and adsorbent column height. In addition, Ma *et al.* (2008) were able to regenerate the bone char powder using 0.5% NaOH, making it a promising material for sustainable purification of drinking water. Compared with traditional F^- removal methods, the authors argued that bone char can be used as a cost-effective biosorbent for efficient F^- removal from groundwater.

6.2.4 *Aluminum and iron oxides and bauxite as adsorbents for fluoride removal from water*

The fluoride ion, F^-, has a strong affinity for metal ions such as Al^{3+} and Fe^{3+} (Wu *et al.*, 2007). Scattering a combination of these metals in a permeable material would afford a high F^- adsorption capacity (Tchomgui-Kamga *et al.*, 2010). As an example of this type of approach, Chen *et al.* (2011) effectively developed an adsorbent by impregnation of porous granular ceramics with aluminum and iron salts to remove F^- from aqueous solution. The Al/Fe dispersed in porous granular ceramic adsorbent was reddish brown and 2–3 mm in diameter (Fig. 6.4b).

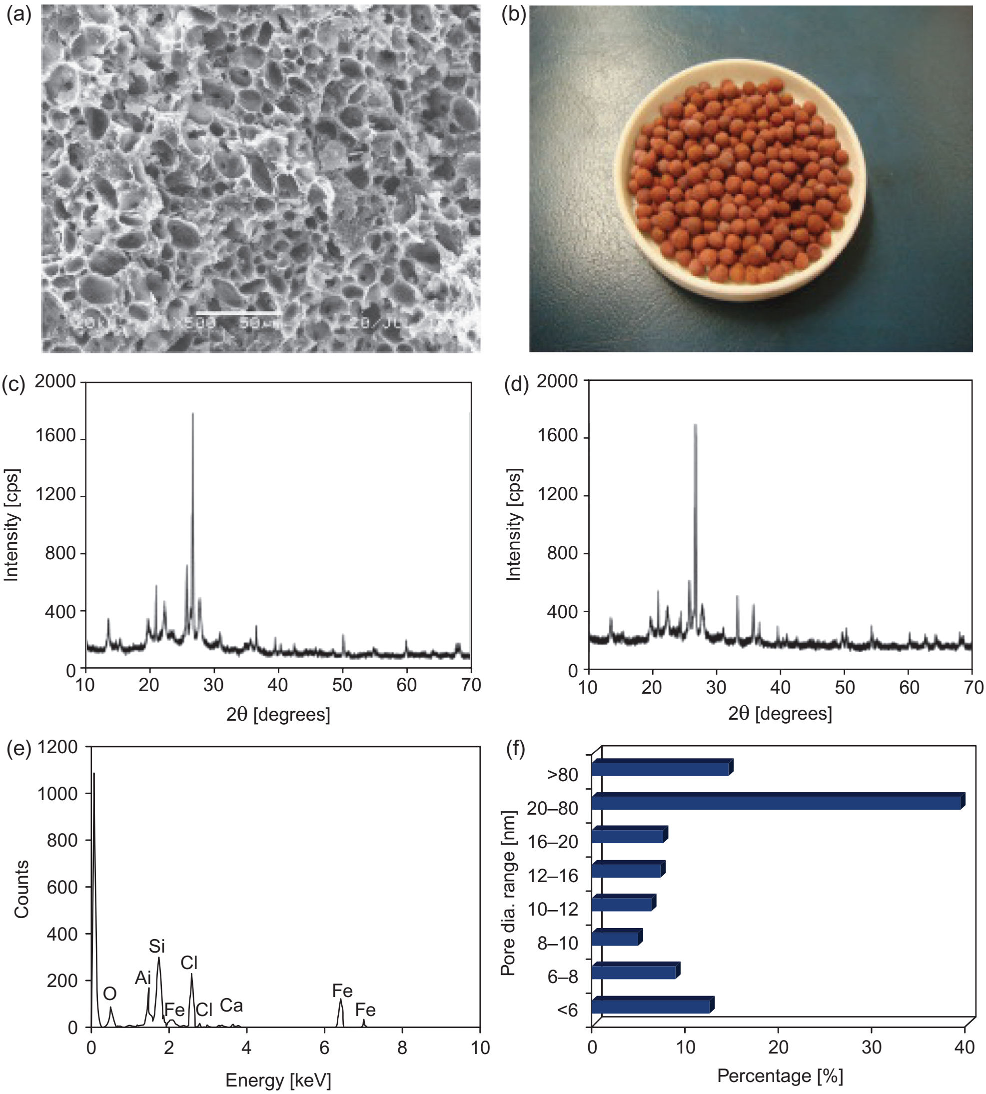

Figure 6.4. SEM images of (a) cross section of pristine granular ceramics and (b) Photo of pristine granular ceramics, Powder XRD patterns of (c) pristine granular ceramics and (d) adsorbed granular ceramics, EDS spectra of (e) pristine granular ceramics, BJH (Barrett–Joyner–Halenda) pore-size distribution of (f) pristine granular ceramics (Chen *et al.*, 2011).

As can be seen from Figure 6.4a, the adsorbent cross section had a very porous structure implying a high adsorption capacity. This pore texture was attributed to the sintering process (i.e., making the granules from powder). The EDS spectrum of Figure 6.4e showed the presence of Fe, Al, Si, O and Cl in the surface of adsorbent, which was attributed to the impregnation process with $AlCl_3$ and $FeCl_3$ salt solutions. Energy-dispersive X-ray spectroscopy (EDS) is an analytical technique normally used for the elemental analysis or chemical characterization of a sample.

Chen *et al.* (2011) argued that these low cost adsorbents showed a good efficiency in F^- removal from aqueous solution and could be useful for environmental protection purposes. The loading capacity of these porous granular ceramics with aluminum and iron salts for F^- was found to be

1.79 mg g^{-1}. The optimum level of F^- removal was observed at pH ranges of 4–9. The presence of carbonate and phosphate ions had a highly negative effect on the F^- removal capacity. Kinetic studies indicated that the adsorption process followed a pseudo-second-order kinetic model. The authors concluded that porous granular ceramics with mixed aluminum and iron oxides have a great potential for F^- removal from ground and drinking water.

In an associated study, Sujana and Anand (2011) confirmed the adsorption efficiency of bauxite for F^- removal from synthetic as well as ground water samples. The adsorption of F^- was highly dependent on pH, temperature and initial adsorbate concentrations in the solutions.

The optimum pH range for F^- adsorption on the bauxite surface was found to be 5 to 7, which was in a similar though slightly narrower range than that observed by Chen *et al.* (2011). Furthermore, a kinetic study by Sujana and Anand (2011) revealed that F^- adsorption on the bauxite surface followed first order with the Langmuir adsorption capacity being 6.16 mg g^{-1}, which was about three times as high as that found for porous granular ceramics with mixed aluminum and iron oxides (Chen *et al.*, 2011). In Sujana and Anand's (2011) work the presence of competing anions like sulfate, nitrate and phosphate showed an adverse effect, whereas carbonate ions only mildly affected the F^- adsorption. Since bauxite is an abundantly available mineral in many parts of the world, the authors concluded that it can provide a simple, effective and yet low cost method for removing F^- from contaminated water.

6.2.5 *Fluoride removal from industrial wastewater using electrocoagulation*

Fluoride ions were removed electrochemically from industrial wastewater by Shen *et al.* (2003) using a combined electrocoagulation and electroflotation process. The experimental results showed that weakly acidic conditions were favorable for this type of treatment, while too high or too low pH could affect the formation of the $Al(OH)_3$ flocs. The optimal retention time in their case was 20 min. Not surprisingly, cations and anions affected the removal process; Ca^{2+} for example was helpful in precipitating F^- and reducing the residual F^- concentration. In general, anions had a negative effect on F^- removal. As the authors explained this may have been due to the competitive adsorption between F^- ion and other anions. As Hu *et al.* (2003) noted, in the electrocoagulation process the F^- ions are attracted to the anode by the electric force. In this process the F^- concentration near the anode is higher than in the bulk solution. However, most of the F^- ions attracted to the anode are replaced by other anions, if F^- is not the dominant anion in solution. Therefore, the defluoridation efficiency may decline because of the presence of co-existing anions.

Khatibikamal *et al.* (2010) in a similar study also employed electrocoagulation (EC) with aluminum electrodes for removing F^- from treated industrial wastewater originating from the steel industry. Effects of different operating conditions such as temperature, pH, voltage, hydraulic retention time (HRT) and number of aluminum plates between anode and cathode plates on removal efficiency were assessed. Experimental results showed that by increasing HRT, removal efficiency increased but after 5 min changes were negligible. Therefore, the total HRT required was only 5 min. After treatment, the F^- concentration was reduced from an initial 4.0–6.0 mg L^{-1} to lower than 0.5 mg L^{-1}. The pH of the influent was established as a very important variable which affected F^- removal. The optimal pH range for the feedwater was 6.0–7.0 at which not only effective defluoridation could be achieved, but also no pH readjustment was needed after treatment. Additionally, increasing the number of aluminum plates between anode and cathode plates in the system did not significantly affect F^- removal.

6.2.6 *Elimination of fluoride from drinking and wastewater using a combination of traditional and membrane techniques*

Reverse osmosis (RO) and nanofiltration (NF) may be used to reduce the concentration of F^- in wastewater. For example Dolar *et al.* (2011) investigated the removal efficiency of RO and NF membranes to reduce fluoride and phosphate load in wastewater from fertilizer factories to

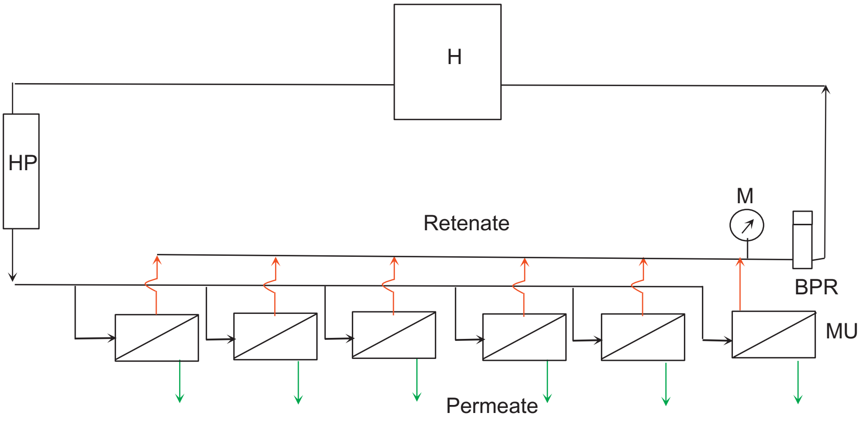

Figure 6.5. Schematic representation of reverse osmosis/nanofiltration (RO/NF) laboratory set up: H – holdup tank, HP – high pressure pump, M – manometer, MU – RO/NF cells, BPR – back pressure regulator. (Dolar *et al.*, 2011).

less than 8 mg L^{-1} and 2 mg L^{-1}, respectively (Fig. 6.5). Their laboratory study indicated that the rejection of F^- with RO membranes was higher than 80% (model waters) and higher than 96% (real wastewater), and with NF membranes it was greater than 40%. However we can argue that this is not sufficient for drinking water quality. As mentioned earlier according to WHO standards, the optimum F^- level in drinking water is considered to be between 0.5 and 1.0 mg L^{-1} (Ghorai and Pantk, 2005; Wang and Reardon, 2001; WHO, 2011). In addition USEPA recently established the effluent discharge standard of 4 mg L^{-1} for F^- from wastewater treatment plant (Khatibikamal *et al.*, 2010; Shen *et al.*, 2003). This suggests that membrane techniques should be combined with traditional methods to reduce the F^- levels to WHO standards.

Kowalchuck (2011) selectively removed F^- from drinking water based on a process which combined precipitation by aluminum hydroxide $Al(OH)_3$ with subsequent removal of the floc by membrane ultrafiltration. A 0.3 gal min^{-1} ($\sim$11.4 L min^{-1}) pilot test plant achieved F^- removal to a concentration of 3.5 mg L^{-1} at an aluminum dose of 30 mg L^{-1}. The former F^- concentration met the USEPA effluent discharge standard of 4 mg L^{-1} for F^- from wastewater. However, it was not in the optimum range since the maximum WHO safe F^- level in drinking water is considered to be between 0.5 and 1.0 mg L^{-1} (Ghorai and Pantk, 2005; Wang and Reardon, 2001; WHO, 2011).

Removal of F^- from drinking water by a membrane coagulation reactor was assessed by Zhang *et al.* (2005), using aluminum sulfate as the major floc forming chemical. The optimum pH value for removal of F^- was found to be in the range from 6.0 to 6.7. In laboratory-scale tests, when proper dosages of aluminum sulfate and sodium hydroxide were added to the reactor, the concentration of F^- was reduced from 4.0 mg L^{-1} in raw water to less than 1.0 mg L^{-1} in the product water, which is within both the WHO and USEPA standards. These were comparable results to those observed by Kowalchuck (2011).

Membrane fouling is a serious problem in any separation process (Goosen *et al.*, 2011). Membrane properties may also be affected by the feed water temperature. Fouling of the membrane surface requires for cleaning using both physical and chemical methods (Al Obeidani *et al.*, 2008). The primary feature of a chemical cleaning process, for example, is a heterogeneous reaction between the detergent solution and the fouled layer (Tran-Ha and Wiley, 1989). The cleaning reaction can be divided into six stages (Fig. 6.6). All six stages do not necessarily always occur.

When cleaning, for example, equipment with fatty fouling, it may be necessary to melt the fat (thereafter the oil could simply be eroded away by hot water), or detergent may be added to emulsify the oil, or it may be dissolved using a suitable solvent (Luss, 1990). The chemicals used as cleaning agents should loosen and dissolve the foulant, keep the foulant in dispersion and solution, avoid spacer fouling, not attack the membrane (and other parts of the system),

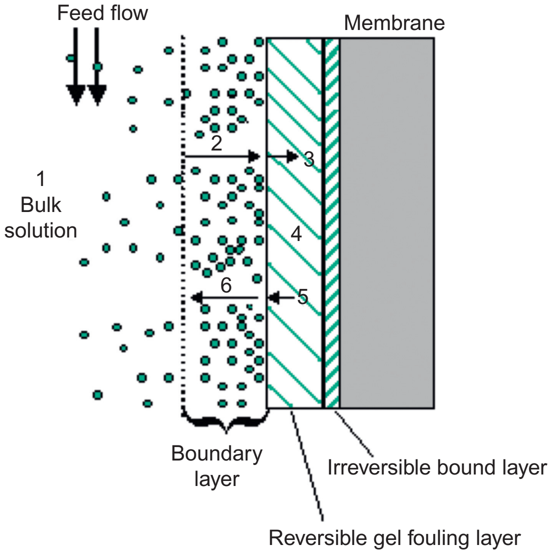

Figure 6.6. Chemical cleaning process at membrane surface: (1) Bulk reactions; (2) Transport of detergent to interface; (3) Transport of detergent into foulant layer; (4) Cleaning reactions in fouling layer; (5) Transport of cleaning reaction products back to interface; and (6) Transport of product to bulk solution (Al Obeidani *et al.*, 2008).

and disinfect all wetted surfaces (Tragardh, 1989). Besides the cleaning ability of a detergent, there are other important factors such as the ease with which it can be dispensed and rinsed away, its chemical stability during use, and cost and safety. All of these will play a key role in determining the large-scale commercial feasibility membrane techniques for removal of F^- and similar pollutants for wastewater.

Zhang *et al.* (2005) in an attempt to overcome fouling problems in the membrane coagulation reactor employed both physical and chemical cleaning to try and regenerate the original flux. While both were effective, chemical cleaning generally achieved better results. For example, at the end of run 4 physical cleaning gave a flux of $38.7\,\mathrm{L\,m^{-2}\,h^{-1}}$ while chemical cleaning gave a flux of $46.2\,\mathrm{L\,m^{-2}\,h^{-1}}$; the latter compares more favorably to the original flux of $49.3\,\mathrm{L\,m^{-2}\,h^{-1}}$ for the unused membrane. In a related study, Al Obeidani *et al.* (2008) in a set of experiments used two chemical agents in a cleaning process starting with alkaline and followed by acid (Fig. 6.7). The results showed that the flux recovery was 93.5% and the operating cycle time was 85% (528 h) of the original cycle time of a new membrane (624 h).

Velizarov *et al.* (2004) in a recommended paper provided an overview of the main membrane-assisted processes that can be used for the removal of toxic inorganic anions from drinking water supplies. The authors emphasized integrated process solutions, which combined traditional and membrane techniques, including membrane bioreactors. It was concluded, for example, that merging the advantages of membrane separation with biological reactions for the treatment of polluted water supplies has resulted in the development of three major membrane bioreactors: pressure-driven, gas transfer, and ion exchange. In the first type, membranes are essentially regarded as porous barriers to promote high biomass for process amplification and avoid contamination of the treated water with microbial cells. Nevertheless, secondary water pollution by an incompletely degraded organic carbon source and other low molecular mass compounds is possible. It was reported by Velizarov *et al.* (2004) that hydrogen gas-transfer membrane bioreactors appear especially attractive for *in-situ* water remediation, while ion exchange membrane bioreactors can provide a highly selective target ion removal and avoid secondary pollution of the treated water.

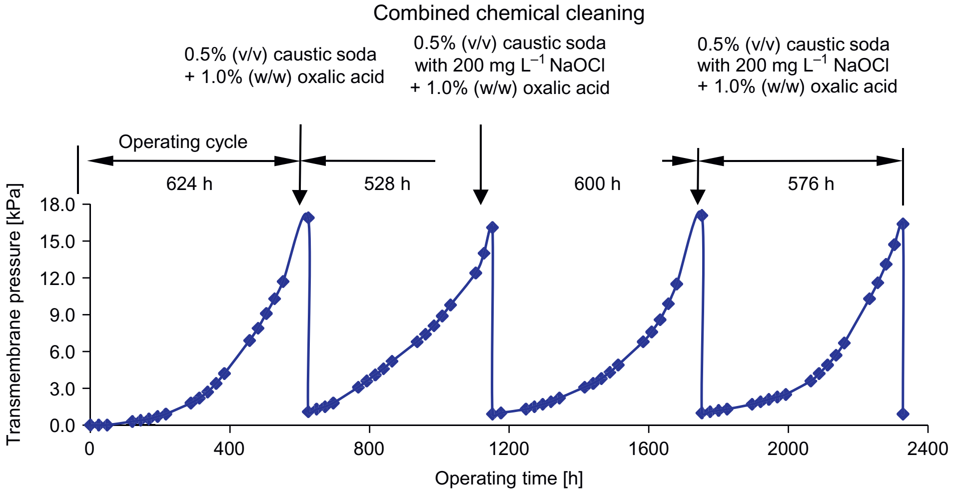

Figure 6.7. Effect of combination of both cleaning agents on flux recovery and operating time (Al Obeidani *et al.*, 2008).

6.2.7 *Potential of adsorbents/fillers in membranes (mixed-matrix membranes) for fluoride removal*

Mixed matrix membranes, a relatively recent development, take advantage of both the relatively low cost of fabricating polymeric membranes and the mechanical strength and functional properties of inorganic materials, such as zeolite, silver, silica as well as nanoparticles (Hoek *et al.*, 2011; Jamshidi Gohari *et al.*, 2013; Vatanpour *et al.*, 2012). Mixed-matric ultrafiltration membranes containing containg inorganic fillers such as silver and zeolite, for instance, can have increased fouling resistance (Hoek *et al.*, 2011). In a recent review of water treatment membrane nanotechnologies Pendergast and Hoek (2011) reported that nanoparticle-containing mixed matrix membranes have the potential to provide enhanced performance, including novel functionalities such as specific adsorption, and improved stability while maintaining the ease of membrane fabrication. Even though such membranes are not yet commercially available, it can be argued that as industrial scale nanoproduction grows, costs will come down. It is hoped that some of these research led improvements will make their way into the open market. While most studies have reported on gas phase purification, it can be reasoned that mixed-matrix membranes due to their specificity and enhanced mechanical strength have great potential for removal of contaminants such as F^-, U and As from wastewater. Zomoza *et al.* (2013) reported the first examples of metal organic framework based mixed-matrix membranes outperforming state-of-art polymers. They noted the high application potential of these composites. Researchers looking at new opportunities should consider studying F^- removal from aqueous solution using mixed-matrix membranes containing various adsorbents/fillers.

6.3 ARSENIC

6.3.1 *Introduction*

Arsenic can be found in two primary forms; organic and inorganic. Organic species of As are mainly found in food, such as shellfish, and include forms as monomethyl arsenic acid (MMAA), dimethyl arsenic acid (DMAA) and arseno-sugars. Inorganic arsenic (i-As) occurs in two valence states, arsenite (As(III)) and arsenate (As(V)). In natural waters, As(III) species consist primarily of arsenious acid (H_3AsO_3) and As(V) species is predominantly present as H_2AsO^{4-} and $HAsO_4^{2-}$

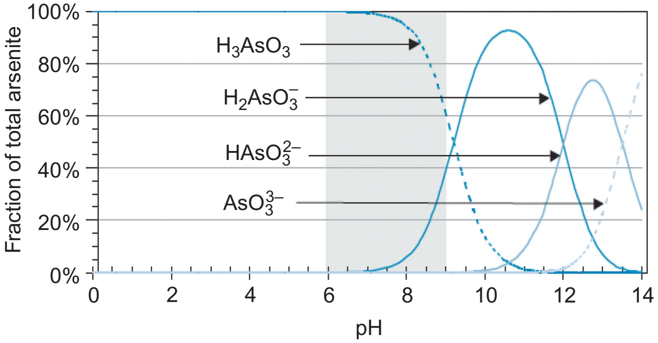

Figure 6.8. Dissociation of arsenite [As(III)] (USEPA, 2003).

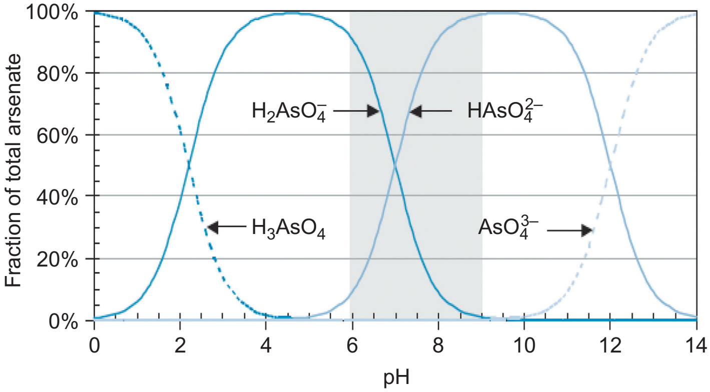

Figure 6.9. Dissociation of arsenate [As(V)] (USEPA, 2003).

(Clifford and Lin, 1995). Most natural waters contain the more toxic inorganic forms of As. Natural groundwater contains predominantly As(III) under reducing conditions whereas As(V) is the principal species under oxidizing conditions.

6.3.2 *Arsenic chemistry*

As is a metal found in the earth's crust, most commonly in the form of iron arsenide sulfide (FeAsS). Arsenic can also be found in the atmosphere as arsenic trioxide dusts, a by-product of industrial smelting operations (http://chemwiki.ucdavis.edu). Through erosion and dissolution, As can enter natural ground and surface waters. Once dissolved, it can take many forms, both organic and inorganic.

Arsenite and arsenate jointly exist in four different forms. The speciation of these molecules changes by dissociation and is pH dependent. The kinetics of dissociation for each are nearly instantaneous. The pH dependencies of arsenite and arsenate are depicted in Figure 6.8 and Figure 6.9, respectively (USEPA, 2003).

Particularly, at any pH less than 9, arsenite will appear as a neutral species H_3AsO_3 where, the neutral form of arsenate H_3AsO_3 is only present at pH < 3. This is very important for determining appropriate treatment technologies (Fig. 6.10).

6.3.3 *Technologies for arsenic removal*

As removal technologies discussed in this chapter are grouped into four broad categories: precipitative processes, adsorption processes, ion exchange processes, and pressure-driven membrane processes. At least, one treatment technology was described for each category.

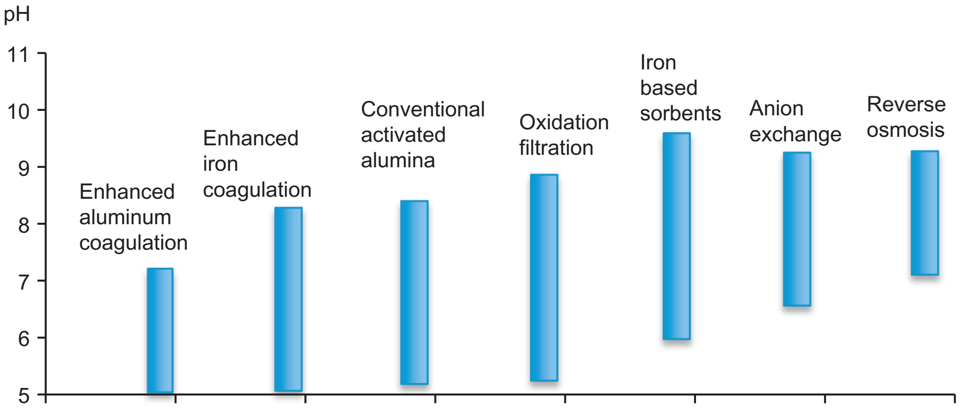

Figure 6.10. Optimal pH ranges for arsenic treatment technologies (adapted from USEPA, 2003).

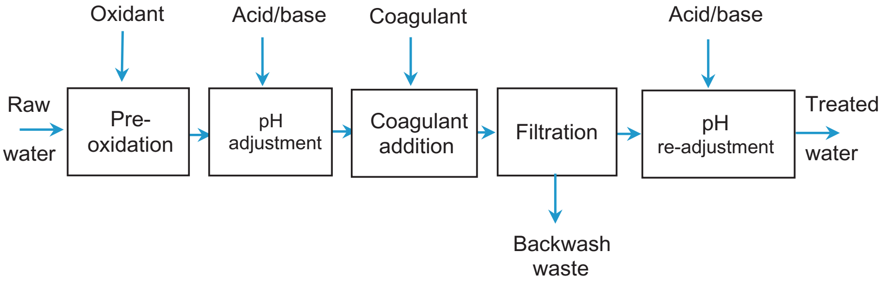

Figure 6.11. Generic coagulation/filtration process flow diagram (adapted from USEPA, 2003).

6.3.3.1 *Coagulation/filtration*

Coagulation filtration is a process based on using an iron or aluminum salt to pretreat water contaminated by As, heavy metals, and dissolved solids. The addition of the salt acts to coagulate the contaminants so that removal using standard filtration can be achieved. This process can be accomplished in large gravity settling basins or in pressure vessels for smaller systems. Major components of a basic coagulation/filtration facility include chemical feed systems, mixing equipment, basins for rapid mix, flocculation, settling, filter media, sludge handling equipment, and filter backwash facilities. Settling may not be necessary in situations where the influent particle concentration is very low. Treatment plants without settling are known as direct filtration plants. As is removed in the pentavalent form, which adsorbs onto coagulated flocs and can be then removed by filtration. As(III) removal during coagulation with alum, ferric chloride, and ferric sulfate has been shown to be less efficient than As(V) under comparable conditions (Edwards, 1994; Gulledge and O'Conner, 1973; Hering *et al.*, 1996; Shen, 1973; Sorg and Logsdon, 1978), thus As(III) has to be previously oxidized (Kartinen and Martin, 1995). Conversion of As(III) to As(V) can be accomplished by providing an oxidizing agent at the head of any proposed As removal process (Fig. 6.11). Chlorine, permanganate and ozone are highly effective for this purpose.

The oxidation-reduction reaction for chlorine, permanganate and ozone are provided in the following equations (USEPA, 2003):

$$H_3AsO_3 + OCl^- \rightarrow H_2AsO_4^- + H^+ + Cl^-$$

$$3H_3AsO_3 + 2MnO_4^- \rightarrow 3H_2AsO_4^- + H^+ + 2MnO_2 + H_2O$$

$$H_3AsO_3 + O_3 \rightarrow H_2AsO_3 \rightarrow H_2AsO_4^- + O_2$$

McNeill and Edwards (1995) reported that Fe and Al based coagulants are mostly used compared to other chemical coagulants. Effective coagulant dosage ranges were 5–25 $mg\,L^{-1}$ of ferric chloride and as much as 40 $mg\,L^{-1}$ of alum (Pallier *et al.*, 2010; USEPA, 2003). Recently, three aluminum based coagulants (aluminum chloride and two types of polyaluminum chloride) were studied by Hu *et al.* (2012). They concluded that each one reduced the concentration of As below the MCL with an initial As(V) concentration of 280 $\mu g\,L^{-1}$. In another study, Ravenscroft *et al.* (2009) found that Fe based coagulants are more effective for water treatment than the Al based coagulants. Unluckily, the production of a large amount of sludge with a considerable concentration of As constitutes the main constraint for the emergence of this treatment technology.

6.3.3.2 *Oxidation and filtration*

Arsenic consists of two major oxyanions, As(III) and As(V) in water (Smedley *et al.*, 2002). These two As species exhibit very different affinities to the mineral surfaces, and the retention of both As(V) and As(III) is strongly pH dependent (Meng *et al.*, 2000) Both inorganic and organic states of the As(III) tend to be more toxic to humans than those of the As(V) forms. The efficiency of most separation methods for As(III) removal is low. To obtain an effective and efficient separation, an oxidation process, which can convert As(III) to As(V), is necessary. Upon efficient oxidation, as a pretreatment, the total removal of As can be effectively improved (Bissen *et al.*, 2003). Different oxidants have been investigated in the As oxidation process, e.g. O_2, O_3, H_2O_2, zero-valent aluminum and iron, activated carbon and manganese (Bissen *et al.*, 2003).

The oxidation efficiency varies when using gaseous oxidants as reported in literature. For example, Frank and Clifford (1986) reported that 8% of As(III) were oxidized within 60 min in solutions purged with pure oxygen. Kim and Nriagu (2000) purged a groundwater containing As(III) with air and pure oxygen and observed that between 54 and 57% of As(III) were oxidized within 5 days. Jiang (2001) noticed that although efficient, utilization of O_3 requires high energy input, thus too expensive for developing countries. Direct application of oxygen sources shows limits in the oxidation efficiency. Consequently, catalysis assisted oxidation, such as MnO_2 coated nanostructured capsules (Criscuoli *et al.*, 2012) was adopted and showed excellent performance. The experimental results show that for the feed with As(III) of 0.1 and 0.3 $mg\,L^{-1}$, complete oxidation was achieved after 3 h and 4 h.

Besides oxidants in the gaseous state, metallic oxidants have also often been employed. Both zero-valent aluminum (ZVAl) (Wu *et al.*, 2007) and iron (Lee *et al.*, 2003) showed preferably oxidation performance for As(III). Leupin *et al.* (2005) reported a positive effect in oxidation of As(III) and a very high removal rate was achieved from an aerated groundwater by filtration through sand and zero-valent iron. A demonstration experiment showed that using 4 oxidation/filtration steps, a 50 $mg\,L^{-1}$ As (total) solution was obtained from a solution of 500 $mg\,L^{-1}$ As(III) solution with an almost complete oxidation.

Iron/manganese oxidation is a commonly used method to treat groundwater Chang *et al.*, 2008; (Driehaus *et al.*, 1995). Hydroxides of metal formed during an oxidation can remove soluble As by a subsequent precipitation or adsorption process. Solar oxidation and removal of As (SORAS) is a simple method that uses irradiation of water with sunlight in PET- or other UV-A transparent bottles to reduce As levels from drinking water from 500 $\mu g\,L^{-1}$ As(III) to 50 $\mu g\,L^{-1}$ As (tot). A typical application of iron oxidation for As(III) was the SONO filter. Inside the filter, there is a top layer composed of coarse river sands (CRS), which is an inactive material as a coarse particulate filter, disperser, flow stabilizer and providing mechanical stability in the filter (Hussam *et al.*, 2007), but generates high concentrations of soluble iron and precipitate as $Fe(OH)_3$ to oxide the groundwater.

Inorganic As(III) species in the feed water is oxidized to As(V) species by the active O_2^-, which is produced by the oxidation of soluble Fe(II) with dissolved oxygen and catalyzed by manganese in the composite iron matrix (CIM). This SONO-filter removes As to concentrations less than

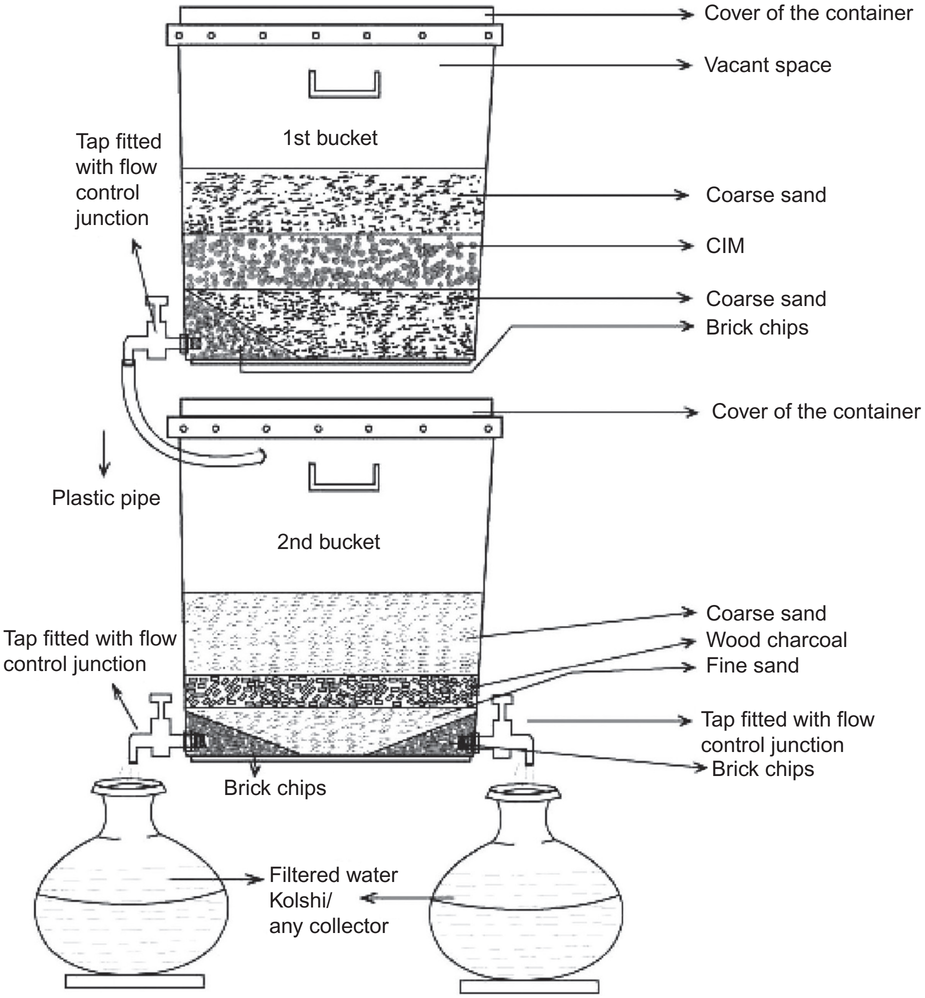

Figure 6.12. Schematic diagram of SONO-filter (Hussam and Munir, 2007).

14 $\mu g\,L^{-1}$ As (total) until reaching the detection limit (2 $\mu g\,L^{-1}$) as well as iron, manganese and many other inorganic species to a potable water (Fig. 6.12).

As a summary, As can be effectively removed by a combined oxidation and filtration process. The cost of the oxidants is low and easily accessible. However, as a simple coarse depth filtration process, the removal rate of the filtration step strongly depends on the saturation of the filter, and the concentration of the feed streams. An absolute separation approach is essential to achieve a stable and much better separation performance. Nonetheless, it is clear that using iron and manganese chemicals is practical for the oxidation of As(III) to As(V). Better performance may be achieved if a better separation technology is available.

6.3.3.3 *Adsorptive processes*

Conventional adsorbents such as alumina, iron oxide, manganesia, titania, and ferric phosphate have been studied extensively to remove As from water (Mohan *et al.*, 2007). Absorption is a physical-chemical process by which the adsorbates (ions of targeted solutes) are adsorbed to the surface of an adsorbent. Cupric oxide and iron oxide adsorbers for instance have been investigated

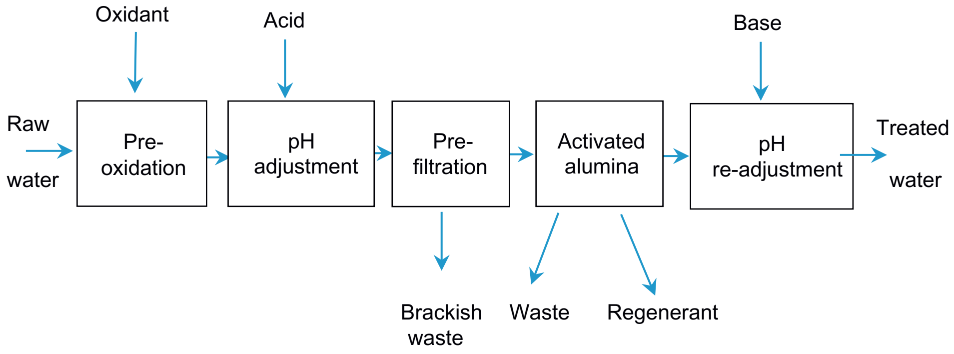

Figure 6.13. Activated alumina process flow diagram (adapted from USEPA, 2003).

as low cost alternatives for rural areas and mobile applications (Chen *et al.*, 2013; Reddy *et al.*, 2013). Rapid small-scale column tests for Arsenate Removal (SCT) in iron oxide packed bed columns have been assessed by Westerhoff *et al.* (2005). It was reported that a simulated 2.5 min empty-bed contact time (EBCT), a model water ($\text{pH} = 8.6$) had q column values of 0.99 to 1.5 mgAs/gGFH *vs.* 0.02 to 0.28 mgAs/gGFH with a comparable pH and EBCT in a natural groundwater indicating a high adsorption efficiency of the SCT.

Fixed-bed filters have been successfully applied for the removal of As in the developing world (Bissen *et al.*, 2003; Sperlich *et al.*, 2005). These filters are simple to operated, feasible for small scale requirements, cost-effective, and normally have low maintenance. Additionally, no dosing of chemicals is required and the amount of residuals is low when adsorbents with high adsorption capacities are used.

Point-of-use (POU) filters have been developed as well (Gurian *et al.*, 2002). The replacement or regeneration frequency of the adsorbents can be minimized if the filtrate is only used for drinking water purposes (Petrusevski *et al.*, 2002). However, the synthesis of most adsorbents, especially efficient adsorbents, are complex, and their performance of re-use is poor, and this process will produce large amounts of As sludge or As containing solid wastes, and other treatment methods are still much desired.

In this section we present two types of commonly used adsorbents, i.e., activated alumina and activated carbon. Activated alumina (AA) is a granulated form of aluminum oxide. It is commonly used to remove As (Guan *et al.*, 2009; Lin *et al.*, 2001). Typically, aluminum oxide (Al_2O_3) granules with a very high internal surface area, in the range of 200 to 300 $m^2\,g^{-1}$ are utilized after a first oxidation step. The As removal efficiency of typically >95% is achieved with a raw water containing arsenite. AA adsorption is a physical/chemical process in which ions in solution are removed on the oxide surface. Feed water is passed continuously through one or more activated alumina beds. Periodically, the activated alumina medium is backwashed to remove any solids that have accumulated in the system. When all available sites are occupied, the activated alumina medium must either be regenerated with a strong base or disposed of entirely. Figure 6.13 shows a typical process flow diagram for Activated Alumina (USEPA, 2003).

The pH has a significant effect on As removal with AA. A pH of 8.2 is significant because it is the "zero point charge" for AA. Below this pH, AA has a net positive charge resulting in a preference for adsorption of anions, including As (USEPA, 2000). Acidic pH levels are generally considered optimum for As removal with AA. The level of competing ions affects the performance of AA for As(V) removal. The following selectivity sequence has been established for AA adsorption (USEPA, 2000):

$$OH^- > H_2AsO_4^- > Si(OH)_3O^- > F^- > HSeO_3^- > TOC > SO_4^{2-} > H_3AsO_3$$

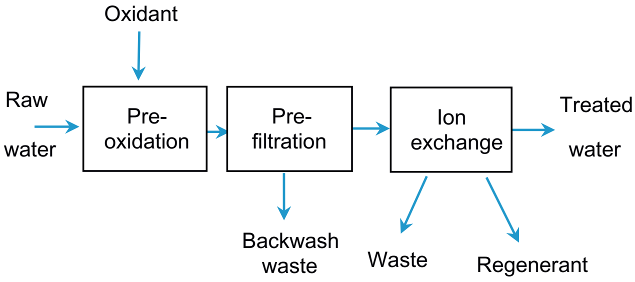

Figure 6.14. Ion exchange process flow diagram (adapted from USEPA, 2003).

The selectivity of AA towards As(III) is poor; therefore, pre-oxidation of As(III) to As(V) is critical.

Activated carbon (AC) as powdered or granulated forms can be used for effective removal of As(III) and As(V) ions from aqueous solutions. AC is a good candidate for the support of the hybrid adsorbents due to the low cost and wide range of available properties (Fierro *et al.*, 2009; Lorenzen *et al.*, 1995; Vitela-Rodriguez *et al.*, 2013). The amount of As uptake by AC is greatly dependent on pH and its oxidation state.

Adsorption of As by AC can be improved by impregnation of AC employing suitable chemicals (e.g., sulfur contain textile dyes for As(III) and Fe(III) salts for removal of As(V) from aqueous solutions (Ansari, 2007). Recently, an interesting study was carried out by Alma *et al.* (2013) on the As removal from water using activated carbon (AC). The authors tested different activated carbons modified with iron hydroxide for their ability to adsorb As from water. They concluded that iron modified activated carbons are efficient adsorbents for As at concentrations lower than $300\,\mu g\,L^{-1}$. According to Mohan and Pittman (2007) Activated carbon can remove 60% As(V) and As(III) but this removal percentage of As is not sufficient to reach drinking water quality. However, sedimentation or filtration processes are required in case of powdered activated carbons, which in turn adds extra cost to the technology.

6.3.3.4 *Ion exchange*

Ion exchange is also frequently used as a treatment technology for arsenic removal. As contaminated water is passed through the resin, contaminant ions are exchanged for other ions in the resin. Ion exchange is often preceded by treatments such as filtration to remove organics, suspended solids, and other contaminants that can foul the resins and reduce their effectiveness. Ion-exchange resins must be periodically regenerated to remove the adsorbed contaminants and replenish the exchanged ions. Regeneration water and spent resin containing high levels of As would require additional treatment prior to disposal or reuse. Alternatively, single-use, non-regenerable ion exchange resins may be used. Figure 6.14 shows a typical process flow diagram for ion exchange.

Before passing As contaminated water, the resin bed are usually flushed with HCl so as to implant labile Cl^- on the surface of the resin, which is later easily exchanged with As. Thus, the effluent contains a considerable amount of Cl^- and additional secondary treatment is needed to improve the quality (Mondal *et al.*, 2013). Since arsenite usually exists as a neutral molecule and is not exchanged, oxidation of As(III) to As(V) is an important pretreatment step for ion exchange processes (Kartinen and Martin, 1995).

The exchange affinity of various ions is a function of the net surface charge. Therefore, the efficiency of the IX process for As(V) removal depends strongly on the solution pH and the concentration of other anions, most notably sulfates and nitrates. These and other anions compete for sites on the exchange resin according to the following selectivity sequence (Clifford, 1999).

Korngold *et al.* (2001) used strong basic anion-exchange resins for the removal of As(V). The resin was regenerated with NaCl or HCl. More than 99% of As was removed by the resins at an initial As concentration of 600 $\mu g\,L^{-1}$. An anion exchanger (AE) prepared from coconut coir pith (CP) was applied for the removal of As(V) from aqueous solutions (Anirudhan *et al.*, 2007) and a maximum removal of 99.2% was obtained for an initial concentration of 1 $mg\,L^{-1}$ As(V) at pH 7.0 at an adsorbent dose of 2 $g\,L^{-1}$. Regeneration of the IE is an issue, particularly that a large amount of water is required to rinse the system.

Phytoremediation has received increasing attention after the discovery of hyperaccumulating plants which are able to accumulate, translocate and concentrate high amounts of certain toxic elements in their above-ground/harvestable parts (Rahman *et al.*, 2011). Phytoremediation of contaminated water by aquatic macrophytes would be a good option in the long term. A large number of aquatic plant species have been tested for the remediation of toxic elements from fresh water systems. Few aquatic plants (mostly macrophytes) have shown the ability to accumulate high levels of As from water. If the term to achieve the desired effect is short enough, the phytoremediation will be an effective As removal process with low energy consumption. The biological process is normally a slow and less efficient process. It is most probably more practical to combine both phytoremediation and other high efficient separation process to remove As.

6.4 URANIUM

6.4.1 *Introduction*

Uranium because of its radioactivity and heavy-metal toxicity is highly lethal not only with respect to human health but also to the whole ecological system (Zou *et al.*, 2009). While dissolved U usually occurs in most natural waters at very low concentrations, U mining, milling, processing, enriching, and disposal all contribute to contaminate surface water and groundwater. Significant amounts of U have also found their way into the environment through the actions associated with the nuclear industry (Ghasemi *et al.*, 2011). Hence, the removal of U from wastewater is important not only for the nuclear industry, but also for environmental remediation. Investigation on separation of U from wastewater is thus vital.

Pollutants from the ore-processing industries, surface and underground mines may find their way into the groundwater in a variety of ways. It can be seen from this scheme, that pollution of surface and ground waters, as well as air takes place during mining. Adsorption by low cost adsorbents, for example, provides an environmentally and economically friendly technique for removing U from wastewaters (Iakovleva and Sillanpää, 2013).

6.4.2 *Biosorption of uranium by algae biomass*

The search for economical and eco-friendly solutions for U removal from water has led to the utilization of biological materials (e.g., microbial and plant origin) as adsorbents since they interact effectively with heavy metals (Ghasemi *et al.*, 2011). Biosorption is described by the removal of heavy metals by dead biomass from aqueous solutions and is attributed mainly to the ligands present in their cell wall biomolecules. There are many natural adsorbents such as marine algae, bacteria, fungi, and industrial wastes that have been used for U removal from water solutions (Bayramoglu *et al.*, 2006; Kalin *et al.*, 2005; Khani *et al.*, 2008; Li *et al.*, 2004; Parab *et al.*, 2005). Among these, algal biomass has received abundant attention due to its low cost, environmental friendliness, and elevated adsorption capacity.

Uranium (VI) biosorption by Ca-pretreated *Cystoseira indica* biomass was studied by Ghasemi *et al.* (2011) using a continuous packed bed column. Metal uptake capacity was found to remain constant with the rise in bed height, while the breakthrough and the exhaustion times increased. Moreover, a decrease in the column bed height resulted in a lower percentage metal removal. It was found that the adsorption breakthrough was strongly dependent on the liquid flow rate, as expected. The authors argued that a successful biosorption process operation requires the multiple reuses of the sorbent, which would greatly reduce the process cost as well as decreasing the dependency of the process on continuous supply of the sorbent. The results of Ghasemi *et al.*

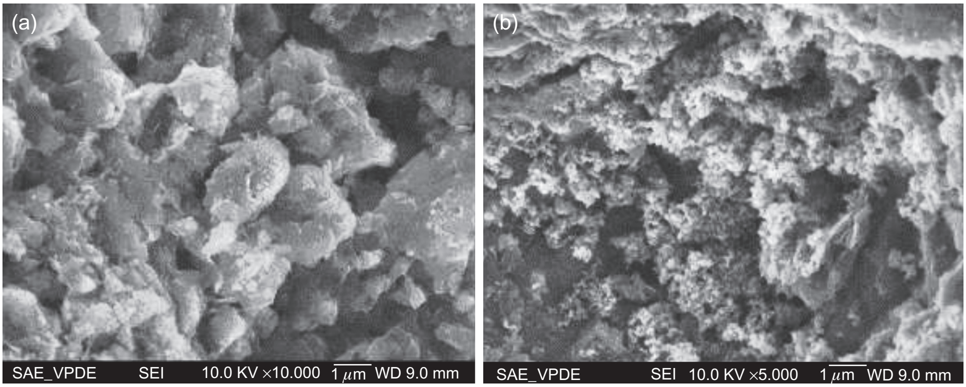

Figure 6.15. SEM micrograph of sample: (a) zeolites; (b) manganese oxide coated zeolites (Zou *et al.*, 2006).

(2011) on column regeneration for three cycles indicated that the usability of *C. indica* biomass for hexavalent uranium (U(VI)) removal and recovery is viable. They concluded that high biosorption efficiency of the alga, low biomass cost, less dependency on the biomass due to reuse, and high efficient elutant make this process an effective, cheap, and alternative technique for treatment of U(VI) bearing solutions.

In a related study, Khani (2011) reported on the removal of U ions from aqueous solutions using *Padina sp*., a brown marine algal biomass. Four main parameters (pH and initial U concentration in solutions, contact time and temperature) were assessed on U uptake. Results showed that the adsorption data adequately fitted a second-order polynomial model. The optimum pH and initial U concentration in solutions, contact time and temperature were found to be 4,778 mg L^{-1}, 74 min, and 37°C, respectively. The maximum U uptake was predicted and experimentally validated. The maximum monolayer adsorption capacity was found to be as high as 376 mg g^{-1}.

6.4.3 *Removal of uranium (VI) from water using zeolite coated with manganese oxide*

Natural zeolites have great potential for heavy metal removal due to their ion exchange ability (Zou *et al.*, 2009). The physical structure of zeolites is highly porous, with interconnected cavities, in which the metal ions and water molecules can interact with the zeolite surface (Fig. 6.15). SEM photographs in Figure 6.15 (a and b) were taken by Zou *et al.* (2006) at 10000×, 5000× magnifications to observe the surface morphology of zeolites and manganese oxide coated zeolites, respectively. At the micron scale, the synthetic coating is composed of small particles on top of a more consolidated coating. SEM images indicated a much rougher surface after the manganese oxide coating. In studies with Cu(II) and Pb(II) Zou *et al.* (2006) showed that adsorption is a spontaneous and endothermic process with a rise in temperature favoring the adsorption.

Manganese oxides, with high adsorptive property, are usually considered as the most significant foragers for trace metals in soil, sediments, and rocks (Zou *et al.*, 2009). The surface charge of manganese oxides is usually negative, so that they can be used as adsorbents to remove heavy metal ions from wastewater. However, pure manganese oxide as a filter medium is not favorable for both economic reasons and unfavorable physical and chemical characteristics, but the coating of manganese oxide on a medium surface such as provided by zeolites may be promising for heavy metal removal from wastewater (Han *et al.*, 2007).

In a study by Han *et al.* (2007), manganese oxide coated zeolites (MOCZ) were synthesized and the adsorption properties for U(VI) by MOCZ were investigated. Their study clearly established that MOCZ is an effective adsorbent for U(VI) removal from aqueous solutions. They reported that the U(VI) binding capacity by MOCZ was strongly dependent on the initial pH, initial U(VI) concentration and temperature. It was noted that an increase in the temperature resulted in a higher metal loading per unit weight of MOCZ. Adsorption capacity increased slightly with increasing temperature. The equilibrium sorption of U(VI) was determined from the Langmuir equation and found to be 15 mg g^{-1} at 293 K and pH 4.0. The authors concluded that the thermodynamics of the U(VI) ion/MOCZ system indicates spontaneous and endothermic nature of the process. This is a similar conclusion as that reached by Zou *et al.* (2006) with zeolite coated with manganese oxide; adsorption is a spontaneous and endothermic process with a rise in temperature favoring the adsorption.

6.4.4 *Removal of uranium from groundwater using biochar, carbonaceous adsorbents and magnetic composite particles*

Kumar *et al.* (2011) argued that the ever-increasing growth of bio-refineries is expected to produce huge amounts of lignocellulose biochar as a by-product. Hydrothermally produced biochar is a porous and amorphous solid rich in active functional groups (e.g., hydroxyl/phenolic, carboxylic, and carbonyl groups). This by-product has great potential for use as an inexpensive adsorbent for heavy metal removal from wastewater. Uranium (VI) removal from groundwater, for example, was assessed by Kumar *et al.* (2011) using biochar produced from hydrothermal carbonization. A batch adsorption experiment at the natural pH (about 3.9) of biochar indicated an H-type isotherm with an adsorption capacity estimated at 2 mg of U g^{-1} of biochar. The adsorption process was highly dependent on the pH of the system. An increase towards neutral pH resulted in a maximum adsorption of 4 mg U g^{-1} of biochar. The authors concluded that the adsorption of U onto biochar is an attractive alternative to treat U(VI)-contaminated groundwater. Compared to other remediation strategies, the feasibility of biochar as U(VI) adsorbent is supported by its environmentally benign nature. The major advantage of biochar is that it could serve as an effective and green adsorbent for U without causing environmental damage.

A low-cost and highly-efficient adsorbent (HTC-COOH) functionalized with carboxylic groups was produced by Liu *et al.* (2013) through oxidizing hydrothermal carbon by HNO_3 solution. Adsorption studies showed that the amounts of U(VI) adsorbed by hydrothermal carbon (HTC) and HTC-COOH were strongly pH-dependent, and increased with the initial concentration of U(VI) and temperature. The adsorption of U(VI) onto HTC and HTC-COOH was well-described by Langmuir isothermal equations and pseudo-second order kinetics models. Calculated monolayer adsorption capacity increased from 62 to 205 mg g^{-1} after carboxylation. There was also increased selectivity. Liu *et al.* (2013) investigated the adsorption of U(U(VI)) from aqueous solution, in the presence of other ions (i.e., Mg^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and Mn^{2+}). The results shown in Figure 6.16 indicated that while HTC showed no selectivity to U(VI), the amount of U(VI) adsorbed on HTC-COOH (15 mg g^{-1}) was much higher than for the other ions. The authors concluded that HTC-COOH is an inexpensive and excellent adsorbent for selective removal of U(VI) in aqueous solution.

In a related study with similar selectivity results, Fan *et al.* (2012) reported on the use of magnetic Fe_3O_4@SiO_2 composite particles as an effective adsorbent material for the removal of U(VI) from aqueous solution. The results shown in Figure 6.17, suggest that the sorption efficiency of U was still high (about 93%) in the presence of other cations. The authors concluded that the presence of other ions had almost no effect on the sorption of U(VI) on the magnetic composite particles. This is a similar result to that obtained by Liu *et al.* (2013) working with a high-efficient adsorbent (HTCCOOH) functionalized with carboxylic groups (Fig. 6.16); the amount of U(VI) adsorbed on HTC-COOH was much higher than for the other ions. Fan *et al.* (2012) concluded that magnetic Fe_3O_4@SiO_2 composite particles could be a perfect candidate as an adsorbent to remove the toxic and radioactive U(VI) from solution.

6.4.5 *Uranium removal from water using ultrafiltration, reverse osmosis, nanofiltration and electrodialysis*

A pilot plant was built by Montaña *et al.* (2013) to assess the effectiveness of ultrafiltration (UF), reverse osmosis (RO), and electrodialysis reversal (EDR) in improving the quality of the

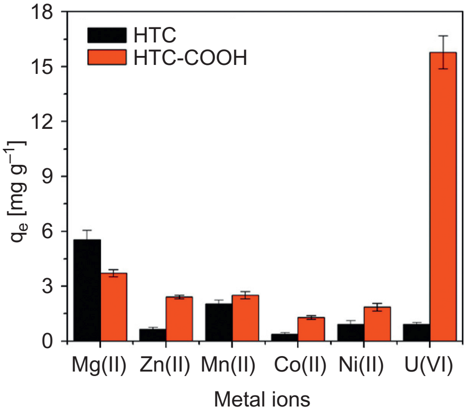

Figure 6.16. Competitive sorption capacity of cations (Mg^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+} and U^{6+}), pH = 4.0, t = 60 min, $C_0 = 5$ mg L^{-1}, $V = 150$ mL, $m = 0.02$ g and $T = 308.15$ K (Liu *et al.*, 2013).

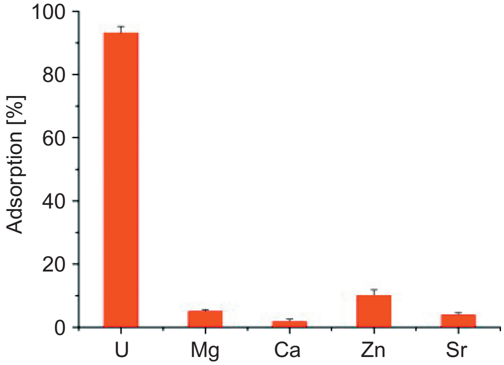

Figure 6.17. Competitive sorption of cations onto $Fe_3O_4@SiO_2$ magnetic composites (50 mg L^{-1} for every ions, pH = 6.0, Time = 180 min, $m/v = 2.5$ g L^{-1} (Fan *et al.*, 2012).

water supplied to the Barcelona metropolitan area from the Llobregat River in Spain. Their paper presented results from two studies to reduce natural radioactivity. The results from the pilot plant with four different scenarios were used to design a full-scale treatment plant (Fig. 6.18 and Fig. 6.19). Samples taken at different steps of the treatment were analyzed to determine gross alpha, gross beta and U activity. The results obtained revealed a significant improvement in the radiological water quality provided by both membrane techniques (i.e., RO and EDR showed removal rates higher than 60%). However, UF did not show any significant removal capacity for gross alpha, gross beta or U activities. RO was better at reducing the radiological parameters studied and this treatment was selected and applied for the full scale treatment plant. The RO treatment used at the full-scale plant reduced the concentration of both gross alpha and gross beta activities and also produced water of high quality with an average removal of 95% for gross alpha activity and almost 93% for gross beta activity at the treatment plant (Fig. 6.19).

In a related study, Khedr (2013) assessed the removal of radium, U, as uranyl cation, or carbonate complexes, and radon by reverse osmosis (RO) and nanofiltration (NF) in comparison with the conventional methods of ion exchange resins (IERs), chemical precipitation/softening, coagulation, and adsorption on surface active media. IERs and chemical softening achieved radionuclide rejection from 32 to 95%, but with loss of process efficiency due to undesired

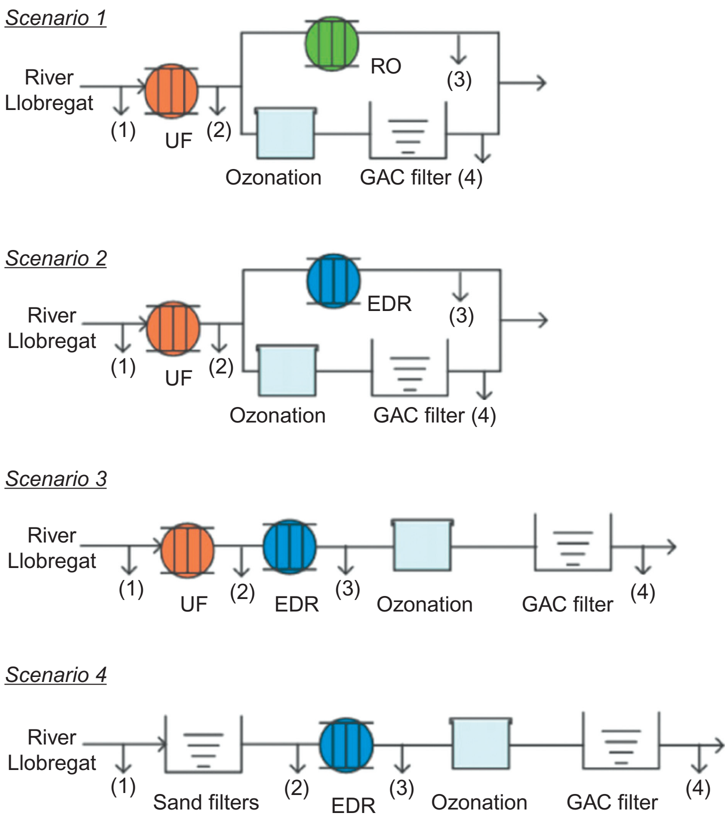

Figure 6.18. Treatment layouts for the four scenarios studied in a pilot plant for removing radionuclides from drinking water. Sampling points are represented by numbers in brackets (Montaña *et al.*, 2013). Code: ultrafiltration (UF), reverse osmosis (RO), electrodialysis reversal (EDR).

parallel removal of similar ions. Removal by IERs was too dependent on the resin form and water pH and required periodical shutdown for regeneration of resin which was slow and seldom complete. Softening required chemical dosing stoichiometric to isotope removal, disposal of contaminated sludge and subsequent water filtration. Coagulation failed to remove radium. In the other hand, the removal of U ranged from zero to 93% depending on pH due to formation of different U complexes. Only RO, parallel to water desalination, showed steady, high rejection of all isotopes (i.e., up to 99%) without interference of similar ions, regeneration, or subsequent filtration. NF showed similar behavior, but with lower water desalination efficiency.

As a final example, Villalobos-Rodriguez *et al.* (2012) reported on the use of ultrafiltration for removal of U from water, with composite activated carbon cellulose triacetate membranes. Uranium removal was found to be 35 ± 7%. Results suggested that co-adsorption of U and iron by the carbon cellulose triacetate membranes during filtration, as the leading rejection path. It can be argued that the U removal reported by Villalobos-Rodriguez *et al.* (2012) was not as good as that presented by Montaña *et al.* (2013) and Khedr (2013) for reverse osmosis membranes (i.e., greater than 90% removal of U).

6.4.6 *Potential of using mixed matrix membranes for removal of uranium from water*

Zomoza *et al.* (2013) reported the first examples of metal organic framework based mixed-matrix membranes outperforming state-of-art polymers. They noted the high application potential of

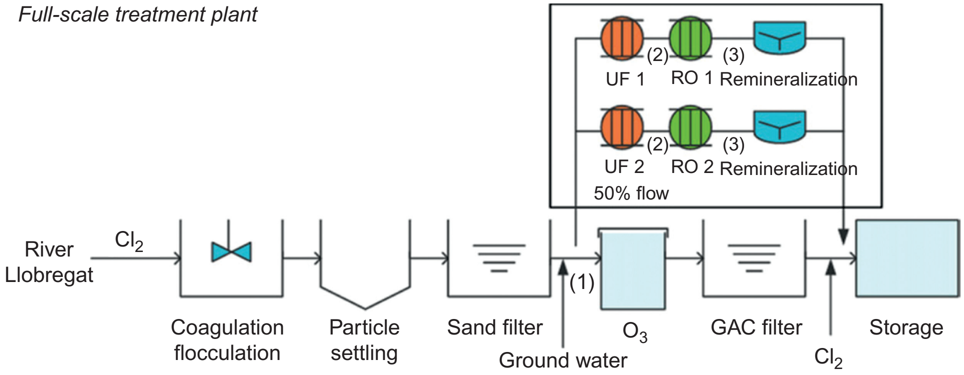

Figure 6.19. Schematic representation of the full-scale treatment plant at Llobregat River in Barcelona Spain. Sample points represented by numbers are in brackets (Montaña *et al.*, 2013). Code: ultrafiltration (UF), reverse osmosis (RO).

these composites. Researchers looking at new opportunities should consider studying U removal from aqueous solution using mixed-matrix membranes containing various adsorbents/fillers such as zeolites. Natural zeolites have great applicability for heavy metal elimination due to their ion exchange ability (Zhou *et al.*, 2009).

Mixed matrix membranes, a somewhat new development, take advantage of both the relatively low cost of fabrication of polymeric membranes and the mechanical strength and functional properties of inorganic materials, such as zeolite, silver, silica as well as nanoparticles (Hoek *et al.*, 2011; Jamshidi Gohari *et al.*, 2013; Vatanpour *et al.*, 2012). Incorporation of the nanoparticles into a nanofiltration coating layer may combine the oxidation and separation of heavy metals in one step as illustrated in Figure 6.14. In a recent review of water treatment membrane nanotechnologies Pendergast and Hoek (2011) reported that nanoparticle-containing mixed matrix membranes have the potential to provide enhanced performance, including novel functionalities such as specific adsorption, and improved stability while maintaining the ease of membrane fabrication. It can be argued that mixed-matrix membranes due to their specificity and enhanced mechanical strength have great potential for removal of contaminants such as F^-, U and As from wastewater.

6.5 CONCLUDING REMARKS AND OUTLOOK

Various treatment methods based on conventional, modern and hybrid technologies have been applied for remediation of F^-, U and As in many parts of the world. These techniques have been critically reviewed in this chapter. Metal organic framework based mixed-matrix membranes have been reported to outperform state-of-art polymers. These composite membranes containing various adsorbents/fillers such as zeolites have high application potential and should be studied further for removal of heavy metals from wastewater.

There is a need for low-cost and proven technologies that can effectively treat polluted water especially in developing countries. Membrane technology has already been successfully used on large-scale for removal of inorganic anions such as nitrate, as well as F^-, U and As. Two disadvantages though are membrane fouling and concentrated brine discharge management and/or treatment. While novel technologies such as membrane bioreactors allow for complete contaminant removal, process operations are insufficiently stable, and also limited due to economic reasons. The major challenges therefore are the design of more efficient membranes. Cost-effective operating conditions are required, especially for long-term processes without or with minimal membrane inorganic and/or biological fouling, and a reduction in the energy consumption requirements.

The applicability of chitin, chitosan and chemically modified chitosan as adsorbents should also be investigated further for the removal of F^-, As and U from drinking water. We can expect this to be one area of rapid development. Chitosan which is derived from chitin one of the mainly components of crustacean shells of prawn, crab, shrimp or lobster, is inexpensive and versatile and has the ability to coordinate various metal ions.

In closing, F^-, As and U removal from wastewater using adsorbent materials and integrated membrane systems are rapidly evolving areas. Mixed matrix membranes containing adsorbent fillers/nanoparticles may be the next stage of growth. It should be kept in mind though that any new process or technology that is produced must be relatively inexpensive and simple to operate so that it can be employed in the developing world where the need is often most acute. This will be the main challenge facing us.

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Part III

New trends in materials and process development

CHAPTER 7

Biosorbent materials and membranes for the treatment of toxic ions from water

Mir Saeed Seyed Dorraji, Vahid Vatanpour & Abdolreza Mirmohseni

7.1 INTRODUCTION

Bioadsorption can be described as the removal of substances from solution by biomass materials. The biomass materials that have been investigated in bioadsorption studies come under the following categories: bacteria, fungi, algae, yeast, waste materials of the food and agricultural industry, lichens and other polysaccharides.

Some confusion has prevailed in the literature regarding the use of terms "*biosorption*" and "*bioaccumulation*". Biosorption (or bioadsorption) is a passive immobilization of metals by the biomass. Mechanisms of cell surface sorption in contrast to bioaccumulation are independent of cell metabolism; they are based upon physicochemical interactions between metal and functional groups of the cell wall. The microorganism's cell wall mainly consists of polysaccharides, lipids and proteins, which have many binding sites for metals. This process is independent of the metabolism and metal binding is fast. Bioaccumulation, in contrast, is an intracellular metal accumulation process which involves metal binding on intracellular compounds, intracellular precipitation, methylation and other mechanisms (Mohan and Pittman, 2007).

In recent years, biosorption has been demonstrated to possess good potential in controlling and removing metal pollutions. Therefore, biosorption has gradually become a hot topic in the field of metal pollution control (Wang and Chen, 2009). Metals are extensively used, produced and discharged into the environment by various industries, including mining, metallurgy, electronic, electroplating, energy production, metal finishing, leather, atomic energy installation, etc. Therefore, metals are one of the most important pollutants in the 21st century.

Biosorption of metal ions can be performed either in the suspension or by the immobilized biomass. The utilizing of an appropriate immobilization technique is important in order to retain the ability of microbial biomass for sorption of metal ions during the continuous industrial process (Das *et al.*, 2008). It has been reported that the immobilization improves mechanical strength, rigidity, porosity and life time of the biosorbent. Polymeric matrices used in the biosorbent immobilization include polysulfone, polyurethane, alginate, polyacrylamide, polyethylenimine (Rangsayatorn *et al.*, 2004). The disadvantages of biosorption by immobilized biomass include additional costs, higher mechanical diffusion resistance, lower capacity, interaction of carrier with active sites. A practical alternative to the immobilization techniques may involve the use of cross-flow (tangential flow) membrane filtration.

7.2 MECHANISM OF METAL BIOSORPTION AND FACTORS AFFECTING ITS PERFORMANCE

A description of the mechanism of biosorption and factors affecting its performance is important for the optimization of the operation conditions for biosorption itself and also for the regeneration of biomass (Chojnacka, 2010).

The imprecise definition of biosorption perhaps gives a clue that the mechanisms involved in biosorption are often difficult to characterize, except perhaps in the simplest laboratory systems

(Gadd, 2009). Biosorption of metal ions is not based on only one mechanism. It is a complicated process and follows complex mechanisms, mainly ion exchange, adsorption by physical forces (e.g., electrostatic), complexation/coordination and precipitation (Volesky and Holan, 1995). Type of biomaterials, properties of metal solution chemistry and environmental conditions such as pH influence the mechanism of metal biosorption (Das *et al.*, 2008).

The initial concentration of metal ion and bisorbent, pH and temperature are the operational conditions which influence the biosorption process. pH determines protonation or deprotonation of the functional groups in the biomass. It affects also the solution chemistry of metals and the competition of metal ions. For these reasons, pH has a strong effect on the biosorption process (Chojnacka, 2010).

Temperature has also an influence on the biosorption of metal ions; however, most reported studies on metal ion sorption on biomass conclude that the influence of temperature is to a limited extent and only in a certain temperature range (Sahmoune *et al.*, 2011). Temperature seems to affect biosorption only to a lesser extent within the range from 20 to 35°C (Veglio and Beolchini, 1997). Higher temperature usually enhances sorption due to the increased surface activity and kinetic energy of the solute, however, physical damage to the biosorbent can be expected at higher temperature (Vijayaraghavan and Yun, 2008). Due to the exothermic nature of some adsorption processes, an increase in temperature has been found to reduce the biosorption capacity (Suhasini *et al.*, 1999).

The initial concentration of metal ions acts as a driving force to overcome mass transfer resistance for metal ion transport between the solution and the surface of the biomass.

By increasing the biomass dosage, the available biosorption sites (i.e., functional groups) also increase, which bring about the improvement of biosorption efficiency.

7.3 EQUILIBRIUM MODELS FOR BIOADSORPTION PROCESS

In order to make the process useful in industrial practice, it is necessary to propose a mathematical description. Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of biosorption systems (Aksu, 2005). A variety of models have been used in the literature to describe the equilibrium between adsorbed metal ions on the biomass (q_{eq}) and metal ions in solution (C_{eq}) at constant temperatures (Table 7.1).

7.4 CHOICE OF METALS FOR BIOADSORPTION STUDIES

Almost all metals in the periodic table have received considerable attention regarding their biosorption, except perhaps those that are highly mobile and do not associate much with biomass, and/or are of low toxicity, e.g. K^+, Mg^{2+} (Chojnacka, 2010). Depending on the angle of interest and the impact of different metals, they could be divided into four major categories: (i) toxic heavy metals, (ii) strategic metals, (iii) precious metals and (iv) radionuclides. In terms of treat of metals in the environment, it is mainly categories (i) and (iv) that are of interest for removal from the environment and/or the point-source effluent discharge (Volesky and Holan, 1995).

7.5 BIOSORBENT MATERIALS AS A PRECURSOR IN MEMBRANE PREPARATION

There are several techniques in the preparation of adsorptive membrane for the adsorption of heavy metals. These procedures include preparation of the membranes by biosorbent polymers as a pure polymer (Vieira and Beppu, 2005) or mixed with other polymers (Han *et al.*, 2007) and blending biomass with membrane polymers (Xin *et al.*, 2011).

Biosorption polymers (biopolymers) are industrially attractive because they are, capable of lowering transition metal ion concentrations to sub-part per billion concentrations, widely available,

Table 7.1. Isotherms and the parameters involved in the different equilibrium sorption isotherms.

Isotherm	Non-linear form	Model parameters	
Langmuir (1916)	$q_e = \frac{Q_o b C_e}{1 + bC_e}$	Q_o, b	Two-parameter isotherms
Freundlich (1906)	$q_e = K_F C_e^{\frac{1}{n}}$	K_F, n	
Tempkin (1940)	$q_e = \frac{RT}{b_T} \ln(A_T C_e)$	b_T, A_T	
Dubinin-Radushkevich (1947)	$q_e = Q_D \exp\left(-K_d\left(RT \ln\left(1 + \frac{1}{C_e}\right)\right)^2\right)$	Q_D, K_d	
Toth (1971)	$q_e = \frac{K_T C_e}{(a_T + C_e)^{\frac{1}{t}}}$	K_T, a_T, t	Three-parameter isotherms
Radke-Prausnitz (1972)	$q_e = \frac{arC_e^{\rho}}{a + rC_e^{\rho-1}}$	a, r, ρ	
Redlich-Peterson (1959)	$q_e = \frac{K_{RP} C_e}{q + a_{RP} C_e^{\beta}}$	K_{RP}, a_{RP}, β	
Sips (1948)	$q_e = \frac{K_S C_e^{\beta_s}}{1 + a_S C_e^{\beta_s}}$	K_S, β_S, a_S	
Koble-Corrigan (1952)	$q_e = \frac{AC_e^n}{1 + BC_e^n}$	A, B, n	

A = Koble-Corrigan isotherm constant [$L^n\ mg^{1-n}\ g^{-1}$]; A_T = Tempkin isotherm equilibrium binding constant [$L\ g^{-1}$]; a_T = Toth isotherm constants [$L\ mg^{-1}$]; ρ = Radke-Prausnitz isotherm model exponent; a_{RP} = Redlich-Peterson isotherm constant [mg^{-1}]; a_S = Sips isotherm model constant [$L\ mg^{-1}$]; B = Koble-Corrigan isotherm constant [$L\ mg^{-1}$]^n; b = Equilibrium constant of biosorption reaction [$L\ mg^{-1}$]; β = Redlich-Peterson isotherm exponent; β_S = Sips isotherm model exponent; C_e = Concentration of biosorbate at equilibrium [$mg\ L^{-1}$]; K_d = Dubinin-Radushkevich isotherm constant [$mol^2\ kJ^{-2}$]; K_F = Freundlich constant indicative of the relative biosorption capacity of the biosorbent [$mg\ g^{-1}$] [$L\ g^{-1}$]^n; K_{RP} = Redlich-Peterson isotherm constant [$L\ g^{-1}$]; K_S = Sips isotherm model constant [$L\ g^{-1}$]; K_T = Toth isotherm constants [$mg\ g^{-1}$]; n = An empirical parameter relating the biosorption intensity; b_T = Tempkin isotherm constant; Q_o = Theoretical maximum biosorption capacity by weight [$mg\ g^{-1}$]; Q_D = Theoretical isotherm saturation capacity by weight [$mg\ g^{-1}$]; q_e = Biosorption capacity by weight at equilibrium [$mg\ g^{-1}$]; q = Biosorption capacity by weight at time t [$mg\ g^{-1}$]; R = Universal gas constant (8.314 $J\ mol^{-1}\ K^{-1}$); r, a = Radke-Prausnitz isotherm model constants; T = Temperature [K]; t = Toth isotherm constants.

and environmentally safe. Also, they possess a number of different functional groups, such as hydroxyls and amines, which increase the efficiency of metal ion adsorption and the maximum chemical loading possibility (Barakat, 2011).

Biopolymers such as chitin, chitosan, cellulose acetate, alginate derivatives, etc., which are polysaccharide-based-materials have been used in the preparation of the adsorptive membrane for removal of heavy metals, dyes and organic materials.

To reduce solubilization of polysaccharides, there are two main procedures for fabrication of insoluble biopolymer membrane: (i) crosslinking reactions, a reaction between the hydroxyl or amino groups of the biopolymer chains with a coupling agent to form water-insoluble crosslinked networks (gels) before or after the preparation of biosorption membrane; (ii) immobilization of polysaccharides on insoluble supports by coupling or grafting reactions in order to give hybrid or composite materials (Barakat, 2011; Crini, 2005).

Among these biopolymers, chitosan has been investigated as a very promising material. Chitosan is a linear polysaccharide based on a glucosamine unit. It is obtained from deacetylation of chitin, which is the major component of crustaceans' shells and is the second most abundant

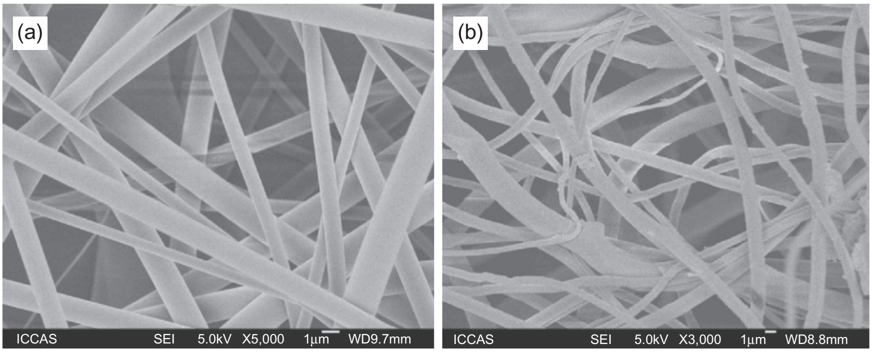

Figure 7.1. SEM images of the (a) non-modified and (b) poly (methacrylic acid)-modified electrospun CA membrane (Tian *et al.*, 2011). Reproduced with permission from Elsevier.

biopolymer in nature. Chitosan was described as an appropriate biopolymer for removal of metal ions from wastewater, since the amino and hydroxyl groups present on chitosan chain can operate as chelation sites (Vieira and Beppu, 2005).

The adsorption and desorption of Hg(II) ions onto natural and glutaraldehyde or epichlorohydrin crosslinked chitosan membranes indicated that Hg(II) ions can be efficiently removed by chitosan membranes, mainly by the glutaraldehyde-crosslinked chitosan, at $\mathrm{pH} = 6.0$, and the adsorbed ions can be easily detached by elution with NaCl (1 M) solution (Vieira and Beppu, 2005).

Electrospun membranes of cellulose acetate (CA) have been prepared for heavy metal ion adsorption by electrospinning and surface modification with poly (methacrylic acid) (Tian *et al.*, 2011). The scanning electron microscopy (SEM) micrographs of the electrospun CA fibers with and without poly (methacrylic acid) surface modification are shown in Figure 7.1. As seen from the figure, the nano- or micro-fibers are randomly deposited to form a nonwoven mat. The surface of the non-modified electrospun CA fibers is smooth and the cross-section is round. After modification, the morphology and diameter of the fibers shows no big difference from the original fibers. The adsorption capacity of heavy metal ions Cu^{2+}, Hg^{2+} and Cd^{2+} increased with the increasing of initial pH value in the system. The adsorbed metal ions can be easily de-adsorbed from the membrane surface, and can be re-used for the metal ion adsorption (Tian *et al.*, 2011).

Chitin/cellulose blend membranes were prepared in NaOH/urea aqueous solution via a freezing/thawing technique to dissolve chitin, and then by coagulating with Na_2SO_4 to regenerate. The resulting composite membranes exhibited efficient removing of heavy metal ions (mercury, copper and lead) from aqueous solution. The uptake capacity of the heavy metal ions increased with the chitin content. The main mechanism of the adsorption of metal ions by chitin/cellulose composite membranes could be described as multi-interactions including complexation, electrostatic attraction, and metal chelation and ionic exchange (Tang *et al.*, 2011).

The other technique in the fabrication of biosorbent membranes is blending of biosorbent materials with a polymer and next, preparation of the membrane using this mixed polymeric solution. For example, a novel biosorbent membrane was prepared by immobilization of waste *Penicillium* biomass with cross-linked chitosan on a fabric carrier. *Penicillium* biomass was dried, then crushed to powder and sieved to particle size $\leq 100\,\mu\mathrm{m}$ for use. Then, chitosan was dissolved in acetic acid (2.5% (v/v)) and the powder of *Penicillium* was added in the above solution, dispersing with ultrasound. Epichlorohydrin as a crosslinking agent of chitosan was used. The mixture slurry was spread between two pieces of fabric as a membrane support, and then soaked into NaOH as the solidifying solutions. Finally, the membrane was washed with distilled water and dried (Xin *et al.*, 2011). The surface texture and morphology of the biomass of *Penicillium* and the biosorbent membrane are showed by the SEM micrographs in Figure 7.2. The Langmuir

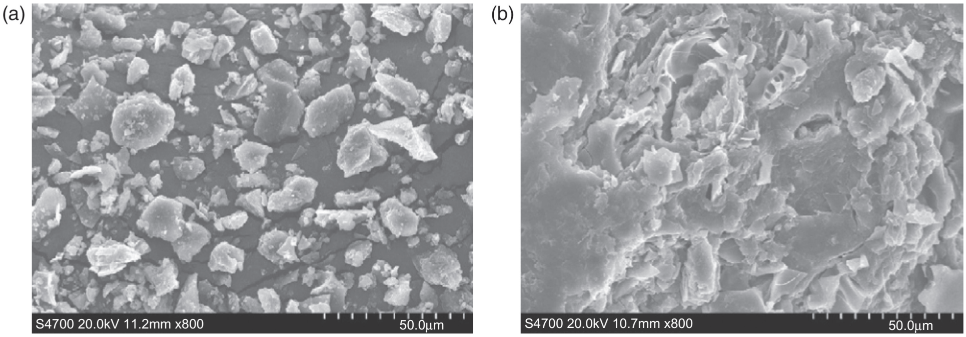

Figure 7.2. SEM images of (a) biomass of *Penicillium* and (b) biosorption membrane (Xin *et al.*, 2011). Reproduced with permission by Elsevier.

isotherm model fitted the sorption data ($R^2 > 0.996$) indicating that sorption was monolayer and the maximum biosorption of Cu(II) was 66 mg g^{-1} at 308 K.

Cellulose/alginic acid ion-exchange membrane have been prepared by coagulating a blend of cellulose cuoxam and alginate solution and used for the adsorption of Cd^{2+} and Sr^{2+} ions (Zhang *et al.*, 1999).

7.6 HYBRID OF BIOSORPTION AND MEMBRANE PROCESSES

Hybrid processes in the separation techniques are described by the combination of two unit operations. Each unit procedure itself is considered to be a separation process, but the combination results in remarkable advantages. In the case of membrane hybrid technology, these advantages are mainly increased product purity and process simplification. This leads to a noticeable reduction in investment costs, discharge costs and energy costs.

There are such techniques for coupling of the membrane process with the biosorption procedure.

The sorption process is generally recognized as immobilization the selected component from the solution by means of various binding materials, which may include several physical and chemical mechanisms of solute separation, i.e., adsorption, biosorption, chemisorption, ion exchange, or complexation, etc.

Integration of these two technologies for the removal of heavy metals minimizes energy consumption, increase product quality and overcome existing separation operations limitations.

From the design view, the hybridization of the biosorption and the membrane processes can be categorized to two groups. In first hybrid system, the biosorption is the beginning step and the resulted pretreated heavy metals effluent introduced to the membrane module (Fig. 7.3). In fact, biosorbent materials have been used as a pretreatment of membrane processes to reducing the membrane fouling and increasing the membrane performance. From other view, membranes were applied for the separation of biosorbent materials from treated aqueous solutions or more treatment of biosorption treated wastewater to reach high quality water (Koltuniewicz *et al.*, 2004).

In the second hybrid system, the membrane is the first step and the membrane permeate is fed to the biosorption step for post-treating with the biosorbent material. Also, the membrane is used to separate suspended particles which cause reduction of biosorbent materials efficiency. Figure 7.4 presents these categories.

Based on the above mentioned arrangement, several techniques were applied for the removal of heavy metals. One of these techniques is called polymer enhanced ultrafiltration process (Cańizares *et al.*, 2005; Geckeler *et al.*, 1986; Juang and Shiau, 2000; Verbych *et al.*, 2005). The used polymer could be biomaterials or other types of polymers, which can complex (chelate) with heavy metals. The polymer enhanced UF process is composed of three steps: (i) complexing of metals with water-soluble polymer, (ii) metal-complex retention by membrane and

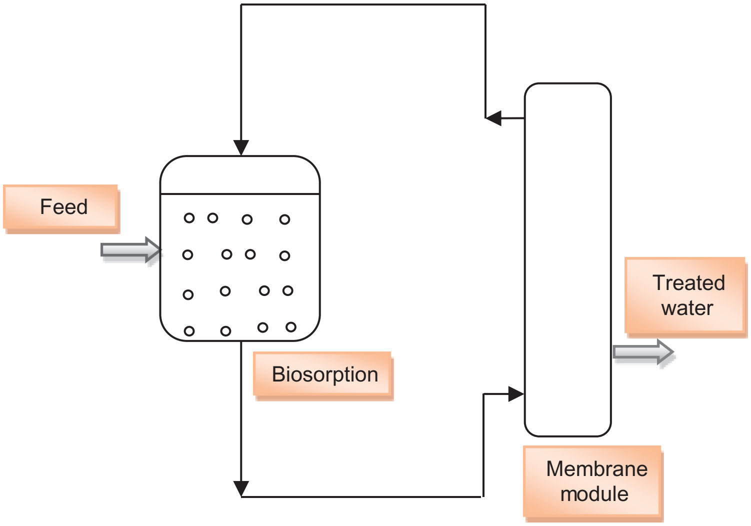

Figure 7.3. Flow sheet of biosorption before membrane process.

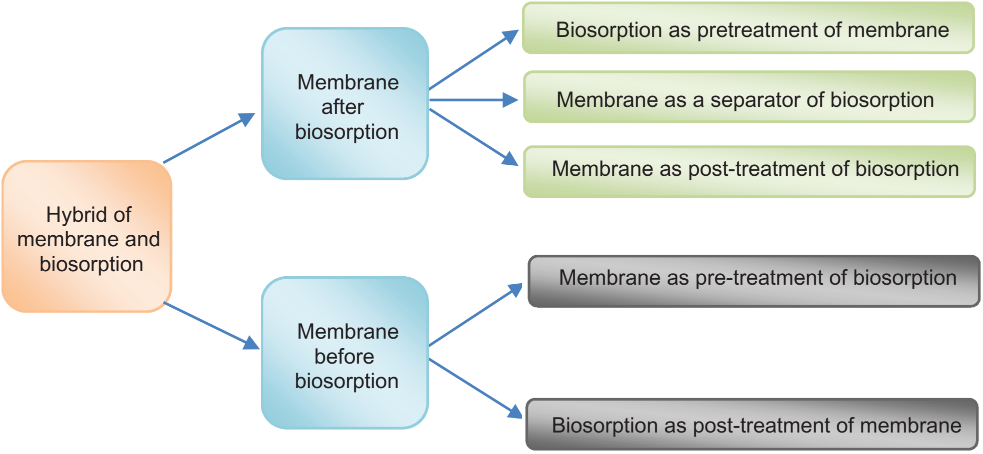

Figure 7.4. Hybridization procedures of the biosorption and the membrane processes.

(iii) polymer regeneration. In the first step, metals ions react with a water-soluble polymer such as chitosan polysaccharide biopolymer (Juang and Shiau, 2000; Verbych *et al.*, 2005; 2006), poly(ethylenimine) (Cañizares *et al.*, 2005; Volchek *et al.*, 1993), poly(acrylic acid) (Cañizares *et al.*, 2005) to form a macromolecular complex. A solution containing macromolecular complex is pumped through an ultrafiltration membrane that retains the complex, and only permits low molecular weight compounds pass through. The almost metal-free permeate stream is collected and the rejected stream returns to the reactor. In the next step, metal-rich rejected stream can be treated (protonated) in order to break down the complex into metal ions and regenerated polymer, capable of being used again in the separation process.

If the size of the obtained polymer-heavy metal binding is suitable, the microfiltration membranes can be applied. For example, As(V) ions have been removed by adsorption onto chitosan in a continuous stirred tank reactor (CSTR) coupled with a microfiltration immersed-membrane unit using 350 hollow organic fibers, with a cutoff of 0.2 µm and a surface area of 0.2 m^2 (Gérente *et al.*, 2010). Cadmium and lead have been adsorbed onto a natural polysaccharide (sugar beet pulp) in a dynamic biosorption process coupled with tubular ceramic MF membrane (Reddad *et al.*, 2003). A ceramic membrane (ZrO_2/TiO_2) was used with a 0.14 or 1.4 mm cutoff and a total area of 94 cm^2.

The other hybrid technologies are membrane biological reactors or membrane bioreactors (MBRs), which combine metal adsorption activated sludge with membrane filtration. Therefore, in addition to removing biodegradable organics, suspended solids, and nutrients, MBRs could retain heavy metal ions and, when operated with membrane pore sizes <1 mm (MF or UF), exclude microorganisms from their discharge (Santos and Judd, 2010). Santos and Judd (2010) compared metal removal in MBRs and conventional activated sludge systems and found that MBRs achieved relatively higher metal removal efficiencies.

Due to this fact that the adsorption of heavy metals onto the activated sludge is related to the functional group of the sludge body not to the living condition of it, the dried activated sludge can be used for sorption of heavy metals (Katsou *et al.*, 2012).

The used membrane can be hollow fiber, tubular ceramic and polymeric spiral wounded membranes.

Biodegradable poly-gamma-glutamic acid (γ-PGA), a linear biopolymer, and its cross-linked nanoparticles were used to capture the metal ions by forming nanosized particles. The polymer-metal ion particles, with sizes in the range of 80–350 nm, were then removed by UF membrane separation. The method is named the combined nano-membrane separation technique (Hajdu *et al.*, 2012).

Fluoride removal by coagulation with *Moringa oleifera* seeds, followed by separation with ultrafiltration membranes, has been reported. The advantage of proposing a sequential process using membrane separation is that it removes color and turbidity, caused by the use of *M. oleifera* as a coagulant, resulting in water that meets portability standards (Bazanella *et al.*, 2012).

Since high levels of heavy metals can inhibit the growth of microorganisms when they are used as biosorbent materials, in some cases direct biological treatment is not usually feasible, and suitable pre-treatment is required. Ultrafiltration (UF) has been applied for the treatment of high metal-contaminated wastewater before of the biosorption process (Katsou *et al.*, 2012; Malamis *et al.*, 2010). UF membrane modules are able to retain suspended solids (SS) and the majority of colloidal matter. Thus, metal forms attached to SS are effectively removed by the UF membranes.

7.7 BIOFILTRATION

Biofiltration is distinguished from other biological waste treatments by the fact that there is a separation between the microorganisms and the treated waste. In biofiltration systems the microorganisms are immobilized (the entrapment of microorganisms within polymer beads) to the bedding material, while the treated fluid flows through it (Geckeler *et al.*, 1986).

The immobilization of microorganisms to the bedding material can be divided into two major immobilization processes (Fig. 7.5): (i) the self-attachment of microorganisms to the filter bedding material, which is defined as “attached growth”, (ii) the artificial immobilization of microorganisms to the bedding material. There are five most important methods for artificial immobilization of microorganisms to a support material. One is the micro-encapsulation method consists of wrapping droplets containing microorganisms with a thin membrane. The microorganisms can freely move within their own capsule, consuming substrates that penetrate through the membrane cover. Many different materials have been used to construct microcapsules; nylon and cellulose nitrate have proven popular. Usually, the diameter of these microcapsules varies from 10 to 100 μm.

The other technique of artificial immobilization is the membrane separation method. The major principle of this procedure is to separate the microorganisms from the bulk fluid by the use of sheets of membrane. The membranes will allow the substrates to penetrate to the microorganism’s zone, while hindering the microorganisms from mixing with the fluid to be treated (Iorio and Calabro, 1995; Sutton and Mishra, 1996).

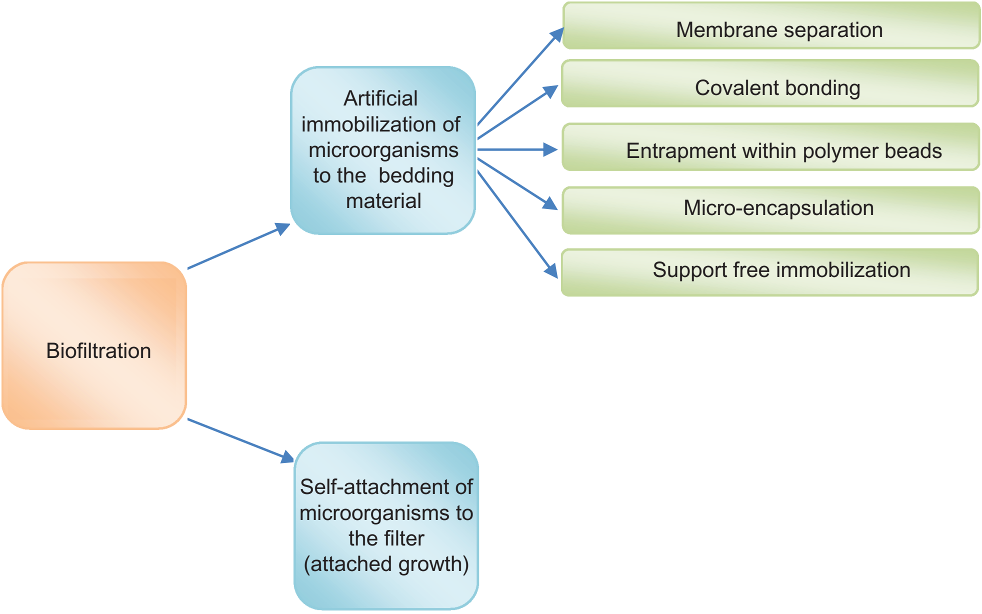

Figure 7.5. Schematic illustration of the immobilization processes in biofiltration process.

The membranes used in this method are usually porous ultrafiltration membranes, but non-porous membranes can also be applied. In some cases, special membranes which are selective to different compounds are used. The main problem associated with this technology is the fouling. The pores in a porous membrane may clog and a non-porous membrane can be covered by a biofilm that alters its performance. The conventional method of membrane cleaning, back flushing against the normal direction of flow, may damage the microbial cells, and other chemical and/or physical methods cannot be applied directly in biofiltration systems, due to the harmful influence they cause to the immobilized microorganisms (Cohen, 2001).

The third technique is the covalent bonding. The outer surfaces of microbial cells contain large quantities of a variety of reactive groups, which can react with the different ligands on the bedding material. Usually different coupling agents are used in order to activate the ligands on the microbial cells and the bedding material. The most commonly used coupling agent is probably glutaraldehyde although carbodiimine, isocyanate and amino silane have also been frequently used (Tampion, 1987).

The fourth technique is the covalent crosslinking method that is called support free immobilization and involves the joining of the microorganisms to each other to form a large, three-dimensional complex structure. This structure is used as a bedding material. The methods of crosslinking normally involve covalent bond formation between the microorganisms. Therefore, this immobilization method usually suffers from the toxicity problem associated with the covalent bonding method.

The last method, which seems to have a potential future application, is the artificial entrapment of microorganisms within polymer beads. This method includes trapping microorganisms within a three-dimensional polymer matrix. The pores in the matrix are smaller than the microbial cells, keeping them trapped within the material, but the pores still allow the penetration of substrates through the polymer matrix towards the trapped microorganisms.

Apart from the immobilization process, biofiltration systems can be divided into two different treatment systems according to the phase of the treated fluid, i.e., systems treating gas and those treating liquids.

In biofiltration systems, the pollutants may be removed from the fluid in several ways. They can be adsorbed to the microbial film or to the bedding material. In biofilters treating gas, the pollutants might be adsorbed to the water that clings to the bedding material. The main way of pollutant removal in biofiltration systems, however, is the biological degradation of the waste. In this way the contaminants are incorporated into the microbial biomass or used as energy sources (electron donors or electron acceptors) (Srivastava and Majumder, 2008).

The main mechanism of heavy metal removal in the biofiltration is adsorption on the microbial film, although the membrane materials can also adsorb the heavy metals if they have been made with adsorptive polymers.

The mechanism of heavy metal removal from contaminated water in biofilters is as follows.

The non-biodegradable water soluble heavy metals are either oxidized or reduced by the microorganisms and produce less soluble species. The less soluble form of these metals which are formed due to microbial reactions are adsorbed or precipitated/co-precipitated on the surface of the adsorbent and the extra cellular protein of the microorganisms in the biolayer (Srivastava and Majumder, 2008; Valls and Lorenzo, 2002). The methylation of metals is also another important route for bioremediation of heavy metals in water (White *et al.*, 1997). Though the microbial action on metal ion transformation is still a matter of research, it is assumed that there are two paths. In one path oxidation or reduction of heavy metal ions takes place by extra cellular enzymes where the metal ions do not enter into the bacterial cell. In the other path the metal ions are transported into the microbial cells by trans-membrane proteins and are converted to other less soluble forms by metabolic actions of enzymes in the cells followed by subsequent excretion from the cells, yet both the paths are plasmid mediated (Valls and Lorenzo, 2002). Whether the microbial action on a metal ion is performed by only one path or by both the paths is a matter of research.

Despite the problems related to this immobilization method, such as diffusion restrictions and the toxicity of some polymer production processes, this technology seems to have many advantages. These advantages include the use of a selected microbial species (this selected microbial species might even be genetically engineered), the potential to carry out complex degradation processes, the ability to carry out oxidative-reductive processes, etc. It seems that with the improvement of the polymer beads, diffusional properties and the development of mild entrapment procedures, this technology has a future potential in commercial biofiltration systems.

In attempts to enhance and improve the attachment of microorganisms in such systems, the most possible option will be to alter the properties of the bedding material. Understanding the forces that are responsible for microbial attachment to the bedding material will help in the selection of a suitable bedding material for a particular application.

The treatment of fluids by biofiltration systems, based upon attached growth and entrapped microorganisms, seems to be, in some environmental conditions, more efficient than the treatment of fluids by suspended microorganisms.

This allows the biofiltration treatment systems to be more compact than the treatment systems based upon suspended microorganisms. However, the existing biofiltration systems suffer from many different problems, such as uncontrolled microbial growth, aeration problems, etc. The improvement of the existing biofiltration systems is still a necessity.

A good biofilter will achieve a high efficiency of pollutant removal by providing the best conditions for the microorganisms it contains. Understanding the microbial needs, the fluid physics, mass transfer calculations, degradation pathways and ways of microbial immobilization will help to utilize the enormous power of the microorganisms in the control of fluid pollution.

7.8 BIOADSORPTION OF ARSENIC, URANIUM AND FLUORIDE

In this section, a summary of recent information concerning bioadsorption of arsenic (As), uranium (U) and fluoride (F^-) has been provided. The reader is strongly encouraged to refer to the original research papers for information on experimental conditions. A summary of biosorption capacity of various biosorbents for removal of F^-, As and U has been presented in Table 7.2.

Table 7.2. Biosorption capacity for the removal of fluoride, arsenic and uranium by various biosorbents.

Ion	Biomass material	Biosorption capacity [mg g^{-1}]	Reference
Fluoride	*Pleurotus ostreatus* 1804 (fungus)	1.272	Ramanaiah *et al.* (2007)
	Spirogyra sp. (algae)	1.272	Venkata Mohana *et al.* (2007)
	Protonated chitosan (biopolymer) bead	7.32	Viswanathan *et al.* (2009a)
	Carboxylated crosslinked chitosan beads	11.11	Viswanathan *et al.* (2009b)
	La(III) incorporated carboxylated chitosan beads	11.905	Viswanathan and Meenakshi (2008a)
	Fe(III) loaded carboxylated chitosan beads	15.385	Viswanathan and Meenakshi (2008b)
Arsenic	Agricultural residue rice polish	As(III): 0.138 As(V): 0.147	Ranjan *et al.* (2009)
	Inonotus hispidus (macrofungus)	As(III): 51.9 As(V): 59.6	Sari and Tuzen (2009)
	Chemically modified *Penicillium chrysogenum* (fungus)	As(V): 57.85	Loukidoua *et al.* (2003)
	Coconut coir pith	As(V): 12.51	Anirudhan and Unnithan (2007)
	Lessonia nigrescens (algae)	As(V): 45.2	Hansen *et al.* (2006)
	Ulothrix cylindricum (algae)	As(III): 67.2	Tuzen *et al.* (2009)
	Maugeotia genuflexa (algae)	As(III): 57.48	Sari (2011)
	Fresh *Garcinia cambogia* (plant)	As(III): 128.1	Kamala *et al.* (2005)
	Immobilized *Garinia cambogia*	As(III): 704.11	
	Chitosan	As(V): 0.739	Gérente *et al.* (2010)
	Fe(III)-pretreated *Staphylococcus xylosus* (bacteria)	As(III): 54.35 As(V): 61.34	Aryal *et al.* (2010)
	shelled *Moringa oleifera* seeds (plant)	As(III): 1.59 As(V): 2.16	Kumari *et al.* (2006)
	Iron-chitosan composite flakes	As(III): 16.15 As(V): 22.47	Gupta *et al.* (2009)
	Iron-chitosan composite granules	As(III): 2.32 As(V): 2.24	Gupta *et al.* (2009)
Uranium	Immobilized *Aspergillus fumigatus* (fungus) beads	34.72	Wang *et al.* (2010)
	chitosan-tripolyphosphate beads	236.9	Sureshkumar *et al.* (2010)
	Cross-linked chitosan	72.46	Wang *et al.* (2009)
	Modified *Rhodotorula glutinis* (yeast)	226	Bai *et al.* (2012)
	Macro marine algae (*Jania rubens*) and yeast *Saccharomyces cerevisiae* immobilized on silica gel	50.25	Aytas *et al.* (2011)
	Penicillium citrinum (fungus)	274.73	Pang *et al.* (2011)
	coir pith	250	Parab *et al.* (2005)
	Spirulina platensis	64.28	Cecal *et al.* (2012)
	Trichoderma harzianum (algae)	496	Akhtar *et al.* (2007)

7.9 CONCLUSION

The potentiality of biosorbent materials and membranes for the treatment of toxic metal ions from water is illustrated in great detail. Disadvantages of biosorption by immobilized biomass such as higher mechanical diffusion resistance and lower capacity can be improved by hybridization with membrane processes. The hybridization of the biosorption and the membrane processes can be categorized into two groups; bioadsorption/biosorption as a pretreatment of membrane processes to reduce the membrane fouling and increasing the membrane performance; and in another hybrid system, the membranes were applied after the bioadsorption step for the separation of biosorbent materials from treated aqueous solutions or more treatment of biosorption treated wastewater to reach high quality water. Sometimes high levels of heavy metals can inhibit the growth of microorganisms when they are used as biosorbent materials, and suitable pre-treatment is required. The membrane is able to reduce the level of contaminants before bioadsorption. In addition, biosorbent materials can be used as precursors in preparation of membranes in different procedures including preparation of the membranes by biosorbent polymers as a pure polymer, mixing with other polymers and blending biomass with membrane polymers.

A good biofiltration system caused high efficiency pollutant removal. Understanding the microbial needs, the fluid physics, mass transfer calculations, degradation pathways and ways of microbial immobilization will help to utilize the enormous power of the microorganisms in the control of fluid pollution and heavy metal removals. Integration of the bioadsorption and the membrane technologies for the removal of heavy metals minimize energy consumption, increase product quality and overcome existing separation operation limitations.

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CHAPTER 8

Liquid membrane separations of uranium

Prasanta Kumar Mohapatra

8.1 INTRODUCTION

Due to growing global energy demands, nuclear power appears to be a long term prospect as an alternative to fossil fuel based power sources. At this moment, most of the nuclear plants operate on enriched uranium (U) based fuels, thus making U as one of the most precious elements.

In the nuclear fuel cycle, U is recovered from various streams (Kumar *et al.*, 2011) to be used as the fuel in the nuclear reactors. The spent fuel is also reprocessed and U and Pu are separated from the fission and activation products by a process called PUREX (plutonium uranium reduction extraction) using TBP (tri-*n*-butyl phosphate) as the extractant from 3–4 M HNO_3 feeds (Sood *et al.*, 1996). As the dissolver solution containing the spent fuel has a high concentration of U (as high as 300 g L^{-1}), even 99.9% U extraction can lead to significant U loss to the raffinate streams. There is, therefore, a need for U recovery from lean solutions and though solvent extraction technique is used in certain cases, it is not economically viable and concerns for the environment in reducing the VOC (volatile organic carbon) burden have prompted the development of alternative low cost 'green' techniques. Membrane based separation methods have been found to be such options which can have different configurations. Pressure driven membrane separation techniques such as ultrafiltration, microfiltration, reverse osmosis, nanofiltration, etc., separate the metal ions based on their ionic size (Saffaj *et al.*, 2004) and sometimes on the size of their complexes (Korus *et al.*, 1999; Zhang *et al.*, 2003). On the other hand, a popular membrane based separation method was developed by Block *et al.* (1967) about 45 years back which is now well known as the liquid membranes method. The liquid membrane separation methods promise to alleviate the problems associated with solvent extraction such as third phase formation, phase separation limitations, flooding, entrapping, etc. and can have the advantage due to their non-equilibrium mass transfer characteristics (Kocherginsky *et al.*, 2007; Mohapatra *et al.*, 2003; Noble *et al.*, 1987; Sastre *et al.*, 1998). Moreover, there is the advantage of simultaneous extraction and stripping which can make the separation methods highly efficient.

There have been a large number of literature reports on separation of metal ions using liquid membrane techniques out of which a major chunk involves U separation. The present review deals with liquid membrane separation of U from a variety of feed solutions. Different types of liquid membrane configurations such as bulk liquid membrane, supported liquid membrane and emulsion liquid membranes will be discussed with several commonly used organic extractants. The structural formulae of these extractants along with their names are presented in Table 8.1. Out of the liquid membrane methods being discussed, the supported liquid membrane technique can be applied in two different configurations, *viz.* flat sheet, and hollow fiber. The different liquid membrane configurations are schematically presented in Figure 8.1. Some of the common literature reports on U recovery using all these liquid membrane techniques with a variety of selective extractants will also be discussed in this chapter. Finally, several specific applications such as U recovery from wet process phosphoric acid (WPPA) and from seawater, considered as lean source of the metal ion, will be discussed.

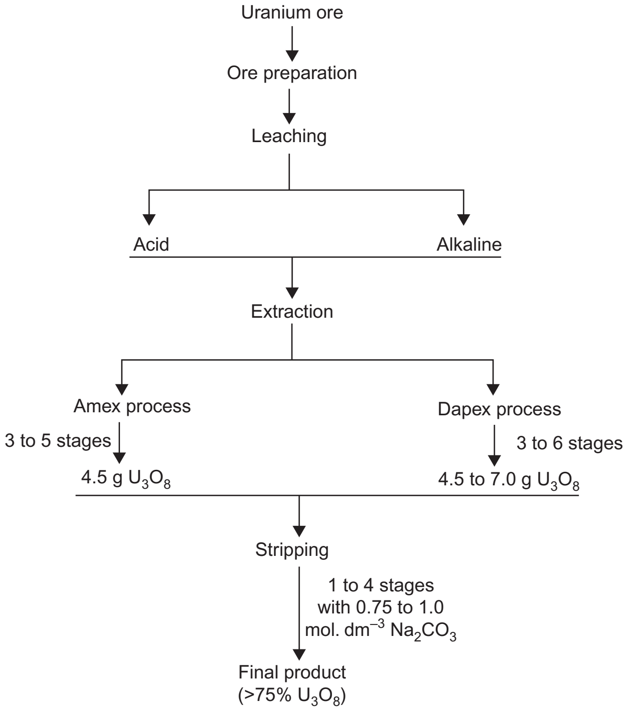
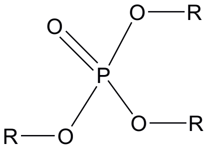
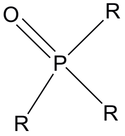
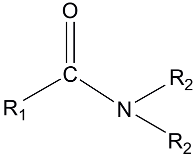
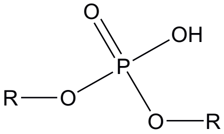
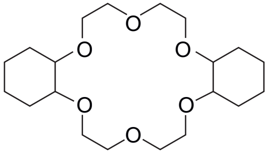


Figure 8.1. Generalized flow sheet for uranium recovery from ore or natural resources by Amex and Dapex process (reproduced with permission from Kumar *et al.*, 2011).

8.2 LIQUID MEMBRANES

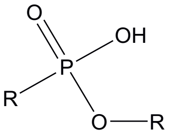
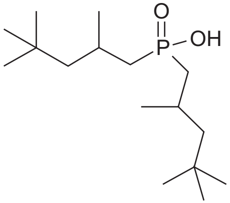
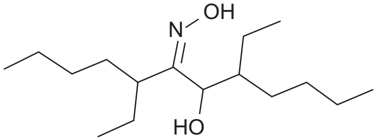
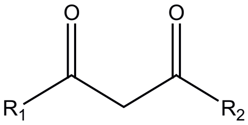
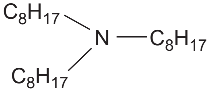
Liquid membranes can be simplistically described as non-aqueous barriers between two aqueous phases, the feed and the receiver, and allow selective permeation of the desired solutes into the receiver phase leaving the undesired substances in the feed phase. Usually, organic solvents containing a specific carrier extractant molecule act as the membrane phase. The separation efficiency in a liquid membrane process is often dependent on the difference in the distribution coefficient of the solutes at the feed and the receiver interfaces and also on the diffusivity of their extracted complexes inside the membrane phase. A solute with higher distribution coefficient and diffusivity is preferentially transported. Therefore, transport through a liquid membrane is also referred to as "pertraction" (permeation and extraction) and closely resembles solvent extraction based separation process (Schlosser *et al.*, 1975). The bulk liquid membrane (BLM) contains an organic phase of higher density than the aqueous phase in a U shaped transport cell (Fig. 8.2). In an emulsion liquid membrane (ELM), the emulsion, made from an extractant, an emulsifier, and strippant (termed as the internal phase) is usually kept in contact with the source phase or feed solution (termed as the outer phase). The ELM method involves kinetically controlled U separation, removing some of the limitations of the thermodynamically dominated solvent extraction process. ELM systems have very high efficiency and are usually leads to pre-concentration with high volume reduction factors. The volume of the internal phase inside the emulsion is at least ten times smaller than that of the outer phase. The ELM has very high surface area which leads to fast separations and high throughputs which can find large scale process applications. The supported liquid membranes (SLM) involve polymeric supports, whose pores contain the extractant solution and the membrane phase separates the feed and the receiver phases. When flat polymeric sheets are used for the transport, also known as flat sheet supported liquid

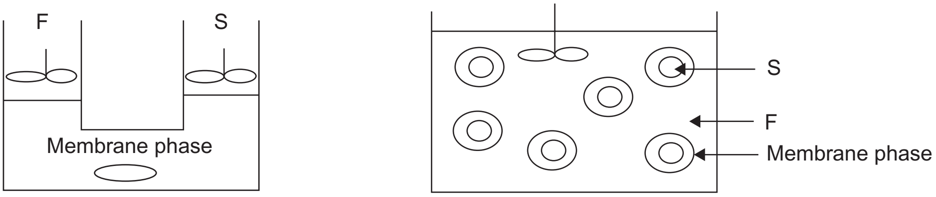
Table 8.1. Structural formulae of some of the organic extractants used for U extraction by liquid membrane methods.

Extractant	Name	Structure		Liquid membrane application (Ref.)
Tri-alkyl phosphate	TBP, T2EHP		**TBP**: R = *n*-butyl **T2EHP**: R = 2-ethyl hexyl	Biswas *et al.* (2011), Chaudry *et al.* (1994; 1995), Chimuka *et al.* (2003), Dharampurikar *et al.* (1997), Joshi *et al.* (2009), Kopunec *et al.* (1994), Rathore *et al.* (2004), Shukla *et al.* (1991),
Tri-alkylphosphine oxide	TOPO		**R** = *n*-octyl	Baker *et al.* (1977), Cahn *et al.* (1981), Bock *et al.* (1982), Dickens *et al.* (1984), El-Hazek *et al.* (2003), El-Reefy *et al.* (1997; 1998), Hayworth *et al.* (1983), Kadous *et al.* (2009), Kulkarni *et al.* (2002; 2003), Macasek *et al.* (1984; 1985), Ramkumar *et al.* (2002), Singh *et al.* (2007)
Dialkyl amide	DHOA, DBOA, D2EHiBA		**DHOA**: R_1 = *n*-heptyl, R_2 = *n*-hexyl **DBOA**: R_1 = *n*-heptyl, R_2 = *n*-butyl **D2EHiBA**: R_1 = iso-butyl, R_2 = 2-ethyl hexyl	Han *et al.* (1998), Patil *et al.* (2003; 2006; 2008), Shailesh *et al.* (2006; 2008)
Dialkylphosphoric acid	D2EHPA, DNPPA		**D2EHPA**: R = 2-ethyl hexyl **DNPPA**: R = nonylphenyl	Akiba *et al.* (1984a), Baker *et al.* (1977), Biswas *et al.* (2012), Bock and Valint (1982), Bock *et al.* (1982), Cahn *et al.* (1981), Dickens *et al.* (1984), El-Hazek *et al.* (2003), El-Reefy *et al.* (1996), El-Sherif (1994), Gill *et al.* (1994), Hayworth *et al.* (1983), Huang *et al.* (1986; 1988), Joshi *et al.* (2009), Kadous *et al.* (2009), Makasek *et al.* (1984), Mikulaj *et al.* (1986), Nanda *et al.* (2002), Sifniades *et al.* (1981), Singh *et al.* (2009), Suripto *et al.* (1998)
Crown ether	DC18C6			Kumar *et al.* (1992), Ramkumar *et al.* (2000), Shamsipur *et al.* (2010), Shukla *et al.* (1992)

(*continued*)

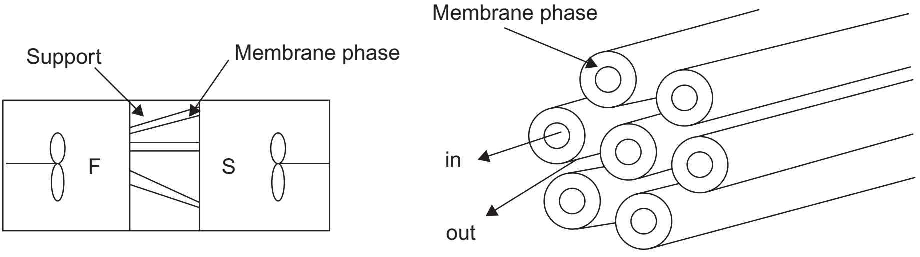
Table 8.1. Continued.

Extractant	Name	Structure		Liquid membrane application (Ref.)
Dialkylphosphonic acid	PC-88A		R = 2-ethylhexyl	Biswas *et al.* (2011), Kedari *et al.* (2001), Nakamura *et al.* (1991), Singh *et al.* (2010),
Dialkylphosphinic acid	Cyanex 272			Akiba *et al.* (1983), Mahmoud *et al.* (1997)
Oxime	LIX 63			Akiba *et al.* (1984b), Chiarizia and Horwitz (1990), Chiarizia *et al.* (1990)
Beta-diketone	TTA, DBM		**TTA**: $R_1 = CF_3$, $R_2 =$ thiophene **DBM**: $R_1 = R_2 =$ phenyl	Nanda *et al.* (2004a; 2004b), Shamsipur *et al.* (2010)
Tri-alkylamines	TOA, Alamine 336			Babcock *et al.* (1980), Chaudry *et al.* (1987), Hirato *et al.* (1991), Lakshmi *et al.* (2004)



(a) Bulk-liquid membrane

(b) Emulsion liquid membrane



(c) Flatsheet SLM

(d) Hollow fibre SLM

Figure 8.2. Some commonly employed liquid membranes for metal ions separations. (Reproduced with permission from Mohapatra *et al.*, 2003).

membrane (FSSLM), the transport flux is significantly lower than that observed with the ELM system. On the other hand, significantly higher mass transfer rates are achieved when hollow fiber contactors are used which is termed as hollow fiber supported liquid membrane (HFSLM). A schematic representation of a hollow fiber set up is shown in Figure 8.3.

In all forms of liquid membrane configurations, the transport efficiency can be changed based on the nature of the organic extractant, feed and receiver phase compositions and the viscosity of the membrane phase. Also, the nature of the diffusing species is important as the diffusion coefficient is dependent on the molar volume of the diffusing species, as per the Wilke-Chang equation (Wilke *et al.*, 1955):

$$D_{\mathrm{o}} = 7.4 \times 10^{-8} \frac{\chi^{0.5} M^{0.5} T}{\eta V_{\mathrm{m}}^{0.6}} \tag{8.1}$$

where, M, χ and η are the molecular weight, solvent association parameter and the viscosity of the solvent, respectively, V_{m} is the molar volume of the diffusing species and T is the temperature. It is important, therefore, that the extracted species should have optimum lipophilicity and size. Though metal ion separation has remained a challenge, with the discovery of novel metal ion specific reagents, this has become much simpler.

8.3 LIQUID MEMBRANE SEPARATIONS USING DIFFERENT EXTRACTANTS

8.3.1 *Neutral donor ligands*

Usually, a neutral donor ligand (L) extracts the metal ion by a solvation mechanism where, a counter anion is needed for charge neutralization of the cation. The difference in the distribution coefficient of the metal ion (D_{M}) between the feed and the strip is generally obtained by a concentration gradient of the counter ion, X^-, which is accompanying the metal ion into the membrane

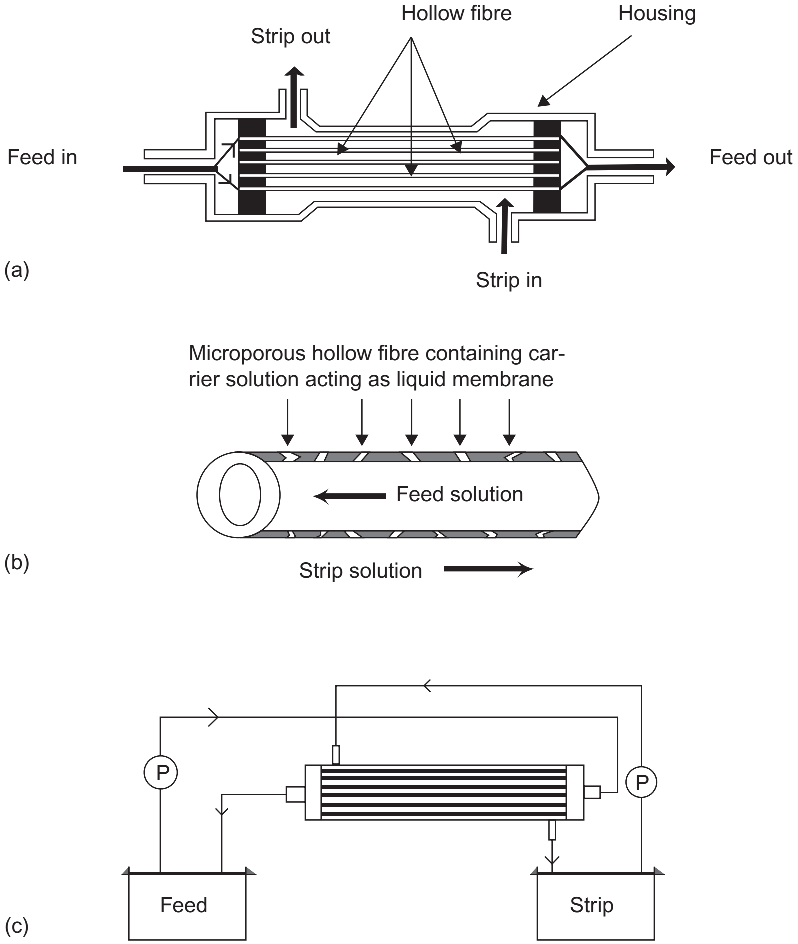


Figure 8.3. Schematic representation of a hollow fiber contactor set up used for supported liquid membrane applications. Flow directions in a hollow fiber module (a), single fiber (b), and hollow fiber set up for simultaneous extraction and stripping. (Reproduced with permission from Ansari *et al.*, 2011a).

and the chemical reaction which is responsible for the coupled transport (or co-transport, indicating the simultaneous transport of the metal ion and the counter anion in the same direction) can be schematized as:

$$M^{+}_{(a)} + X^{-}_{(a)} + L_{(o)}\ (\text{membrane}) \rightarrow MXL_{(o)}\ (\text{membrane}) \tag{8.2}$$

8.3.1.1 *Tri-alkyl phosphate*

Common examples of such cases are those involving metal ion transport using tri-*n*-butyl phosphate (TBP). TBP has been the workhorse of the nuclear industry as it is used at many stages of metal ion recovery in the nuclear fuel cycle, including the U refining cycle, PUREX process cycle, etc. Consequently, it has also been extensively used for U recovery using liquid membrane based separation methods (Table 8.2). As mentioned in a review by Kopunec and Manh (1994), one of the early studies on the transport behavior of U using TBP as the carrier extractant was from a Russian group who have determined the purification coefficients with respect to lanthanides which was >200 in 0.5 M HNO_3 which decreased to 25 when a mixture of 0.1 M HNO_3 and

6 M NH_4NO_3 was used as the feed due to favorable permeation of the lanthanides under these conditions. Usually, the feed containing nitric acid has an extraction equilibrium the same as that reported in the solvent extraction reactions:

$$UO^{2+}_{2(a)} + 2NO^{-}_{3(a)} + 2TBP_{(o)} \rightarrow UO_2(NO_3)_2 \cdot 2TBP_{(o)} \qquad (8.3)$$

As per Equation (8.3), pertraction rates of U were expected to increase with increasing HNO_3 concentration. In order to facilitate stripping, the receiver phase should either contain very dilute nitric acid or even simply distilled water to reverse the above extraction equilibrium reaction. Alternatively, a complexing agent such as carbonate or sulfate can also be used. Chaudry *et al.* (1987) studied the transport of uranyl ions from nitric acid feed solutions into ammonium carbonate receiver solutions through Celgard 2400 polypropylene microporous membrane filters containing TBP in kerosene as the carrier solvent. Based on flux measurements at varying concentrations of nitric acid, TBP and the stripping agent, the mechanism of U transport was predicted considering $UO_2(NO_3)_2{\cdot}2TBP$ as the stoichiometry of the diffusing species in the liquid membrane phase. They have also reported increase in U flux with increase in the feed U concentration (Chaudry *et al.*, 1994). It was also reported that the nitrate ion transport is rather fast as compared to U transport when the feed contained a mixture of nitric acid and sodium nitrate and the diffusing species co-transporting with the uranyl ion complex (*vide supra*) were suggested as $HNO_3{\cdot}2TBP$ (Chaudry *et al.*, 1995).

Transport of U(VI) from aqueous nitric acid feed solutions was also investigated by Shukla *et al.* (1991) using TBP as the carrier extractant in both BLM as well as SLM configurations. These transport studies involved 30% TBP in *n*-dodecane as the carrier solution, similar to that used in the PUREX process, while 2 M HNO_3 and 1 M $(NH_4)_2CO_3$ were used as the feed and the strip solutions, respectively. An increase in U transport was reported with increasing HNO_3 as well as TBP concentration and maximum flux were obtained at 2 M HNO_3 and 30% TBP. Though it is expected that increasing carrier extractant concentration and nitric acid concentration should increase the U transport flux, the decrease beyond 30% TBP and 2 M HNO_3 was attributed to viscosity effects and strong competition from $TBP{\cdot}\,HNO_3$ adducts (as discussed above), respectively. In another study, Na_2SO_4 has been used as the complexing agent for effective stripping of the uranyl ion from the supported liquid membrane containing TBP as the carrier extractant (Chimuka *et al.*, 2003). The method was successfully used for U estimation from natural water samples using adsorptive stripping voltammetry on a hanging mercury drop microelectrode which resulted in a detection limit of 0.5 $\mu g\,L^{-1}$ of U. Hollow fiber supported liquid membrane (HFSLM) technique was used to understand the permeation behavior of U(VI) and Pu(IV) in the presence of fission products from medium active acidic waste employing 30% TBP as the carrier extractant (Rathore *et al.*, 2004). The recovery of U was found to be enhanced by using fresh strippant solutions each time. TBP has also been used as an auxiliary extractant in several synergistic extraction systems which are discussed below.

Tris(2-ethylhexyl) phosphate (T2EHP) is a tri-alkyl phosphate extractant analogous to TBP with higher selectivity due to its branched substituents. Selective transport of U(VI) across an SLM containing T2EHP as the carrier extractant was investigated by Dharmapurikar *et al.* (1997) who have reported >90% U extraction from a feed containing about 0.2 $g\,L^{-1}$ of U in 4 M HNO_3 in to a receiver phase solution containing 0.5 M Na_2CO_3 while using 0.6 M T2EHP in *n*-dodecane as the carrier solvent.

8.3.1.2 *Trialkylphosphine oxide*

Another phosphorous based neutral donor ligand commonly used for U extraction is TOPO (tri-*n*-octylphosphine oxide), which has higher basicity as compared to TBP (Mansingh *et al.*, 1996). The major part of the U transport studies by liquid membranes containing TOPO involved emulsion liquid membranes (ELM) though there are limited reports involving supported liquid membranes as well (Table 8.2). Singh *et al.* (2007) studied U recovery using supported liquid membrane (SLM) from phosphoric acid medium (0.5 M) and its mixture with nitric acid using TOPO in *n*-dodecane as the carrier and ammonium carbonate as the receiving phase. Negligible transport of U(VI) was reported (in 6 h) from pure phosphoric acid (0.5 M) medium, which increased remarkably if 2 M nitric acid was added to the feed phase. Decreasing H_3PO_4 concentration to $\sim 1.0 \times 10^{-3}$ M, while keeping HNO_3 concentration as 2 M resulted in $>90\%$ U transport in 6 h.

In emulsion liquid membrane studies involving TOPO, Macasek *et al.* (1985) investigated the pre-concentration of U using H_2SO_4 and H_3PO_4 as the internal phase. In another ELM study (El-Reefy, *et al.*, 1997) using 0.1 M TOPO in cyclohexane, about 98% U and 82% Th(IV) extraction was observed from 0.1 M HNO_3 feed solution under identical conditions. U(VI) and Th(IV) were found to be stripped from their organic phase by 0.1 M sodium citrate solution which was subsequently used as the internal phase in the ELM studies where the emulsion was prepared from a mixture of TOPO and Span 80 apart from sodium citrate. U(VI) permeation rate was found to be mainly dependent on TOPO concentration and the concentration of U(VI) and HNO_3 in the external phase had relatively less significant role. It was also reported that U(VI) had significantly higher permeation rate (98%) as compared to Th(IV) (78%) while most of the other metal ions were not transported at all. Further, it was possible to back extract U(VI) and Th(IV) from the organic phase using sodium citrate while the other metal ions were remained in the organic phase. The same authors have attempted to recover low concentrations of U from Th matrix (about 10 times higher concentration as compared to U) involving HCl feed solutions, using an ELM containing the same composition mentioned above. The isolated U was found to be contaminated with less than 3% of Th (El-Reefy *et al.*, 1998).

Kulkarni *et al.* (2002) used TOPO as the extractant in an ELM study involving U transport where carbonate was used as the complexing agent in the internal phase. Optimization of the internal phase carbonate concentration indicated 0.5 M sodium carbonate to yield maximum recovery of U while the feed phase pH has been found to be critical for U recovery. The proposed U transport mechanism inside the emulsion is presented in Figure 8.4. Similar to the extraction mechanism observed with TBP (*vide supra*), diffusion of the complexed species, $UO_2(NO_3)_2.2TOPO$ is the key step in the metal ion pertraction kinetics. The acidic wastes generated during U purification and processing was used for U recovery in another study involving ELM containing TOPO in paraffin as the carrier and sodium carbonate as the stripping agent. Studies with the waste, having a composition of nearly 600 mg L^{-1} U(VI), 360 mg L^{-1} Fe(III), 325 mg L^{-1} Ca(II) and 390 mg L^{-1} Mg(II) in 1.2 M HNO_3, indicated selective permeation of uranyl ions to $>70\%$ (Kulkarni *et al.*, 2003).

8.3.1.3 *Dialkylamides*

Dialkylamides have been proposed as the 'green' alternatives to TBP (Manchanda *et al.*, 2004; Musikas *et al.*, 1988) and there are several reports on their application for U and Pu recovery from PUREX type feed solutions. There have been some reports on the use of this interesting class of compounds for U transport from acidic feed solutions as well (Table 8.2). Patil *et al.* (2003) used one of the widely studied amides *viz.* di-*n*-hexyl octanamide (DHOA) for U transport from 4 M nitric acid to a strip solution containing either dilute nitric acid (pH 2.0) or complexing solution (1.0 M Na_2CO_3). Di-2-ethylhexyl-iso-butyramide (D2EHiBA), a sterically modified dialkylamide has been used by Shailesh *et al.* (2008), for the selective transport of U(VI) from nitric acid feed solutions also containing large concentrations of Th. TBP was found to display much higher transport rates as compared to D2EHiBA which was attributed to the lower viscosity of the former. The superior transport property of TBP was also reflected in its acid transport capacity. The role of organic diluent was also investigated which indicated most favorable U transport with diethylbenzene and the trend was explained in terms of viscosity, density as well as acid uptake by the organic phase (Shailesh *et al.*, 2006). With a view to apply this method for THOREX type applications, U(VI) transport was also investigated in the presence of large excess of Th(IV). While the U(VI) and Th(IV) transport was found not to be significantly affected with increasing Th concentration, nitric acid permeation increased with increasing Th concentration in the feed (Fig. 8.5). Lower nitric acid transport rates were seen as compared to TBP/*n*-dodecane system which suggested favorable decontamination factors. Transport of U(VI) was also investigated

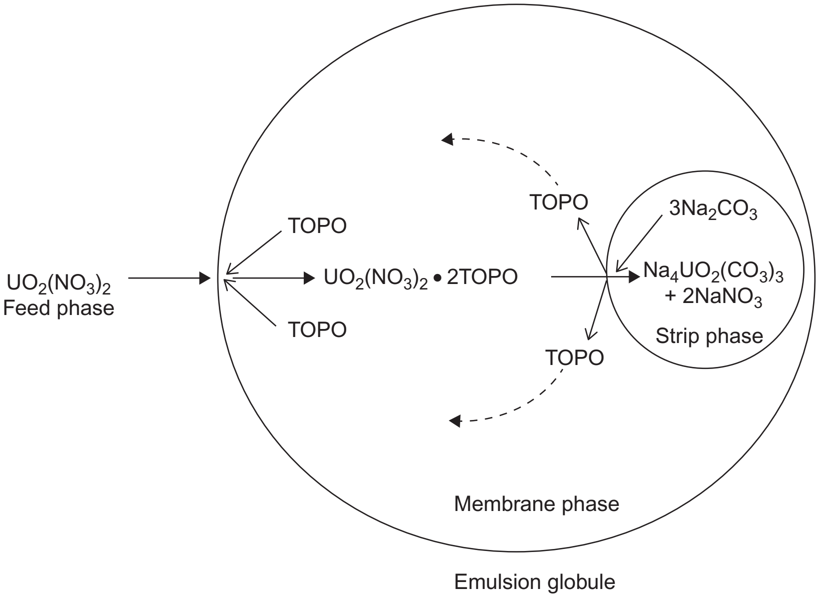


Figure 8.4. A typical transport of a uranyl nitrate ion across the emulsion globule. (Reproduced with permission from Kulkarni *et al.*, 2002).

using a ELM containing *N*,*N*-dibutyloctanamide (DBOA) as the mobile carrier (Han *et al.*, 1998) and reported effective concentration of U from nitric acid medium.

Non-dispersive solvent extraction of metal ions has been reported using hollow fiber contactors (Alonso *et al.*, 1999; Prasad *et al.*, 1990). Patil *et al.* (2006) have carried out non-dispersive solvent extraction (NDSX) of U(VI) from aqueous nitric acid medium using solutions of DHOA in normal paraffin hydrocarbon (NPH) and a commercial hollow fiber module which enabled higher U flux due to the large surface area available in this configuration. Their studies indicated that the U(VI) mass transfer rates were positively influenced by the nitric acid as well as DHOA concentrations. The same authors have also investigated Th(IV) transport under comparable experimental conditions and have observed significantly lower Th(IV) transport as compared to U(VI) transport (Patil *et al.*, 2008) which could be applied for the separation of U from Th. As shown in Figure 8.6, quantitative U(VI) transport was possible with negligible fraction of Th(IV) being co-transported from a feed containing 1 g L^{-1} U and 200 g L^{-1} Th in 4 M HNO_3 which was used as a simulated Thorex feed.

8.3.1.4 *Other neutral donor extractants*

There are limited reports on the transport of U using neutral donor extractants such as CMPO which are proposed for actinide partitioning (Ansari *et al.*, 2011b; Mathur *et al.*, 2001). Ramanujam *et al.* (1999) reported significantly lower transport rates for UO_2^{2+} as compared to Am(III), Np(IV), Np(VI) and Pu(IV). This was rather surprising considering significantly higher extraction of U(VI) as compared to that of Am(III). However, the transport rates of the other metal ions were affected by the presence of macro concentrations of U in the feed solutions. Macrocyclic ligands such as crown ethers have been found to be reasonably good extractants of uranyl ions from aqueous acidic solutions (Agrawal *et al.*, 2000; Mohapatra *et al.*, 1998). In supported liquid membrane studies, uranyl ion transport was studied by Shukla *et al.* (1992) using crown ethers in various organic diluents and the results indicated superior transport properties of aromatic diluents like toluene and o-dichlorobenzene compared to chlorinated hydrocarbons such as chloroform, 1,2-dichloroethane, dichloromethane. In another study, U(VI) transport was investigated using SLM

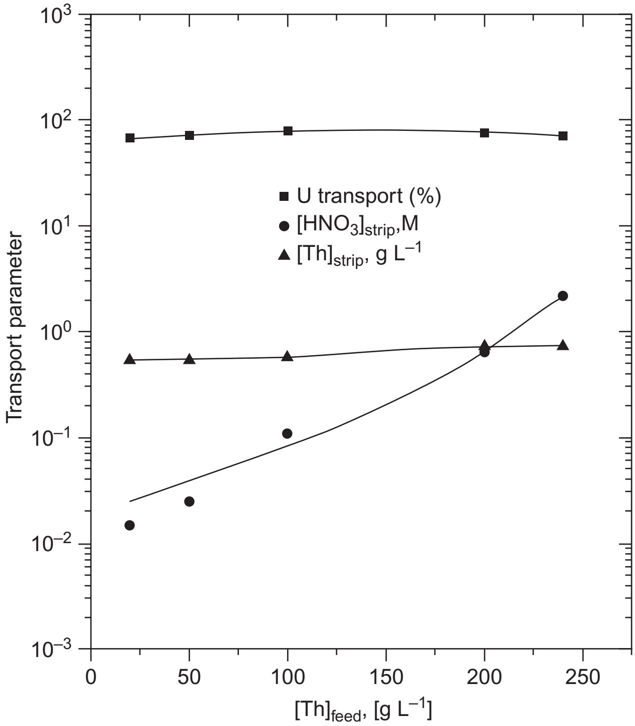


Figure 8.5. Variation of U, Th and nitric acid transport with feed Th concentration; carrier: 1 M D2EHiBA/*n*-dodecane; strip: pH 2 solution; feed acidity: 4 M HNO_3; $[U]_{feed}$: ~200 mg L^{-1}; duration: 8 h. (Reproduced with permission from Shailesh *et al.*, 2008).

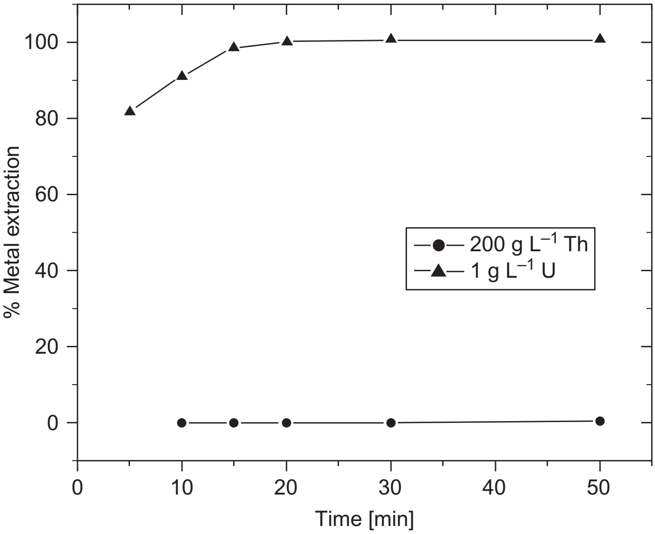


Figure 8.6. Comparative NDSX data of U (1 g L^{-1}) and Th (200 g L^{-1}) through the hollow fiber module. Organic phase 1.1 M DHOA; aqueous phase flow rate 3.5 mL s^{-1}; organic phase flow rate 4.5 mL s^{-1} (reproduced with permission from Patil *et al.*, 2008).

containing DC18C6 in toluene (Kumar *et al.*, 1992). The studies on the effect of absorbed dose on the polymeric membranes indicated that the permeation of U(VI) was relatively less affected when irradiated membranes containing the carrier were used as compared to dry membranes which became fragile. In another study, the transport behavior of the anionic thiocyanate complex, $[UO_2(SCN)_4]^{2-}$, across a bulk liquid membrane using 18 crown 6 and dibenzo 18 crown 6 as the carriers was studied and ~90% U transport was reported. The interference from cations such as Th(IV) was minimized by using EDTA in the feed solution (Ramkumar *et al.*, 2000).

Other macrocyclic extractants such as calixarenes have been reported to form stable complexes with uranyl ions (Jung *et al.*, 1999; Tabusi *et al.*, 1980). A bulk liquid membrane containing a lipophilic ion-associate of methyltrioctylammonium ion and hydroxycalix[*n*]arene-*p*-sulfonate ion was used as uranyl ion carrier from a feed containing an aqueous sodium hydrogen carbonate solution of pH 4–8 into a receiver phase containing dilute sulfuric acid solution (Lee *et al.*, 1999). Ramkumar *et al.* (2002) have used several calixarenes along with neutral donors such as TOPO and 18 crown 6 for the selective transport of U from seawater. There have been several other reports on the liquid membrane transport of U using calixarenes for possible applications of the method in the recovery of U from seawater (*vide infra*).

8.3.2 *Acidic extractants*

If the metal carrier is an acidic extractant, HL, the pH of the feed decides the extent of metal ion extraction and hence, the transport/separation efficiency. In contrast to the co-transport mechanism seen for neutral donor extractants, usually, a counter transport mechanism is realized, i.e., the metal ion transport is opposed by a hydrogen ion transport process as per the following equation:

$$M^+_{(a)} + HL_{(o)}\ (\text{membrane}) \rightarrow ML_{(o)}\ (\text{membrane}) + H^+_{(a)} \qquad (8.4)$$

The results of U transport studies using several acidic extractants such as D2EHPA, PC-88A, oximes and beta-diketones are summarized below.

8.3.2.1 *Dialkylphosphoric acid*

One of the most commonly used acidic extractant is di-2-ethylhexylphosphoric acid (D2EHPA), which has been employed by many researchers for U transport studies by liquid membranes (Table 8.2). Separation of Th from U was reported using an ELM containing D2EHPA in cyclohexane as the carrier, polyethylene glycol dioleate as surfactant and HCl as a stripping solution (El-Sherif, 1994). Pilot plant scale extraction of U from wet process phosphoric acid (WPPA) was demonstrated in a feed containing $100\,\text{mg L}^{-1}$ U where ELM contained D2EHPA + TOPO mixture as the extractant (Dickens *et al.*, 1984). The major problem of the ELM has been the stability of the membrane, which has been affected by swelling of the emulsion. Akiba *et al.* (1984a) investigated uranium extraction by emulsion liquid membranes containing D2EHPA as the mobile carrier and reported increase in the apparent rate constant (k_{obs}) with increase in the extractant concentration and with the pH of the external phase, while it was almost independent of the acidity of the internal phase. Demulsification of the emulsion was done by a high voltage electrostatic method and the extracted U was almost quantitatively recovered from the liquid membrane phase.

Suripto *et al.* (1998) have extracted U from 2 M nitric acid solution using an emulsion containing D2EHPA as the extractant and Span 80 as the surfactant, and phosphoric acids as the strippant in the internal phase and the extraction of U was found to be fast as >94% transport was observed in 5 minutes. U extraction was also studied Macasek *et al.* (1984) using ELMs containing various extractants such as TOPO, D2EHPA, TOA, etc. while SPAN 80 was used as the surfactant. Though significant acid extraction was seen while using TOPO as the extractant, the use of carbonate in the internal phase resulted in the breaking of the emulsion (due to carbon dioxide formation). D2EHPA was, however, reported to yield >99% U extraction when diluted sulfuric acid was used as the strippant in the internal phase.

Table 8.2. Summary of U liquid membrane studies using various commonly used extractants.

Carrier	Membrane configuration	Nature of feed	Strip composition	Highlight	Ref.
TBP	BLM containing 30% TBP in *n*-dodecane	2 M HNO_3	1 M $(NH_4)_2CO_3$	Increase in U flux with increasing TBP and HNO_3 concentration up to 30% TBP and 2 M HNO_3	Shukla *et al.* (1991)
	SLM	1–8 M HNO_3	1.9 M $(NH_4)_2CO_3$	Quantitative transport (>99%) of uranyl ion is possible as acid transport is found to be insignificant	Chaudry *et al.*, (1987; 1994; 1995)
	SLM containing 50% TBP in kerosene	Dilute nitric acid solutions	Na_2SO_4	Used for U estimation in natural water using adsorptive stripping voltammetry	Chimuka *et al.* (2003)
	HFSLM containing 30% TBP in *n*-dodecane	3 M HNO_3	NH_2OH. HCl in 0.3 M HNO_3	>99% U transport was reported from feed containing fission products	Rathore *et al.* (2004)
T2EHP	SLM containing 0.6 M T2EHP in *n*-dodecane	0.2 g L^{-1} of U in 4 M HNO_3	0.5 M Na_2CO_3	More than 90% U transport in a single run	Dharampurikar *et al.* (1997)
TOPO	SLM	$H_3PO_4 + HNO_3$	$(NH_4)_2CO_3$ solution	>90% U transport was possible at mM concentration of H_3PO_4 in 2 M HNO_3	Mansingh *et al.* (1996)
	Emulsion liquid membrane containing 0.1 M TOPO in cyclohexane	0.1 M HNO_3	0.1 M sodium citrate	>98% U and 78% Th was extracted from nitric acid medium. Form HCl medium, however, only 3% Th contamination was noticed.	El-Reefy *et al.* (1997; 1998);
	ELM	U(VI), Fe(III), Ca(II) and Mg(II) in 1.2 M HNO_3	0.5 M sodium carbonate	>70% permeation of U was observed selectively.	Kulkarni *et al.* (2003)
DHOA	Non-dispersive extraction using hollow fiber contactor containing 1.1 M DHOA in NPH	12 g L^{-1} U in 1 M HNO_3	–	>90% U extraction was possible after 1 h when U concentration was lower and HNO_3 and DHOA concentration was higher	Patil *et al.* (2008)

D2EHPA	SLM containing D2EHPA in kerosene	Millimolar solutions of uranyl nitrate	5 M H_3PO_4	The U transport increased with D2EHPA concentration, and was controlled by the chemical reaction and the aqueous film diffusion occurring at the feed side interface	Huang *et al.* (1986)
	ELM containing D2EHPA and Span 80 and H_3PO_4 as internal phase	2 M HNO_3	H_3PO_4	>94% U extraction was possible in 5 minutes. It was not possible to use Na_2CO_3 as strippant as it broke emulsion	Suripto *et al.* (1998)
D2EHPA + TOPO	SLM containing D2EHPA and TOPO in kerosene	5–6 M H_3PO_4	>5–6 M H_3PO_4	Reduction to U(IV) was done by Fe(II) and the flux was low which due to slow diffusion and U complexation/decomplexation kinetics	Hurst *et al.* (1974)
	ELM containing D2EHPA + TOPO in a surfactant	WPPA	NaOH, Na-citrate, EDTA and Na_2SO_4	Reduction to U(IV) has been proposed for efficient stripping	Sifniades *et al.* (1981)
PC-88A	SLM containing PC-88A or its mixture in Cyanex-923 in *n*-dodecane	Dilute acid solutions/analytical waste	H_2SO_4 or $(NH_4)_2CO_3$ solutions	U transport results were encouraging and it was applied to recover U from analytical wastes	Nakamura *et al.* (1991); Singh *et al.* (2010)
Alamine 336	SLM containing Alamine 336 in aromatic 150	1 g L^{-1} uranyl sulfate	Acetate buffer at pH 4.5	The extraction mechanism was dependent on the feed phase pH. Increased Alamine 336 concentration led to lower transport rates due to increased viscosity	Babcock *et al.* (1980a; 1980b)

Huang and Huang (1988) have investigated the kinetics of the coupled transport of U(VI) from nitric acid solutions containing millimolar concentrations of U(VI) through an SLM containing D2EHPA in kerosene as a mobile carrier. The resistances of aqueous film diffusion, chemical reaction, and membrane phase diffusion were used for the calculation of the rate equations describing U transport. It was also reported that the transport of U was found to be controlled by chemical reaction and aqueous film diffusion at the feed-membrane interface. The same authors (Huang and Huang, 1986) have tried to understand the mechanism of uranyl ion transport by TBP by measuring the permeability of the uranyl nitrate-TBP complex, and the interfacial resistances. They have observed higher U flux across the SLM than that calculated with the measured permeability. While the flux was nearly independent of the membrane-strip phase resistances, it was reported to be dependent on the distribution ratio of U at the feed-membrane interface.

U(VI) transport across SLM containing D2EHPA and TOPO was also studied by Kadous *et al.* (2009) and quantitative U transport was seen when two SLMs were used in series. Selective U pre-concentration from phosphoric acid feed solutions was studied by Joshi *et al.* (2009) using a mixture of D2EHPA and neutral donor extractants like tri-*n*-butyl phosphate (TBP), di-butyl butyl phosphonate (DBBP), tri-*n*-octyl phosphine oxide (TOPO), and Cyanex 923 in *n*-dodecane as the carrier extractant while $(NH_4)_2CO_3$ was used as the receiving phase. The results suggested that the SLM formed by TOPO and D2EHPA was best suited for U(VI) transport from phosphoric acid feed solutions though an increase in the feed acidity to 6 M H_3PO_4 found to retard the transport rate of U(VI) across the SLM. This was in sharp contrast to some ELM studies using the same extractants (*vide infra*). In another study, Gill *et al.* (1994) investigated U(VI) transport using a mixture of 1 M D2EHPA and 30% TBP as the carrier extractants in silicone membranes with comparable flux with other polymeric supports such as polypropylene and PTFE (1994). Singh *et al.* (2009) reported the SLM transport of U from phosphoric acid medium using D2EHPA in *n*-dodecane as the carrier solvent and ammonium carbonate as the receiving phase. As expected, the transport of U decreased with an increase in H_3PO_4 concentration while increasing D2EHPA concentration increased the transport rates. The method was reported for application to the recovery of U(VI) from its lean sources like wet process phosphoric acid and wastes generated from the Davis-Gray method used for U analysis. D2EHPA in chloroform was also used for the transport of uranyl ion across a bulk liquid membrane where pH solutions (pH 4–5) were used as the feed while 0.1 M HCl was used as the receiver. >98% Uranium was selectively transported in <3 h from feeds containing a binary or a multi-component mixture of cations. Though reasonably good decontamination was obtained from Zn^{2+} and Fe^{3+} without any complexing agent, Th(IV) co-transport was suppressed by the addition of EDTA to the feed solution. About 98% recovery of U with a hundred fold pre-concentration was reported in about 3h (Nanda *et al.*, 2002).

An ELM containing D2EHPA was used for the pre-concentration of 20–30 L samples to result in a pre-concentration factor of >100 (Mikulaj *et al.*, 1986). The poor extraction of U from HCl medium in to an ELM containing D2EHPA was used for the selective and rapid permeation of Th as the latter was found to be quantitatively extracted in less than one minute while about 6% U extraction was noticed after 3 minutes. This was used for the separation of ^{234}Th from natural U with high radiochemical purity of more than 98% (El-Reefy *et al.*, 1996).

Several other dialkylphosphoric acids have also been employed as carrier extractant for the liquid membrane transport of U. Biswas *et al.* (2012) have used dinonyl phenyl phosphoric acid (DNPPA) and its mixture with several neutral oxodonor ligands in *n*-dodecane as a synergistic solvent system for the carrier facilitated transport of U(VI) from nitric acid feeds in to a receiver phase containing 2 M H_2SO_4. The permeability coefficient (P) was determined using 0.1 M DNPPA and 0.05 M neutral donors and showed the U(VI) transport order as: Cyanex 923 $\approx$ TOPO > TBP > T2EHP. As expected, the P of U(VI) transport decreased with increase in HNO_3 concentration and with metal ion concentration in the feed solution. An optimized solvent system containing 0.1 M DNPPA and 0.05 M Cyanex 923 was used for U recovery from uranyl nitrate raffinate (UNR) solution generated during the purification of U through U(VI)-HNO_3-TBP route. The authors have also used DNPPA alone while using 6 M H_2SO_4 as the strippant solution in the receiver phase. They have fitted the transport data to a kinetic model to calculate the diffusion coefficient and mass transfer coefficients (Biswas *et al*., 2013). Han *et al.* (1999) have used di-1(1-methylheptyl) phosphoric acid (DMHPA) as a mobile carrier for U(VI) transport and investigated the mass transfer kinetics and reported $>96\%$ recovery from the feeds.

8.3.2.2 *Phosphonic acids*

Phosphonic acids such as PC-88A (2-ethylhexyl 2-ethylhexylphosphonic acid) have also been used for U transport studies. Nakamura *et al.* (1991) have investigated the transport behavior of U(VI) using PC-88A from a feed solution into a sulfuric acid solution receiver phase by maintaining a large concentration gradient of hydrogen ions across two sides of the SLM. The stability of the SLM was improved by the addition of 1-decanol to the carrier solution. Kedari *et al.* (2001) have investigated the transport of U(VI) from nitric acid solutions across immobilized liquid membranes (ILM) containing PC-88A in *n*-dodecane as the carrier in to a receiver phase containing oxalic acid. U flux across ILM decreased significantly when concentration of PC-88A in ILM was increased beyond a particular concentration.

A mixture of 0.6 M PC-88A and 0.15 M Cyanex 923 in *n*-dodecane as the carrier for U(VI) transport in to a receiver phase containing $(NH_4)_2CO_3$ (Singh *et al*., 2010). More than 95% U(VI) was recovered from the 0.5 M H_3PO_4 feed in 6 h using 0.5 M $(NH_4)_2CO_3$ as the stripping phase. This method was also applied to recover U from analytical waste in phosphoric acid medium generated in the laboratory. Biswas *et al.* (2011) have studied the permeation of U(VI) from nitric acid medium using SLM containing PC-88A either alone or in a mixture of neutral donors like tri-*n*-butyl phosphate (TBP), tris(2-ethylhexyl) phosphate (T2EHP), and tri-*n*-octyl phosphine oxide (TOPO) dissolved in *n*-parrafin as the carrier and oxalic acid or Na_2CO_3 solutions as the receiving phase. Uranium permeation was also investigated from its binary mixtures with metal ions such as Zr(IV), Th(IV), and Y(III) from feed containing 2 M HNO_3 employing 0.1 M PC-88A in *n*-paraffin as the carrier solvent and 0.5 M oxalic acid as the receiver phase. The presence of the auxiliary neutral donor ligands enhanced the permeation of U(VI) across the SLM in the following order: T2EHP $\sim$ TBP $>$ TOPO. There was significant enhancement in U transport when 1 M Na_2CO_3 was used as the receiver phase.

8.3.2.3 *Phosphinic acids*

Similar to the dialkyl phosphoric acids and dialkyl phosphonic acids, dialkyl phosphinic acids have also been used as extractants of actinide ions including U(VI). Chiarizia *et al.* (1990a) have used di(2,4,4-trimethylpentyl)phosphinic acid (DTMPPA or Cyanex-272) for the removal of U from contaminated groundwater after adjusting the feed acidity to pH 2 while using 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) as the strippant in the receiver phase. Good selectivity for U was observed over accompanying metal ions, *viz*. Ca^{2+} and Fe^{3+}. While Ca^{2+} was poorly extracted by the carrier extractant, Fe^{3+} transport was kinetically disfavored. This SLM based method was employed for the decontamination of Hanford site groundwater at a *DF* (decontamination factor) values >800. The same authors (Chiarizia *et al*., 1990b) used Cyanex 272 in *n*-dodecane as the carrier solvent in polyproylene hollow-fibers and studied U mass transfer in a recycling mode, using a synthetic groundwater feed (at pH 2). Encouraging results were obtained with the proposed HFSLM system to separate and concentrate U(VI) in the strip solution with synthetic as well as real contaminated groundwater with a *DF* value $>3.5 \times 10^3$.

8.3.2.4 *Oximes*

Liquid membrane transport of U(VI) was studied by a ELM containing 5,8-diethyl-7-hydroxy-6-dodecanone oxime (LIX 63) using U tracer (10^{-5} M) solutions in pH 3–4.5 while the strippant used in the internal phase was sulfuric acid (pH 1.5) (Akiba *et al.*, 1984b). The apparent rate constants were calculated for U mass transfer and were found to increase with an increase in the carrier concentrations and external phase pH values. On the other hand, the mass transfer rates were slightly dependent on the stripping phase acidity. In another study by the same author (Akiba *et al.*, 1983) using LIX 63 as the carrier extractant in SLM, Uranium transport was effective from a feed containing U(VI) at pH 4–5 to the receiver solution containing 0.1 M HNO_3 as the strippant.

The mass transport rate of U was found to be inversely proportional to the feed volume and was independent of U(VI) concentration and >99% of U was recovered in this SLM system.

The solvent extraction and SLM transport behavior of U(VI) was also investigated by Mahmoud *et al.* (1997) using LIX 63 as the extractant, where U(VI) containing species were extracted in a nearly neutral region and selectively stripped with a dilute acid. The transport studies indicated that U(VI) was selectively transported to the product side, while Mo(VI) with similar ionic species was retained in the SLM in the low pH region and remained in the feed solution at near neutral pH conditions suggesting facile separation of the metal ions.

8.3.2.5 *Beta-diketones*

Beta-diketones have been used as efficient extractants for actinides from weakly acidic medium (Manchanda *et al.*, 2009). In view of being acidic extractants, an increase in the feed acidity decreases the metal ion extraction. On the other hand, the presence of neutral donor ligands leads to synergism and hence to higher metal ion extraction compared to the beta-diketone alone at a given acidity.

A solution of benzoyltrifluoro acetone (BTA) in carbon tetrachloride was used as the bulk liquid membrane for U(VI) transport from mildly acidic feed solutions (pH 6.0) in to a receiver phase containing 0.1 M hydrochloric acid. >99% Transport of U was possible and its separation from binary mixtures containing metal ions such as Th^{4+}, Hf^{4+}, Zr^{4+}, Fe^{3+}, La^{3+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+} was demonstrated using trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid (DCTA) as a masking agent in the feed compartment (Shamsipur *et al.*, 2009). Chloroform solutions of TTA (2-thenoyltrifluoro acetone) was used for the transport of uranyl ion across a bulk liquid membrane from feed solutions whose pH was maintained at 4 to 5 while the receiver phase contained 0.1 M hydrochloric acid (Nanda *et al.*, 2004a). EDTA was found to be an effective masking agent to eliminate the interference from Th(IV) and transition metal ions. The BLM system was applied to the recovery of U from synthetic seawater and a forty-fold pre-concentration and >96% recovery of U was reported in a single stage operation. A uranyl ion selective electrode was developed by Nanda *et al.* (2004b) using PVC membranes containing TTA as the carrier ligand while dibutyl phthalate and sodium tetraphenyl borate have been used as plasticizer and anion excluder, respectively.

Shamsipur *et al.* (2010) have also investigated the carrier-mediated transport of U(VI) using a mixture of TTA and dicyclohexyl-18-crown-6 (DC18C6) in chloroform in a bulk liquid membrane transport system from pH 2.0 solution in to a mixture of 0.2 M hydrochloric acid and 4.0×10^{-3}M sodium dodecylsulfate (SDS), an anionic surfactant. Though only about 20% U transport was observed after 9 hours when only TTA was used as the carrier extractant, it sharply rose in the presence of the crown ether to result in the quantitative transport of the metal ion under identical experimental conditions. When several crown ether ligands were used as the auxiliary ligand, the transport efficiency of the crown ether ligands followed the order, DC18C6 > DB18C6 > DB24C8 > DB21C7 > DB15C5. A kinetic model was developed to describe the U(VI) transport behavior which indicated the stripping rate constant to be three times than the extraction rate constant. The interference from metal ions such as Fe^{3+}, Cu^{2+} and Th^{4+} was also investigated and EDTA was used in the feed to suppress their transport leading to selective U permeation.

8.3.3 *Basic extractants*

The mechanism of extraction of uranyl ion by basic extractants such as the amines primarily involves formation of anionic complexes of the metal ion. This is usually favored in media containing moderately high concentration of the complexing anions and also involves (in many cases) moderate concentrations of the acid. Out of the basic extractants investigated, tri-*n*-octyl amine (TOA), also known as Alamine 336 (a commercial product known as tri-capryl amine or tri-caprylyl amine) is one of the most studied for uranyl ion extraction. In this context, the transport studies involving TOA or Alamine 336 (Table 8.2) as the carrier extractant will be discussed first followed by other basic extractants.

The chemical reaction which is responsible for the coupled transport involving the co-transport of H^+ ion in case of a basic extractant can be presented as:

$$M^{n+}_{(a)} + mX^-_{(a)} + (m-n)H^+ + (m-n)L_{(o)} \rightleftharpoons (MX_m^{(m-n)-})((m-n)LH^+)_{(o)} \tag{8.5}$$

As the complex formation is dependent on the anion concentration and acidity of the medium, these are considered as the driving forces.

Babcock *et al.* (1980a) have studied the coupled transport of U(VI) through liquid membranes containing Alamine 336 in Aromatic 150 as the diluent while the feed contained $1\,g\,L^{-1}$ U as uranyl sulfate and the receiver phase comprised of acetate buffer at pH 4.5. A pH dependent U transport behavior was seen as the transport rates were high in the pH range of 0.5–2.5 and were low outside this range. The mechanism of transport involved formation of complexed species such as $(R_3NH)_4UO_2(SO_4)_3$ and at pH value above the pK_a value of Alamine 336 (2.5), the following reaction destabilized the extraction reaction:

$$(R_3NH)_4UO_2(SO_4)_{3(o)} \rightleftharpoons 4R_3N_{(o)} + 4H^+_{(a)} + UO_2(SO_4)^{4-}_{3(a)} \tag{8.6}$$

On the other hand, at pH lower than 2.5, the following reaction, which favored sulfuric acid transport predominates:

$$(R_3NH)_4UO_2(SO_4)_{3(o)} + 4HSO^-_{4(a)} \rightleftharpoons 4(R_3NH_2SO_4)_{(o)} + UO_2(SO_4)^{4-}_{3(a)} \tag{8.7}$$

The transport mechanism is schematically presented in Figure 8.7. Babcock *et al.* (1980b) have also reported that the U transport efficiency increased with increasing concentration of Alamine 336 which also led to increased viscosity of the liquid membrane phase which has a significant effect on the flux. The optimum extractant concentration was found to be 30% Alamine 336 in Aromatic 150. The studies with varying membrane pore size indicated lower flux for membranes with lower pore size which was attributed to interaction of the diffusing species with the side wall. Lakshmi *et al.* (2004) have studied the transport of uranyl ions from HCl medium using 30% Alamine 336 in toluene as the carrier while distilled water was used as the strippant. The role of U transport on the nature of the organic diluent was investigated using several diluents which showed the trend: toluene > *tert*-butylbenzene > chloroform > 1,2-dichloroethane > hexane > 1-decanol. Studies carried out using PTFE membranes of varying pore size indicated, however, highest flux at membranes of 0.2 micron pore size and continuous decrease with increasing pore size which was in sharp contrast to the observation made by Babcock *et al.* (1980b) (*vide supra*). Tri-*n*-octyl amine (TOA) in xylene was used as a carrier solvent by Chaudry and Mohammad (1987) for U transport studies from nitric acid solutions to an alkaline aqueous phase which required about 10 hours for the quantitative transport of U from the feed phase composition of 6 M HNO_3. In another study involving TOA in an ELM system with Span 80 as the surfactant, Hirato *et al.* (1991) have reported >99% U extraction in to the internal phase containing 1 M Na_2CO_3 solution. The liquid membrane extraction was reported by the authors to be more efficient as compared to the conventional solvent extraction process using the same extractant.

Mohapatra *et al.* (2006) have investigated the transport of uranyl ion from HCl medium using 30% Aliquat 336 (a quaternary ammonium extractant which acts as a liquid anion exchanger) in $CHCl_3$ as the carrier solvent and reported >90% transport of U in about 3 h which was due to significant amount of acid transport (about 15%). Subba Rao *et al.* (1999) have also studied U transport behavior from hydrochloric acid medium using Aliquat 336 in xylene as the carrier solvent and observed higher U flux values at lower carrier concentration which was attributed to the aggregation of Aliquat 336 in the liquid membrane phase. The authors have also investigated the effect of phase modifier on U permeation from hydrochloric acid medium (Subba Rao *et al.*, 1999).

El Sayed *et al.* (2003) have extracted U from a leach liquor (in H_2SO_4 medium) using an ELM separation system containing Aliquat 336, 5% Span 80 in kerosene while the internal phase was composed of 1 M Na_2CO_3 solution. In another study (Pancharoen *et al.*, 2011) involving

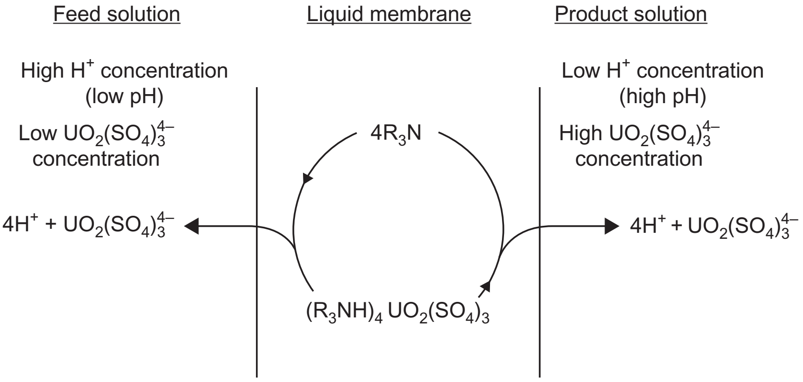


Figure 8.7. Schematic representation of co-transport of uranium with a tertiary amine. (Reproduced with permission from Babcock *et al.*, 1980b).

a binary extraction system of Aliquat 336 and TBP in the liquid membrane phase, in hollow fiber contactors, an enhanced U flux was seen as compared to that observed with Aliquat 336 alone. Effective separation of U from a feed containing trisodium phosphate solution (a by-product of monazite processing) was reported suggesting its potential applications. Lothongkum *et al.* (2009), have demonstrated in another study that for the feed containing 45 mg L^{-1} of U in trisodium phosphate, a hollow fiber contactor can be used effectively using 0.1 M Aliquat 336 and 0.06 M TBP mixture as the solvent system, and 0.5 M HNO_3 as the receiver phase to achieve 99% U extraction.

The nature of the anionic complex and feed acid concentration has a role in the extent of U transport in the liquid membranes containing amine extractants. Apparently, the anionic complexes formed in HCl medium are better transported by this class of extractants. Lakshmi *et al.* (2005) have studied the role of mineral acid type on U pertraction using SLM containing Aliquat 336 in chloroform and the results (Fig. 8.8) indicated the ease of U transport as: $HCl > H_2SO_4 > HNO_3$.

Guo *et al.* (2008) have studied the recovery of U(VI) from chloride solution using an emulsion liquid membrane (ELM) consisting benzyloctadecyldimethyl ammonium chloride (BODMAC) in kerosene as the solvent system, Span 80 as the emulsifying agent and 0.5 M Na_2CO_3 as the internal phase and reported about 80% U transport. The stability of the emulsion was reported to be good at low pH in the presence of NaCl and $MgCl_2$.

8.4 APPLICATIONS OF LIQUID MEMBRANES FOR URANIUM RECOVERY

8.4.1 *Wet process phosphoric acid*

Wet-process phosphoric acid (WPPA) is considered a lean source of U with concentration in the range of 50–200 mg L^{-1}. The commonly used solvent extraction methods for the recovery of U from WPPA involve mainly three processes, *viz.* OPPA (octylpyrophosphoric acid), D2EHPA-TOPO and OPAP (octylphenylacid phosphate) (IAEA, 1989). While the D2EHPA-TOPO solvent system preferentially extracts U(VI) (Hurst *et al.*, 1972), OPPA preferentially extracts U(IV) (Hurst *et al.*, 1974). These solvent systems have also been extended to liquid membrane based separations. The application of liquid membrane technology for the quantitative recovery of U from WPPA has been discussed in many published papers. Transport of U(VI) from 5–6 M phosphoric acid solution through a SLM containing D2EHPA and TOPO in kerosene was studied by Sifniades *et al.* (1981). The receiver phase contained Fe(II) in H_3PO_4 and U flux was rather low to be competitive with liquid-liquid extraction processes for the recovery of U from WPPA as >10 days were needed for the quantitative transport of U from 5–6 M phosphoric acid.

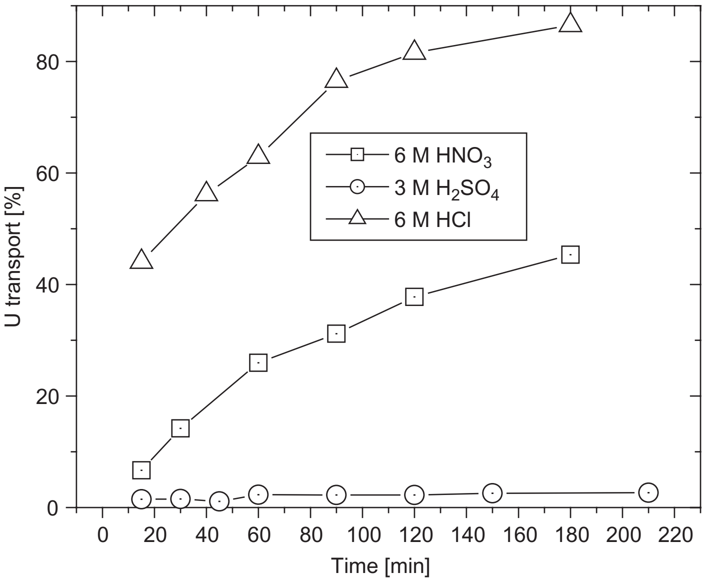


Figure 8.8. Dependence of U(VI) transport rates on the nature of mineral acid. Carrier: 30% Aliquat 336 in chloroform; receiver: distilled water. (Reproduced with permission from Lakshmi *et al.*, 2005).

Emulsion liquid membrane (ELM) based processes have been reported to be far more efficient as compared to the solvent extraction methods when U recovery was attempted from WPPA feeds (Hayworth *et al.*, 1983). ELM based methods have shown to have much larger U flux and are extensively used for U from WPPA. Usually, a water-in-oil emulsion containing the carrier extractant has been used for the simultaneous removal of U from a WPPA feed and concentrates it in the internal phase containing the strippant solution. The general strategy has been to use either DEHPA and TOPO synergistic extraction system in a hydrocarbon diluent as the carrier which facilitated the pertraction of U(VI) in to the internal phase where the metal ion was reduced to the +4 state. Alternatively, U(IV) extraction was carried out using OPPA (octylphenylphosphoric acid) followed by oxidation in the internal phase. It was reported that the role of mixing rate and temperature was quite pronounced on the U mass transfer coefficient while the complexing agent and acid concentration had very little effect. The operative cost was cheaper in the ELM method as compared to the SX method (Baker *et al.*, 1977; Cahn *et al.*, 1981). Though Na_2CO_3 was a good strippant for U(VI) due to the strong complexation of the uranyl ion by the carbonate anion, the ELM stability was rather poor (*vide supra*). On the other hand, while NaOH, Na-citrate, EDTA and Na_2SO_4 could be used for effective stripping of U into the internal phase, the yield was not better than the SX methods. The schematics of U recovery by the ELM method are shown in Figure 8.9. The proposed ELM process is suggested to be more efficient than the analogous solvent extraction process. Bock and Valint (1982) and Bock *et al.* (1982) have also investigated the liquid membrane separation of U from wet process phosphoric acid. Bock and Valint (1982) reported that the ELM extraction of U exhibited an inverse temperature response compared to the solvent extraction method, insensitivity to phosphoric acid strength and the concentration of complexing agent. El-Hazek *et al.* (2003) have reported an ELM process for U extraction from either dihydrate 28–30% P_2O_5 (DH) or hemi-dihydrate 42–45% P_2O_5 (HDH) wet process phosphoric acid using a binary extraction system of 0.1 M di-2-ethyl hexyl phosphoric acid (D2EHPA) and 0.025 M trioctyl phosphine oxide (TOPO) with 4% Span 80 while using 0.5 M citric acid as the internal phase. The emulsion was found to be stable in 42–45% P_2O_5 acid suggesting its possible application to U recovery from the phosphoric acid produced by the

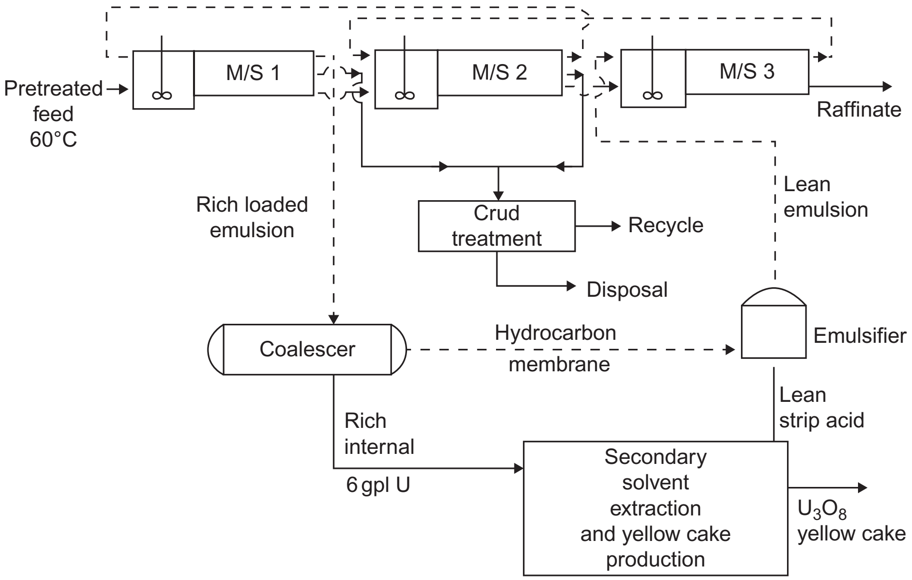


Figure 8.9. ELM process flow sheet for U recovery from WPPA. (Reproduced with permission from Hayworth *et al.*, 1983).

hemi-dihydrate (HDH) process. A flow-sheet proposed by the authors for U recovery from the DH or HDH process is given in Figure 8.10.

8.4.2 *Uranium recovery from seawater*

Uranium present in the seawater ($\sim$3.3 μg L^{-1} concentration range) is being considered as a secondary source. U present in the sea (total amount estimated as 4×10^9 metric tons) is about 1000-fold of the amount existing in mines all over the world. However, this separation process is rather complex in view of the presence of a large number of elements in the seawater, high salt concentration (0.6–0.7 M) and also the different ionic species in which U exists, *viz.* the carbonates and the hydroxides. Though there have been various resin based U separation methods available (Tabushi *et al.*, 1984) several membrane based methods are also reported. Extraction of U from seawater (spiked with ^{237}U tracer) has been attempted by Akiba *et al.* (1985) by using a supported liquid membrane containing 0.1 M 7-dodecenyl-8-quinolinol (Kelex 100) in kerosene and inferred that about 10 hours were required for the quantitative transport of U from seawater. The authors, however, have not reported the interference from other matrix elements. In view of the poor stability of the SLM, especially under actual seawater conditions, grafted membranes have been proposed to be more suitable for such applications and some of those are discussed below.

A porous, amidoxime-group-containing membrane made by radiation-induced graft polymerization of acrylonitrile was found to adsorb 0.85 g of U per kg of the adsorbent in 50 days which was considered fast compared to the available literature reports (Saito *et al.*, 1987). It was interesting to note that the selectivity of the membrane for U uptake was apparent from its high concentration factor (10^5) which was four orders of magnitude higher than that for Mg. The authors have made hollow fibers from the amidoxime polymer which showed improved U uptake kinetics (Takeda *et al.*, 1991). Das *et al.* (2008) have also prepared amidoximated macroporous membranes and determined their water uptake capacity in seawater, Na$^+$-exchange capacity, and U loading capacity from seawater as 200 $\pm$ 10 wt%, $(3.1 \pm 0.2) \times 10^{-4}$ mol g^{-1}, and $(1.60 \pm 0.18) \times 10^{-3}$ mol g^{-1},

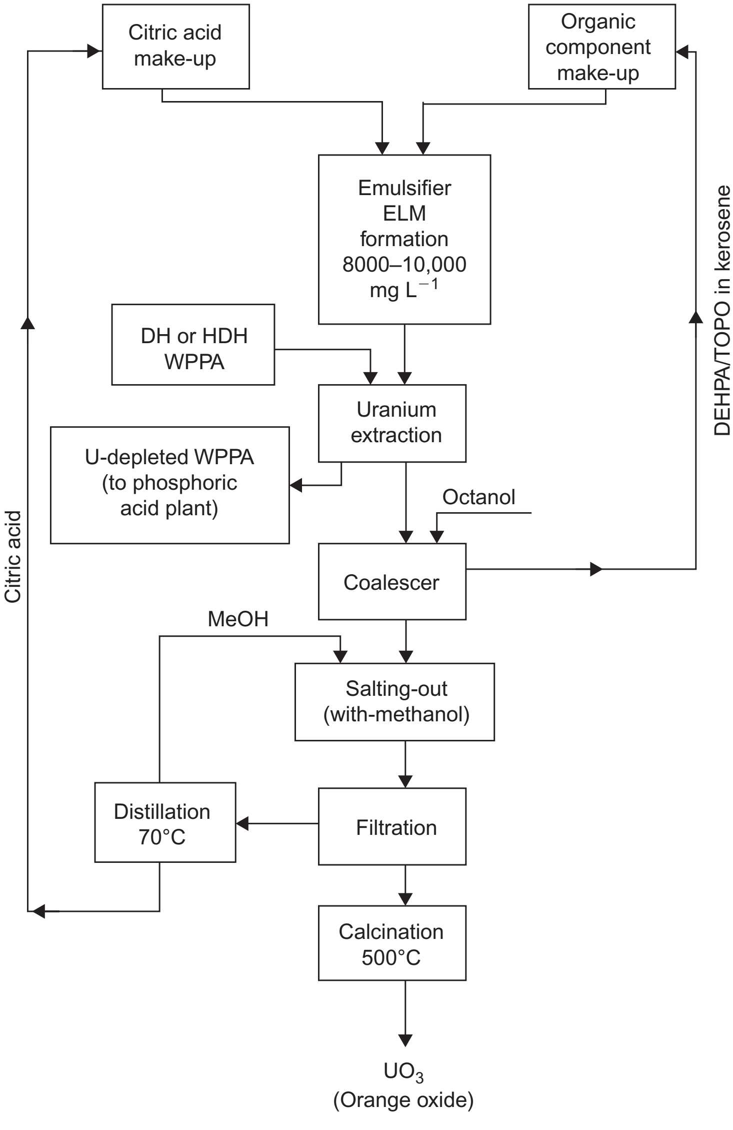


Figure 8.10. Proposed flow-sheet for uranium recovery by DEHPA/TOPO/citric acid ELM system from DH or HDH process phosphoric acid. (Reproduced with permission from Akiba *et al.*, 1985).

respectively. These authors have also postulated that the uranyl ion formed a complex with the amidoxime groups in 1:4 proportion which could be quantitatively desorbed (>90%) using sodium carbonate and HCl solutions. The same authors have prepared poly(ethylene glycol methacrylate phosphate) macroporous membranes (PEGMP-membrane) and investigated the U uptake under seawater conditions (Das *et al.*, 2012) which suggested that the uranyl ion formed complex with EGMP units in 1:2 proportion (Fig. 8.11). Near quantitative (>95%) desorption of the sorbed U was possible in 10 minutes using 0.5 M Na_2CO_3.

A macrocyclic ligand containing several carboxylate functional groups (Kobuke *et al.*, 1988) was used in a membrane separation method where the feed contained uranyl acetate (3.3×10^{-5} M) at a pH value of 4–5, while the receiver phase contained 1.0 M $NaHCO_3$ and U was found

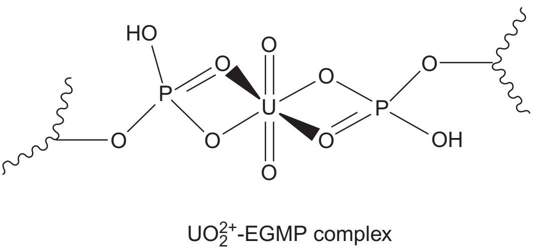


Figure 8.11. Proposed structure of the UO_2^{2+}-EGMP complex. (Reproduced with permission from Das *et al.*, 2012).

to selectively transport from a mixture of cations such as Na^+, K^+, Mg^{2+}, Ca^{2+}, etc. Ca^{2+} was found to compete with the uranyl ion though the kinetic factors favored a selective U transport. In a separate study, amidoxime grafted membranes were tested for the recovery of U from seawater (Kawai *et al.*, 2000).

8.5 CONCLUSION AND PERSPECTIVES

The liquid membrane technique has been extensively evaluated for U recovery from lean solutions. Though BLM has been one of the early configurations tested for metal ion transport, it has not been considered beyond laboratory tests, due to slow diffusion rates and relatively large solvent inventory. The SLM based methods though also show slow transport rates, the limitation can be alleviated using hollow fiber contactors. Both SLM and ELM use very low extractant inventory and can have high mass transfer rates to find applications in actual processes. Additionally, ELM methods can achieve high volume reduction factors making them a very versatile technique. ELM studies were found to be the most promising though recent studies with hollow fiber contactors have shown promise. ELM studies for the recovery of U from WPPA feeds, using a mixture of D2EHPA and TOPO as the carrier extractants, have shown better economy as compared to the solvent extraction studies. SLM methods based on tri-alkyl amines have been suggested by Babcock *et al.* (1980c) to be cheaper as compared to the analogous solvent extraction methods.

The major hurdles include the scale up issues, which is related to lower flux and fouling problems. Also, sustainability possibilities need to be explored wherein the long term reusability of the liquid membranes need to be studied in detail. These issues include chemical stability of the solvent systems and long term liquid membrane stability. Grafted membranes can partially solve the stability issues and several of them have been successfully tested for U recovery from seawater. It is required to develop membranes with higher flux, higher stability, higher VRF and lesser fouling problems. With a large number of scientists and technologists working on these areas, it appears that application of such 'smart' membranes to actual U containing feeds can be possible to make in the near future.

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CHAPTER 9

Supported liquid membrane technology in the removal and recovery of toxic ions from water

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9.1 INTRODUCTION

Several methods are being used at present to treat polluted waters regarding the removal of heavy metal ions. These technologies include solvent extraction, chemical precipitation, ion-exchange, adsorption, membrane filtration, coagulation-flocculation, flotation and electrochemical methods (Kocherginsky and Yang, 2007a; Liu *et al.*, 2008; Matsumoto *et al.*, 2007; Muthuraman and Palanivelu, 2006; Vilar *et al.*, 2007). These techniques generally meet legislation requirements, but they have some important drawbacks. Solvent extraction has the main problem of employing large quantities of organic phase, especially when processing dilute solutions (Kumbasar, 2009), making this process not very cheap and safe, since the used solvents are often chlorinated and sometimes carcinogenic. Precipitation is a very simple technique, but it is unselective, produces a large amount of sludge containing contaminants and residuals of the precipitating agents are often in high concentration, for which disposal/treatment is a very costly affair and it is not eco-friendly. Adsorption and ion exchange are not continuous processes, because of the regeneration need, which negatively affects process economy.

Use of membrane-based separation processes represents a promising alternative to traditional processes, since they do not require high energy and chemical consumption, thus significantly improving the sustainable energy approach. In particular, innovative methods based on the carrier facilitated transport across a liquid membrane (LM) show great potential since they do not produce by-products of difficult disposal and they can be operated continuously.

A LM is a thin layer of an organic phase separating two aqueous solutions. The organic phase can contain an extractant compound, indicated as carrier, which promotes the facilitated transport from the donor phase (feed) to the acceptor phase (strip). Liquid membrane based processes have become an attractive alternative to conventional techniques for selective separation and concentration of both organic and inorganic compounds from dilute aqueous solutions, because they combine the extraction process of the species of interest and the subsequent stripping process into a single process, thus reducing the solvent inventory requirement, the volume of the contacting equipment and the cost significantly (Molinari *et al.*, 2009a). These processes also allow the use of expensive and highly selective extractants owing to their cyclical use, which otherwise would be uneconomic in solvent extraction. Other potential advantages of LM based processes in comparison to the convectional separation techniques, that make these processes interesting for a sustainable future, are: (i) high separation factors; (ii) higher flux or permeability compared to solid membranes, since diffusion coefficients in liquids are at least three/four orders of magnitude higher than in solids; (iii) uphill concentration and separation, because of facilitated transport making the system as a matter pump; (iv) minimization of chemical additives use, thus reducing the costs and the ecological impact of the treatment; (v) high feed/strip volume ratios; (vi) ability to separate low concentration species from very dilute solutions, because of the effective binding; (vii) high flexibility and easy scale up; and (viii) low capital and operating costs.

LM systems include bulk liquid membrane (BLM), emulsion liquid membrane (ELM) and supported liquid membrane (SLM).

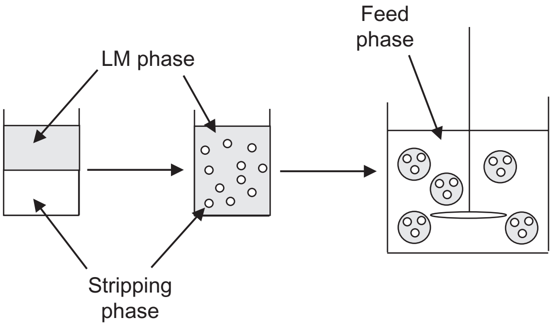

Figure 9.1. Schematization of ELMs preparation.

BLMs usually consist of a water-immiscible liquid membrane phase, which separates two aqueous phases (feed and strip). The most important drawback of this LM configuration is the small membrane surface area per unit volume, making it not attractive in view of large-scale applications.

ELMs are characterized by a large surface area per unit source phase volume, which enhances the transport rate of this membrane. They are usually described as a bubble inside a bubble contained in the feed phase, where the inner bubble is the strip phase, closed by the LM membrane phase (Ahmad *et al.*, 2011; Zhao *et al.*, 2010). Their preparation usually involves two steps (Fig. 9.1): (i) emulsion formation, in which a stable water-in-oil emulsion is formed between an aqueous stripping phase and an organic LM phase, which can contain an extractant together with a surfactant to stabilize the emulsion droplets; (ii) emulsion dispersion into a continuous third phase (an aqueous feed phase) by agitation. The most important limitation of ELMs is the low emulsion stability, so that if for any reason, the membrane does not remain intact during operation, the separation achieved to that point is destroyed. Thus, ELMs are not technologically attractive.

SLM consists of a LM phase impregnated in the pores of a thin hydrophobic microfiltration membrane and kept there by capillary forces (Kocherginsky *et al.*, 2007b; Molinari *et al.*, 2009a), Molinari *et al.*, 2009b). This LM phase may also contain a mobile extractant agent (carrier), which mediates the transport across the SLM binding very selectively one or a class of components in the donor phase (feed), transporting it (or them) into the acceptor phase (strip), resulting in the so called facilitated transport (Molinari *et al.*, 2006a). SLM systems combine the typical advantages of liquid membrane with the mechanical resistance of solid membranes. They meet the energetic sustainability criteria because lower amount of energy is required compared to pressure driven membrane processes.

SLMs have been studied in the transport of various cationic metals (Altin *et al.*, 2010; Ata, 2007; Chaudry *et al.*, 2008; Tarditi *et al.*, 2008) and anions (Güell *et al.*, 2010) from wastewater, as well as different molecules of biological interest (Hassoune *et al.*, 2009; Matsumoto *et al.*, 2007; Muthuraman and Palanivelu, 2006; Venkateswaran and Palanivelu, 2006; Yang and Chung, 2006) and organics (Ravanchi *et al.*, 2010).

Common SLM configurations include flat-sheet, hollow fiber and spiral wound. The latter two configurations are usually more expensive but they provide much higher surface area to module volume ratio (up to 500 m^{-1}). Commercially available hollow fiber modules can have up to 220 m^2 area per module. Usually the LM phase is embedded in the pores of microporous hollow tubes and feed and strip solutions are circulated in the lumen and in the shell side of the hollow fibers, respectively (He, 2008). In view of large-scale applications, the first level of method development is usually represented by the flat sheet configuration. During operation with this system arrangement, the technical feasibility and the performance of a particular system

Table 9.1. Summary of the principal advantages/disadvantages of BLM, ELM and SLM LM-based processes.

Advantages	Disadvantages
High separation factors	BLM: small membrane surface area per unit volume
Higher flux compared to solid membranes	ELM: low emulsion stability
Very high selectivity	SLM: low system stability
Uphill concentration and separation	
Possibility to use expensive extractants	
Minimization of chemical additives use	
High feed/strip volume ratios	
Ability to operate on very dilute solutions	
High flexibility and easy scale up	
Low capital and operating costs	

(e.g., metal ion, carrier) are evaluated before scaling-up the hollow fiber or the spiral wound configurations (Alguacil, 2004).

Despite the above-mentioned advantages, the application of SLMs at large scale in industrial applications has been limited because of the insufficient system stability (Kemperman *et al.*, 1996; Yang *et al.*, 2007). The principal causes of instability, as evidenced by many studies, is the LM phase (carrier and/or solvent) loss from the pores of the support followed by its substitution with feed and/or strip solutions, influencing both flux and selectivity (Hill *et al.*, 1996; Kemperman *et al.*, 1998; Yang and Fane, 1997; Zhang *et al.*, 2001). This loss can be caused by one or a combination of various factors, like a pressure difference over the membrane (Danesi *et al.*, 1987), solubility of the carrier and liquid membrane solvent in the adjacent feed and strip solutions (Zha *et al.*, 1995), progressive wetting of the pores in the membrane support by the aqueous phases (Takeuchi *et al.*, 1987), blockage of support pores by precipitation of carrier complex (Zhu and Li, 1990), or emulsion formation (Neplenbroek *et al.*, 1992). Most likely, only two mechanisms are the major important factors resulting in membrane stability/instability: the solubility of the SLM components in the adjacent feed or strip solutions and an emulsification of the SLM phase caused by lateral shear forces. SLM stability can also be affected by the type of polymeric support, its pore radius, organic solvent used in the LM phase and method of preparation (Yang *et al.*, 2007).

Table 9.1 reports a summary of the advantages and disadvantages of the previous reported LM based processes.

In this chapter, the main theoretical aspects of transport in SLMs will be described and possible applications of this technology in the removal and recovery of toxic ions from water will be reported. Particular attention will be devoted to the separation and recovery of As from environmental matrices. Possible large-scale applications of SLMs will be also described, evidencing that if the LM separation process is carried out avoiding the production of byproducts, it can be considered as a green process.

9.2 THEORY

9.2.1 *Main transport mechanisms across a LM*

Solute permeation from the donor feed to the receiving strip phases across a LM can be mediated by a mobile extractant (carrier), resulting in the so-called facilitated transport, or simply due to a different solubility of the solutes in the above mentioned two phases, resulting in the so-called non-facilitated transport.

In the facilitated transport, mass transport is due to a concentration difference of bound and unbound extractant, existing between the two internal interfaces of the LM, generated by a chemical gradient of another species between feed and strip (facilitated coupled transport).

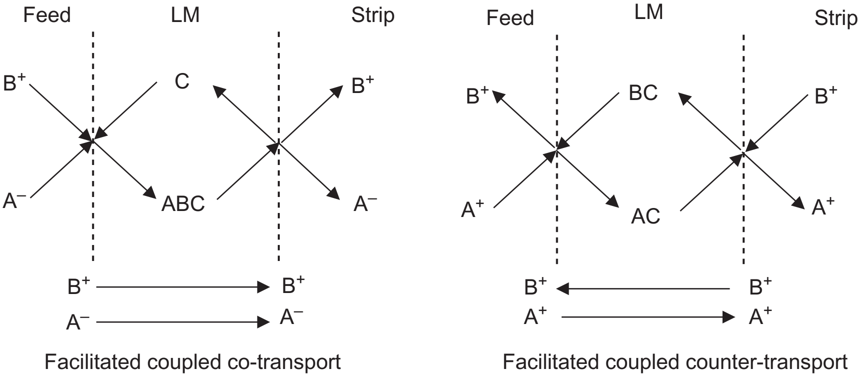

Figure 9.2. Facilitated coupled transport of ionic solutes across a liquid membrane.

Two main transport mechanisms are known (Fig. 9.2): (i) facilitated coupled co-transport and (ii) facilitated coupled counter-transport.

In the former case, a basic carrier like amines or phosphates is used to transport negatively charged species (A^-) and the counter-ion (B^+) across the membrane in the same direction. At feed-LM interface, the carrier C selectively binds the charged species A^- and the counter ion B^+. The so formed ABC complex diffuses through the LM where at LM-strip interface A^- and B^+ ions are released in the strip. The so regenerated carrier molecule C diffuses back to the feed and the transport cycle begins again.

In the case of facilitated coupled counter-transport, at feed-LM interface the carrier C selectively binds charged species A^+ and releases the charged species B^+. The so formed AC complex diffuses through the LM. At LM-strip interface, the A^+ ion is released into the strip and the B^+ ion is bound. The BC complex diffuses back to the feed and the transport cycle begins again. The ion A^+ has the same charge as B^+, and the electrical neutrality is preserved because the carrier acts as a shuttle transporting A^+ and B^+ in opposite directions. This transport mechanism is typical for the transport of metal ions (Me^{n+}) through the SLM with an acidic carrier CH (Molinari *et al.*, 2006b), where the reaction scheme is the following:

$$(Me^{n+})_F + n(CH)_{org} \leftrightarrows (MeC_n)_{org} + n(H^+)_F \tag{9.1}$$

$$(MeC_n)_{org} + n(H^+)_S \leftrightarrows (Me^{n+})_S + n(CH)_{org} \tag{9.2}$$

where the subscript ‘F’, ‘org’ and ‘S’ mean feed, organic and strip phases, respectively, and MeC_n is the metal ion-carrier complex.

As a consequence of the coupled transport of A and B ions, the target ionic species (A^+ or A^-) can be transported across the LM against their concentration gradient. This so-called “uphill” or active transport will continue until the driving force (difference of chemical potentials of B ions (usually H^+) between feed and strip phases) is balanced by the difference of the chemical potentials of the targeted transported ions.

In the case of non-facilitated transport, solutes are transported from the feed to the strip phase by the following steps: (i) diffusion in the boundary layer on the feed side from the bulk of the feed solution to the feed-LM interface; (ii) solubilization (capture) in the organic phase at the feed-LM interface; (iii) diffusion across the LM under the action of the concentration gradient; (iv) solubilization (release) in the receiving strip phase at the LM-strip interface; and (v) diffusion in the boundary layer on the strip side from the LM-strip interface to the bulk of the receiving phase. Based on this, non-facilitated transport can be indicated simply as solution-diffusion transport. The efficiencies of solubilization steps are determined by the partition coefficient while the diffusion is by the diffusivities of the solutes in the organic phase. A not very selective separation is achievable, as it is simply due to the difference in the partition coefficients and diffusivities of solutes. Furthermore, the targeted species cannot be transported across the LM against their concentration gradient. These limitations can be overcome by coupling a chemical reaction with the release in the strip phase (e.g., phenol conversion to sodium phenolate with sodium hydroxide) thus promoting solute stripping and reaching counter-transport.

9.2.2 *Fundamental parameters of SLM separations*

A fundamental parameter in the liquid-liquid extraction process is the partition coefficient k_d. It is a key parameter of SLM separations, influencing both the permeation and process selectivity. It is defined as the ratio between the amount (moles) of a target species in organic and aqueous phases at equilibrium:

$$k_d = (n_A)_{org}/(n_A)_{aq} \tag{9.3}$$

where A is the target component and the subscripts "org" and "aq" mean organic and aqueous phases, respectively. When the organic and aqueous phase volumes are equal ($V_{org} = V_{aq}$), the partition coefficient can be expressed as follows:

$$k_d = (c_A)_{org}/(c_A)_{aq} \tag{9.4}$$

where c_A is the molar concentration of the target component A.

Another important parameter, strictly related to the partition coefficient, is the extraction percentage, defined as follows when $V_{org} = V_{aq}$:

$$E\% = ((n_A)_{org}/(n_A)_{in}) \times 100 = (k_d/(k_d + 1)) \times 100 \tag{9.5}$$

where $(n_A)_{in}$ represents the initial amount (moles) of the target ionic species in the feed phase.

Selectivity can be calculated as the ratio $E\%(A)/E\%(B)$, where A is the target species and B represents another generic species contained in the aqueous phase. However, it must be noticed that previous selectivity considers only the extraction process and not also the permeation one. Thus, it can be indicated as thermodynamic (static) or extraction selectivity (Molinari *et al.*, 2006b). It can be quite different with respect to the transport (kinetic) selectivity, which must be determined by the ratio of the permeation flux J of the species of interest compared to another one (J_A/J_B).

The permeation flux is defined as the rate of mass transport of a solute through the membrane. It is the parameter frequently used to evaluate SLM performance (Singh *et al.*, 2010). Calculation of fluxes can be done by using the following equation:

$$J_A = -(V_F/S_{exp}\varepsilon_m) \times (dc_A/dt)_F \tag{9.6}$$

where A represents the target species and V_F is the feed phase volume. S_{exp} is the membrane surface exposed to feed and strip phases. It is related to the effective membrane surface (S_{eff}) where transport really occurs by means of membrane porosity $\varepsilon_m = S_{eff}/S_{exp}$.

The flux can be also calculated referring to strip concentration, thus considering only the recovered A:

$$J_A = -(V_S/S_{exp}\varepsilon_m) \times (dc_A/dt)_S \tag{9.7}$$

where V_S is the strip phase volume.

When diffusion of the carrier complex through the membrane is the limiting step, the permeation flux J can be calculated by an appropriate formulation of the Fick's first law of diffusion, as follows (Altin *et al.*, 2010):

$$J_A = (D/L)(c_{A,FI} - c_{A,SI}) = P(c_{A,FI} - c_{A,SI}) \tag{9.8}$$

where D is the diffusion coefficient of the complex through the membrane phase, L is the membrane thickness and $c_{A,FI}$ and $c_{A,SI}$ are the concentrations of the target species at the membrane/feed interface and at the membrane/strip interface, respectively. P is the permeability; it is another fundamental parameter frequently used to evaluate SLM performance (Güell *et al.*, 2010; Zidi *et al.*, 2010).

Operating under efficient stripping conditions $c_{A,FI} >> c_{A,SI}$ and ignoring the aqueous diffusion layer $c_{A,FI} \approx c_{A,F}$ (the complex diffusion in the membrane phase is the limiting step) and combining Equations (9.6) and (9.8):

$$P = -(V_F/S_{eff}) \times (dc_{A,F}/dt) \times (1/c_{A,F}) \tag{9.9}$$

Integrating Equation (9.9) and assuming constant the permeability P, the following equation is obtained:

$$\ln(c_{A,F}/c_{A,F0}) = -(S_{eff}/V_F) \times P \times t \tag{9.10}$$

where $c_{A,F}$ and $c_{A,F0}$ are the concentrations of the target species in the aqueous feed phase at the times t and 0 (initial feed concentration). By plotting $\ln([A]_F/[A]_{F0})$ *vs.* the time and determining the slope of the obtained straight line the permeability (P) of the SLM system can be evaluated.

9.3 SLM APPLICATION IN THE REMOVAL AND RECOVERY OF TOXIC IONS FROM WATER

9.3.1 *Separation and recovery of arsenic from environmental matrices*

Due to its high toxicity it is of great importance to develop efficient separation systems for As removal from natural water intended to be used as a source of drinking water, as well as to help in their monitoring in terms of As(III)/As(V) speciation. In 1993, the World Health Organization (WHO) changed the provisional guideline for As from $50\,\mu g\,L^{-1}$ to $10\,\mu g\,L^{-1}$ as a drinking water standard (WHO, 2011). This standard was accepted both within the European Union (European Union, 1998) and by the Environmental Protection Agency of the USA (Code of Federal Regulations, 2006).

Arsenic is generated from the processing of a variety of ores including those of copper, gold, nickel, lead and zinc (Bey *et al.*, 2010). Considering the hydrometallurgical production of copper at an industrial level by the electro-refining of impure anode copper to produce cathodes with high purity, As is the most commonly found impurity dissolved in the copper-bearing acidic electrolyte solution. The electrolyte composition is: copper 30–60 $g\,L^{-1}$, arsenic 1–7 $g\,L^{-1}$, nickel 1–20 $g\,L^{-1}$, antinomy 0.1–0.7 $g\,L^{-1}$ and H_2SO_4 150–250 $g\,L^{-1}$. Therefore, As could be contained in high purity Cu cathodes, affecting their properties such as conductivity and malleability (Martinez Perez *et al.*, 2007). Among the methods used to decrease As concentration in Cu-electrolytic baths, liquid-liquid extraction is a versatile technique that can be easily included in industrial production lines, but it employs large amounts of solvent, which can result in environmental problems.

On the basis of this, Martinez Perez *et al.* (2007) reported a study on the selective recovery of As(V) from 2 M H_2SO_4 aqueous solutions also containing Sb and Bi, species which are present together with As in copper electrolytic baths, by using a SLM with trioctylphosphine oxide (Cyanex 921) as extractant diluted in kerosene. The influence of various parameters on system performance, as nature of stripping solution, extractant concentration and stirring rate, has been evaluated to determine optimal conditions for an efficient separation system, i.e., high recovery percentage of As(V) in a reduced transfer time.

The transport process of As through the SLM using Cyanex 921 as extractant takes place in five steps in series: (1) As(V) diffusion from feed bulk to membrane surface in the non-stirred boundary layer at the feed-membrane interface; (2) complexation As(V) at membrane interface feed side, thus forming the As(V)-Cyanex 921 complex; (3) diffusion of the As(V)-Cyanex 921 complex through the membrane thickness; (4) stripping of As(V) from the As(V)-Cyanex 921 complex at membrane interface strip side; (5) As(V) diffusion from membrane surface (strip side) to strip bulk, through the non-stirred boundary layer at the strip-membrane interface.

Obtained results showed that 94% As(V) recovery in 120 minutes was achieved and minimum quantities of organic phase were required, thus confirming the great potentialities of the SLM process. Moreover, under the optimized operating conditions, the transfer of Bi(III) and Sb(III) was practically zero, evidencing good selectivity for As(V) of the prepared SLM. The observed selectivity was explained by considering that the extraction mechanism of As(V), Bi(III) and Sb(III) should happen by the formation of neutral complexes, which can be extracted by Cyanex 921 (solvating extractant) into the organic phase. In 2.0 M sulfuric acid media, As(V) is found in the neutral form H_3AsO_4 ($pK_{a1} = 2.22$, $pK_{a2} = 6.98$, $pK_{a3} = 11.50$). In opposition, Bi(III) and Sb(III) neutral complexes cannot be formed, so that their extraction by SLM, under the same extraction conditions as for As(V), is limited. Hence, SLM based processes are source of great expectations in the separation and recovery of As(V) from copper electrolytic baths.

Another important source of As polluted waters is represented by offshore oil and gas operations, which increased dramatically in the last few years. To increase oil and gas recovery, water is usually injected into the reservoirs. The co-produced water is usually contaminated with organic and inorganic compounds, salts, hydrocarbons, radioactive elements, trace heavy and toxic metals/metalloids (e.g., arsenic, chromium, mercury, lead, nickel, copper, cadmium and zinc), and chemical additives used during well drillings. As a consequence, these large quantities of contaminated water can have significant environmental impacts if they are not handled properly (Pancharoen *et al.*, 2010). In practice, co-produced water is partially reused and treated before discharging it into the environment or re-injecting it into the origin reservoir depending on its quality and the environmental constraints. Six traditional water treatment technologies, i.e., carbon adsorption, air stripping, membrane filtration, UV light, chemical oxidation and biological treatment were tested offshore for this purpose. Although each method presented technical problems, none of them was insuperable. In particular, a chemical process must be found to remove As and Hg from the produced waters prior to overboard discharge. However, in certain fields of the Gulf of Thailand, the concentrations of As and Hg in the produced waters are high. The As appears in As(V) form whereas the Hg appears predominantly in the elemental form with the rest in inorganic (such as $HgCl_2$), organic (such as dimethyl and diethyl mercury) and organo-ionic compounds (such as $ClHgCH_3$). According to the permissible discharge limits by the government of Thailand, the operators must remove As and Hg from the offshore waste discharges to values no greater than 250 and 5 $\mu g\,L^{-1}$, respectively. In accordance with several studies using LM systems to remove trace metal ions from aqueous solutions, hollow fiber supported liquid membrane (HFSLM) is a promising method to treat effectively water with a very low metal ions concentration thanks to the high selectivity and rapid transport of the desired metal ions.

Because of this, Pancharoen *et al.* (2009) applied a lab-scale microporous HFSLM system to remove and recover As ions from produced waters coming from a gas separation plant in the Gulf of Thailand, thus controlling its concentration in the produced waters. Different molecules were used as the extractant, and an aqueous solution of NaOH was the stripping phase.

Obtained results evidenced that of all the extractants used, Aliquat 336 permitted both high extraction and recovery percentages of As ions to be obtained, since it reacted with both undissociated As (H_3AsO_3) and dissociated As ($H_2AsO_4^-$ and $HAsO_4^{2-}$). In particular, the HFSLM with 0.75 M (35%, v/v) carrier concentration and 0.5 M NaOH as the stripping solution permitted to reduce the concentration of As ions in produced water from the gas separation plant in the Gulf of Thailand at a level lower than the permissible limit. Among the other carriers, Cyanex® 923 and tri-*n*-butylphosphate (TBP) reacted only with undissociated forms while TOA reacted only with dissociated forms, resulting in lower extraction percentage. Although the extractant Cyanex® 301 showed relatively high percentage of extraction, it achieved very low percentage of recovery in the strip phase as it formed very strong complexes with As ions, which made the stripping difficult. These results evidence that the choice of the carrier molecule is a fundamental step in order to achieve the technical feasibility of the SLM system.

The influence of various numbers of runs through the hollow fiber module on the concentration of As ions in the outlet solutions was studied by using 35% (v/v) Aliquat 336 and 0.5 M NaOH as the stripping solution. The percentages of extraction and recovery for As ions increased when

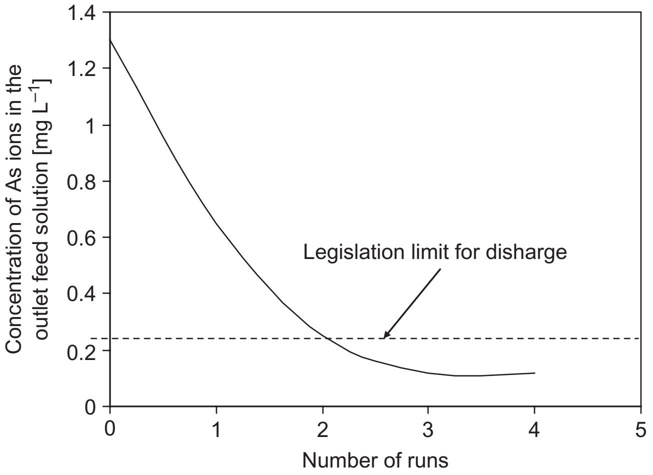

Figure 9.3. Concentration of As ions in the outlet feed solution *vs*. the numbers of runs through HFSLM (Aliquat 336, 35% (v/v), 0.5 M NaOH, flow rates of feed and stripping solutions 100 mL min^{-1}; elaborated from Pancharoen *et al*. (2009)).

the number of runs increased. At the third run, the extraction and recovery percentages of As ions were 91 and 72%, respectively. Accordingly, the concentration of As ions left in the feed solution was 120 μg L^{-1} (Fig. 9.3), which was in accordance with the legislation limits for discharge of industrial effluent in Thailand.

Considering that, in the Gulf of Thailand, trace heavy and toxic metals in co-produced water are As and Hg, Lothongkum *et al*. (2011) focused their work on the synergistic extraction of As and Hg from natural-gas-co-produced water via HFSLM. The basic idea of their work is that As and Hg amounts can be reduced respecting their regulatory discharge limits because various combinations of two or more extractants can produce a synergistic effect (the extractability of a mixture of the extractants is greater than the sum of their individual extractabilities). The influence of several variables on the performance of the separating system was studied: types of extractant, concentration of the synergic extractant, concentration of H_2SO_4 (co-extractant) in the feed phase, composition of stripping solution and number of separation cycles. The results evidenced that a greater Hg extraction was obtained than As extraction by every single extractant considered. Of all the considered mixtures of extractants, the synergistic effect on As and Hg extraction was found by using the mixture of 0.06 M Cyanex 471 and 0.22 M Aliquat 336 and 0.1 M thiourea as the stripping solution with 0.2 M H_2SO_4 in feed solution (Table 9.2). In particular, Hg discharge to the environment not higher than 5 μg L^{-1} was attained within 1-cycle separation, while 3-cycle separation, corresponding to 94% As extraction, was required for As abatement below legislation limits. The highest percentages of As and Hg extractions were achieved at 4-cycle separation.

Summarizing, the results obtained by Pancharoen *et al*., 2009 and Lothongkum *et al*., 2011 evidenced that the use of an appropriate HFSLM permits to remove and recover As and Hg ions from produced waters coming from gas separation plants, producing an effluent which was in accordance with the legislation discharge of industrial effluents.

Besides the total As removal, as reported in the previous works, in some cases an efficient separation of As(V) from As(III) (indicated also as As speciation) could be of extreme importance due to the different toxicity of these two inorganic arsenic (i-As) forms. Guell *et al*. (2010) therefore checked the capability of the SLM system to selectively transport As species from synthetic spiked water and different natural spiked samples, such as tap water and river water. For this purpose, an aqueous solution prepared dissolving equal amounts of As(III) and As(V) species in Milli-Q ultrapure water was used as the feed phase, the anion exchanger mobile carrier

Table 9.2. Percentages of As and Hg ions extraction and recovery in the stripping phase against the number of separation cycles through HFSLM (operating conditions: mixture of 0.22 M Aliquat 336 and 0.06 M Cyanex 471 as the extractant; 0.1 M thiourea as the stripping solution; 0.2 M H_2SO_4 in the feed phase as the co-extractant; data from Lothongkum *et al.*, 2011).

Number of separation cycles	As extraction/recovery [%]	Hg extraction/recovery [%]
1	62/11	97/46
2	84/22	100/91
3	94/32	100/95
4	94/35	100/95

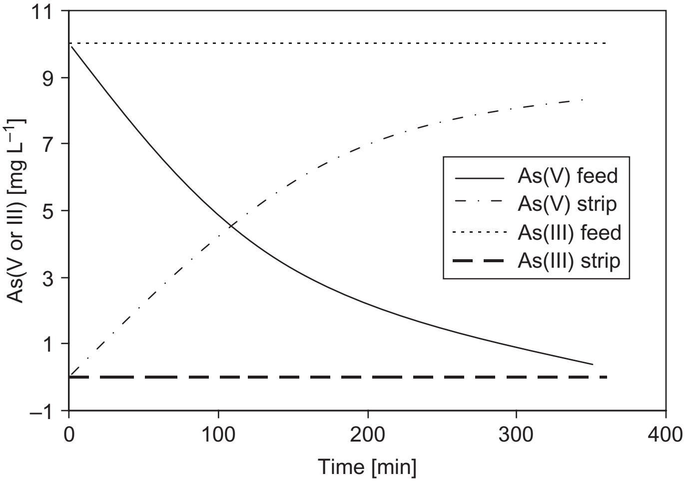

Figure 9.4. As(V) and As(III) separation using the SLM system (elaborated from Guell *et al.*, 2010).

Aliquat 336 (a quaternary ammonium salt) in dodecane modified with 4% dodecanol to increase the solubility of the extractant was the LM phase and 0.1 M HCl was the stripping phase. The results, summarized in Figure 9.4 in terms of As(III) and As(V) concentration in the feed and in the stripping solution, demonstrate the viability of using the SLM system for the speciation and separation of As species in water samples, since As(V) was quantitatively transported across the SLM after 6 h decreasing to $\mu g\,L^{-1}$ level in the feed, whereas no As(III) transport in the strip was observed.

This selectivity was caused by the different kinetics of As(III) and As(V) complexation by the carrier. Indeed L-L extraction tests evidenced that the rate of extraction depends on the oxidation state of As: in the case of As(V) the extraction equilibrium was attained in less than 5 min, whereas in the case of As(III) it took more than 2 h. Hence, the As(V)-Aliquat 336 system is kinetically more favorable than the As(III) system.

To test the possible application of the SLM system in As speciation from real matrices, aqueous solutions prepared by dissolving As species in tap water and river water were submitted to SLM separation. The results obtained in terms of As(V) permeability for the different aqueous matrices, summarized in Table 9.3, evidence that no significant differences were obtained in the permeability values, despite the presence of different anions (Cl^-, SO_4^{2-}, NO_3^-) at high concentration in the real matrices.

Then the SLM system is a feasible and promising separation technique when it is necessary to treat As-polluted environmental samples. Some difficulties were encountered when an As

Table 9.3. As(V) permeability through the SLM system for different environmental matrices (data from Guell *et al.*, 2010).

Aqueous matrix	Permeability [cm min^{-1}]
Milli-Q water	0.100
Tap water	0.109
River water	0.102

Table 9.4. Effect of the pH of the feed solution on As(V) transport in SLM and AEMs systems. (Feed phase: [As(V)] = 10 mg L^{-1}. SLM: 0.5 M Aliquat 336 in dodecane and 4% dodecanol. Stripping phase: 0.1 M NaCl (data from Guell *et al.*, 2011).

	Transport efficiency [%] (24 h)	
Feed pH	SLM	AEMs
3	65	–
5	–	100
7	100	95
10	100	92
13	20	30

level of 280 mg L^{-1}, typical for polluted groundwater, was considered. Indeed, using synthetic wastewater, prepared with Milli-Q water, a 100% As(V) recovery was achieved after 6 h while using tap water as matrix, the recovery decreased to 44%, probably because of the presence of other interfering anions in the solution. Then, it was demonstrated that an SLM system with Aliquat 336 as the mobile carrier effectively and selectively transported As(V) from the feed phase at pH 13 to a 0.1 M HCl solution. However, most As polluted waters stay at neutral pH (about 6.7–8.8).

In a successive work (Guell *et al.*, 2011) the same authors reported a comparison between two different membrane-based techniques for the separation and recovery of i-As species in natural waters at neutral pH: two different anion-exchange membranes (AEMs) and a SLM practically identical to the one previously used (Guell *et al.*, 2010). Parameters affecting the membrane system were investigated, giving special emphasis on the pH effect. Obtained results, summarized in Table 9.4, evidence that in both the cases acidic pH such as 3 and very basic pH such as 13 gave poorer results, while As(V) was quantitatively transported at pHs of 10 and 7, the latter being the best one.

In order to test the feasibility of using these membrane systems for i-As speciation, the transport of As(III) was investigated under the best experimental conditions found for As(V) permeation (pH 7), and different behavior was observed for SLM and AEMs. Transport of As(III) through the SLM system containing the anion exchanger Aliquat 336 as the carrier was not possible, as at pH 7 As(III) is present in its neutral form H_3AsO_3, which cannot be extracted via an anion exchange mechanism. On the contrary, transport of As(III) at pH 7 through the AEMs occurred even though its rate was lower compared to that of As(V). These results evidenced that if separation of As(III) from As(V) is desired, SLM is the membrane system of choice.

Taking into account that the arsenate transport is based on an anion-exchange mechanism, the presence of other anions in natural waters could affect the rate of the As transport and its removal efficiency. For this purpose, Milli-Q water was spiked with 10 mg L^{-1} of As(V)

Table 9.5. Summary of the main results obtained for As removal using liquid membrane based processes.

Type of separation	Carrier	Main results	Reference
As(V) removal from simulated copper electrolytic baths *via* SLM.	Cyanex 921	94% As recovery in 120 minutes; 100% selectivity to Arsenic with respect to Bi(III) and Sb(III)	Martinez Perez *et al.* (2007)
As removal from waters coming from a gas separation plant in the Gulf of Thailand *via* HFSLM.	Aliquat 336	91% As extraction; 72% As recovery; 120 $\mu g\,L^{-1}$ As level in treated water, below Thai legislation limit	Pancharoen *et al.* (2009)
Synergistic extraction of As and Hg from natural gas coproduced water *via* HFSLM.	Cyanex 471 and Aliquat 336	As: 94% extraction/32% recovery; Hg: 100% extraction/95% recovery; As and Hg level in the treated water below the legislation limits	Lothongkum *et al.* (2011)
As(V)/As(III) speciation from synthetic, tap and river water *via* SLM.	Aliquat 336	100% selectivity to As(V); 100% As(V) recovery from synthetic wastewater; 44% As(V) recovery from tap water, because of the presence of other interfering anions in the solution	Guell *et al.* (2010; 2011)

and the following anions: $[NO_3^-] = 12.4\,mg\,L^{-1}$; $[SO_4^{2-}] = 9.6\,mg\,L^{-1}$; $[HCO_3^-] = 12.2\,mg\,L^{-1}$; $[H_2PO_4^-] = 19.4\,mg\,L^{-1}$. These concentrations were chosen to be the same equivalents as As(V). Obtained results permitted the conclusion that although the anions were co-transported with the inorganic As species their presence did not affect the As removal.

Table 9.5 summarizes the most significant results discussed in this section on the recovery and separation of As from matrices of environmental interest. It can be observed that use of appropriate LM configurations permits satisfactory results to be obtained in terms of As extraction from the feed phase, As recovery in the strip phase, and selectivity to As (also in As speciation). All the treated effluents present As level below the legislation limits of industrial effluents, thus permitting their safe discharge.

9.3.2 *Copper removal and recovery from ammoniacal etching solutions*

Ammoniacal etching solutions are widely used in the electronic industry to etch a thin copper layer on printed circuit boards. During this process a spent etching solution with Cu(II) content up to $160\,mg\,L^{-1}$ is formed. Traditionally this solution is submitted to neutralization in order to achieve copper precipitation. After this treatment, the generated ammoniacal wastewater still contains several $mg\,L^{-1}$ of copper and must be appropriately managed. In particular, copper concentration in this wastewater must be reduced to less than $5\,mg\,L^{-1}$ in order to be reused or safely discharged. The predominant form of copper (II) ions in this wastewater is $[Cu(NH_3)_4]^{2+}$.

In this context, in two different works Yang and Kocherginsky, studied the technical feasibility of the treatment of ammoniacal etching solutions as a possible application of the SLM process (Kocherginsky and Yang, 2007; Yang and Kocherginsky, 2007). The basic idea was that the treatment of this wastewater using the SLM technology is potentially feasible and attractive.

In the first work Kocherginsky and Yang (2007) evidenced that concentration and recovery of copper from these ammoniacal complexes is possible by using a flat sheet SLM system with LIX54 as the carrier and sulfuric acid as the stripping agent. In particular, in the presence of sulfate ions (SO_4^{2-}) in the stripping solution copper (II) permeation through the SLM takes place and when

Table 9.6. Summary of the main results obtained for Cu(II) removal using liquid membrane based processes.

Type of separation	Carrier	Main results	Reference
Copper removal from industrial ammoniacal wastewater (e.g., ammoniacal etching solutions)	LIX54	$5\,\mathrm{mg\,L^{-1}}$ copper level in the treated water; High selectivity to copper; Long term stability	Yang and Kocherginsky (2007)

its concentration in the strip reach the solubility level, copper precipitates as sulfate pentahydrate crystals with quality comparable to a commercial chemical grade product. Thus, the separation process does not result in any secondary waste and can be considered as a green chemistry process. However, the small membrane surface area of this system configuration ($10\,\mathrm{cm^2}$) did not allow it for any practical application.

Based on this in the successive work, Yang and Kocherginsky (2007) demonstrated that HFSLM represents a very attractive solution to apply SLM for copper removal from industrial ammoniacal wastewater. A Liqui-Liqui-Cel® (6.35 cm × 20.32 cm) membrane contactor ($1.4\,\mathrm{m^2}$ membrane area) was used as the support, and the HFSLM module was operated at a flow rate of $4\,\mathrm{L\,h^{-1}}$. Obtained results showed that the copper level in the ammoniacal solution was reduced to less than $5\,\mathrm{mg\,L^{-1}}$. The treated solution can be reused as the rinse water for printed circuit boards PCB production or discharged directly in compliance with the environmental regulations. The results also evidenced the selectivity in Cu(II) separation over other cationic contaminants in the ammoniacal wastewater (copper separation factors were 103, 17 and 3.8 over Cd(II), Zn(II) and Ni(II), respectively). SLM stability was evaluated by monitoring the overall mass transfer coefficient in the time of the hollow fiber membrane contactor operating in co-current mode and same flow rate in the lumen (feed wastewater) and shell (strip solution) in order to obtain a stable SLM. The results showed a transport efficiency which decreased by half in the first half month and then it was practically constant. The membrane could be washed, dried, reimpregnated and then reused. This possibility of hollow fiber membrane contactor reuse is important in terms of economical sustainability.

In summary, Cu level in the treated feed solution below the legislation limits, high selectivity to Cu(II) over other cations in the ammoniacal wastewater and long-term stability of HFSLM system proposes the HFSLM technology a promising effective way to concentrate and recover copper from the industrial wastewater (Table 9.6).

9.3.3 *Ni(II) recovery from wastewater from the stainless steel industry*

Wastewaters from a stainless steel manufacturing plant usually contain various heavy metals, mainly Fe(II), Cr(VI) and Ni(II), with concentrations ranging from few $\mathrm{mg\,L^{-1}}$ to thousands $\mathrm{mg\,L^{-1}}$. Therefore, this wastewater needs to be treated to remove toxic components before discharge, since heavy metals are non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders.

On the basis of this, Lothongkum *et al.* (2009) proposed the application of a HFSLM in the selective stripping and recovery of nickel ions from wastewater of the stainless steel-cold rolled plate process. The percentage of extraction and selective recovery of Ni(II) highly depends on: (i) feed pH; (ii) types and concentration of the extractant; (iii) concentration of the stripping solution (sulfuric acid); and (iv) flow rates of both the feed and the stripping solutions and feed to strip volumetric ratio.

Of all the carriers tested, LIX 860-I at 0.8 M concentration was the most effective carrier to selectively recover nickel ions from wastewater at pH 4, obtaining nickel extraction from the feed phase and recovery in the strip phase 80% and 52%, respectively, for a single module operation. The percentage of the selective extraction and recovery of nickel increased by increasing carrier

Table 9.7. Summary of the main results obtained for Ni(II) removal using liquid membrane based processes.

Type of separation	Carrier	Main results	Reference
Selective stripping and recovery of Ni(II) from a real effluent coming from the Thai stainless steel industry by HFSLM	LIX 860-I	87% nickel recovery in the strip; 1 mg L^{-1} Ni remaining in the feed solution, below the legislation limits	Lothongkum *et al.* (2009)

concentration to 0.8 M. Above that value, the recovery percentage decreased, because the increase in the viscosity of the film becomes dominant and obstructs mass transfer. Besides, obtained results evidenced a progressive increase of nickel recovery with the increase in the stripping solution concentration in the range 0.5–2.5 M. Since too much acid concentration in the strip solution can damage the hollow fiber module, resulting in system destabilization, the sulfuric acid concentration in the strip was fixed to 2.0 M.

The flow rates of feed and strip phases play a significant role in the percentage of extracted and recovered nickel and on system stability. Based on this, some tests were performed at different feed and strip flow rates. Obtained results evidenced that by operating at feed and strip flow rates of 100 mL min^{-1} the highest recovery percentage of nickel (60% for single module operation and 87% from a double-module operation) and system stability was obtained. Nickel recovery percentage and SLM stability decreased when the flow rates increased above the previous value, because of lower residence time of the two solutions in the HFSLM module and of higher lateral shear forces at the membrane-aqueous interfaces, resulting in the gradual loss of the LM phase to the aqueous feed and stripping solutions and then in system destabilization.

Once having determined the optimal operating conditions for the selective recovery of nickel, some tests with a real effluent coming from the Thai stainless steel industry were carried out in a double module operation (i.e., two HFSLM modules in series) for the maximum recovery of nickel ions. For a single module operation the recovery of nickel ion was 58% while, by operating with a double module operation, its recovery increased to 87% and the amount of Ni remaining in the feed solution after passing double-module operation was 1 mg L^{-1}, which was in accordance with the permissible limits of Thailand.

Summarizing, the results obtained by Lothongkum *et al.* (2009) confirms the promising feasibility and applicability of the HFSLM for wastewater treatment with low concentration of heavy metals (Table 9.7).

9.3.4 *Mn(II) extraction from sulfuric acid solutions*

Manganese is an essential trace nutrient for living organisms, as it is a necessary constituent of metallo-proteins including enzymes, as it optimize enzymes and membrane transport function. Despite the toxicity of its compounds being lower than those of other common metals (e.g., nickel and copper) its excess or deficiency in the body can cause serious impairment of vital physiological and biochemical processes. Excessive manganese intake is frequently associated with the so-called "manganism", a rare central nervous system disorder, which symptoms are similar to those of Parkinson's disease.

Manganese compounds, in which it has various oxidation states, are widely used in the industry. For example, manganese oxide is used as a depolarizer in dry cell batteries and as a drying agent in glassmaking. Besides, since manganese ions have various colors depending on their oxidation state, they are used industrially as pigments. Furthermore, permanganates of alkali and alkaline earth metals are used as a bactericide and algaecide in water treatment and as an oxidant in organic chemical synthesis because of their good oxidizing power.

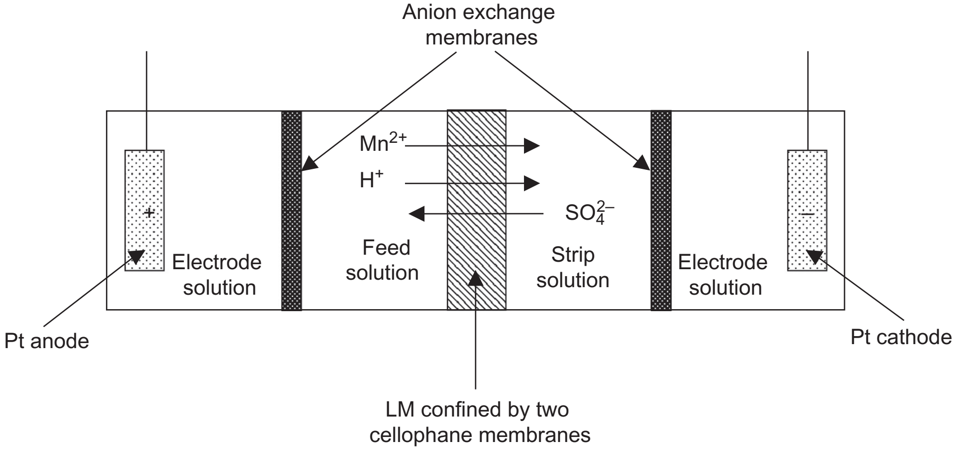

Figure 9.5. Schematization of the HLM-electrodialysis system proposed by Sadyrbaeva to perform the permeation experiments (elaborated from Sadyrbaeva, 2011).

Then manganese separation and/or recovery from the various liquid effluents or wastewater is of practical value. As for the other metal ions, a variety of separation processes have been developed for industrial needs, but all entail some drawbacks. SLM can be proposed as interesting alternative.

A widely used important acidic extractant in hydrometallurgy in metal separation and/or recovery is di(2-ethylhexyl)phosphoric acid (D2EHPA). It was extensively used also in the extraction and recovery of manganese from neutral and weakly acidic solutions using SLM and ELM (Mohapatra and Kanungo, 1992). Yongtao *et al.* (1992) studied the simultaneous extraction and recovery of manganese and cadmium from wastewaters, obtaining recovery percentages in the order of 92–100%.

Sadyrbaeva (2011) proposed a novel method, called hybrid liquid membrane-electrodialysis process (HLM-electrodialysis), for Mn(II) extraction from sulfuric acid solutions.

The proposed system, schematized in Figure 9.5, is constituted by an electrodialytic cell in which two electrode aqueous solutions (0.15 M H_2SO_4) were separated from feed and strip aqueous solutions by two solid anion-exchange membranes. A free LM containing D2EHPA as the carrier was separated from feed and strip aqueous solutions by two vertical cellophane solid membranes. The solutions were not stirred. In this system, ion transfer through the liquid ion-exchange membrane is accelerated by a direct electric current supplied to the plane platinum electrodes. Thus, the unselective electrodialytic process was coupled with the LM process, which provides greater selectivity and permeability with respect to the traditional solid ion-exchange membrane. Indeed, Mn(II) is transported across the system as follows: Mn(II) diffuses from the bulk of the feed phase to the feed/LM interface where it is complexed and extracted by the carrier. Mn(II) migration to cathode accelerates this phenomenon. The carrier-Mn(II) complex is then transferred by diffusion across the organic layer and dissociates at the interface LM/strip solution. The carrier's molecules return back according to their concentration gradient and its transport cycle begins again. Hydrogen ions contained in the acidic feed solution permeate across the membrane in the same direction as Mn^{2+} ions. The high acidity of the aqueous strip solution and correction of pH value, usually necessary in traditional SLM transport with acidic extractants as D2EHPA, are not necessary during electrodialysis. Sulfate ions are transported through the organic layer simply by electromigration in the opposite direction.

Obtained results showed that a Mn(II) extraction degree about 6.5% per hour and no transport in the strip solution have been obtained without applying the electric field. The imposition of the electric field enhanced the extraction of Mn(II) from the feed to the LM phase and the stripping into the strip solution of 0.25 M H_2SO_4. A maximum current efficiency of 28% was obtained,

Table 9.8. Summary of the main results obtained for Mn(II) removal using liquid membrane based processes.

Type of separation	Carrier	Main results	Reference
HLM-electrodialysis for Mn(II) extraction from sulfuric acid solutions.	D2EHPA	100% removal of Mn(II) from the feed; 88% Mn(II) extraction degree.	Sadyrbaeva (2011)

as the current was transferred across the liquid membranes mainly by hydrogen ions of the feed solution and sulfate anions of the strip solution.

Complete removal of Mn(II) from a feed solution containing 0.01 mol L^{-1} of $MnSO_4$ and a maximum extraction degree of 88% was obtained operating under optimized conditions.

Considering the results, summarized in Table 9.8, it is possible to state that the proposed novel method for Mn(II) extraction permitted to efficiently obtain an effective one-stage extraction of manganese (II) from sulfuric acid solutions into diluted solutions of sulfuric, nitric, hydrochloric, perchloric acids and water.

9.3.5 *Remediation of nuclear waste*

The recovery of U and Pu in the closed nuclear fuel cycle usually produces an high level waste (HLW) stream containing high concentration of fission/activation products (e.g., U, Pu, Am, Eu, Sr) and process/structural materials (Fe, Ni, Cr, etc.). This concentrated HLW is typically submitted to immobilization in glass/ceramic matrices, followed by their disposal in geological repositories. Considering the half-lives of the fission products (in the range of hundred-millions years) this solution result is unsustainable. The treatment of HLW by SLM represents a possible alternative.

Because of this, Ansari *et al.* (2007) evaluated the feasibility of using a SLM in the remediation of HLW. The results obtained during preliminary transport studies on various actinide ions, as well as fission products, showed that Am(III), Eu(III), Pu(IV), Np(IV) and U(VI) were quantitatively recovered from nitric acid solution by using the facilitated SLM transport. The permeability coefficients of the considered metal ions were in the order: Am(III)/Ln(III) > Am(IV) > Am(VI) > Sr(II) > Tc(VII). No transport of monovalent cation like Cs(I) was observed. Some transport tests were carried out by using a simulated HLW also containing structural materials, which can interfere on system performance. Obtained results showed that transport rates were marginally affected by the presence of Fe(III) as structural material.

The radiolytic stability of the liquid membrane phase is a fundamental parameter to be evaluated to effectively use the SLM system for the separation of metal ions from HLW. For this purpose, some tests were carried out increasing the radiation dose from 0 MGy to 1.8 MGy. Obtained results evidenced no significant decrease of the permeability of Am(III) when the radiation dose was lower than 0.46 MGy. However, the permeability decreased almost linearly by increasing the radiation dose from 0.46 to 1.8 MGy (Table 9.9).

Two intrinsically linked factors were responsible of this behavior: (i) the capability of the LM phase to extract Am(III) decreased linearly with the irradiation dose, because the carrier was degraded; and (ii) the density of the LM phase was almost insensitive to the dose, but the viscosity increased with the irradiation dose, affecting the transport behavior. This phenomenon is indicated as radiolytic degradation of the LM phase.

On the same research topic, Singh *et al.* (2010) studied the separation of U(VI) from a phosphoric acid medium by a SLM. The influence of various parameters, such as feed acidity, nature of the stripping solution, carrier concentration, membrane pore size and thickness was studied. The results showed that membrane support characteristics affect the transport of the target ionic species (such as U(VI)) and confirmed that U(VI) separation from phosphoric acid medium by SLM is feasible. System stability was studied by performing ten continuous experimental cycles with 6 hours duration each. The results evidenced a good operational stability, with a quite linear

Table 9.9. Permeability *vs.* radiation dose for Am(III) transport across the SLM used (data elaborated from Ansari *et al.*, 2007).

Permeability [cm min^{-1}]	Radiation dose [MGy]
3.67	0.00
3.65	0.30
3.65	0.46
1.50	0.80
0.60	1.10
0.06	1.80

Table 9.10. Summary of the main results obtained by treating nuclear waste by liquid membrane based processes.

Type of separation	Carrier	Main results	Reference
Remediation of high level waste (HLW) stream by using a SLM	TODGA	Quantitative recovery of Am(III), Eu(III), Pu(IV), Np(IV) and U(VI) from simulated HLW; No transport of monovalent cation like Cs(I); Transport rates marginally affected by the presence of structural materials; Linear decrease of permeability by increasing the radiation dose over 0.46 MGy	Ansari *et al.* (2007)
Separation of U(VI) from phosphoric acid medium by a SLM	Binary mixture of PC88A and Cyanex 923	More than 95% U(VI) recovered in 360 min; high selectivity of U(VI) over fission products; good operational stability	Singh *et al.* (2010)

decrease of the permeation performance, for the first eight cycles. The percentage of permeation decreased drastically with the 10th cycle.

The results obtained by Ansari *et al.* (2007) and by Singh *et al.* (2010) suggest that the separation of minor actinides and U(VI) from the HLW solutions and phosphoric acid medium, respectively, is technically feasible as application of SLM. Despite the encouraging results described in this section, in order to effectively use the SLM system for the separation of metal ions from HLW, it is fundamental to consider the problems related to the radiolytic stability of the liquid membrane phase.

9.4 CONCLUSION

In the present chapter, the main theoretical aspects of transport in supported liquid membranes (SLMs) have been described and possible applications of this technology in the removal and recovery of toxic ions from water have been reported.

Arsenic (As) is a toxic element and its contamination of water, especially groundwater, has been receiving worldwide attention by the scientific community, since significant water contamination by As was observed in many countries. The experimental results reported clearly show that the SLM based processes are of great expectations in the separation and recovery of As(V) from copper electrolytic baths. The use of an appropriate hollow fiber SLM (HFSLM) also permits to remove and recover As and Hg ions from produced waters coming from gas separation plants, producing an effluent that was in accordance with the legislation discharge of industrial effluents. The SLM system is also a feasible and promising separation technique when it is necessary to obtain an efficient separation of As(V) from As(III) which could be of extreme importance due to the different toxicity of these two inorganic arsenic (i-As) forms.

The HFSLM technology is also a promising effective way to concentrate and recover: (i) Cu from industrial ammoniacal wastewater, e.g., ammoniacal spent etching solutions widely used in the electronic industry to etch a thin Cu layer on printed circuit boards, obtaining Cu(II) levels lower than regulation limits; (ii) Ni from wastewater of stainless steel industry.

A novel method called HLM-electrodialysis represents an effective one-stage extraction process for heavy metals (e.g., Mn(II)) from acidic wastewaters. In particular, the application of a direct electric field significantly intensifies the transport of ions through the liquid membrane and facilitates the stripping of metals from the organic phase.

The SLM technique has also been tested in the remediation of nuclear waste, but the radiolylic stability of the LM phase, in addition to the operational stability, has to be opportunely considered.

On the basis of this it can be stated that the SLM based techniques represent today a feasible and effective way to separate, concentrate and purify inorganic solutes from industrial wastewaters fulfilling sustainability criteria, as they are characterized by: (i) high selectivity with respect to the target ions over other cations or with different oxidation states; (ii) long-term stability mainly in the HFSLM configuration; (iii) possibility to treat solutions at ng L^{-1} level and (iv) optimal quality of treated water in compliance with environmental regulations; (v) high sustainability in terms of energy management, as they significantly reduce energy consumption. Besides, if opportunely designed, these separation processes do not produce by-products and can be considered as green processes.

Despite these interesting results, some practical problems (e.g., system stability and flux) have to be appropriately solved to make the SLM based separation processes technically and economically attractive in view of large-scale applications.

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CHAPTER 10

Polymer inclusion membranes for the separation of uranium and arsenic from dilute aqueous solutions

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10.1 INTRODUCTION

Polymer inclusion membranes (PIMs) are a relatively novel type of self-supporting liquid membranes for the extraction and separation of metallic and non-metallic ionic species and small organic molecules from dilute aqueous solutions. PIMs entrap a solute-selective extraction reagent, often referred to as the carrier, in a base polymer matrix, which consists of a base polymer and in some cases may contain plasticizers and chemical modifiers. When the PIM is placed in contact with the dilute aqueous solution, the extractant reactively couples with the solute of interest and transfers it into or through the membrane.

PIMs share considerable similarities with the more well-known liquid-liquid extraction techniques, commonly known as solvent extraction (SX), in which an extractant is dissolved in a large volume of solvent. PIMs are principally differentiated by the replacement of the solvent with a polymer matrix. Solvents used in SX are commonly volatile, toxic and flammable (e.g., kerosene, decane) and extractants are commonly corrosive and harmful to the environment if released (e.g., substituted alkylamines, substituted alkylphosphorus compounds). By replacing the solvent with a relatively inert polymer matrix, the chemical hazards associated with separation processes are considerably reduced and solvent-associated fire hazards are essentially eliminated. Additionally, by entrapping the extractant in the polymer matrix, occupational exposure to the extractant could be considerably reduced.

PIMs have shown potential for the separation of a number of metallic and non-metallic species (Almeida *et al.*, 2012; Nghiem *et al.*, 2006; O'Rourke *et al.*, 2009). Target solutes for PIM separation have included a range of chemical species of metals/metalloids such as gold (Au), lead (Pb), cadmium (Cd), copper (Cu), cobalt (Co), uranium (U), zinc (Zn), and arsenic (As); non-metals such as halide, thiocyanate and nitrate anions; and small organic compounds such as thiourea, glyphosphate and 2,4-dichlorophenoxyacetic acid (2,4-D). PIM techniques have inherited a large body of knowledge from the literature on solvent extraction and much of the research into PIMs has focused on adapting existing solvent extraction technologies. Many researchers have demonstrated promising systems for safe and effective separation of target solutes, but these systems have exhibited poorer mass transfer rates than comparable SX systems. This has limited their commercial application to date; however, the performance of new PIMs now equals or exceeds other comparable membrane technologies.

The separation of U, both in industrial and environmental contexts, has attracted a considerable volume of research since the discovery of nuclear fission in the 1940s. The need to purify U from its ores gave rise to large-scale modern solvent extraction techniques. Considerable effort has been made to improve the efficiency and lower the cost of U processing; the techniques used to separate U from its ores have been subsequently applied to the separation and/or purification of numerous other elements and compounds. The purification of U is still conducted using solvent extraction techniques, which has led to a number of unfortunate industrial accidents (Bacon and Mihaylov, 2002) and the application of PIMs is one method proposed to improve the safety of U purification.

The advantages of PIMs as a safe, cheap and effective separation technique have also led to the investigation of the suitability of PIMs for the environmental cleanup of contaminated water.

Arsenic (As) is a pollutant of major concern worldwide; as it is a potent human carcinogen, its presence in natural and wastewaters presents a serious health hazard (Choong *et al.*, 2007; Villaescusa and Bollinger, 2008). PIMs are simple and cheap to fabricate, which makes them ideal for use in developing economies where As contamination is often a problem.

Unlike many other separation processes, PIM-based separation is usually driven only by chemical forces and hence can have low energy intensity in their operation. Moreover, the underlying technology required to utilize PIMs for separation of target solutes from aqueous solutions is relatively simple and could be easily adapted to a range of applications.

This chapter will describe the operation of PIMs and explore progress made on the development of PIMs for the separation of U and As from aqueous solutions. The separation of U and As illustrates the applicability of PIM-based technology to industrial separation and environmental remediation with low energy requirements.

10.2 EXTRACTION AND SEPARATION OF SOLUTES

In all cases, PIMs encapsulate the extractant in a base polymer such as poly(vinyl chloride) (PVC) or ester-substituted cellulose derivatives (e.g., cellulose triacetate, CTA), frequently with the addition of plasticizers or chemical modifiers. These components are held inside the polymer matrix by a combination of physicochemical interactions (Pereira *et al.*, 2009) and the process of polymer entanglement (Wool, 1993). Each component has a different function. The extractant reactively complexes with the solute of interest and acts as the phase-transfer agent, extracting the solute from the aqueous phase into the membrane phase by forming a hydrophobic ion-pair or a complex which subsequently diffuses within the membrane. Plasticizers lower the diffusive resistance of the membrane, allowing the extracted species to diffuse more easily through the membrane, and give a PIM its characteristic flexibility. Chemical modifiers act as stabilization agents, keeping the extracted solute or even the extractant 'soluble' in the membrane liquid phase. It should be pointed out that very often extractants have plasticizing properties.

10.2.1 *Carrier-facilitated mass transport*

In contrast to osmotic, dialysis, filtration or size-exclusion type membranes, PIMs as other liquid membranes (i.e., bulk liquid membranes, emulsion liquid membranes and supported liquid membranes) rely on the action of a chemical agent to extract the solute of interest from an aqueous phase (Kolev, 2005). The action of this chemical agent is the most important factor in the performance of any PIM and its behavior shares considerable similarities with SX applications (e.g., hydrometallurgy).

The chemical and physical behavior of the extractant is of great importance in the separation process and generally determines the suitability of a particular separation system for a given application. Although PIM extraction and SX are not identical, they are based on similar principles. It is therefore appropriate to discuss at this point the basic principles of SX systems, which are fairly well understood, to provide a better theoretical understanding of PIM-based separations.

10.2.1.1 *Overview of SX*

In the simplest SX scenario, two immiscible phases are brought into contact, where one phase (source phase) contains a dissolved species, A, and the other phase (receiving phase) does not. Almost invariably, the two phases involved are an organic phase and an aqueous phase. Assuming that A has finite solubility in both phases it will be partitioned between them and at equilibrium the SX system is characterized by the distribution ratio (D_A):

$$D_A = \frac{[A]_{org}}{[A]_{aq}} \tag{10.1}$$

where $[\mathrm{A}]_{\mathrm{aq}}$ and $[\mathrm{A}]_{\mathrm{org}}$ are the equilibrium concentrations of the solute A in the aqueous and organic phases, respectively. The distribution ratio is sometimes referred to as the partition coefficient (K_{p}). Technically the distribution ratio is distinct from the partition coefficient[1], although they are often used as synonyms in SX literature. The distribution ratio is unique to each system. It is convenient to characterize extraction by the so-called percentage extraction (%E):

$$\%E = 100\left(\frac{[\mathrm{A}]_{\mathrm{aq,i}} - [\mathrm{A}]_{\mathrm{aq,e}}}{[\mathrm{A}]_{\mathrm{aq,i}}}\right) \tag{10.2}$$

where $[\mathrm{A}]_{\mathrm{aq,i}}$ and $[\mathrm{A}]_{\mathrm{aq,e}}$ are the initial and equilibrium concentrations of solute A in the aqueous phase, respectively. Extraction is the process of transferring A from the source to the receiving phase. It is important to maximize the distribution ratio of the target solute, while minimizing the distribution ratios of any other solutes, so as to reduce their co-extraction. This selectivity may be achieved by manipulation of a number of SX variables such as the chemical composition of the two immiscible phases. Very often SX is followed by back-extraction of the extracted solute from the receiving organic phase into another aqueous phase with a suitable chemical composition. The organic phase in most large-scale SX processes consists of an extractant dissolved in a suitable organic solvent (generally to improve the mobility, stability and economy of the process), which extracts the solute via a reactive process (Cox and Rydberg, 2004; Lo *et al.*, 1983; Ritcey, 1996).

10.2.1.2 *Carrier-facilitated extraction*

The introduction of an extraction reagent, often known as an extractant or carrier, adds a layer of complexity into the extraction process. In contrast to ‘passive’ SX, where a neutral molecule is transferred from the aqueous phase into the organic phase by solvation only, carrier-facilitated extraction relies upon the action of an extractant chemical species, normally resident in the organic phase, reacting with the aqueous solute (most often by complexation and/or ion-exchange) at the interface between the organic and aqueous phases. The resulting reaction product is then distributed through the organic phase, leading to an appreciable concentration of the original aqueous solute in the organic phase, albeit in a different chemical form to the aqueous solute.

The use of an extractant to facilitate the extraction process provides a number of opportunities for expanding the utility of the SX process as a separation and/or purification technique. For example, although molecules must be electrically neutral to diffuse into the organic phase, there are many extraction reagents which are capable of extracting charged species into the organic phase in the form of neutral complexes or ion-pairs. Extractants may be targeted to the selective extraction of a certain solute, minimizing co-extraction of other species and allowing for enhanced separation of a particular species from a mixture of species.

Carrier-facilitated extraction may be described by the following generic stoichiometric equation:

$$\mathrm{A}_{(\mathrm{aq})} + \mathrm{B}_{(\mathrm{org})} \leftrightarrows \mathrm{AB}_{(\mathrm{org})} \tag{10.3}$$

where aqueous solute A is complexed by organic extractant B and the resulting complex AB is distributed throughout the organic phase. The distribution ratio for this system is given by:

$$D_{\mathrm{A}} = \frac{[\mathrm{AB}]_{\mathrm{org}}}{[\mathrm{A}]_{\mathrm{aq}}} = \frac{[\mathrm{A}]_{\mathrm{org}}}{[\mathrm{A}]_{\mathrm{aq}}} \tag{10.4}$$

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[1] The partition coefficient technically refers to the quotient of the solute concentration in the organic phase divided by the concentration of un-ionized solute in the aqueous phase, whereas the distribution ratio counts both ionized and un-ionized solute in the aqueous phase. This distinction is important in systems where the extracted species is present as a neutral and an ionized species in the aqueous phase and only the neutral species can be extracted into the organic phase. In carrier-facilitated extraction, the distinction is less important as solutes must be complexed by the extractant or form an ion-pair with it prior to extraction into the organic phase; the solute is often in its ionized form prior to complexation.

as in this case $[\mathrm{AB}]_{\mathrm{org}} = [\mathrm{A}]_{\mathrm{org}}$. Although the distribution ratio characterizes the separative capacity of the system, such systems are commonly described by the extraction constant:

$$K_{\mathrm{ex}} = \frac{[\mathrm{AB}]_{\mathrm{org}}}{[\mathrm{A}]_{\mathrm{aq}}[\mathrm{B}]_{\mathrm{org}}} \tag{10.5}$$

In the case where the solute to be extracted is not neutral, the following ion-exchange stoichiometric equation describes the extraction process:

$$\mathrm{A}^{+/-}_{(\mathrm{aq})} + \mathrm{BX}_{(\mathrm{org})} \leftrightarrows \mathrm{AB}_{(\mathrm{org})} + \mathrm{X}^{+/-}_{(\mathrm{aq})} \tag{10.6}$$

The extraction constant for such a reaction is given by:

$$K_{\mathrm{ex}} = \frac{[\mathrm{AB}]_{\mathrm{org}}[\mathrm{X}^{+/-}]_{\mathrm{aq}}}{[\mathrm{A}^{+/-}]_{\mathrm{aq}}[\mathrm{BX}]_{\mathrm{org}}} \tag{10.7}$$

In the case of carrier-facilitated extraction, the receiving phase is generally only permeable to the solute of interest after complexation or ion-pair formation with the extractant. This means that in many SX processes, the reaction of the solute with the extractant is one of the most important factors determining the extractive performance of the system.

A vast number of extractants have been synthesized and reported in the literature for a wide variety of applications. Many reagents have been developed to separate specific solutes from each other, or to suit other unique conditions in a certain application. The criteria for evaluating the performance of such reagents include not only those generally applied for industrial reagents (low cost, safety) but also selectivity for the species of interest over other species and the equipment and expertise needed to use the reagents (Cox and Rydberg 2004; Lo *et al.*, 1983).

10.2.1.3 *Carrier-facilitated membrane separation systems*

As mentioned earlier, although SX is a mature and well-developed art, the process possesses several drawbacks; whilst the process is efficient and relatively cheap, it is of considerable environmental and public health concern because of the use of large amounts of diluents which are often volatile, flammable and toxic. Additionally, the substantial reagent inventory required by solvent extraction processes has driven study into more efficient extractive separation technologies. In particular, a great deal of research into new forms of membrane systems has been undertaken.

Membrane technologies have a particular advantage over SX techniques as membrane systems often allow for extraction to be coupled in the same system with simultaneous back-extraction, rather than the extraction and back-extraction being conducted in sequential steps as is necessary in SX operations. Where a membrane acts as the organic phase, which separates two distinct aqueous phases, the phase from which the solute is extracted is referred to as the source phase and the aqueous phase into which the solute is back-extracted is called the receiving phase.

Other techniques have been developed to improve upon SX; among them of particular interest are liquid membranes with the main types of these membranes being bulk liquid membranes (BLMs), emulsion liquid membranes (ELMs) and supported liquid membranes (SLMs) (Kolev, 2005) (Fig. 10.1). While these all have advantages compared to SX systems, they have not yet achieved wide commercial acceptance. The following paragraphs present a brief description of the principles utilized by BLMs, ELMs and SLMs. For more information about liquid membranes please refer also to Chapters 7 and 8 of this volume.

BLM systems have strong similarities to conventional SX systems; in this case the source phase contacts with the liquid organic phase, which is simultaneously contacted with an aqueous receiving phase. The liquid organic phase is referred to as the BLM. The extractant reacts with the solute of interest at the interface between the source aqueous phase and the liquid organic phase, diffuses through the liquid organic phase and the solute is back-extracted from the liquid organic phase into the aqueous receiving phase. The organic-aqueous interface can either be formed as a result of density difference between the two immiscible liquid phases in a suitably

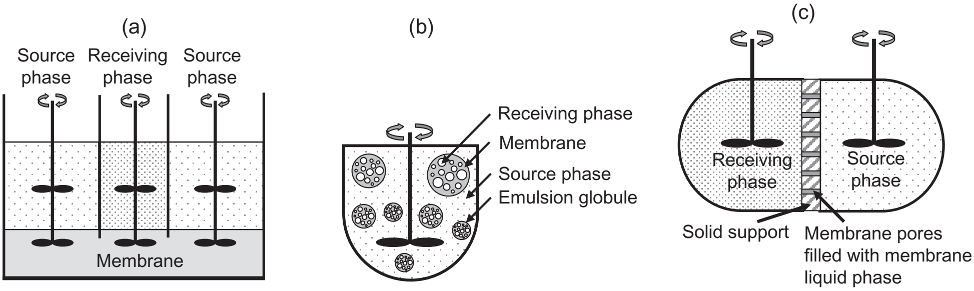

Figure 10.1. Schematic of a BLM (a), ELM (b) and SLM (c) (Kolev, 2005, with permission from Elsevier).

designed reaction vessel (especially if the organic phase is denser than the aqueous phase), or via hydrophilic or hydrophobic semi-permeable membranes separating the liquid organic phase from both the source and the receiving aqueous phases. The latter setup is usually preferred as it allows all three phases to be agitated vigorously, greatly speeding up the separation process (Mulder, 1996; Nanda *et al.*, 2002; 2004; Ramkumar *et al.*, 2002; Shamsipur *et al.*, 2009; 2010) without the formation of an emulsion.

ELMs are formed by creating a double emulsion of the source aqueous solution and emulsion globules of the receiving phase dispersed within the liquid organic phase. The species of interest is extracted across the liquid organic phase, acting as a membrane, into the receiving aqueous phase. At the end of the extraction process the emulsion globules are separated from the source aqueous phase and demulsified to form two separate layers, i.e., a liquid organic layer and a receiving aqueous layer, enriched with the species of interest (El-Hazek and El Sayed, 2003; El-Reefy *et al.*, 1996; Han *et al.*, 1999; Hirato *et al.*, 1991; Kulkarni, 2003; Kulkarni *et al.*, 2002; Macasek *et al.*, 1985; Saidi and Khalaf, 2004; Yang *et al.*, 2005).

SLMs differ greatly from the previous two types of liquid membranes. In general, an SLM is composed of an inert microporous membrane into which the extractant is impregnated. The extractant is often diluted in a solvent prior to impregnation, and the diluted extractant is held within the pores of the membrane by capillary forces and forms liquid organic channels through the solid membrane support. The SLM is then used to separate the aqueous source and receiving phases and the species of interest is transported along the channels of the membrane by the extractant (Chaudry *et al.*, 1995; Chiarizia and Horwitz, 1990; Chiarizia *et al.*, 1990; Fontàs *et al.*, 2005; Huang and Huang, 1988; Kadous *et al.*, 2009; Rathore *et al.*, 2004; Singh *et al.*, 2009; 2010).

PIMs form a different type of self-supporting liquid membranes. PIMs operate in a similar fashion to SLMs, except that the route of transport through the membrane is less clear; the transport of the solute might occur as in SLMs at a certain carrier concentration, that facilitates a closed organization of the components of the PIM and allows transmembrane diffusional mass transfer (Fontàs *et al.*, 2007), or the solute-extractant complex might diffuse through the membrane intact, with the polymer acting as a super-viscous ‘solvent’ (Bayou *et al.*, 2010; Nghiem *et al.*, 2006; O’Rourke *et al.*, 2009). Further studies on the structure of PIMs are expected to allow better understanding of the transport mechanism across these membranes.

PIMs share many characteristics with polymer ion-selective electrode (ISE) membranes which have been known for many years and are often referred to as plasticized membranes (Nghiem *et al.*, 2006). PIMs are designed for fast transport of the target chemical species across the membrane. They often completely extract a particular species from a solution, as is common with separation techniques for hydrometallurgical or remedial environmental applications (Cox, 2004; Lo *et al.*, 1983). These properties of PIMs are in sharp contrast with those of the plasticized membranes used in ISEs where the transmembrane transport is negligible.

10.2.1.4 *Comparison of membrane separation techniques*

Each of the membrane separation techniques outlined above has advantages and disadvantages; none have yet proved the ideal replacement for SX. BLMs have perhaps seen the most commercial applications as their setup is relatively simple and they are effective at reducing reagent losses compared to SX. However, the limited surface area at which the corresponding immiscible phases are in contact with one another and the distance across the liquid organic phase which the extracted species must diffuse to the receiving phase introduces some retardation of the speed of the separation process compared to SX (Kentish and Stevens, 2001; Kolev, 2005).

ELMs do not suffer from the same mass transport inhibitions as BLMs as the distance that the extracted species must travel is much shorter, and the contact surface area of these membranes is much higher. However, ELMs can prove difficult to implement because of potential problems associated with the formation and breakdown of the double emulsion and high sensitivity to suspended solids. All these drawbacks have limited their commercial applications (Kentish and Stevens, 2001; Kolev, 2005).

SLMs have relatively high mass transfer rates, as the distance that the species must diffuse between the source and receiving phases is very small. SLMs are however prone to reagent loss as a result of leaching of the membrane liquid phase into the adjacent aqueous phases and as there is a relatively small amount of extractant in the membrane, any loss can seriously impact separation performance (Kentish and Stevens, 2001, Kolev, 2005).

PIMs have the potential to overcome many of these limitations mentioned above. The encapsulation of the extractant within the membrane polymer matrix significantly lessens reagent losses to the aqueous solutions in contact with the membrane. Although PIMs suffer from relatively slow mass transport through the membrane, due to their mechanical stability the membranes can be made into very thin films which can somewhat mitigate the diffusive resistance effects (Nghiem *et al.*, 2006).

As mentioned previously, PIMs also offer vast improvements in terms of health, safety and environmental concerns for process operations compared to the other types of membranes and conventional SX. Handling fabricated PIMs is effectively as safe as handling other plastic products. The discrete and robust nature of PIMs also allows for off-site fabrication; this means that the *in-situ* organic solvent hazard can be completely removed when PIMs are used. Chemical exposure and its associated hazards continue to be more stringently regulated with time so PIMs may present an opportunity to reduce compliance costs.

Although PIMs offer great advantages in terms of health, safety and environmental concerns, their extractive performance has generally been regarded as slightly inferior to other membrane technologies and substantially poorer than SX operations. The diffusive resistance of PIMs is higher than that of the other liquid membranes, due to the requirement for the extracted species to 'diffuse' through the polymer matrix. The polymer matrix is much more viscous than a liquid-phase solvent, through which the extracted solute diffuses in the other liquid membranes and in SX. However, as research into PIMs progresses, the performance gap between PIMs and other liquid membranes is lessening and their advantages become more attractive. It is for these reasons that PIMs are currently generating a large body of research which is expected to lead to efficient industrial separation techniques in the future (Almeida *et al.*, 2012; Argiropoulos *et al.*, 1998; Lo *et al.*, 1983; Macasek *et al.*, 1985; Nghiem *et al.*, 2006; Sifniades *et al.*, 1981; Wang *et al.*, 2000).

10.2.1.5 *Unique features of PIMs*

PIMs occupy a unique place in the sphere of membrane technologies. The behavior shown by PIMs is influenced by both the chemical factors which characterize SX systems, but also by the physical phenomena associated with membranes. It is difficult to describe PIMs by either classical membrane models or by solution chemistry alone; the observed behavior of PIMs is a combination of both.

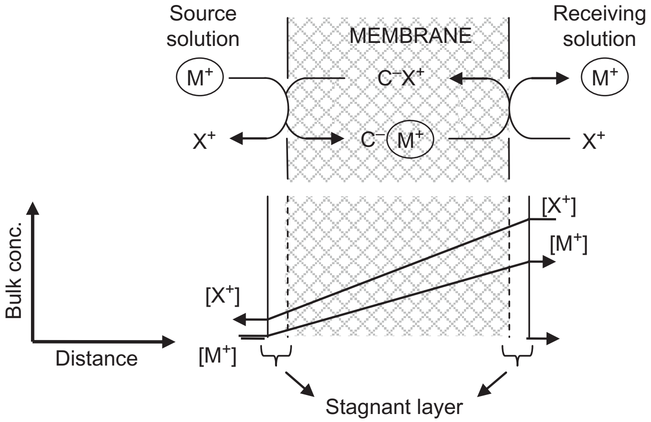

Figure 10.2. Schematic description of carrier-facilitated extraction and transport of a cation (M^+) across a PIM with a cation exchange carrier (Nghiem *et al.*, 2006, with permission from Elsevier).

For example, the one dimensional diffusion of a species through a semipermeable inert membrane is often characterized by Fick's first law of diffusion:

$$J_m = -D_m \frac{\partial C_a}{\partial x} \tag{10.8}$$

where D_m and J_m are the diffusion coefficient and flux of species a through the membrane, respectively, C_a is the concentration of species a, and x is distance. Although Fick's law represents membrane behavior well in the case of passive diffusion of a species through a membrane, it cannot fully take into account the influence of solution chemistry, which is an important factor in carrier-facilitated extraction. Similarly, it is hard to explain the effect of membrane phenomena (such as diffusive resistance) on the extraction of a solute by a membrane by chemical reasoning alone. The effect of the polymer matrix on the rate of extraction is a problem unique to PIMs; the membrane polymer matrix largely does not participate in the extraction processes as in the other types of membranes (Cussler, 2009; Mulder, 1996; Nghiem *et al.*, 2006).

Carrier-facilitated membrane extraction and transport therefore can be viewed as a combination of solvent extraction and membrane diffusion processes and the extent to which each process contributes to the overall process is an area of particular importance to PIM technology. Figure 10.2 illustrates the principles of carrier-facilitated membrane separation of a cation (M^+). In this example the stripping reagent (X^+) is in sufficiently high concentration to allow the target cation to be transported quantitatively from the source to the receiving solution.

10.2.1.6 *Composition of PIMs*

The composition of a PIM is tailored to a particular application. The components of the PIM (base polymer, extractant and any plasticizers and/or modifiers) play an important overall role in the separative efficiency of any PIM and must be chosen with care. Examples of various PIM components are shown in Figure 10.3.

The role of the base polymer is to provide the membrane with mechanical strength, whilst presenting as little diffusive resistance as possible. Ideally, the membrane should possess sufficient strength to withstand simple mechanical stress (such as stretching and bending) without damage; brittle or fragile membranes are difficult to handle and are easily broken. The polymer must also entrap the active component of the membrane (the extractant) and minimize any loss of the extractant to the surrounding solution. The polymer should also be relatively inert to any chemical species that it is likely to come into contact with (such as acids and bases). Although a vast number of polymers exist, the literature on PIMs primarily focuses on PVC and CTA,

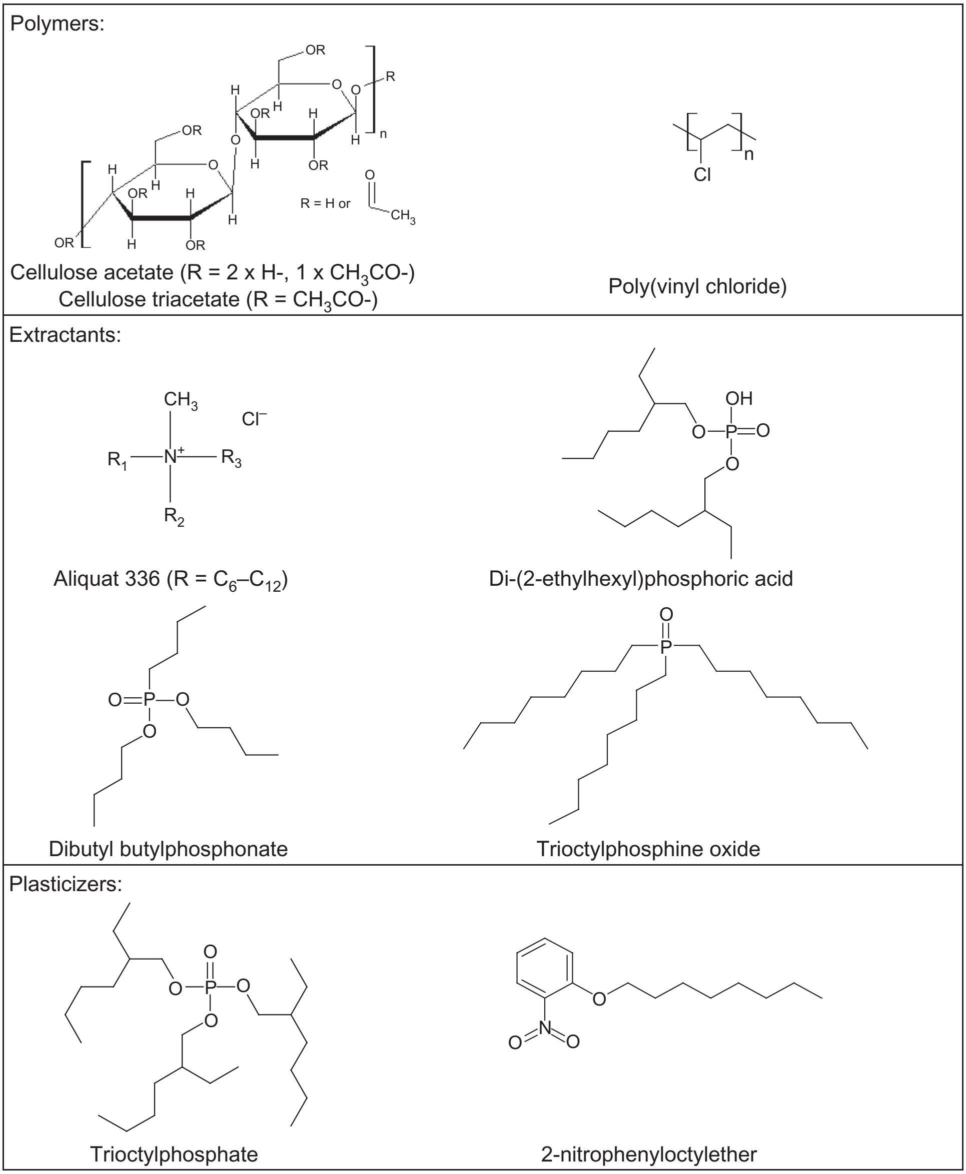

Figure 10.3. Structural formulae of various PIM components.

although polyvinylidene fluoride (PVDF) is also being studied as a base polymer. Both of these polymers are relatively cheap, combine well with active PIM components and are relatively inert under a wide range of aqueous conditions.

In contrast, a far wider range of extractants has been used in PIM studies. The extractant has the central role in the extraction process; extractants are often synthesized with a target solute in mind and are designed to minimize co-extraction of non-target solutes. Ideally, extractants have low water solubility, are relatively cheap and react quickly with the solute of interest. Extractants should also be relatively inert to other species in the extraction system, although this is seldom fully achieved in practice.

Extractants are often grouped by their mode of extractive action. A commonly used group of extractants, particularly for the extraction of U and As, are the basic extractants. These extractants are commonly designed around a basic nitrogen center; examples include the widely used trioctylamine and quaternary ammonium salts (and the related commercial preparations Alamine 336 and Aliquat 336). Substituted pyridine oxides also form part of this group. Basic extractants rely on the formation of aqueous anionic complexes between the target solute and a counter ion, such as chloride or sulfate. The basic extractant then forms a complex or ion-pair with the aqueous complex of the target solute and extracts it into the membrane, most frequently by an ion-exchange mechanism. These extractants are very useful for the extraction of As(V) found in natural waters. At neutral pH arsenate is present as anionic species, which readily form ion-pairs with the cation of quaternary ammonium salts such as Aliquat 336.

Acidic and chelating extractants are another important group of extractants. A wide variety of substituted phosphoric, phosphonic and phosphinic acids are used as solvent extraction reagents, particularly for U. Hexavalent uranium (U(VI)) is highly oxophilic and readily complexes with phosphoryl oxygen moieties. Di-2-ethylhexyl phosphoric acid (D2EHPA) is an example of an extractant which has long been used for the extraction and separation of U. Additionally, acidic reagents with chelating properties, such as β-diketones, quinolones and hydroxyaryloximes, are also often used as highly specific extraction reagents. Acidic extractants generally extract target solutes by exchanging a proton for the solute species of interest, transferring it into the membrane phase at the same time.

Another category of extractants is the neutral or solvating category. These are often phosphorus based, commonly consisting of substituted phosphine oxides or phosphate esters. Common examples applied to the extraction of U include tri-*n*-butyl phosphate and trioctyl phosphine oxide, whereas dibutyl butyl phosphonate has been used for the extraction of As species. They 'solvate' the species of interest, thus making the target solute soluble in the membrane liquid phase.

The final category of extractants, considered in this chapter, is the macrocyclic/macromolecular group. These are frequently based on large crown ether moieties and are particularly useful in extracting oxophilic species. Macrocycles can often be tailored to a specific application and they have been applied to the separation of a wide number of metallic species, although not extensively for the PIM separation of U to date (Nghiem *et al.*, 2006).

Modifiers and plasticizers are the third group of PIM components. These components often play a vital part in the extractive efficiency of a membrane. Plasticizers, well known in the plastics industry, are used to make PIMs more flexible and provide better separation between polymer chains inside the PIM. In turn, this makes it easier for solutes to diffuse through the membrane due to a reduction in steric constriction. Examples include 2-nitrophenyloctylether, dioctyl phthalate and trioctyl phosphate. Modifiers are used to aid solubility inside the membrane, either of the extractant or of the extractant-solute complex. Examples include long-chain alcohols and phenols.

These components are incorporated into a PIM by a relatively simple process, illustrated in Figure 10.4; all components are dissolved using a suitable solvent, mixed, cast in a mould (e.g., a glass ring positioned on a flat glass plate) and the solvent is allowed to evaporate. Once this has been achieved, a transparent, flexible and homogeneous film is left; this film is a PIM. This ease of fabrication makes PIMs particularly attractive for the development of low-cost separation technologies, although it may be desirable to mechanize their production in commercial situations.

For the PIM to be cast successfully, the components must be miscible with each other in each specific formulation. Poorly miscible formulations will phase-separate upon drying and suffer from poor extractive performance. Poorly designed formulations often result in brittle and inhomogeneous membranes. PIM components may be miscible only in limited, specific formulations, or only in the presence of particular modifiers or plasticizers. Similarly, the formulation of a PIM composition must be appropriate for its intended application – for example, CTA can undergo hydrolysis in strongly acidic or alkaline solutions and is therefore an inappropriate base polymer for these conditions. This means that PIM development typically includes a significant period of optimizing the composition of the PIM formulation.

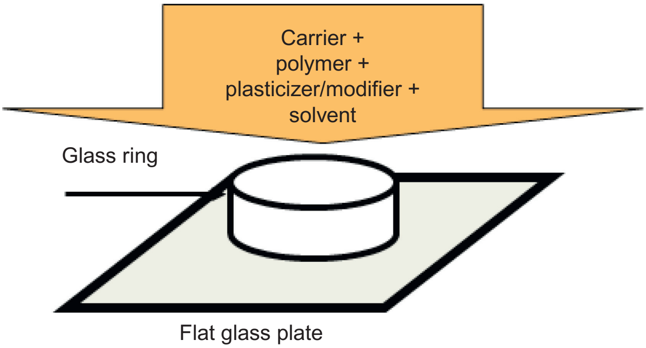

Figure 10.4. Schematic description of PIM preparation.

The compatibility of the PIM components relies on two principal factors; firstly the successful entanglement of the polymer chains and secondly, the physicochemical interactions between the components. Polymers have a critical molecular weight of entanglement, which must be exceeded for entanglement to occur successfully. The majority of polymers used for PIMs exceed this critical weight by a significant margin. Internal physicochemical interactions can be more difficult to predict. The full range of intermolecular forces contributes to the compatibility and stability of a PIM. If the intermolecular interactions between components are attractive on average, the PIM components will remain miscible and the PIM will be stable and homogeneous. Conversely, if these interactions are repulsive on average, the resulting PIM will suffer from poor stability, if it even forms properly at all. For example, a PIM will form well between PVC and Aliquat 336, due to an attractive interaction between the electronegative chlorine on the PVC backbone and the partial positive charge on the ammonium center in Aliquat 336. In contrast, a membrane will not form between Alamine 336 and PVC due to the strong repulsion between the lone electron pair on the nitrogen center in Alamine 336 and the electronegative chlorine in PVC (Pereira *et al.*, 2009).

If the PIM has been designed well, the resulting film should be mechanically stable, hydrophobic and safe to handle. Compatibility and homogeneity can often be judged visually or with the use of a microscope, although instrumental methods are being used more frequently to characterize PIMs at a micro- and nanometer scale (St John *et al.*, 2011).

10.2.1.7 *Polymer inclusion membrane systems for transport experiments*

The study of PIMs almost always involves characterization of the extraction of the target solute from a source solution (sometimes called the ‘feed’) into a PIM; this is frequently combined with simultaneous back-extraction on the other side of the membrane into a receiving solution (sometimes called the ‘strip’). Where extraction and back-extraction occur simultaneously, the solute is *transported* across the membrane. These experiments are often carried out in a system consisting of two compartments (cells) with mechanically stirred solutions and a membrane sandwiched between them (Fig. 10.5).

One of the compartments contains the source solution with a known initial concentration of the target solute while the other one contains the receiving solution with a suitable stripping reagent. The concentration of the target solute in each cell is monitored in time. The change in concentration in each cell allows the determination of the rate of transport of the solute across the membrane.

In some instances, it may not be possible (or desirable) for the solute to be transported across the membrane; in these cases both left and right cell will be filled with the same source solution that contains the solute. Any solute lost from the solution phases is assumed to be extracted into the membrane and therefore the change of concentration of the solute in the cells can be used for calculating the rate of extraction.

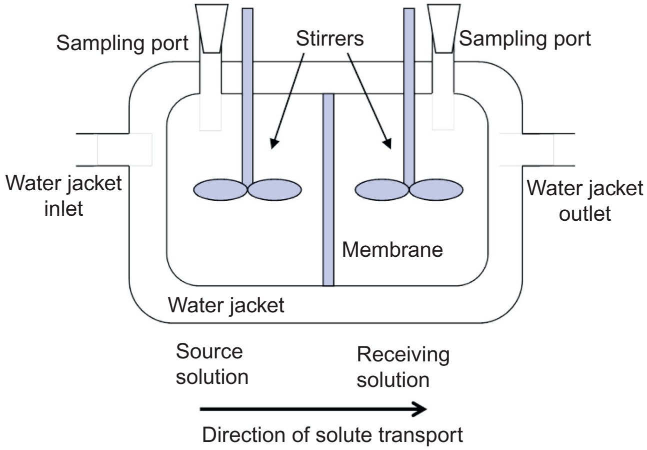

Figure 10.5. Schematic diagram of a PIM transport system.

10.3 SEPARATION OF URANIUM

10.3.1 *Separation of uranium from its ores*

The majority of research that has been conducted on the separation of U relates to its purification from its parent ores. The production of the commercial U concentrate known as 'yellowcake' from the parent U ore is a mature and routine metallurgical process and is described extensively in the literature (Musikas *et al.*, 2004; Ring, 2000; Ritcey, 1996). Although a wide range of techniques have been developed for this process, this section will consider U separation where conventional mining is used to recover the U ore body (as opposed to *in-situ* leaching).

In Australia, for instance, U is leached from mined ores using sulfuric acid in the presence of an oxidant, such as the ferric ion, prior to separation. Australian ores contain some tetravalent U, but given that U(VI) (as the uranyl ion, UO_2^{2+}) is more soluble in aqueous solutions than tetravalent U compounds; oxidation is employed to maximize recovery. The dissolved U is subsequently separated from its matrix by solvent extraction procedures where impurities are removed prior to precipitation, drying and calcining. Ion-exchange techniques (IX) are also sometimes used for purification processes in tandem with SX. *In-situ* leaching (ISL) processes are substantially different from conventional mining operations; ISL processes leach the U from orebodies located underground by injecting sulfuric acid into suitable aquifers and performing purification steps (in this case, IX) on the returned pregnant leachate (Musikas *et al.*, 2004; Ring, 2000; Ritcey, 1996).

10.3.1.1 *Solvent extraction of uranium*

In the production of U the separation of U from other species is principally achieved in the SX step. While other approaches have been used in the past, SX and IX techniques are now used almost universally. Solvent extraction techniques involve the contact of the impure leachate with an extractant, chosen for its selective affinity to the species of interest (in this case U), which then extracts the species of interest into an immiscible organic phase. The chosen reagent is normally diluted in an inexpensive solvent such as kerosene to improve the efficiency and speed of the process. Concentrated reagent solutions tend to be viscous, which can present engineering difficulties; in contrast, a dilute solution of the extractant may be mixed and transported with greater ease.

This U-rich phase may then undergo further steps to remove remaining impurities, prior to being back-extracted into a clean aqueous phase, ready for drying and calcining. The most commonly used extractants for U are mixtures of long-chain tertiary amines, such as Alamine 336 used in the AMEX process, and organophosphorous acids such as D2EHPA used in the DAPEX process (Musikas *et al.*, 2004; Ring, 2000; Ritcey, 1996). It should be noted that the aqueous waste from the initial extraction step (also called the raffinate) contains low concentrations of U and other environmental contaminants, making it unsuitable for further use or release. This is often discharged to retention ponds or other storage. This low-concentration raffinate is an ideal target for a low-cost, low-energy and efficient separation technique (such as those involving PIMs) to remove residual U from the aqueous waste prior to its re-use or disposal.

10.3.2 *Polymer inclusion membrane systems for uranium separation*

10.3.2.1 *TBP based PIMs*

Several early attempts at the creation of a PIM system for the transport and separation of U from aqueous solutions were based around the use of the extractant tri-*n*-butylphosphate (TBP). The first of these was reported by Bloch and co-workers, who described a system in which a membrane was fabricated using a mixture of 75 wt% TBP and 25 wt% CTA (Bloch *et al.*, 1967). Given data from later systems, this is a very high concentration of extractant; this PIM was not properly self-supporting and generally had to be supported on Kraft paper. Although the membrane showed poor stability, it successfully extracted U from nitric acid solutions.

The general reaction for the extraction of the aqueous uranyl cation is given by:

$$UO_2^{2+}{}_{(s)} + 2NO_3^-{}_{(s)} + 2TBP_{(m)} \rightarrow UO_2(NO_3)_2 \cdot 2TBP_{(m)} \tag{10.9}$$

where m and s refer to the membrane and solution phases, respectively. The reaction is driven by a high ionic strength of the uranyl and nitrate ions in the source solution; the reaction may be reversed by contacting a U-loaded membrane with a stripping solution of relatively low ionic strength (e.g., water).

This membrane was successfully shown to separate uranium nitrate from nitrates of iron (III), aluminum (III) and sodium. However, it was significantly permeable to nitric acid; the permeability to nitric acid was shown to be about 40% of the permeability to uranium. Permeability to nitric acid allows the system to reduce the difference in chemical potential across the membrane by transporting nitrate ions across the membrane without necessarily transporting U at the same time. This reduces the separative efficiency of the membrane.

Bloch's membrane also suffered from serious stability problems lasting only 1 to 2 days in contact with solution. This is due in no small part to the high water solubility of TBP. This suggests that a large amount of the extractant was leached out of the membrane, rendering the PIM unable to transport U after only a short period of time. Altering the extractant to include longer aliphatic side chains increased the membrane's stability considerably.

Another system for the separation of U based on TBP was described by Matsuoka and co-workers (Matsuoka *et al.*, 1980). Their PIM incorporated 62 wt% TBP and 38 wt% CTA and was shown to be able to transport uranium nitrate. Again, the effect of a high difference in concentration of the nitrate ion across the membrane was exploited to allow U to be transported in this system. However, a stripping agent (sodium carbonate) was used to improve the system's performance. The carbonate anion forms a stable complex with U and is widely used as a stripping reagent; it assists in removing U from the membrane. This membrane had extremely poor stability, lasting only 2 hours in contact with solution before its ability to transport U was removed. Again, this poor stability is attributed to the high water solubility of TBP. In this study, the authors were only able to demonstrate any useful lifetime by saturating both source and receiving solutions with TBP, limiting the leaching of TBP from the membrane. Even with this treatment, the PIM lasted less than 50 hours (Matsuoka *et al.*, 1980).

10.3.2.2 *Trioctylphosphine oxide (TOPO) based PIMs*

A more recent system for the separation of U was based on TOPO, another commonly-used U extractant. TOPO is not often used in PIMs as it is solid at room temperature; most PIM components (other than the polymer) are usually liquid. Solid components are frequently incapable of forming homogeneous membranes with the polymers used and generally have no plasticizing ability of their own. TOPO makes no exception and its inclusion in a PIM requires the addition of a large amount of a plasticizer to the membrane formulation to compensate for TOPO's poor endogenous plasticizing ability.

Despite these difficulties, Bayou *et al.* (2010) managed to produce a PIM based on TOPO and CTA, which was able to partially separate U from molybdenum. These researchers used 2-nitrophenyloctylether (NPOE) to dissolve TOPO inside the membrane and provide sufficient plasticizing ability – the PIM contained 18 wt% TOPO, 42 wt% NPOE and 40 wt% CTA.

Bayou's membranes showed excellent stability. According to their report, their PIM system was capable of functioning for more than 16 days without any serious detriment to the membrane. The stability of the membrane was compared to an analogous SLM, which lasted less than half as long as the PIM.

However, the PIM's stability was accompanied by relatively poor separative performance. The transport of U across the membrane by TOPO proceeds by a similar scheme to that by TBP; TOPO forms a neutral complex with uranyl nitrate which is extracted into the membrane. In this case, U was transported from a solution containing only uranyl nitrate and molybdenum nitrate into water. This means that the reaction had no driving force other than the difference in concentration of the respective metal on each side of the membrane. Under these circumstances, 'uphill' transport (Fig. 10.2) and separation is impossible, and this system reflects that limitation. Less than 50% of the U in the source phase was transferred to the receiving phase. Additionally, the system was not able to completely separate U from Mo, leaving an appreciable quantity of Mo and U in both source and receiving phases. Nonetheless, this research clearly demonstrated the superiority of PIMs over SLMs in this application.

10.3.2.3 *D2EHPA based PIMs*

A more recent approach to the separation of U using PIMs has been based on the widely-used extractant D2EHPA. Sodaye and co-workers designed a PIM in 2004 for extraction and analytical pre-concentration of U based on D2EHPA and CTA; however, they did not extend their work to quantitative separation (Sodaye *et al.*, 2004).

Another system based on D2EHPA showed greater potential for the separation of U from mixtures (St John *et al.*, 2010). The PIM used in this system was composed only of D2EHPA (45 wt%) and PVC (55 wt%). The plasticizing properties of D2EHPA itself in PVC were sufficient to form a homogeneous and flexible membrane.

In contrast to the other systems based on the solvating properties of TBP and TOPO, D2EHPA is an acidic extractant. The extraction of U by a D2EHPA PIM is described by:

$$\mathrm{UO_2^{2+}}_{(s)} + 2(\mathrm{HA})_{2(m)} \leftrightarrows \mathrm{UO_2(AHA)_{2(m)}} + 2\mathrm{H^+_{(aq)}} \tag{10.10}$$

where HA is a molecule of D2EHPA, $(\mathrm{HA})_2$ represents a dimer of D2EHPA and AHA is the D2EHPA dimer after the loss of a proton. The stripping of U from the membrane is described by the same reaction, however, in this case it is shifted towards the dissociation of the U/D2EHPA complex. As the reaction indicates, the extraction of U by D2EHPA is very sensitive to pH. Uranium extraction into the membrane is hindered by high acidity in the source phase; conversely the stripping of U from the membrane is aided by high acidity in the receiving phase (St John *et al.*, 2010).

This pH reliance can be manipulated to provide a useful driving force for the transmembrane transport of U. Under transport conditions, the source solution is of low acidity (0.1 mol $\mathrm{L^{-1}}$ $\mathrm{H_2SO_4}$), whereas the receiving solution is of high acidity (6 mol $\mathrm{L^{-1}}$ $\mathrm{H_2SO_4}$). The large difference in chemical potential of sulfuric acid across the membrane can be used to drive the transport of U. As the PIM has poor permeability to $\mathrm{H_2SO_4}$, the only way that the system can move to reduce the chemical potential difference is by transporting uranyl cations from the source phase to the receiving phase; this allows the counter-coupled transport of $\mathrm{H^+}$ ions from the receiving phase

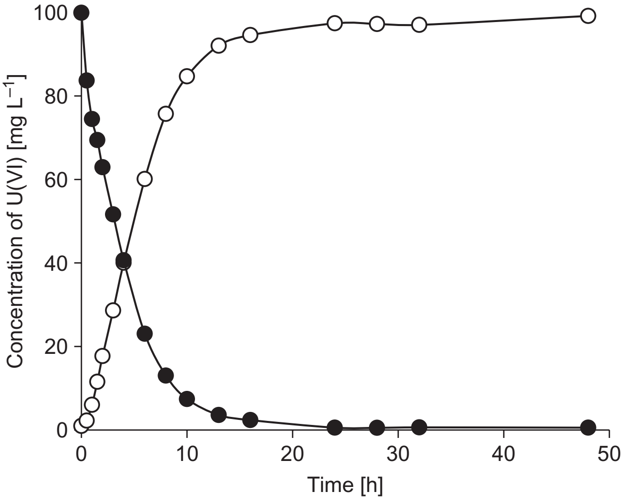

Figure 10.6. Transport of uranium(VI) across a PIM containing 45 wt% D2EHPA and 55 wt% PVC. The concentration of uranium is shown in the source (●) and receiving (○) solutions. The source solution contained 0.1 mol L^{-1} H_2SO_4 and 100 mg L^{-1} U(VI) as uranyl sulfate. The receiving solution contained 6 mol L^{-1} H_2SO_4 (St John *et al.*, 2012).

to the source phase. As long as a large excess of H_2SO_4 is maintained in the receiving phase, the transport of U from the source phase to the receiving phase will continue. This means that U may easily be transported uphill, almost regardless of the U concentration in the receiving phase, thus leading to U being completely transported from the source phase to the receiving phase, as shown in Figure 10.6 (St John *et al.*, 2012).

The pH-sensitive nature of the extraction can also be used to facilitate separation of U from a number of other metal ions. D2EHPA is in fact a relatively non-specific extractant; it complexes with many metal ions under the right solution conditions. However, each metal has a specific pH-extraction relationship. The relationship between extraction and pH is different for each metal. An example, Figure 10.7 shows how the extents of extraction of Fe(III) and U(VI) by a D2EHPA PIM vary considerably from each other at different pH values. Almost all other metals are extracted by D2EHPA only at much higher pH. This means that the uranyl cation can be separated from most other metal ions by maintaining the acidity of the source solution at relatively high levels. This system was demonstrated to be able to completely separate U(VI) from the common base metal ions such as Al(III), Cu(II), Mn(II), and Zn(II). The system could also separate U(VI) from Fe(III), however some co-extraction of Fe(III) was observed under some conditions. The system can kinetically separate U(VI) from Fe(III) under conditions of high source phase acidity (1.0 mol L^{-1} H_2SO_4).

These D2EHPA/PVC membranes showed excellent durability. The PIMs were subjected to 10 cycles of extraction and back-extraction and showed negligible leaching of extractant from the membranes and no observable loss in performance (St John *et al.*, 2012). PVC is an excellent base polymer for PIMs as it is inert under a wide range of chemical conditions and unlike CTA is not susceptible to acid or base hydrolysis.

However, the stability of these membranes is limited to a certain set of solution conditions. D2EHPA's own pK_a is around 3.5, which means that if D2EHPA PIMs are exposed to solutions of about pH 3 or higher, D2EHPA dissociates, leaches from the membrane and frequently forms an insoluble third phase in the source solution. In the extraction of U D2EHPA PIMs are exposed to solutions with a pH substantially lower than 3.5 and therefore leaching of D2EHPA is negligible.

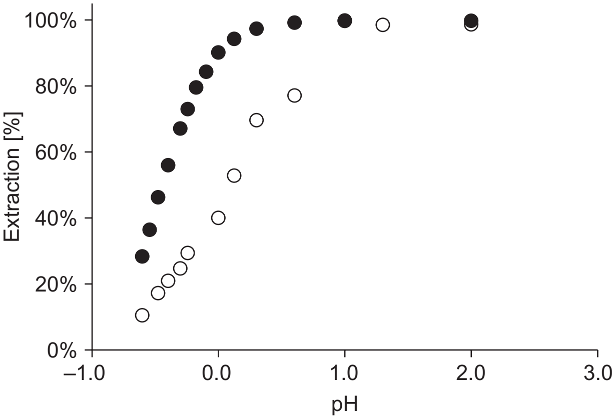

Figure 10.7. Relationship between the pH of the source solution and the extent of extraction of uranium(VI) (•) and iron(III) (○) by a D2EHPA PIM at equilibrium (pH isotherm) (St John *et al.*, 2012, with permission from Elsevier).

The separative performance of the D2EHPA/PVC membrane system was also found to be superior to the other PIM systems that had been used for the separation of U. The permeability of the D2EHPA/PVC membrane to U was calculated to be 6.96 m s^{-1}, while it was 4.76 m s^{-1} for Matsuoka's TBP/CTA PIM (Matsuoka *et al.*, 1980), 2.40 m s^{-1} for Bloch's TBP/PVC PIM (Bloch *et al.*, 1967), and 2.15 ms^{-1} for Bayou's TOPO/NPOE/CTA PIM (Bayou *et al.*, 2010). The permeability of the D2EHPA/PVC membrane is comparable to or even higher than that of many SLMs, and it should be noted that the stability of PIMs far outclasses that of SLMs.

The advances in PIM technology continue to narrow the gap between SX systems and membrane systems. Although it is likely that U production technology will continue to rely on SX systems for the foreseeable future, the continued development of safer, cleaner and more efficient PIM systems is expected to result in their gradual implementation in the U and other industries in the not too distant future.

10.4 SEPARATION OF ARSENIC

10.4.1 *Arsenic occurrence in natural waters and technologies for its removal*

Conventional As removal technologies include adsorption, coagulation/precipitation and ion-exchange processes (Mohan *et al.*, 2007; Mondal *et al.*, 2013). Membrane processes are considered a promising technology for removing As from groundwater for its subsequent use as drinking water. The membrane separation processes currently in use (microfiltration, ultrafiltration, nanofiltration, and reverse osmosis) utilize pressure difference as the driving force (Shih, 2005). The main drawback of using these membrane technologies in As removal, besides the high operation and capital cost, is the high consumption of electrical energy. A possible alternative is the use of functionalized membranes in which the separation process is based on chemical pumping instead of physical rejection.

10.4.1.1 *Aliquat 336 based PIMs for As separation*

A CTA based PIM which incorporated Aliquat 336 was described by Güell *et al.* (2011a) with the aim to develop a suitable separation system to treat natural waters containing trace levels of As. The basis of this study was the extended knowledge on the extraction of arsenate (As(V)) and arsenite (As(III)) by Aliquat 336 in both SX and SLM systems.

It has been reported that As(V) and As(III) species can be extracted from an aqueous solution at pH 13 to an organic phase containing Aliquat 336 in dodecane modified with 4% dodecanol via the formation of ion-pairs with As:Aliquat 336 ratios of 1:2 and 1:3 (Güell *et al.*, 2010). At this basic pH both arsenate and arsenite are present in anionic forms and the values of the corresponding extraction constants are similar. This fact indicates a comparable stability of the As:Aliquat 336 species in the organic phase. However, it should be noted that the As(V)-Aliquat 336 system reached equilibrium after 5 min of contact between the membrane and solution, whereas the As(III) extraction system needed between 2 and 7 h to reach equilibrium (Güell *et al.*, 2010). This difference in the rate of extraction was the basis for the separation of As(V) and As(III) at pH = 13 using an SLM consisting of 0.5 M Aliquat 336 in dodecane and 4% dodecanol and a 0.1 M HCl solution as the receiving phase. Under these conditions, As(V) was quantitatively transported after 6 h, whereas no transport of As(III) took place (Güell *et al.*, 2010).

The performance of the Aliquat 336 based SLM system, outlined above, was also applied to the extraction of As(V) from neutral solutions. The extraction of As(V) in this case was described by the following stoichiometric equation (Güell *et al.*, 2010):

$$\mathrm{HAsO_4^{2-}} + 2(\mathrm{R_3R'N^+Cl^-})_{\mathrm{org}} \leftrightarrows [(\mathrm{R_3R'N^+})_2\mathrm{HAsO_4^{2-}}]_{\mathrm{org}} + 2\mathrm{Cl^-} \qquad (10.11)$$

where $R_3R'N^+Cl^-$ is a quaternary ammonium chloride of Aliquat 336.

To ensure quantitative transport of arsenate from the source to the receiving phase, a 0.1 M NaCl solution was found to provide efficient stripping of $HAsO_4^{2-}$ in the receiving phase, while a 0.1 M HCl solution only allowed the transport of 40% of As(V) across the membrane. This low transport efficiency was related to the observed decrease in pH of the source solution (from 7 to 2), indicating that transport of HCl occurred across the membrane from the receiving solution to the source solution. This fact was attributed to both the ability of Aliquat 336 to transport HCl (Kagaya *et al.*, 2012) and to the difference of ionic strength between the solutions on the two sides of the membrane. The accumulation of HCl in the source solution led to the protonation of the anionic As(V) species to H_3AsO_4 which could not be extracted into the membrane.

The proposed SLM system showed how to quantitatively remove As(V) from its solutions in the presence of other anions normally encountered in natural waters (e.g., nitrate, sulfate, bicarbonate, and phosphate) which were also transported across the membrane but to a lesser extent than As(V).

The same SLM system was found to be incapable of transporting As(III) under the conditions used for the complete removal of As(V). This can be explained by the fact that at neutral pH arsenite is completely protonated (i.e., H_3AsO_3) and therefore cannot be extracted via an ion-exchange mechanism. Thus, the SLM incorporating Aliquat 336 can be viewed as an effective system for the speciation of As(III)/As(V) in water samples (Güell *et al.*, 2011b).

Aliquat 336 has also been used as a carrier in other SLM configurations such as hollow fiber SLMs to effectively transport As species. This carrier dissolved in kerosene (35% v/v) showed the highest As transport efficiency in the case of 1 M NaOH receiving phase when compared to other extractants such as the neutral extractants Cyanex 923 and TBP, the acidic extractant Cyanex 301 and the basic extractant tri-*n*-octylamine (TOA) (Pancharoen *et al.*, 2009). As(V) was removed from an aqueous stream by non-dispersive solvent extraction in a hollow fiber membrane contactor using Aliquat 336 (30% v/v) dissolved in kerosene and octanol (4% v/v). This extraction system was affected by the pH of the source solution and maximum removal was obtained in the pH range from 7.0 to 8.2, where divalent and monovalent As(V) species were the predominant As(V) species (Bey *et al.*, 2010). However, in the SLM investigated by Güell and co-workers (2010), it was found that the highest permeability value was achieved at pH 9, where the dominant As(V) species is $HAsO_4^{2-}$.

Albeit the source solution pH plays a key role in the extraction of As by Aliquat 336, the membrane composition has also been found to affect significantly the extraction efficiency of the As-Aliquat 336 system. In the case of the Aliquat 336 based PIM system developed by Güell and co-workers, the effect of the membrane composition was found to be crucial in ensuring an effective As(V) transport at pH 7. Taking CTA as a base polymer (28.8 wt%) and Aliquat 336

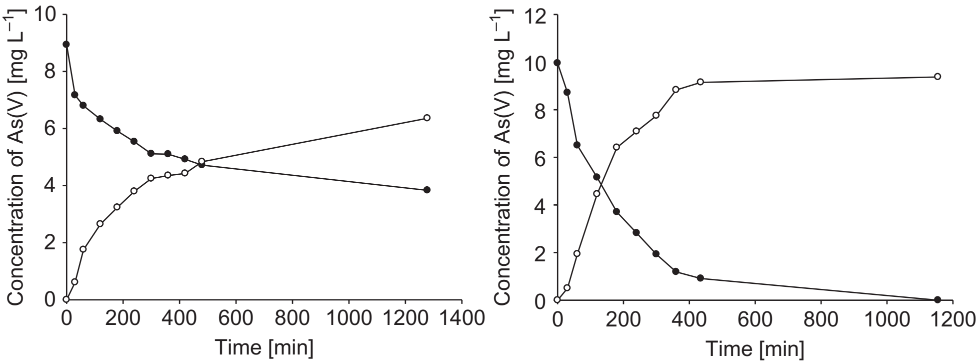

Figure 10.8. Effect of membrane composition on the transient concentration curves in As(V) transport. PIM containing Aliquat 336 (26.2 wt%), CTA (26.2 wt%) and NPOE (45 wt%) (left) and PIM containing Aliquat 336 (26 wt%) and CTA (74 wt%) (right). (●) source phase: 10 mg L^{-1} As(V), pH = 7; (○) receiving phase: 0.1 M NaCl.

as a carrier (26.2 wt%), the effect of the addition of the plasticizers NPOE and dibutyl sebacate (DBS) to the PIM composition (45 wt%) was investigated. These PIMs provided poor transport of As(V), i.e., only 43% of As(V) was transported to a 0.1 M NaCl receiving solution in the first 5 h in the case of NPOE and 57.8% in the case of DBS. At the same time a PIM containing no plasticizer and the same amount of Aliquat 336 (26 wt%) with the rest being only CTA (74 wt%) allowed the transport of 78% of total arsenate. Figure 10.8 compares the transport of As(V) across membranes with (Fig. 10.8 left) and without (Fig. 10.8 right) NPOE. The results clearly show that the PIM made only with CTA and Aliquat 336 provided faster transport of As(V) which was completely removed from the source phase after 24 h. These results indicate that even though NPOE is a suitable plasticizer and interacts well with the other components of the PIM, it has a negative effect on the extraction and transport of arsenate, and thus, it should not be incorporated in the membrane composition. It should be noted that Aliquat 336 has plasticizing properties itself and often there is no need of adding a separate plasticizer to the membrane composition.

The maximum permeability value for As(V) was obtained with a PIM consisting of 52.4 wt% CTA and 47.6 wt% Aliquat 336, and this membrane composition was further used in studying the effect of source solution pH on both arsenate and arsenite transport. Albeit different As(V) species were the dominant species at the different pH values studied (i.e., $H_2AsO_4^-$ at pH 5, $H_2AsO_4^-/HAsO_4^{2-}$ at pH 7, and $HAsO_4^{2-}$ at pH 10) the membrane permeability values were found to be similar (0.17 cm min^{-1}, 0.26 cm min^{-1}, and 0.23 cm min^{-1} at pH 5, 7 and 10, respectively) (Güell *et al.*, 2011a). However, in an analogous SLM system a much stronger pH effect on permeability was observed (i.e., 0.016 cm min^{-1} at pH 5, 0.103 cm min^{-1} at pH 7 and 0.32 cm min^{-1} at pH 10) even though the As(V) species transported across both membranes ($HAsO_4^{2-}$) was the same (Güell *et al.*, 2011b). This result suggests that the incorporation of the carrier into the polymeric structure of a PIM leads to a more efficient separation process which is less dependent on external parameters such as pH.

The transport of As(III) through the same PIM was insignificant during the first 5 h (the period that allowed 100% transport of As(V)) and was not affected by the pH. This fact reveals the suitability of the Aliquat 336/CTA PIM for speciation purposes. When the transport lasted 24 h, 20% of arsenate was transported to the receiving phase by passive diffusion of the neutral arsenious acid due to the concentration gradient between the two solutions. Hence, the same PIM system can be efficient for the removal of total As (As(III) + As(V)) from water if the separation processes is allowed to run for longer time periods.

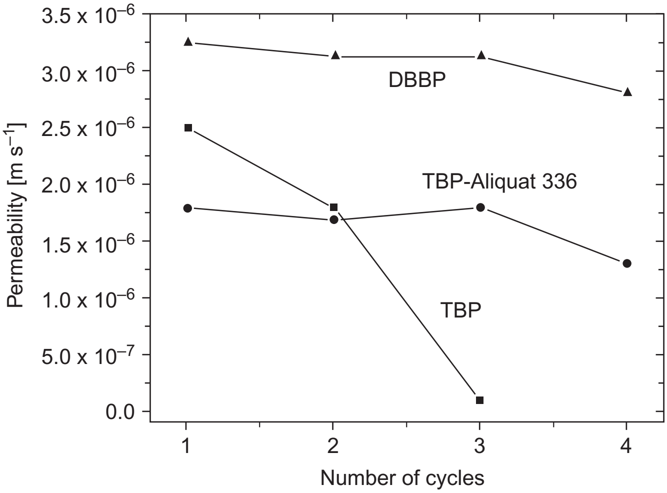

Figure 10.9. Comparison of the performance (permeability and stability) of different carriers in PIMs. TBP – 2.04 mg cm^{-2}; DBBP – 2.04 mg cm^{-2}; mixture of TBP and Aliquat 336 – 1.75 and 0.24 mg cm^{-2}, respectively. Source: 3000 mg L^{-1} As(V), 2 M H_2SO_4 (Ballinas *et al.*, 2004, with permission from American Chemical Society).

10.4.2 *Arsenic removal from copper electrolytic baths*

As(V) is a common impurity in copper processing since it is present in copper sulfide concentrates. Its occurrence varies from 0.010–2%. During copper electro-refining As is dissolved along with Cu from the anode in the electrolyte and its gradual accumulation results in a variety of problems such as damage to the high purity Cu cathodes. Hence, several methods have been developed to decrease As concentration in Cu-electrolytic baths. Among them, solvent extraction with tri-n-butyl phosphate (TBP) as the main extracting agent, was employed in some copper refineries for As removal. TBP extracts As(V) together with H_2SO_4 according to the following stoichiometric equation (Iberhan *et al.*, 2002):

$$H_3AsO_4 + H_2SO_4 + TBP \cdot H_2O_{(org)} \leftrightarrows H_3AsO_4 \cdot H_2SO_4 \cdot TBP \cdot H_2O_{(org)} \qquad (10.12)$$

Under these acidic conditions neutral As species are formed and the use of solvating extractants is justified. Other phosphine derivatives have also been reported to extract arsenate from sulfuric acid solutions (e.g., Cyanex 923, Cyanex 921 and Cyanex 301) and SLM incorporating these extractants have been developed. Martinez *et al.* (2007) developed an SLM system based on Cyanex 921 dissolved in kerosene to transport As(V) from a 2 M H_2SO_4 source solutionto a Na_2SO_4 receiving solution. In this system, the extraction of As(V) by Cyanex 921 also occured via a solvation mechanism, including both sulfuric acid and water molecules.

10.4.2.1 *A PIM system for As(V) removal from sulfuric acid media*

Ballinas *et al.* (2004) developed a separation system to transport As(V) from sulfuric acid source solutions into a LiCl receiving solution using a CTA based PIM. PIM stability (number of cycles) and performance (permeability towards As(V)) were investigated for three different carriers: dibutyl butyl phosphonate (DBBP), TBP, and a mixture of TBP and Aliquat 336 (Fig. 10.9).

The advantage of DBBP over the other 2 carriers was evident and this carrier was selected for the subsequent As removal studies. It was suggested that polymerization between CTA and DBBP occurred spontaneously at all CTA/DBBP ratios studied (Ballinas *et al.*, 2004). A typical PIM used in this work was composed of 8 wt% CTA and 92 wt% DBBP. Hence, the intermixing between the two components is crucial for the formation of a stable membrane. Otherwise, the low concentration of the base polymer would not be enough to embed the carrier and, thus, to form a stable PIM.

Ballinas *et al.* (2004) also stated that the number of cycles that the membrane could undergo without deterioration in performance depended on the thickness of the membrane. Thicker membranes ($15 \pm 2\,\mu$m instead of $8 \pm 2\,\mu$m) could undergo 8 cycles instead of 5 before the permeability dropped to 20% of its initial value. However, thicker PIMs resulted in lower permeability values. Hence, a compromise between stability and permeability must be reached for optimal membrane performance.

The selectivity of the PIM, mentioned above, was investigated by carrying out experiments using sulfuric acid solutions of As(V) which also contained relatively high concentrations of Cu, Ni and Bi. No significant transport of other species was noticed, and, moreover, the transport of As was not compromised under these conditions.

In contrast, As transport was strongly influenced by the sulfuric acid concentration. The carrier was shown to be capable of transporting both As and H_2SO_4 molecules through the formation of the H_3AsO_4-[DBBP]$_2$ and H_2SO_4-[DBBP] species. To ensure As uphill transport through a DBBP/CTA PIM a difference in sulfuric acid concentration between the receiving and source solutions was required. Therefore the use of two identical PIMs in a triple-cell configuration was proposed. The first compartment contained initially a source solution consisting of 3000 mg L^{-1} As(V) and 220 g L^{-1} H_2SO_4 while both the second and third compartments contained 2 M LiCl solution. As sulfuric acid and As(V) were transported from the source solution to the second compartment, transport to the third recovery phase also started. In this way, sulfuric acid concentration continuously varied in all compartments. In this way, high As recovery factors (90% in 800 min) were obtained using this PIM system.

10.5 CONCLUSION AND OUTLOOK

Research on PIMs carried out to date has demonstrated their potential for the development of membrane systems for separation in both industry and chemical analysis. However, the relatively modest rate of membrane transport of the current generation of PIMs, based mainly on the use of PVC or CTA as base polymers, is an obstacle for the adoption of separation utilizing these membranes as an economically viable alternative to conventional solvent extraction. It can be expected that this crucial membrane transport characteristic could be significantly improved by using other base polymers, manufacturing of thinner membranes with sufficient mechanical stability, operating the separation process at elevated temperatures, or applying ultrasound. Research on the applicability of some these approaches by Zhang *et al.* (2012) has produced encouraging results. These authors have implemented for the first time PIMs in the on-line extractive separation of analytes from complex sample matrices prior to their determination in flow injection analyzers (Zhang *et al.*, 2011). It has been demonstrated in this study that the transport performance of a D2EHPA/PVC PIM for the separation of Zn(II) can be improved approximately 200 times by decreasing the membrane thickness from 40 to 22 μm and over one order of magnitude by increasing the temperature of the membrane separation module and the source and receiving solutions from 20 to 50°C (Zhang *et al.*, 2012). The membrane remained stable in this temperature range. The exposure of the on-line separation module mentioned above to ultrasound produced only a modest 2-fold improvement in the rate of membrane transport though it should be taken into account that equipment design was not optimized (Zhang *et al.*, 2012).

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CHAPTER 11

Removal of arsenic by nanofiltration: a case study on novel membrane materials

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11.1 INTRODUCTION

The removal of arsenic (As) by means of nanofiltration (NF) membranes is discussed. In particular, the separation mechanism, state of the art and, limitations of NF related to arsenic removal are reported. Directions for new development are pointed out by analysis of the latest literature on the preparation of high performance NF membranes. The aim of this chapter is to give a comprehensive overview on the use of NF membrane-based processes for As removal, which not only provides a critical analysis of the current treatment status using membrane based processes, but also points out new development directions that may help the advancement of arsenic removal in a more energy efficient manner.

11.2 NANOFILTRATION (NF)

11.2.1 *Nanofiltration and membrane*

Nanofiltration (NF) is a pressure-driven membrane process based on effective membrane pores in the nanometer range. The separation characteristics are between ultrafiltration and reverse osmosis. The specific features of a nanofiltration membrane is its high rejection towards multivalent ions but low to moderate for monovalent ions, as well as high rejection of organic compounds with a molecular weight of 150–1000 Da (Nagy, 2012; Uddin *et al.*, 2007a). Compared to reverse osmosis, nanofiltration membranes show also relatively high removal rate for As; however, at a relatively lower pressure, or lower energy demand. These characteristics indicate that the nanofiltration membrane process may be an alternative technology of high potential for the developing countries.

Nanofiltration membranes consist of an active layer and a support, which determine the separation properties and mechanical strength, respectively. The active layer may be integrally connected to the support structure, such as membranes prepared via an immersion precipitation process (Bowen *et al.*, 2001; He *et al.*, 2002). This type of membrane has distinct pores in the nanometer range at the skin layer. The active layer can also be an extra coating layer on to a tailor-made support structure via interfacial polymerization or dip-coating.

11.2.2 *Separation mechanism of nanofiltration*

There are several theories to explain the nanofiltration mechanism and the understanding of the transport mechanism reveals a contradictory picture of how the active layer behaves in NF (Bardot *et al.*, 1995; Bhattacharyya *et al.*, 1974; Bowen *et al.*, 1996; 1997; 1998a; 2001; 2005; Garba *et al.*, 1999; Hagmeyer *et al.*, 1998; Hall *et al.*, 1997; Jitsuhara *et al.*, 1983; Levenstein *et al.*, 1996; Mehiguene *et al.*, 1999; Perry *et al.*, 1989; Rios *et al.*, 1996; Schirg *et al.*, 1992; Spiegler *et al.*, 1966; Tsuru *et al.*, 1991; van der Horst *et al.*, 1995; Wang *et al.*, 1995a; Xu *et al.*, 1997; Yaroshchuk, 2000). A dense skin layer was assumed by the Torell-Meyer-Sievers model (TMC) and the hybrid model. On the other hand, the space-charge model and the Donnan-steric pore model (DSPM) described a porous skin layer (Bowen *et al.*, 1998b; Wang *et al.*, 1995b).

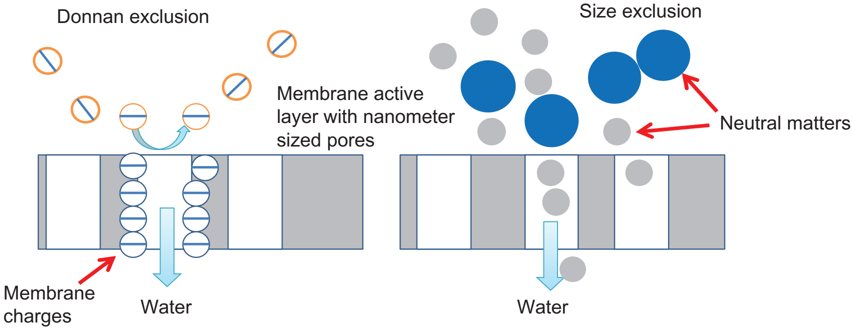

Figure 11.1. Schematic of the principle of Donnan exclusion and size exclusion.

These models have been applied in the prediction of electrolyte rejection by NF membranes in aqueous solutions, successfully for specific cases. Bowen *et al.* (1997) reported the observation of distinctive pores by atomic force microscopy (AFM) in the surface of commercial membranes prepared by IP process. The research supported the hypothesis that a dense coating layer swells at working conditions, resulting in water passages and NF properties.

According to DSPM model, the separation of nanofiltration is mainly dependent on the pore size and the solute, or the sieving effect, and the net charge of the material in the active layer and solute, or the Donnan exclusion effect, as illustrated in Figure 10.3. A membrane with negative charges is able to reject the negatively charged species but allow neutral matter to permeate through; for species of size significantly larger than the pore size, the rejection rate might be high as well. Nanofiltration has important applications in water softening, decolorization of industrial dye wastewater, purification and concentration of low molecular weight organic substances, etc.

11.2.3 *Modeling of nanofiltration*

Assuming that the active layer of the nanofiltration membrane is porous in nature, the extended Nernst-Planck equation is applicable to describe the transport of multicomponent systems in nanofiltration membranes. It represents transport due to diffusion, electrical potential gradient and convection. The equations can be written as:

$$j_i = -D_{i,\mathrm{p}}\left(\frac{dc_i}{dx} + \frac{Z_i c_i F}{RT}\frac{d\psi_\mathrm{m}}{dx}\right) + K_{i,\mathrm{c}} c_i J_\mathrm{v} \tag{11.1}$$

with

$$D_{i,\mathrm{p}} = K_{i,\mathrm{d}} D_{i,\infty} \tag{11.2}$$

where j_i is the flux of solute i, and $D_{i,\mathrm{p}}$ is the hindered diffusion coefficient corrected from the bulk diffusion coefficient, $D_{i,\infty}$ by diffusion hindrance, the factor $K_{i,\mathrm{d}}$. j_v is the solvent flux and $K_{\mathrm{i,c}}$ the convective hindrance factor. The equation does not include the influence of the pressure on diffusion and specific ion membrane matrix interaction on $D_{i,\mathrm{p}}$.

For uncharged solutes, no electrostatic term is in Equation (11.1); thus the solute flux can be expressed as:

$$j_i = -D_{i,\mathrm{p}}\frac{dc_i}{dx} + K_{i,\mathrm{c}} c_i V \tag{11.3}$$

To obtain an expression for the rejection of the solute, Equation (11.3) is integrated across the membrane. The Hagen-Poiseuille equation gives the relationship between the pure water flux and the applied pressure across the membrane:

$$J_\mathrm{w} = \frac{r_\mathrm{p}\Delta P}{8\mu(\Delta x/A)} \tag{11.4}$$

where r_p is derived from the MWCO and hence the value for $\Delta x/A$ can be calculated.

For charged solutes, the concentration at the interface can be determined using the following equilibrium conditions, which will be taken as a combination of the Donnan and steric effects:

$$\left(\frac{c_i}{C_i}\right) = \phi \exp\left(-\frac{z_i F}{RT}\Delta\psi_{\mathrm{D}}\right) \tag{11.5}$$

The term ϕ is the steric partitioning term to account for the steric effects on the entrance to the membrane, and can be described as:

$$\phi = (1 - \lambda)^2 \tag{11.6}$$

where λ is the ratio of the solute to the pore radius. The activity coefficients for both bulk solution and inside the membrane are also taken to be 1 based on relatively low salt concentration in bulk and difficulty to know that in membrane.

Once r_{p} and $\Delta x/A$ are obtained, the rejection data of salts can be used to estimate the effective charge density X_{d}, of that membrane at the specific concentration. Since there is strong concentration polarization in a hollow fiber configuration, the concentration next to the membrane is a function of the flux. X_{d} is specific for the concentration. Therefore, it is a function of the flux as well. The exact calculating procedure can be found in the literature (Bardot *et al.*, 1995; Bowen *et al.*, 1996; 1997; 1998b; 2001; 2005; Garba *et al.*, 1999; Hagmeyer *et al.*, 1998; Hall *et al.*, 1997; Levenstein *et al.*, 1996; Mehiguene *et al.*, 1999; Rios *et al.*, 1996; van der Horst *et al.*, 1995; Wang *et al.*, 1995a; Xu *et al.*, 1997; Yaroshchuk, 2000).

11.3 REMOVAL OF ARSENIC BY NANOFILTRATION

NF membranes are usually employed in the separation of multivatent ions from monovalent ones. Arsenic is mostly presented as multivalent negatively charged chemical spieces in the normal pH range for drinking water. Fortunately, most NF membranes are negatively charged under neutral and alkaline conditions (Hilal *et al.*, 2004). Therefore, As removal in drinking water by NF is achievable by both size exclusion and Donnan effect. A number of studies concerning the As removal from water by NF membrane were reported in literature, as listed in Table 11.1. Some of the typical results are summarized as follows:

(1) Nanofiltration membranes are able to remove most of the As(V) but the removal rate for As(III) is low. Urase *et al.* (1998) studied the rejection of As by ES-10, an aromatic polyamide composite membrane (Nitto-Denko Co. Ltd.). The rejection of As(V) and As(III) increased with the increase of pH and rejections of 93% at pH 10 for As(V) and 50–89% for As(III) were found. A "loose" nanofiltration (NF) membrane, NF-45 (polyamide thin film composite membranes) was reported by Vrijenhoek *et al.* (2000) and a rejection of 90% for As(V) and fairly low rejection of 10–20% for As(III) were found.

(2) Low pressure nanofiltration membranes made by interfacial polymerization technology were often chosen for As removal. NF300 (Saitua *et al.*, 2005), NF90, NF-200 (Uddin *et al.*, 2007b), NF30 (Figoli *et al.*, 2010) were systematically investigated by researchers. Low-pressure nanofiltration, e.g., ES10, NTR729HF and NTR7250, were investigated for removal of As and anionic salts in groundwater (Sato *et al.*, 2002). Oh *et al.* (2004) reported a rather high water permeability of $53\,\mathrm{L\,m^{-2}\,h^{-1}\,MPa^{-1}}$ and 90% rejection for As from a systematic research on selected ES-10, NTR729, NTR7250 membranes.

Commercial application of nanofiltration membrane and reverse osmosis membrane is not yet realized for the removal of As from drinking water. The high energy consumption as well as low removal rate for the As(III) is the major obstacle. Classical interfacial polymerization membranes are negatively charged, but of low charge density, leading to low rejection of As (Seidel *et al.*, 2001).

Table 11.1. Literature concerning nanofiltration membranes for the removal of As(V) and As(III).

As concentration in feed	Membranes	Rejection and permeate flux	Reference
600 $\mu g\,L^{-1}$ As(total)	ES10	Rejection As(Ill) 50% to 89%; As(V): 87% to 93%	Urase *et al.* (1998)
Total As: 35–1800 $\mu g\,L^{-1}$, As(III)/As ~25%; sources: wells, rainwater, ponds	ES-10 HS5110	ES10: rejection As(III) around 55%; 99% for As(V); Flux: 30.5 $mL\,min^{-1}\,cm^{-2}$ at 0.7 MPa HS5110: rejection As(V) around 90%; Flux: 5.7 $mL\,min^{-1}\,cm^{-2}$ at 0.7 MPa	Oh *et al.* (2000)
10,32,100, 316 $\mu g\,L^{-1}$ As(V) and As(III)	NF-45	Rejection: 60–90% for As(V) and around 20% to 5% for As(III) Flux: 8 $\mu m\,s^{-1}$ at 0.55 MPa	Vrijenhoek *et al.* (2000)
10 to 316 $\mu g\,L^{-1}$ As(V) and As(III)	BQ01	Rejection: 60 to 90% for As(V) and 28 to 50% for As(III) Flux: 8 $\mu m\,s^{-1}$ at 0.55 MPa	Seidel *et al.* (2001)
50 $\mu g\,L^{-1}$ As(V) and As(III)	ES-10 NTR-7250 NTR-729	Rejection As(III): NTR-729/NTR-7250, >22% ES-10: >75% As(V): >95%, all NF membrane	Sato *et al.* (2002)
200 $\mu g\,L^{-1}$ As(III), dimethyl arsinic acid and As(V) was added; groundwater	ES-10 NTR-7250 NTR-729	ES-10: 0.18 $m^3\,m^{-2}$ per day at 0.25 MPa NTR-7250: 0.16 $m^3\,m^{-2}$ per day at 0.25 MPa NTR-729: 0.32 $m^3\,m^{-2}$ per day at 0.25 MPa	Oh *et al.* (2004)
142 to 233 $\mu g\,L^{-1}$, both natural and synthetic	NF270 NFC	Rejection As(V): 78.8% to 99.3% (NF270), Flux: 53.9 to 62.6 $kg\,m^{-2}\,h^{-1}$, at 0.689 MPa; Rejection: 84.6% to 99.3% (NFC), Flux: 7.3 to 10.9 $kg\,m^{-2}\,h^{-1}$, at 0.689 MPa	Košutić *et al.* (2005)
100 and 382 $\mu g\,L^{-1}$ As(V), synthetic water	192-NF300	Rejection As(V): 93–99% Flux: around 8 to 12 $\mu m\,s^{-1}$ at 0.724 MPa	Saitua *et al.* (2005)
440 μg/L, As(V), synthetic water	NF from Nitto Denko	Rejection As(V): more than 94%	Nguyen *et al.* (2006)
100–1000 $\mu g\,L^{-1}$ As(V), 50–25 $\mu g\,L^{-1}$ As(III), synthetic water	NF-60 NF-200	Rejection: >98% As(V) for NF60 and NF200 for As(III): NF60, from 16% at 0.5 MPa to 30% at 2.0 MPa; NF200, 50% at 0.5 MPa to 63% at 2.0 MPa	Uddin *et al.* (2007b)
20–90 $\mu g\,L^{-1}$ As(V) and As(III), synthetic water	NF from Toray	Rejection As(V): 90 and 100%; Rejection As(III): about 5%; the mean value of permeability: 365 $L\,m^2\,h^{-1}\,MPa^{-1}$	Xia *et al.* (2007)
As(V) and As(III), 0.5, 1.0, 2.0, 5.0 $mg\,L^{-1}$, synthetic water	NF-200 DS-5	Rejection: NF200, 23% and 25% at 1.0 MPa for As (0.5 and 1.0 $mg\,L^{-1}$), nearly 90% for 0.5 and 1.0 $mg\,L^{-1}$; DS-5, from around 40% to more than 90% at 1.0 MPa Flux: NF200 around 10 to 20 $L\,m^{-2}\,h^{-1}$ at 1.0 MPa; 40 to 50 $L\,m^{-2}\,h^{-1}$ for DS-5 at 1.0 MPa	Cakmakci M. *et al.* (2009)
20–100 $\mu g\,L^{-1}$ As(III) and As(V), synthetic	NE-90	Rejection about 89–96% for As(V), 44–41% for As(III); Flux: from 2 to 9 $L\,m^{-2}h^{-1}$ at 0.138 to 0.552 MPa	Nguyen C.M. *et al.* (2009)

50–1000 $\mu g\ L^{-1}$, As(III) and As(V), synthetic water	tailor-made NF	72.3 to 98.6% for As(V), 52.3 to 70.4% for As(III)	Perez-Sicairos *et al.* (2009)
Source waters in Australia	NF90-TFC-S	Average retention 65% for TFC-Sand 78% for NF90	Richards *et al.* (2009)
As(V) from 100–1000 $\mu g\ L^{-1}$, synthetic water	NF90-2540 N30F-2440	Rejection of NF-90 higher than NF30 The As(V) rejection from 94–98.4% for NF-90; 74%–88% for NF90 at pH 3.4 to 10 and 0.6 MPa; The flux for N30F, around 20 L/m^2 h at 0.2 MPa to nearly 80 $L\ m^{-2}\ h^{-1}$ at 0.8 MPa; 20 $L\ m^{-2}\ h^{-1}$ at 0.2 MPa to nearly 60 $L\ m^{-2}\ h^{-1}$ at 0.8 MPa for N30F at $pH = 8$	Figoli *et al.* (2010)
50 $\mu g/L$ of As(III) and As(V), synthetic water	NTR-7450 UTC-70	Rejection for As(V): UTC-70, 95% to 99.2%, NTR-7450, 74% to 82.5% at pressure from 0.2 MPa to 1 MPa, For As(III): UTC-70, 75% to 80.5%. NTR-7450, 13.5% to 21.5% at pressure from 0.2 MPa to 1 MPa; Both membranes can reach the 13.25 $\mu m\ s^{-1}$ at 0.55 MPa	Ahmed *et al.* (2010)
As(V) from 120 to 1026 $\mu g\ L^{-1}$ As(III) from 118 to 985 $\mu g\ L^{-1}$, synthetic water	NF90	Rejection of 96.59% to 98.35% for As(V) and 87% to 94.07% for As(III) at 0.6 MPa, as increasing initial As in feed	Akbari *et al.* (2010)
7.49, 22.47, 37.46 $mg\ L^{-1}$ As(V), synthetic water	NF-300	The rejection of As(V): around 90% to 99.99% with pressure from 1.0 to 5.0 MPa, The flux can reach 3280 $L\ min^{-1}$ at 3.0 MPa with the TDS was 1875 $mg\ L^{-1}$	Harisha *et al.* (2010)
30–400 $\mu g\ L^{-1}$ As(V), groundwater and synthetic water	NF-300	The rejection: 97% for single salt and 95.2% at 0.7 MPa for groundwater, and 1.0 MPa show a As(V) rejection over 95%. The flux: from around 10 $L\ m^{-2}\ h^{-1}$ at 0.2 MPa to nearly 80 $L\ m^{-2}\ h^{-1}$ at 1.0 MPa	Saitua *et al.* (2011)
As(V) 200 $\mu g\ L^{-1}$ As(V)	ESNA-1-K1, NF270, ESNA-1-LF, HODRA-CORE.	The rejection: higher than 94% for the ESNA-1-LF and 37% to 47% at 1 MPa with difference ion concentration; the rejection also higher than 86% for ESNA-1-LF, lower than 50% for HODRA-CORE with difference pressure from 0.4 MPa to 1.2 MPa. The flux of ESNA-1-LF from nearly 10 $L\ m^{-2}\ h^{-1}$ to 40 $L\ m^{-2}\ h^{-1}$; nearly 20 $L\ m^{-2}\ h^{-1}$ to 80 $L\ m^{-2}\ h^{-1}$ for ESNA-1-K1, around 30 $L\ m^{-2}\ h^{-1}$ to 130 $L\ m^{-2}\ h^{-1}$ for NF270 and more than 50 $L\ m^{-2}\ h^{-1}$ to nearly 160 $L\ m^{-2}\ h^{-1}$ for HODRA-CORE with the pressure from 0.4 MPa to 1.2 MPa.	Yu *et al.* (2013)

11.4 HIGH PERFORMANCE NF MEMBRANES

Based on the Donnan-steric pore model (Bowen *et al.*, 1996), separation and permeation characteristics are able to be tuned by the pore size and the surface charges at the active skin layer. Theoretically, it is possible to create a very open nanofiltration membrane with a high permeability as well as high rejection. Arsenic is multivalent, neutral or negatively charged in nature. It is essentially in a relatively low concentration as well. Based on the Donnan exclusion mechanism, a membrane with strong active negative charges or a high charge density repulses negatively charged anions, thus preventing the diffusion of the chemicals through the membrane. Recently, a new type of NF membrane based on this concept was reported by He *et al.* (2012) and Song *et al.* (2013). Different from the commercial NF membranes, this new membrane was prepared by a simple dip-coating process. The coating layer was a tailor-made sulfonated polyether ether ketone (SPEEK) with exceptionally high sulfonation degree (SD), or a high density of surface charges. Instead of a spiral wound module, a hollow fiber membrane module was prepared. A description in detail will be presented in the following sections.

11.4.1 *Sulfonation of PEEK*

Polyetheretherketone (PEEK) is a semicrystalline polymer insoluble in most of the polar and apolar solvent, except concentrated acid, such as sulfuric acid. Figure 11.2 shows the chemical structure of the PEEK. Sulfonation of the PEEK is often used for the preparation of the sulfonated PEEK (SPEEK), which can be used as the coating layer for the preparation of a high permeability, or low energy nanofiltration (LENF) membranes. Sulfonation of the PEEK takes place by the replacement of aromatic hydrogens with $–SO_3H$ groups in a concentrated sulfuric acid. The chemical structure of the SPEEK is shown in Figure 11.2B. The sulfonation procedure is straight forward: starting from mixing the PEEK resins in the concentrated sulfuric acid at a pre-determined concentration and temperature; at the end of the sulfonation, the solution of SPEEK/sulfuric acid is precipitated in an ice water to obtain the swollen SPEEK beads; after the complete rinsing of the sulfuric acid, these beads are then dried at ambient temperature to remove the majority of absorbed water; consequently, the water in SPEEK is completely removed in an vacuum oven for certain period of time and specific temperature to obtain a dry polymer.

Controlling the sulfonation degree (SD) of SPEEK is crucial in designing the separating characteristics of the active separation layer. It is required that the coating layer is soluble in a volatile organic solvent but not in water. In general, SPEEK is soluble in polar solvents, such as NMP, DMAc, DMF, etc., when the sulfonation degree is above a certain value; further increase in the sulfonation degree leads to a SPEEK soluble in a wider range of solvents, such as alcohols, water. There is a narrow range of sulfonation degree at which the SPEEK is soluble in a volatile solvent such as alcohols, but not water. The advantages of being soluble in a volatile solvent are reflected in the quick drying of the coating to form a dense separating layer.

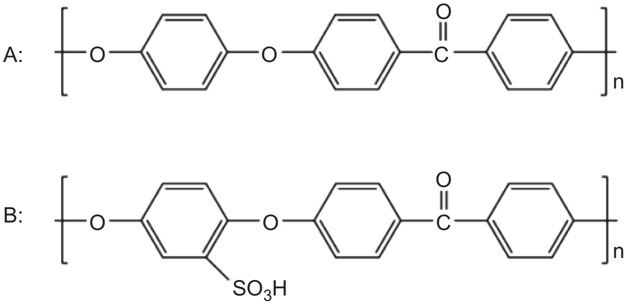

Figure 11.2. Chemical structure of PEEK (A) and SPEEK (B).

Separation characteristics of the composite NF membranes are mainly determined by the charges and the pore size in the SPEEK layer. Higher sulfonation degree (SD) results in a higher rejection towards anions, however, at a higher SD value, the swelling of the SPEEK in aqueous solution is larger, thus leading to a bigger water channels (He *et al.*, 2008) and subsequently lower rejection. Therefore, a balance exists between the sulfonation degree and NF performance. Furthermore the ionic electron conductivity (IEC) is another property of the SPEEK membranes to be considered for evaluating its proton-conducting behavior and it is related to the sulfonated groups present. Selection of PEEK is another important factor for controlling the membrane properties. PEEK is a semi-crystalline and highly solvent stable polymer. It is known that the sulfonation degree and the homogeneity in the sulfonation are related to the sulfonation temperature, the sulfonation time, the approach for precipitation, and the degree of the crystallinity in the polymer, etc. For the crystalline part, the dissolution of PEEK in the sulfuric acid tends to be slower than an amorphous counterpart. This leads to a difference in the sulfonation time in the two parts. Most probably, the amorphous sections will have a higher sulfonation degree than the crystalline sections. At longer reaction time, the degree of sulfonation is higher. It has been reported that the final polymer tends to be inhomogeneous with a wide distribution of sulfonation degree (Wijers *et al.*, 1998). It is thus desirable to select a more homogeneous PEEK polymer for preparation of SPEEK.

11.4.2 *Preparation of composite membranes*

The composite membrane is prepared by dip-coating a porous support membrane with a diluted SPEEK solution. Selection of a suitable solvent is important. The groups of the potential solvents for SPEEK vary with the sulfonation degree (*SD*) and counter ions (Bishop *et al.*, 1985). The solvency strength of the solvents can be expressed by solubility parameter. This parameter is determined by dispersive contribution (δ_d), polar force contribution (δ_p) and hydrogen bonding contribution (δ_h). According to the rule-of-the-thumb, "similar-like-similar", SPEEK is soluble in a polar solvent due to the sulfonic groups. High sulfonation degree may result in a soluble polymer in a solvent of strong hydrogen bonding contribution and polar contribution, such as NMP, DMAc, or even methanol, ethanol and water. Table 11.2 lists the solubility of a SPEEK prepared from a Victrex 450P of Mw 102,000 g mol^{-1}. It shows that SPEEK does not dissolve in solvents such as NMP, DMAc at sulfonation time of 48 h. SPEEK becomes soluble in polar solvents at sulfonation time above 100 h, such as NMP, DMAc, Acetone. Only when the sulfonation time is no less than 140 h, the polymer is ethanol soluble, but still not water soluble. Further increase in the sulfonation time will lead to a water soluble SPEEK. However, for the preparation of a composite nanofiltration membrane, the SPEEK layer should be stable enough in aqueous solution to maintain a stable membrane performance.

Table 11.2. Solubility of SPEEK with different sulfonation time (He, 2001).

Polymers	S-48*	S-100	S-120	S-140
Sulfonation time [h]	48	100	120	140
IEC [meq g^{-1}]	1.21	1.65	2.33	2.79
Sulfonation degree, *SD*	0.38	0.55	0.83	1.03
Solvent	**Solubility****			
NMP	+	–	–	–
DMAc	+	–	–	–
Methanol	+	–	–	–
Ethanol	NC	+	++	–
Acetone	NC	–	–	–
H_2O	NC	+	+	++

*The sulfonation was at 20°C; **NC, no change; –: dissolved; +: swollen; ++: highly swollen.

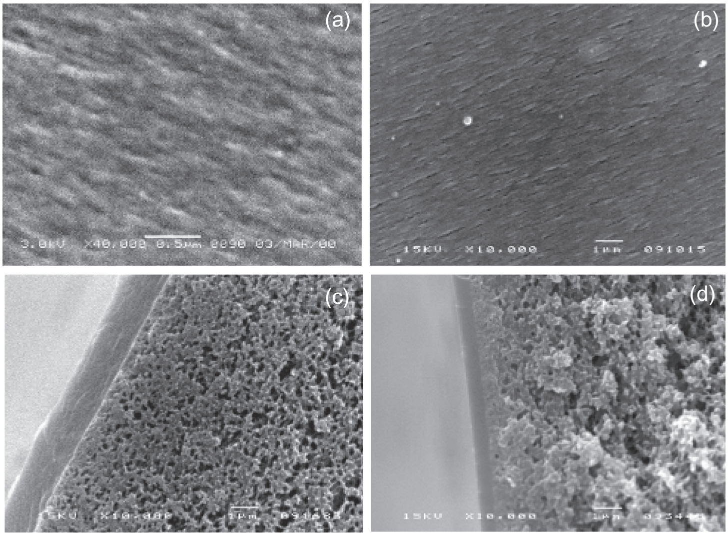

Figure 11.3. Scanning electron microscopy photos of the surface morphology of a PES and PSf hollow fiber membranes and the inner skin layers of the composite membranes. (a) Inner surface of PES membrane (FESEM); (b) Inner surface of PSf membranes; (c) skin layer of composite PES membranes; (d) skin layer of composite PSf membranes. Coating solutions: S-120 at 5 wt%. The pore radius of PES and PSf membranes are 10 nm and 26 nm, respectively (He, 2001).

The second criterion for the preparation of a composite membrane is the choice of the support membrane structure. A wide variety of support membranes is potentially available: ceramic and metallic membranes, polymeric microfiltration and ultrafiltration membranes. From an economic point, polymeric membranes are the primary choice. Besides the membrane materials, the membrane pore size is also critical for the performance of the final composite membranes. In the case of small pore size, the coating solution penetration is shallow, thus forming a thin layer on top of the support surface, instead of deeply penetrated composite. In Figure 11.3, the SEM images of composite membranes prepared with support of different pore size are reported. It appears that for the small pore PES membrane, a thicker layer with a sharp interface (at the SPEEK/PES boundary) is formed. On the polysulfone (PSf) support with a larger pore size, a "thinner" coating is formed on top of the PSf support, which indicates that there is penetration of the SPEEK into the substrate. Furthermore, the wettability of the support membrane also affects the performance of the composite membrane (He *et al.*, 2003). Therefore, the chemical physical properties of the support membrane are important to determine the final performance of the nanofiltration membranes. Other preparation parameters influencing the composite membranes include the polymer concentration, viscosity, contact time, drying temperature, and post-treatment, etc. Readers may refer to the literature (e.g., Song *et al.*, 2013) for detailed information on the basis of the relationship between the process parameters for dip-coating and the membrane performance. Hollow fiber support membranes allow a more compact membrane module and potentially a compact water treatment system.

11.4.3 *Membrane performance for arsenic removal*

Based on a commercial polyethersulfone ultrafiltration hollow fiber membrane, a SPEEK-coated composite membrane was tested for the separation of As(V) from drinking water sources. The characteristics of the support membrane and the composite membrane are listed in Table 11.3. The membrane has typical properties (dimensions, water permeability, pore size etc.) of a UF

Table 11.3. Characteristics of PES ultrafiltration hollow fiber membrane.

Properties	Unit	Value
ID/OD	mm	0.8/1.3
Molecular weight cutoff (MWCO)[1]	Da	70000
Burst pressure	MPa	>1
Maximal temperature	°C	40
pH range during cleaning at 30°C	–	1–13
Pure water permeability[2]	$\mathrm{L\,m^{-2}\,h^{-1}\,MPa^{-1}}$	6000 ± 500
SPEEK coated nanofiltration membrane		
Pore size	nm	1.56
MWCO	Da	6000
Rejection for Na_2SO_4	%	96.2
Rejection for NaCl	%	42.8
Rejection for $CaCl_2$	%	34.0

[1] Rejection for BSA at 90%, [2] Water permeability measured at 20°C. *Salt concentration $=1000\,\mathrm{mg\,L^{-1}}$, trans-membrane pressure = 0.5 MPa, MWCO: molecular weight cutoff.

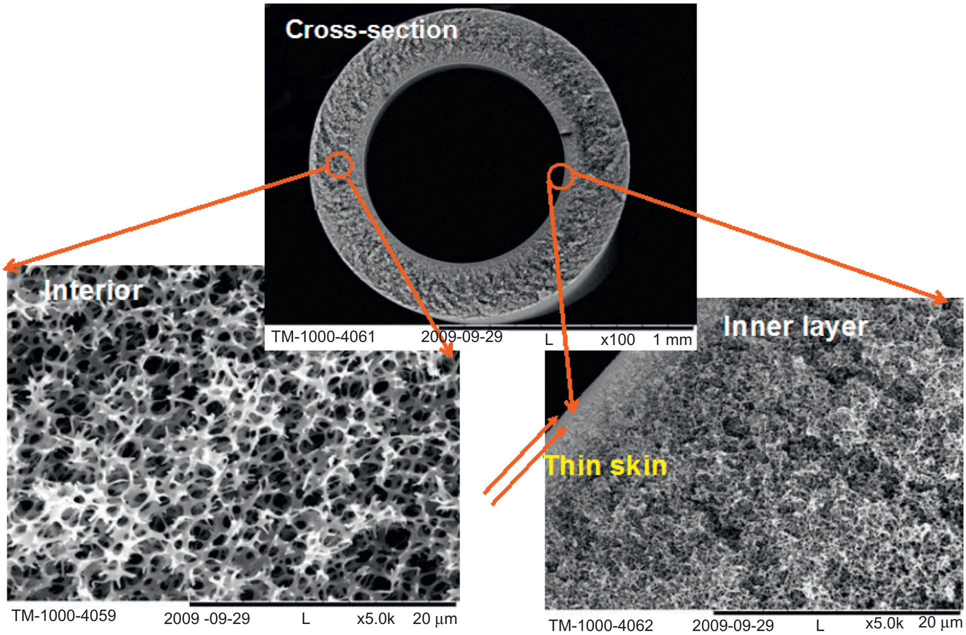

Figure 11.4. SEM photos of polyethersulfone ultrafiltration hollow fiber membrane. The membrane shows a sponge-like morphology with very open interior structure and a rather thin skin layer (Song *et al*., 2013).

membrane as used in a large scale water treatment plant. The coating layer was a tailor-made sulfonated polyether ether ketone (SPEEK) with a sulfonation degree of 0.69 and it is readily soluble in methanol but not in water. As shown in Figure 11.4, this PES membrane has a very open interior morphology and rather thin skin layer and a sponge-like morphology. In Figure 11.5, the composite nanofiltration shows a dense inner surface (the SPEEK coating was located at the inner surface). The nanofiltration membranes show a rejection toward sodium sulfate of 96.2%, but to sodium chloride of 42.8% and to calcium chloride of 34.0%.

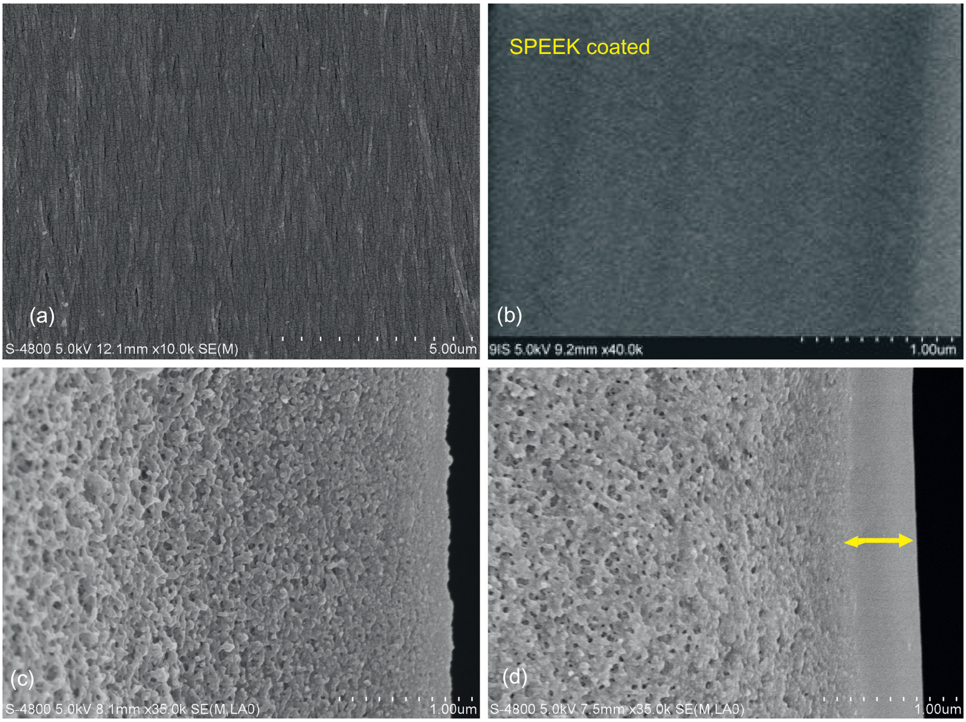

Figure 11.5. SEM photos of the inner surfaces and inner skins of the PES ultrafiltration membrane and SPEEK coated nanofiltration membranes: (a): inner surface of PES membrane; (b): inner surface of nanofiltration membrane; (c): inner skin of the PES membrane; (d): inner skin of the nanofiltration membrane (Song *et al*., 2013).

The rejection against As(V) *versus* the operation pressure of the above composite NF membrane is shown in Figure 11.6. The rejection for the As(V) was about 97% at a transmembrane pressure of 0.3 MPa and a water flux around 32 $\mathrm{L\,m^{-2}\,h^{-1}}$. At a feed As(V) concentration of 360 $\mu\mathrm{g\,L^{-1}}$, one throughout using the nanofiltration membrane results in a permeate water quality slightly higher than the WHO MCL limit of 10 $\mu\mathrm{g\,L^{-1}}$ level. At elevated operation transmembrane pressure, the rejection increases, leading to a lower permeate arsenic concentration. At 0.4 MPa, the permeate As(V) concentration is lower than 10 $\mu\mathrm{g\,L^{-1}}$ and the water flux reaches about 43 $\mathrm{L\,m^{-2}\,h^{-1}}$. These results indicate that the SPEEK-coated nanofiltration membrane is capable of reducing the As(V) at a rather high rejection.

11.5 COST EVALUATION

Cost estimation for the removal of As from drinking water source was pursued. The assumptions and key cost parameters for such a treatment system are listed in Table 11.4. Two scenarios are selected for the evaluation based on two potential cases:

(1) An area of high population density, where tap water is supplied; thus a high capacity is assumed to be 1000 $\mathrm{t\,h^{-1}}$;
(2) An area of low population density, where no tap water is supplied, and the infrastructure is less developed, particularly for remote villages; the drinking water plant may be transported from site to site. Thus, a small capacity is assumed to be 100 $\mathrm{t\,h^{-1}}$.

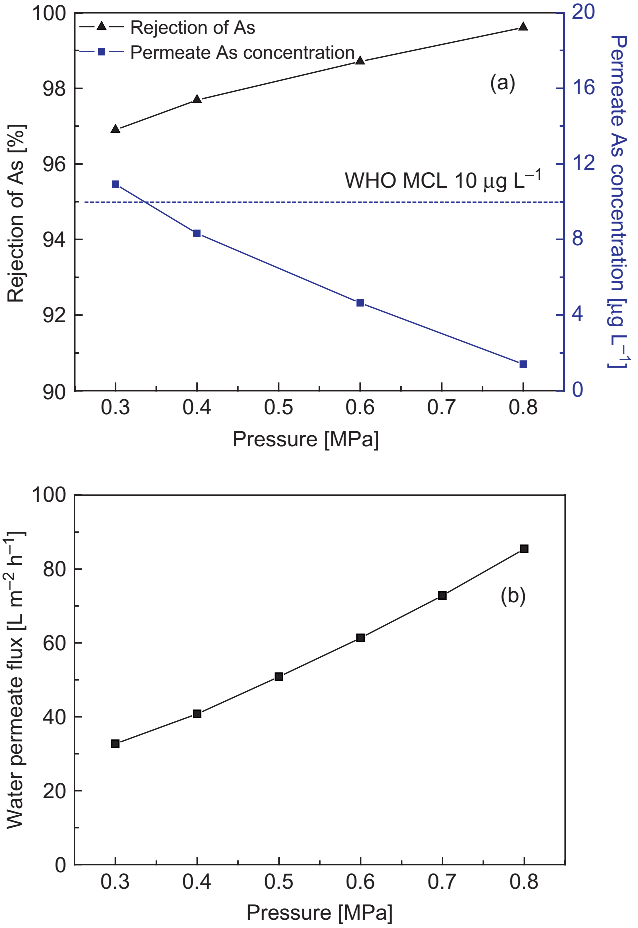

Figure 11.6. Effect of operating pressure on the rejection (a) and water flux (b) of SPEEK nanofiltration membrane. The feed concentration of 360 μg L^{-1}, temperature: 25°C.

The membrane permeability was assumed to be 100 L m^{-2} h^{-1} MPa^{-1} and the operating pressure was 0.5 MPa. Based on an 8 inch (≈20.3 cm) hollow fiber membrane module, the number of membrane modules is estimated to be 715 pieces for the large plant and 72 pieces for small plant (assume an 80% recovery due to low salinity in the feed water). The cost for the membrane module was assumed be 50 US\$ m^{-2}. By adopting the rule-of-thumb in reverse osmosis process, the lifetime of the membrane system was set to be 30 years, and the cost for a membrane system was 3 times the cost of the membranes (Valadez-Blanco *et al.*, 2008). Based on the membrane cost, the cost for the nanofiltration system was 3.75 million US\$ for the large plant and 375,000 US\$ for the small plant.

To justify the assumptions, the estimated cost in power consumption, labor, and membrane replacement was compared with that in a seawater reverse osmosis desalination (SWRO) plant (Atikol *et al.*, 2005). For SWRO, the reported cost for power was 0.04 US\$ m^{-3}, we estimated 0.022 US\$ m^{-3} for our system. The lower cost in energy consumption is mainly due to the low operating pressure and significantly higher water recovery in this system. The cost for pre-treatment was assumed to be lower than seawater plant due to the significantly much better water quality in the drinking water sources. The maintenance cost was adopted from the

Table 11.4. Cost estimation of the nanofiltration membranes in removal of arsenic from drinking water.

	Items	Values		Remarks
Assumptions	System capacity [m^3 h^{-1}]	1000	100	Assume two scenarios: a full scale water treatment plant and a medium size plant loaded on trucks
	Working days [day]	300		
	Membrane lifetime [year]	5		Suitable pre-treatment
	Membrane permeability [kg m s Pa]	2.78×10^{-8}		Based on this work
	*Recovery rate [%]	80		The TDS and scaling potential of surface water is generally much lower than seawater, high recovery rate is possible
	Membrane cost [US$ m^{-2}]	50		Include support membrane and coating
	Module [m^2]	35		8 inch (≈20.3 cm), 1.5 m module
	Module No [pieces]	715	72	
	Operation pressure [MPa]	0.5		Based on this work
	Membrane cost [1000 US$]	1250	125	
	System cost [1000 US$]	3750	375	As a rule-of-thumb, triple the membrane cost (Valadez-Blanco *et al.*, 2008)
	*System life time [years]	30		Assumption based on seawater reverse osmosis desalination plant
	Labor cost [US$ $year^{-1}$]	80000	40000	4 full time operator for large plant and 2 for small plant
	Cost of electricity [U$ kWh^{-1}]	0.1		
Estimated cost	Electricity [US$ m^{-3}]	0.022		Power efficiency = 0.8
	Membrane replacement [US$ m^{-3}]	0.035		
	*Pre-treatment [US$ m^{-3}]	0.018		Quality of the drinking water sources requires less pre-treatment, thus assume half of the cost as seawater desalination
	Manpower [US$ m^{-3}]	0.011	0.056	Based on labor cost
	*Maintenance [US$ m^{-3}]	0.010	0.010	2% of system cost every year
	Depreciation in system [US$ m^{-3}]	0.017		System cost divided by the amount of the annual treated water
	Total cost [US$ m^{-3}]	0.111	0.158	

*Reference (Atikol *et al.*, 2005).

SWRO plant, which might be slightly higher than the real case. Eventually, the replacement for the SPEEK membrane was estimated to be 0.035 US$ m^{-3}, which falls in the range of the SWRO, in which the membrane replacement cost is about 0.018–0.05 US$ m^{-3}. The cost for the SPEEK membrane may decrease if the market becomes large enough to cover the investment in the manufacturing of such membranes. Thus, the cost for membrane may be lower in the future. Less labor was assumed because nanofiltration operates at a much lower pressure than RO and the hollow fiber membrane may perform rather stably. The final gross estimation for the cost of the nanofiltration process in treating one cubic water was 0.113 US$ m^{-3}, for 1000 t h^{-1} plant and 0.158 US$ $m^{-3}$for 100 t h^{-1}, as listed in Table 11.4. The value is significantly lower than a reverse osmosis process. The cost breakdown of the nanofiltration system shows that the membrane cost takes 22% and labor 35% in the small plant, which amounts to 31% and 9.8%, respectively in the large plant. Therefore, it is clear that the main target to lowering the cost is different as the scale of the plant varies: (i) for large nanofiltration system, the power

Table 11.5. Comparison of main arsenic removal technologies.

	Advantages	Disadvantages
Oxidation/precipitation		
Bissen *et al.* (2003); Borho *et al.* (1996); Leupin *et al.* (2005); Wu *et al.* (2013)		
Air oxidation	Relatively simple, low-cost; *in-situ* arsenic removal; also oxidizes other inorganic and organic constituents in water	Slow process, mainly removes arsenic(V) and accelerate the oxidation process;
Chemical oxidation	Oxidizes other impurities and kills microbes; relatively simple and rapid process; minimum residual mass	Efficient control of the pH and oxidation step is needed; Couple with other technologies is needed.
Coagulation/coprecipitation		
Bilici Baskan *et al.* (2010); Cheng *et al.* (1994); Lee *et al.* (2003); Sancha (1999)		
Alum coagulation	Durable powder chemicals are available; relatively low capital costand simple in operation; effective over a wider range of pH	Produces toxic sludges; low removal of arsenic; pre-oxidation may be required
Iron coagulation	Common chemicals are available; more efficient than alum coagulation on weight basis	Medium removal of As(III); sedimentation and filtration needed
Lime softening	Chemicals are available commercially	Readjustment of pH is required
Sorption and ion-exchange techniques	Korngoldm, *et al.* (2001); Mohan *et al.* (2007); Tuna *et al.* (2013)	
Activated alumina	Relatively well known and commercially available	Needs replacement after four to five regenerations
Activated carbon		
Iron coated sand	Cheap; no regeneration is required; remove both As(III) and As(V)	Not standardized; produces toxic solid waste
Ion-exchange resin	Well-defined medium and capacity; pH independent; exclusive ion specific resin to remove arsenic	High cost medium; high-tech operation and maintenance; regeneration creates a sludge disposal problem; As(III) is difficult to remove; life of resins
Membrane techniques		
Nguyen V.T. *et al*. (2009b)		
Nanofiltration	Well-defined and high-removal efficiency	Very high-capital and running cost, pre-conditioning; high water rejection
Vrijenhoek *et al*. (2000)		
Reverse osmosis	No toxic solid waste is produced	High tech operation and maintenance
Kang *et al*. (2000)		
Microfiltration ultrafiltration		Highly dependent on the size distribution of arsenic-bearing particles
Ghurye *et al*. (2004)		

and membrane replacement is critical, thus striving in cutting the membrane cost down and optimization of the energy consumption are crucial; (ii) for a small system as 100 t h^{-1}, the costs for membrane and manpower are more important; therefore, besides the membrane, automatization of the plant to save manpower to the system is critical; nowadays, remote monitoring and control systems are easily accessible and thus saving in manpower is possible. It is expected that at least a 20% decline in the total cost is realistic from the membrane, manpower and further savings in electricity. It should be noted that the costs for interest rates, land, and other peripheral facilities were not taken into consideration, which may affect the total amount slightly.

11.6 SUMMARY AND OUTLOOK

The chapter describes the use of the nanofiltration process for As removal. In general, As(V) is more effectively removed than As(III). Therefore, pre-oxidation of As(III) to As(V) is essential. Most of the arsenic removal systems such as oxidation/precipitation, coagulation/coprecipitation, sorption and ion-exchange techniques require a secondary treatment process to reduce the arsenic concentration to MCL standard. A large amount of chemical reagents is used for adsorption and flocculation processes. These processes produce a large volume of secondary waste with a high concentration of arsenic, which requires further treatment before disposal (Uddin *et al.*, 2007a). MF and UF processes require less chemical reagents, but it is a prerequisite to increase size of the arsenic-containing particles to reach acceptable rejection rate of arsenic, resulting in the secondary solid waste. The removal of arsenic by RO membrane processes needs no coagulants/flocculants, thus no sludge is produced. However, RO processes require high energy input, and the costs of the system are higher compared to other technologies. All these technologies employed for As removal have their merits and weak points (Table 11.5).

The main advantage of NF technology is the combination of a high rejection to arsenic with relatively low energy cost and consequently low cost in systems. In combination of a nanoparticle-based oxidation process, a low energy SPEEK coated composite NF membrane may achieve a high removal rate for the total arsenic from the water sources. Further research should be directed to the design of highly efficient, reliable, easy-to-handle and cost-effective removal technologies for the treatment of arsenic contaminated water, especially for developing regions and countries.

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NOMENCLATURE

A_{k}	porosity of the membrane
c_{i}	concentration in the membrane [$\mathrm{mol\,m^{-3}}$]
C_i	bulk solution concentration [$\mathrm{mol\,m^{-3}}$]
$D_{i,\mathrm{p}}$	hindered diffusivity [$\mathrm{m^2\,s^{-1}}$]
$D_{i,\infty}$	bulk diffusivity [$\mathrm{m^2\,s^{-1}}$]
F	faraday constant [$\mathrm{{}^\circ C\,mol^{-1}}$]
j_i	ion flux [$\mathrm{mol\,m^{-2}\,s^{-1}}$]
J_{w}	water flux (based on membrane area) [$\mathrm{m\,s^{-1}}$]
$K_{i,\mathrm{c}}$	hindrance factor for convection

$K_{i,\mathrm{d}}$	hindrance factor for diffusion
ΔP	applied pressure difference [Pa]
r_p	effective pore radius [m]
R	gas constant [J mol^{-1} K^{-1}]
Re	Reynolds number
T	absolute temperature [K]
x	distance normal to membrane [m]
Δx	effective membrane thickness [m]
X	effective membrane charge density [mol m^{-3}]
z_i	valence of ion
ϕ	steric partitioning term
μ	viscosity of solution [Pa s]
ψ	electric potential in axial direction [V]

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CHAPTER 12

Fate and removal of trace metals/metalloids and fluoride from urban wastewater by membrane bioreactors: pilot and full-scale experiences

Evina Katsou, Simos Malamis, Franco Cecchi & Francesco Fatone

12.1 INTRODUCTION

The membrane bioreactor (MBR) technology is an advanced biological treatment process which has been increasingly adopted in the last fifteen years for the treatment of industrial and municipal effluents (Di Fabio *et al.*, 2013a; Fatone *et al.*, 2008a; Kraemer *et al.*, 2012; Lin *et al.*, 2012;). In the MBR process, as opposed to the conventional activated sludge (CAS) process, the separation of the treated effluent from the solids is achieved through the filtration of the mixed liquor by microfiltration (MF) or ultrafiltration (UF) membranes (Metcalf and Eddy, 2003); hence, settling problems are not encountered. The quality of MBR permeate is superior to that of secondary effluents from the CAS process, as the permeate is completely free from suspended solids; also the MBR achieves physical disinfection, increasing the potential reuse options (Judd, 2006; Malamis and Andreadakis, 2009; Melin *et al.*, 2006; Yang *et al.*, 2006).

Only specific polymers are suitable for membrane filtration in MBRs. This material includes polyvinylidene fluoride (PVDF), polyethylsulfone (PES), polyethylene (PE), polypropylene (PP). The membrane modules that are employed in MBRs are the hollow fibers, the plate sand frame and the tubular ones (Judd, 2006). MBRs have two potential configurations depending on the positioning of the membrane module: the external, side-stream or pressurized MBR and the immersed or submerged MBR (Fig. 12.1). In the external MBR the membrane modules are located outside the tanks and the mixed liquor is fed under pressure to the membrane modules. The filtration process results in the production of two liquid streams: the permeate (i.e., treated water) and the concentrate which is recycled back to the aeration tank. Excess sludge is usually removed by the concentrate stream. In the submerged or immersed MBR the membrane modules are immersed either inside the biological reactors or in a separate filtration tank. Low vacuum is applied to remove the permeate from the mixed liquor. The waste activated sludge can be removed directly from the tanks.

The continuous reduction in the cost of MBR plants and its increase in process effectiveness over the few last years have facilitated their wider application (Coté *et al.*, 2004; Judd, 2006). The main drawback associated with MBR processes is that of membrane fouling due to the gradual deposition of foulants on the membrane surface and interior. As a result, the transmembrane pressure increases for a given permeate flux. Several measures are usually taken to retard membrane fouling, including air scouring of the membrane module, backwash with the produced permeate (or pressure relaxation by intermitted filtration) and frequent chemical cleaning to restore the membrane's permeability. Also, the membrane modules must be replaced after some years, thus increasing the operating expenses. The membrane air scouring significantly increases the system's operational cost. Even with the adoption of these methods fouling gradually builds up and intensive chemical cleaning is required in which case the module is removed from the biological reactor and is placed in a suitable chemical cleaning solution for several hours. The latter method is the most effective for restoring membrane permeability, but shortens the life-time of the membrane.

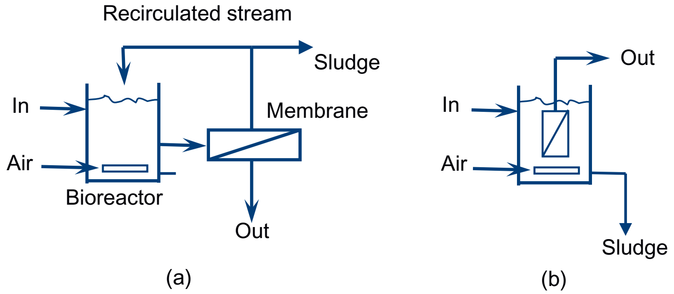

Figure 12.1. (a) External (side-stream) SBR and (b) immersed (submerged) MBR configuration (adapted from Judd, 2006).

12.2 MYTHS AND REALITIES ABOUT MBR

MBR technology is now considered a mature technology since it has been widely implemented for the treatment of municipal and industrial wastewater. MBR technology is an attractive solution for medium size plants, with a population equivalent of 5000–100,000. However, MBR plants still remain an expensive solution for most decentralized schemes. Despite the development of MBR technology, less than 1% of Europe's population was serviced by MBR in 2011 and it is unlikely that this technology will extensively replace CAS in the near future (Lesjean *et al.*, 2011).

Often in research works and in technical reports, the presence of membranes is overemphasized, shadowing the importance of biological processes. The main function of the membranes is to achieve complete rejection of suspended particles. However, in biological reactors the processes of biodegradation, precipitation, adsorption, nitrification/denitrification are the prominent ones (Lesjean *et al.*, 2011). In fact, it is the combined biological treatment with effective filtration that can ensure the desirable effluent quality. Another two misconceptions related to MBR plants is that they can achieve higher removal of organic micropollutants compared to the CAS process and that they produce less amount of excess sludge (Lesjean *et al.*, 2011). These statements are attributed to the operating conditions (i.e., higher solids retention time (*SRT*), higher mixed liquor suspended solids (*MLSS*) rather than the MBR technology per se. Current research has shown that for given *SRT*, organic loading and temperature, the removal of organic micropollutants is similar in MBR and CAS processes (Abegglen *et al.*, 2009; Bouju *et al.*, 2009; Joss *et al.*, 2006; Lesjean *et al.*, 2011; Weiss and Reemtsma, 2008). In terms of sludge production for given operating conditions the MBR processes are expected to produce more sludge than the CAS due to the complete retention of suspended solids by membranes (Lesjean *et al.*, 2011). The advantage of operating the MBR, at very high *SRT* and *MLSS*, is usually offset by the increased operating expenses associated with the higher oxygen requirements of biomass.

As far as heavy metals and metalloids are concerned, the processes of adsorption on activated sludge and precipitation in conjunction with the complete rejection of suspended solids and of colloidal matter may enhance their removal compared to CAS. In addition, the metals/metalloids that have higher affinity with soluble macromolecular ligands may also be rejected to a certain extent by MBR (Comte *et al.*, 2006; Fatone *et al.*, 2008b). Recently, the role of problematic biofilm (fouling and clogging layers) has been investigated and their effect on metals/metalloids removal was outlined (Di Fabio *et al.*, 2013b). In the section that follows the mechanisms involved in trace metal/metalloid removal are discussed in greater depth.

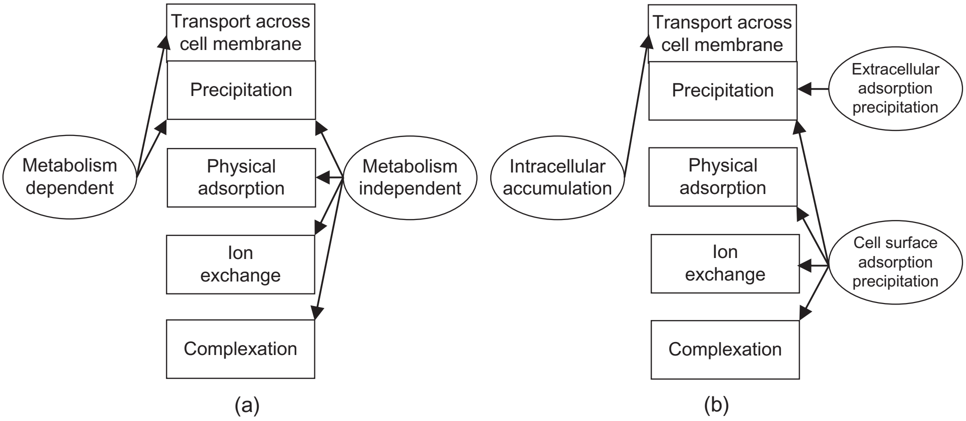

Figure 12.2. Sorption mechanisms for the removal of metals/metalloids from activated sludge according to (a) the dependence of the metal on the metabolism of cells and (b) location where the metal is found (Cho *et al.*, 2010; Veglio and Beolchini, 1997).

12.3 OCCURRENCE, FATE AND REMOVAL OF TRACE METALS, METALLOIDS AND FLUORIDE

12.3.1 *Mechanisms involved*

The main mechanisms involved in the removal of metals/metalloids by activated sludge consist of precipitation, adsorption of soluble metal/metalloid species on the extracellular polymeric substances (EPS), uptake of soluble metal forms by the cells (i.e., bioaccumulation) and for specific metals, volatilization (Brown and Lester, 1979; Kelly *et al.*, 2004). Figure 12.2 summarizes the most prominent mechanisms. The contribution of each mechanism depends on the type and concentration of metals and metalloids, the presence of competing cations, the ionic strength of the liquid phase of the mixed liquor, the *MLSS* concentration and the *SRT*.

The MBR achieves complete retention of the particulate matter, thus ensuring the rejection of the particulate metal/metalloid forms. Precipitates are either entrapped within the sludge flocs as biological precipitates or form due to chemical precipitation (Fig. 12.3). Metal/metalloid adsorption on activated sludge flocs takes place mainly through physicochemical processes. Biosorption is defined as the passive sorption of metals on the negatively charged surfaces of flocs and is independent from bacterial metabolism. Metal sorption is carried out through:

- Complexation on the cell's surface due to the interaction between metals and the sorption sites.
- Ion exchange: cations such as K^+, Na^+, Ca^{2+} and Mg^{2+} which are found in the cell wall and in the cell membrane are exchanged with other metals found in soluble form in the mixed liquor.
- Microprecipitation which takes place due to the interaction between the metals and the cell's surface.

The metals/metalloids are entrapped in the cellular structure and are sorbed onto the available adsorption sites. The adsorption process is mainly accomplished through the diffusion of metals/metalloids inside the bacteria. The available sorption sites consist of EPS and the functional groups of the cell wall like amino, carboxylic and phosphoric groups (Cho *et al.*, 2010; Pagnanelli *et al.*, 2009). The role of EPS is very important in the removal of metals and metalloids from the liquid phase and has been extensively examined (Arican *et al.*, 2002; Brown and Lester, 1982; Guibaud *et al.*, 2009; Guine *et al.*, 2006; Ha *et al.*, 2010; Joshi and Juwarkar, 2009; Santos *et al.*, 2010; Sheng *et al.*, 2010; Toner *et al.*, 2005). Metal precipitation in the form of metal sulfides and hydroxides is favored by the presence of certain bacteria through the production of

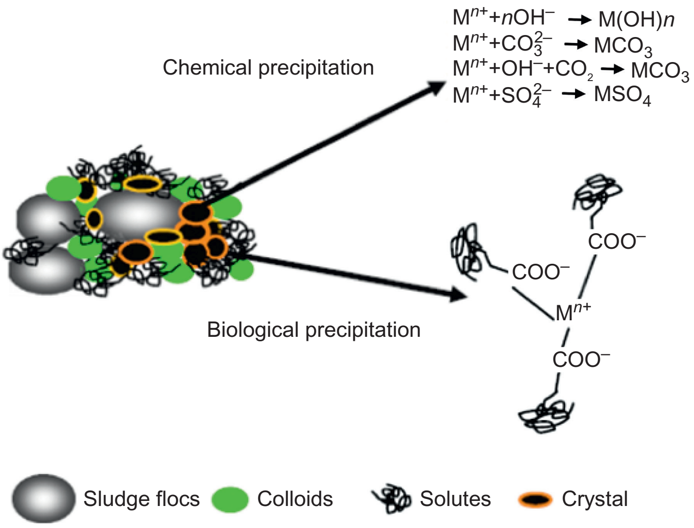

Figure 12.3. Schematic representation of chemical and biological precipitation of metals in activated sludge (Meng *et al.*, 2009).

organic bases and hydrogen sulfide. Laurent *et al.* (2010) mentioned that the contribution of metal precipitation is important to the overall removal of copper and cadmium from activated sludge. Sterritt and Lester (1981) evaluated the influence of precipitation on metal removal and found different behavior depending on the type and initial metal concentration. Precipitation was found to be dominant in the removal of Pb and Cr(III), while Cd, Cr(VI), Mn and Ni mainly remained in soluble form in the mixed liquor. However, it was difficult to determine whether the rejection of lead and chromium (III) was due to independent precipitation or to the uptake of metal precipitates by biomass. In practice the presence of activated sludge enhances precipitation. Stephenson *et al.* (1987) examined metal removal in batch reactors of activated sludge and concluded that the most important removal mechanism for copper and cadmium was the interaction of insoluble metals with the settling sludge. On the contrary, nickel was mainly in soluble form and was not effectively removed. Chang *et al.* (2007) isolated the contribution of precipitation in the removal of metals by CAS and found that a significant part of the metals (11–29%) precipitated. Precipitation may or may not depend on bacterial metabolism. In the first case, metal removal depends on the bacterial immune system, as the microorganisms react in the presence of toxic metal forms resulting in the formation of products that favor metal precipitation. In the second case, precipitation is related to the interaction between the metal and the cell's surface (Ahalya *et al.*, 2003) or to the independent formation of precipitates in the liquid. In practice, it is difficult to distinguish between metal precipitation that takes place independent of the biomass and the one that is entrapped within the activated sludge matrix (Ziolko *et al.*, 2011).

The adsorption of metals by activated sludge takes place in two stages. During the first stage the adsorption of metal ions on activated sludge is fast (3–60 minutes), with the process being passive and reversible. The adsorption on the negatively charged cellular surfaces is rather physicochemical than biological. The second stage takes place at a lower rate (may last for several hours), depending on the viability of cells (Cheng *et al.*, 1975; Ziolko *et al.*, 2011).

Ion exchange is also an important mechanism that results in the uptake of metals by activated sludge. As has been documented by several researchers (Gai *et al.*, 2008; Laurent *et al.*, 2010; Yuncu *et al.*, 2006) during the sorption of Ni, Cu and Zn on bound EPS a simultaneous release of Ca and Mg in the solution was observed indicating that ion exchange also took place. Laurent *et al.* (2010) concluded that ion exchange was a more important metal uptake mechanism by EPS for cadmium than for copper. Pagnanelli *et al.* (2009) found that the carboxylic and amino groups are mainly responsible for the uptake of cadmium and lead in activated sludge. Apart from metal cations, the amino groups can also bind with anionic metal species through the electrostatic interaction or through hydrogen bonds. Brown and Lester (1982) mention that the cellular capsule can significantly affect the removal of soluble copper and cadmium depending on the operating conditions. The EPS composition changes when the cells are exposed to heavy metals. For example, the microorganism *Pseudomonas aeruginosa* excretes EPS when copper is present and as a result an increased retention of this metal is observed (Kazy *et al.*, 2002). Furthermore, the variation on the C/N and C/P ratios influences the adsorption of metals on EPS (Brown and Lester, 1982; Yuncu *et al.*, 2006). The metals concentration is also very important; Li (2005) found that the increase in iron concentration in the mixed liquor affects the EPS composition. Certain bacteria in activated sludge do not produce capsules or extracellular material and the metals are sorbed on the cellular wall due to adsorption and/or accumulate in the cytoplasm where they form complexes with ligands having the highest affinity for metals. Also, certain metals have a tendency to accumulate at the cellular membrane.

Another important mechanism of metal/metalloid uptake is that of bioaccumulation which depends on the cell's metabolism and is carried out by living cells. The soluble metals penetrate the cell membrane and enter the cell where they accumulate (Malik, 2003). This mechanism requires the consumption of energy (Wang and Chen, 2006). Several researchers believe that this mechanism has a very limited contribution to metal removal in CAS and MBR processes (Aksu *et al.*, 2002; Lamb and Tollefson, 1976; Patrick and Loutit, 1976; Santos *et al.*, 2010), particularly when the metal concentrations in the mixed liquor are significant. Living cells are sensitive to their exposure to significant metal concentrations and as a result the intracellular accumulation of metals is low (Vijayaraghavan and Yun, 2008).

The contribution of intracellular accumulation to the removal of metals/metalloids depends on the operating conditions, since higher *SRT* usually increase the metal uptake. The metals diffusion is adversely affected by the presence of metal cations having the same charge and similar ionic radius. Rudd *et al.* (1983) found that the operating conditions are more important than biomass activity in the removal of metals, with bulking sludge resulting in higher metal sorption. Figure 12.2 summarizes the main sorption mechanisms involved in metal/metalloid removal by biomass.

The conversion of specific metals/metalloids to volatile forms is due to microbial action. This process can take place for the elements that can be converted to organometallic forms through methylation. These elements include As, Hg, Pb, Se and Te. The methylation in wastewater treatment plants is usually limited (Goldstone *et al.*, 1990; Santos and Judd, 2010).

12.3.2 *Influential parameters*

The fate and removal of trace metals/metalloids in biological wastewater treatment plants depends on a variety of parameters including (Lester, 1987; Santos *et al.*, 2010):

- Operating parameters such as *SRT*, dissolved oxygen (DO), *MLSS*, sludge volume index (SVI), suspended solids removal. The two last parameters are important in CAS processes where secondary clarification is employed for the solids/liquid separation (Rossin *et al.*, 1982; Santos and Judd, 2010; Sterritt and Lester, 1981).
- Physicochemical parameters including the type, species and initial concentration of the metals, the type and concentration of ligands, the presence and concentration of competing cations (Comte *et al.*, 2008; Kempton *et al.*, 1987a; 1987b; Santos and Judd, 2010; Stephenson and Lester, 1987).
- Biochemical parameters with the most important one being the concentration and content of EPS (i.e., bound/soluble, proteins/carbohydrates) (Comte *et al.*, 2008; Pagnanelli *et al.*, 2009; Santos and Judd, 2010). Other biochemical parameters are the ligands that are produced through bacterial activity, products from cell lysis, bacterial species that favor metal uptake.

The aforementioned parameters define the distribution of heavy metals/metalloids between the solid and the liquid phase (Nelson *et al.*, 1981). At relatively high *MLSS* concentrations the number of available sorption sites increases and consequently metal sorption and entrapment by sludge flocs may also increase. Furthermore, at higher *SRT* the metal removal is favored since the concentration of certain organic chelators in the mixed liquor decreases due to more effective biodegradation (Santos *et al.*, 2010). However, at very high *SRT*s the amount of waste sludge is very low and this may result in a potential saturation of the sorption sites and a limited metal rejection. On the contrary, at lower *SRT* and lower *MLSS* concentrations the wasting of higher amounts of sludge results in higher bacterial activity resulting in new, unsaturated sorption sites for metals (Crane *et al.*, 2010). At very high *SRT*, conditions of expended aeration prevail resulting in the deflocculation of metabolic bacterial products and of EPS. This increases the concentration of metals in the liquid phase and decreases their retention by MBR (Santos *et al.*, 2010). The decrease in the removal of metals at very high *SRT* is also partly attributed to the increased production of organic chelators, which bond with metals and increase their solubility. As a result, metals remain in the liquid phase and can penetrate through the UF/MF membranes.

The presence of metabolic by-products of activated sludge at high *SRT* has been observed by several researchers (Baskir and Hansford, 1980; Saunders and Dick, 1981). Sterritt and Lester (1981) and Rossin *et al.* (1982) have shown that these substances can maintain the metal solubility. Liao *et al.* (2001) observed changes in the activated floc surface at high *SRT* as the flocs become more hydrophobic and negatively charged, thus affecting metal removal. Kempton *et al.* (1983) investigated the impact of *SRT* on metal solubility, metal removal and accumulation in CAS processes. The increase of *SRT* from 3 to 18 days and the consequent increase of *MLSS* resulted in a gradual decrease of metal solubility in the mixed liquor and a greater accumulation of metals in activated sludge. Lawson *et al.* (1983) noted the high affinity of Cd, Cu, Co, Mn, Ni, and Ti for *MLSS*, which was highest for copper and cadmium. The researchers mention that the amount of metals sorbed per unit mass of activated sludge reduces as the *MLSS* concentration increases. This shows that the activated sludge has a limited sorption capacity for metals. Similar results have been reported by Brown and Lester (1982) and Cheng *et al.* (1975).

EPS consist of several negatively charged sorption sites which are available for metals and for organic substances such as aromatic, aliphatic in proteins and the hydrophobic regions in carbohydrates (Flemming and Leis, 2002). Several functional groups in EPS such as carboxylic, phosphoric, sulfhydryl, phenolic and hydroxyl groups can form complexes with heavy metals (Ha *et al.*, 2010; Joshi and Juwarkar, 2009; Liu and Fang, 2002). EPS protect to a certain extent the cell from the potentially toxic action of metals since they can adsorb different types of metals (Arican *et al.*, 2002). The bonds created between metals and EPS are strong. The EPS composition impacts on the activated sludge selectivity towards specific metals instead of other ones. Consequently, the EPS concentration and composition significantly impacts on the metal removal from MBR and CAS processes. The increase of *SRT* usually results in a decrease of EPS concentration (normalized per g VSS) since the low availability of organic substrate results in the consumption of some EPS (Malamis, 2009; Zhang *et al.*, 2006). However, the increase in *SRT* for given HRT results in an increase of *MLSS* concentration and consequently the total EPS content given as $\mathrm{mg\,L^{-1}}$ increases due to the presence of more biomass. Increased EPS concentration favors metal removal as more sorption sites are available.

Rossin *et al.* (1982) concluded that the increased metal removal at high *SRT* of CAS processes is due to the increase in the *MLSS* concentration, to the change in the composition of EPS and the metal species. *SRT* changes influence the distribution between the bound and the soluble EPS, the biomass concentration in the mixed liquor and the bacterial population. Changes in bacterial populations are accompanied by changes in the composition of the bacterial cell surface and in the metabolic products of the cell which are released in the liquid phase. Also, very high *SRT* result in conditions of extended aeration and in the deflocculation that increases the secretion of EPS and metal solubility.

The work of Comte *et al.* (2008) demonstrated that the EPS which mainly consist of proteins and carbohydrates favor the uptake of lead compared to copper due to the higher affinity of lead to form complexes with ligands that are composed of -O and -N. The contribution of each active group in the removal of specific metals depends on the number of available sorption sites, the accessibility for the metal cations to these sites, the chemical composition of the sites and the selectivity of the sorption sites for these metals. Soluble EPS (i.e., SMP) may be able to bond more easily with metals than bound EPS (Comte *et al.*, 2006; Pan *et al.*, 2010). The latter is attributed to the higher proportion of proteins in SMP which increase their potential bonding with metals. The SMP-metal bonding increases the proportion of metals found in the liquid state and thus decreases their rejection by the MBR and CAS processes (Holakoo *et al.*, 2006).

The presence of soluble organic and inorganic ligands in the mixed liquor and the formation of complexes with metals impacts on their removal and decreases the proportion of metals that can be sorbed to activated sludge. The ligands in the mixed liquor form complexes with metals and only a small proportion of the metals remain in ionic form (Cantwell *et al.*, 1982; Laxen and Harrison, 1981; Sterritt and Lester, 1985). The extent depends on the complexation potential of the soluble ligands found in the mixed liquor with the metals (Stephenson and Lester, 1987).

The pH critically affects metal sorption on activated sludge. An increase in the pH introduces OH^- ions which form complexes with metals, and results in the deprotonation of organic ligands and of the surface functional groups of bacteria which are potential sorption sites for metals (Aksu *et al.*, 2002). At pH values higher than the isoelectric point, the activated sludge is negatively charged and the ionic state of ligands favors the metal uptake. At pH lower than the isoelectric one, the cellular surfaces become positively charged since H^+ ions are introduced and as a result the uptake of metal cations is inhibited. At the operating pH of biological wastewater treatment plants (i.e., 6.7–8.5) the activated sludge is negatively charged and thus metal adsorption is more favorable (Arican *et al.*, 2002; Comte *et al.*, 2008). Also, ion exchange is more effective when fewer protons compete with metal cations for the available sorption sites. Changes in the pH may also affect the selectivity order of activated sludge for the different metals which are present in the mixed liquor (Comte *et al.*, 2008). Changes in pH within the normal range of biological wastewater treatment processes can affect the metal solubility of specific metals and thus increase/decrease the rejection of the metals by MBR. This depends on the type of metal and its interaction with biomass. The results from the work of Comte *et al.* (2008) have shown that even small changes in the pH can affect the metal precipitation on the surface of activated sludge.

Pagnanelli *et al.* (2009) found that the dominant removal mechanism for Cd was adsorption and for Pb precipitation. Karvelas *et al.* (2003) found that in wastewater treatment plants, the majority of copper, chromium, cadmium, zinc and particularly lead are in particulate form, while manganese and particularly nickel remain mainly in the liquid phase. Nickel has a low affinity for suspended solids and has the tendency to form soluble complexes (Karvelas *et al.*, 2003; Sorme and Lagerkvist, 2002). In agreement with this, Buzier *et al.* (2006) observed that Cu, Pb, Cd and Cr are found mainly in particulate form, while Ni and Co are in soluble species. Several studies have shown that the concentration of the soluble metal forms in the mixed liquor is similar or higher to the influent soluble metal concentration (Buzier *et al.*, 2006; Karvelas *et al.*, 2003; Santos *et al.*, 2010). This could be attributed to the formation of soluble complexes between the metals and certain ligands thus maintaining the metals in their soluble form and favoring the release of metals from the solid to the liquid phase through biochemical processes such as cell lysis (Buzier *et al.*, 2006).

The oxidation state of metals significantly impacts on their removal. The most prominent example is chromium. The trivalent chromium is usually removed in CAS by 70−>90% while hexavalent chromium only by ~15–25% (Imai and Gloyna, 1990; Lester, 1987; Stasinakis *et al.*, 2003). In the case of manganese, the conversion of soluble Mn^{2+} to insoluble Mn^{4+} during biological treatment results in its effective removal by CAS (Karvelas *et al.*, 2003). Metal removal is also influenced by the size distribution of activated sludge particles. Chen *et al.* (1974) found that 50% of Cu, Zn, Cd, Cr and Hg was sorbed to flocs having size larger than 8 μm. On the other hand, 50% of Ni, Pb and Mn was sorbed to flocs having a size smaller than 8 μm which are associated with poor settling characteristics.

12.3.3 *MBR pilot and full scale experiences*

Table 12.1 summarizes the most important studies concerning the removal of metals/metalloids from municipal wastewater using MBR. In several cases the metal removal is significant showing that the trace metals are mainly in particulate form.

The results summarized in Table 12.1 show a general tendency in the removal of trace metals/metalloids which follows the order: As $<$ B $\approx$ Se $<$ Co $<$ Ni $<$ Pb $<$ Zn $<$ Cd $<$ Cu $<$ Ba $<$ Mg $<$ Cr $<$ Fe $<$ Ag $\approx$ Al $\approx$ Hg $\approx$ Sn. However, this order cannot be generalized since variations are observed depending on the specific environmental and operating conditions, the mixed liquor characteristics and the composition of municipal wastewater. Although the composition of municipal wastewater is rather stable in terms of organic content and macronutrients, its composition in trace metals can vary significantly in the order of $\text{ng L}^{-1}-\mu\text{g L}^{-1}$.

Fatone *et al.* (2008b) found that copper and chromium are effectively removed by MBR, while the removal of nickel is lower. Yang *et al.* (2009) found that the rejection of Fe and Mn was very effective by MBR with removal efficiencies being 99 and 92.3% respectively. Dialynas and Diamadopoulos (2009) operated an MBR at $MLSS = 5\text{ g L}^{-1}$ and found that lead and nickel were completely rejected by the MBR, showing that these metals were in particulate form. The removal of chromium was 89% and that of copper much lower (i.e., 49%) showing that it was mainly in soluble forms. Malamis *et al.* (2012) found significant variations in the removal efficiencies of metals in a pilot scale MBR used to treat municipal wastewater which was attributed to fluctuations in the mixed liquor pH, the *MLSS* concentration and the initial metal concentration. The authors concluded that usually the higher metal removals were obtained when at least one of the following was observed: high pH, high *MLSS*, low competing cation concentration and relatively high concentrations of the metals under examination. Specifically, lead removal ranged from 50–98%, copper from 76–99%, Fe from 62–98%, Mn from 64–93%, chromium from 66–92, Zn from 49–99% and nickel from 51–86%. The reported sequence of average metal removal by MBR was Cu $>$ Fe $>$ Mn $>$ Cr $>$ Zn $>$ Pb $>$ Ni and is in good agreement with the order Hg $>$ Cu $>$ Cr $>$ Zn $>$ Cd $>$ Pb $>$ Ni given by the review of Santos and Judd (2010). Fatone *et al.* (2006) found similar removal for Cu, Pb and Cr with those found by Carletti *et al.* (2008) and Malamis *et al.* (2012). Yang *et al.* (2009) found higher removal of iron and manganese compared to the work of Malamis *et al.* (2012). For municipal wastewater there is no study showing a clear trend between the removal of trace metals and the operating parameters.

Bolzonella *et al.* (2010) distinguished three groups of trace metals/metalloids depending on their tendency to be removed from municipal wastewater with MBR or the CAS process: (i) metals/metalloids which are easily removed (i.e., removals $>$75% for Al, Ag, Ba, Cd, Cr, Cu, Fe, Hg, Sn, V), (ii) yhose which partially rejected (i.e., removal efficiencies of 40–60% for Co, Mn, Ni, Pb, Zn) and (iii) those which are very difficult to remove (i.e., removal efficiencies $<$40% for As, B, and Se) (Innocenti *et al.*, 2002). Innocenti *et al.* (2002) reported that at pH $<$ 8, the Cd(II) ion is the dominant form (found in more than 95%) and this facilitates its adsorption on sludge (Leyva-Ramos *et al.*, 1997). The high affinity of Cu for organic and humic substances can explain its high rejection by MBR processes. The insufficient removal of B and Se is usually not a serious concern, as these trace metals are met in very low concentrations.

Innocenti *et al.* (2002) studied metal removal in an MBR at *SRT*s of 10, 190 and >200 d for *MLSS* of 3.7, 9.0 and 16.6 g L^{-1} respectively. The increase of *SRT* from 190 d to $>$200 d increased the removal of most metals (i.e., Zn, V, Ni, Mn, Fe, Co, Ba, Al). However, for some metals (i.e., Cu, Pb) the opposite trend was obtained and for some metals/metalloids no significant change was observed (i.e., As, Se, B). The increase of *SRT* in an MBR from 10 to 30 days resulted in an increase of chromium removal from 56 to 81% (Conklin *et al.*, 2007), while the *SRT* increase from 11 to $>$1000 d resulted in an increase of Ni from 40 to 89% and of Pb from 50 to $>$98% (Cecchi *et al.*, 2003; Fatone *et al.*, 2008b). Cecchi *et al.* (2003) found that the MBR removed Cd, Cu, Pb, Ni and Zn at $>$50%, 90%, 88%, 50% and 51% respectively and observed that the increase in *SRT* enhanced the removal of lead, nickel and zinc, while it did not impact on copper removal. Fatone *et al.* (2008b) did not find any increase in metal removal by an MBR operating

Table 12.1. Trace metals/metalloids concentration [$\mu g\,L^{-1}$] and removal efficiencies [%] in municipal wastewater by MBR technology (adapted from Santos and Judd, 2010 and extensively integrated by the authors).

	Cd	Sn	Mn	Ag	Al	V	Ba	As	B	Se	Co	Cr	Cu	Pb	Ni	Zn	Fe	Hg	Conditions	Reference
Concentration	0.3				1980			1.8				18.8	43.4	9.6	9.7	427	1763	7.9	*MLSS*: 4.8–9 g L^{-1}	Fatone
Removal	>27				98			48				75	95	74	86	94	97	94	*SRT*: 40–60 d	*et al.* (2006)
Concentration	1.8							2.7				38	56	62	28	–		2.8	*MLSS*: 4 g L^{-1}	Fatone
Removal	>90							29				>95	85	58	40	–		>95	*SRT*: 11 d	*et al.* (2008b)
Concentration	1.8							2.7				38	56	62	28	–		2.8	*MLSS*: 9 g L^{-1}	
Removal	>90							37				>95	89	63	46	–		>95	*SRT*: 200 d	
Concentration	1.8							2.7				38	56	62	28	–		2.8	*MLSS*: 18 g L^{-1}	
Removal	>90							33				>95	72	50	66	–		>95	*SRT*: >1000 d	
Concentration	1.8							2.7				38	56	62	28	–		2.8	*MLSS*: 16 g L^{-1}	
Removal	>90							35				>95	90	70	64	–		>95	*SRT*: >1000 d	
Concentration	0.5				1592			2				18.5	53.9	9.6	8.7	461	1766	7.9	*SRT*: 55–67d	Fatone
Removal	>50				>97			65				75	96	74	79	>90	>97	94	HRT: 8 h *MLSS*: 4.0–5.6 g L^{-1}	*et al.* (2005)
Concentration	1.0											–	53	50	74	274			*SRT*: 190 d	Cecchi
Removal	>50											–	90	88	50	51			HRT: 14 h	*et al.* (2003)
Concentration	1.0												53	50	74	274			*SRT*: >300 d	
Removal	>50												79	>98	89	94			HRT: 14 h	
Concentration	–											–	–	–	–	–			*SRT*: 190d	Innocenti
Removal	>99		78	>99	∼85	∼47	∼78	∼38		∼30	∼47		89	65	45	54	∼86		HRT: 14 h	*et al.* (2002)
Concentration	–												–	–	–	–			*SRT*: >200 d	
Removal	>99		90	>99	>99	∼90	∼90	∼35	∼28		∼78		72	50	65	80	∼98		HRT: 14 h	
Concentration	–											–	–	>68	–	–			*SRT*: 10 d	Conklin
Removal	–											56	75	–	32	59			–	*et al.* (2007)
Concentration	–											–	–	–	–	–			*SRT*: 20 d	
Removal	–											–		–	–	–			–	
Concentration	–											–		–	–	–			*SRT*: 30 d	
Removal	–											85	89		–	66			–	

(*continued*)

Table 12.1. Continued.

	Cd	Sn	Mn	Ag	Al	V	Ba	As	B	Se	Co	Cr	Cu	Pb	Ni	Zn	Fe	Hg	Conditions	Reference
Concentration	–											56.6	9.8	8.6	16.6	1233				Carletti
Removal	–				89							72	90	74	72	83	89	92		*et al.* (2008)
Concentration	–											–	–	–	–	–			*MLSS*: 18.4 g L^{-1}	Cattaneo
Removal	80											–	–	90	95	–			HRT: 7.9 h	*et al.* (2008)
Concentration	–											<1–746	<1–1345	<1–16	<1–34	–			*MLSS*: 5.0 g L^{-1}	Dialynas and Diamadopoulos
Removal	–											89	49	100	–	–				(2009)
Concentration	0.9	3.3	118	101	2121	4.7	145	8.7	439	3.5	2.6	18	79	51	71	306	4232	1.3	*MLSS*: 9.2 g L^{-1} *SRT*: ~200 d	Bolzonella *et al.* (2010)
Removal	>99	>99	77	99	90	79	82	31	– 56	79	62	>99	94	88	48	77	90	>99		
Concentration	0.9	3.3	118	101	2121	4.7	145	8.7	439	3.5	2.6	18	79	51	71	306	4232	1.3	*MLSS*: 16.6 g L^{-1} *SRT*: >600 d	
Removal	>99	>99	84	>99	98	79	86	43	87		62	>99	49	16	65	77	94	>99		
Concentration													10–40			100–400			*MLSS*: 9.72 g L^{-1}	Crane
Removal													48			8			*SRT*: >40 d	*et al.* (2010)
Concentration			124									20	40	98	10	411	235		*MLSS*: 5.91 g L^{-1}	Malamis
Removal			82									80	90	73	67	75	85		*SRT*: 15 d	*et al.* (2012)
Concentration																				Yang
Removal			95														>99.9			*et al.* (2009)
Concentration	≤3	3–10	3–10		10–1600	≤3	10–100	3–10		≤3	≤3	10–100	10–100	10–100	10–100	100–1600	100–1600			Choubert *et al.* (2011)
Removal	~56	~93	~57		~97	~2	~54	~23		~59	~2	~75	~82	~78	~41	~55	~80			

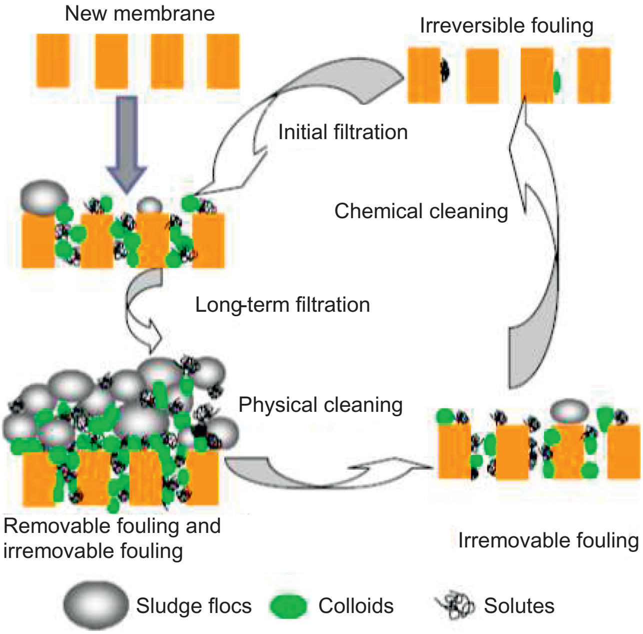

Figure 12.4. Diagrammatic representation of foulants on the membranes of an MBR during the various processes (i.e., filtration, physical and chemical cleaning) (Meng *et al*., 2009).

at very high *SRT* (>1000 d) during the co-treatment of municipal and industrial effluents. At the same time, the energy demands at such high *SRT* are higher (Judd, 2006; Germain *et al*., 2007). Bolzonella *et al.* (2010) concluded that the *MLSS* increase in an MBR from 9.2 to 16.6 g L^{-1} did not change significantly metal removal. It seems that *SRT* is not influential in the removal of metals which have high affinity to be adsorbed on activated sludge and are therefore retained at very high levels irrespective of the operating conditions. Such behavior has been demonstrated by cadmium (Innocenti *et al*., 2002). To conclude, most research works examining the impact of *SRT* and *MLSS* have found that an increase of these two parameters can enhance metal removal. However, very high *SRT* does not seem to favor metal removal.

Di Fabio *et al.* (2013b) studied the characteristics of problematic biofilms (i.e., fouling and clogging layers) with regards to the removal and fate of trace metals and metalloids (contents well under 100 µg L^{-1} during the long-term operation of a pilot-scale MBR for the treatment of real wastewaters from a large petrochemical industrial area. Results showed that a clogging layer was more effective than suspended activated sludge in the biosorption of As > Zn > Ni > Cd > Sb > Fe > Se due to the synergic effects of extracellular polymeric compounds and metal-resistant bacteria. Compared to the suspended activated sludge, the clogging layer (aerobic and anaerobic) enhanced the biosorption of very toxic substances such as As, Cd and Ni. In fact, the metal contents for suspended activated sludge and clogging sludge (aerobic and anaerobic) were respectively: 1.0 *vs*. 7.9–7.4 mgAs/kg total solides (TS); <0.01 *vs*. 1.5–2.2 mg Cd/kgTS; 18.0 *vs*. 58.8–71.7 mgNi/kgTS. Figure 12.4 summarizes diagrammatically the deposition of sludge matter due to reversible and irreversible fouling.

12.3.4 *Arsenic, fluoride and uranium in activated sludge systems*

Limited information exists concerning the occurrence, fate and removal of trace uranium (U) in/from urban wastewaters. In fact, effluents from mining and industrial processes are a major source of this metal contamination in water. On the other hand, arsenic inputs originate from natural background sources and from household products such as washing products, medicines, garden products, wood preservatives, old paints and pigments (European Commission, 2001).

The removal of As is usually very low (0–37%) by MBR processes (Innocenti *et al.*, 2002). Nevertheless, the As concentrations in wastewater are generally below the limit of 10 $\mu g\,L^{-1}$ specified in the WHO drinking water guidelines. (Bolzonella *et al.*, 2010; Cecchi *et al.*, 2003; Mohan and Pittman, 2007). The low removal of As is probably attributed to its particular chemistry in wastewater processes (Carbonell-Barrachina *et al.*, 1999; Meng *et al.*, 2001). At the pH range of 6–8 and redox values range from −100 to +300 mV that are typical for activated sludge processes Arsenic is usually dominant in the form of arsenate (As(V)) and arsenite (As(III)). Arsenate can be present in various protonated states, such as $H_2AsO_4^-$ and $HAsO_4^{2-}$ that are soluble and negatively charged and thus they do not react with the binding sites of activated sludge. Arsenite is present as a neutral molecule (H_3AsO_3) with low chemical reactivity (Bolzonella *et al.*, 2010). Hence, As can only be partially removed in the activated sludge process, and other processes/technologies should be integrated in order to enhance its removal. Di Fabio *et al.* (2013b) found that, compared to activated sludge suspended in MBRs, the clogging sludge enhanced the bio-sorption of heavy metals according to the descending order: As > Zn > Ni > Cd > Sb > Fe > Se. Thus, very remarkable enhanced biosorption was obtained with amphoteric and toxic substances such as the As.

Choubert *et al.* (2011) found that the removal of As, Se and U in nine full scale wastewater treatment plants (including one MBR) ranged from 0–50% (average 20%), 40–75% (average of 60%) and 55–70% (average of 60%) respectively. The authors found that the concentration of Se and U in influent municipal wastewater was very low and ranged from 1–4.5 $\mu g\,L^{-1}$ and 0.1–1 $\mu g\,L^{-1}$ respectively.

Membranes can remove As through filtration by adsorption of As-bearing compounds on their surface. Electric repulsion of UF plays an important role in As rejection beyond that achievable with only pore size-dependent sieving and that of uncharged membranes showing poor rejection of both As(V) and As(III). The scarce removal of As could be due to the decrease in electrostatic forces by adsorption of organic matter to the membrane surface that can reduce the surface charge of the membrane and increase the repulsion towards negatively charged As compounds. Thus, it seems necessary to integrate the UF with other processes in order to achieve effective As removal. Alternative options can be the use of granular or powder activated carbon (Mnju *et al.*, 1998; Jiang, 2001) and metallic salts of La, Al, Ca and Fe (Sengupta *et al.*, 2001; Sutherland and Woolgar, 2001; Tokunaga *et al.*, 1999) that result in enhanced removal of arsenate and arsenite species. In any case, for influents containing high concentrations of As, B, and Se, some form of tertiary treatment is required in order to reduce their content in the reclaimed water (Bolzonella *et al.*, 2010).

Fluoride exists as a natural occurring anion (F^-) in many waters, or can be added to water artificially as a fluoro-silicate solution, since in some countries it is used for water fluoridation. Fluorine up to 4% is also present in aluminum and phosphate fertilizers (Velizarov *et al.*, 2004). The prescribed concentration allowable in drinking water is 1.5 $mg\,L^{-1}$. However, natural F^- concentration in groundwater can reach values higher than 40 $mg\,L^{-1}$, and may cause health related problems wherever groundwater is used for drinking purposes. Studies on the ecotoxicology of fluorides demonstrated that F^- is not removed by primary sewage treatment methods (Wallis *et al.*, 1996). Marier and Rose (1977) have shown that primary treatment of raw wastewater would have little or no effect on F^- levels, but secondary treatment (presumably biological) would result in F^- removal of up to 70%. Smith and Moollan (2004) demonstrated that the average removal achieved ranged from 0–44%. This fluctuation could be due to plant performances.

From the data of another treatment plant, where approximately half the wastewater is treated using an activated sludge system and the other half by trickling filters, the F^- removal was similar (Smith and Moollan, 2004).

12.3.5 *MBR versus CAS processes*

MBR processes retain particulate and colloidal matter. Thus, substances, including metals and metalloids that are bound-adsorbed to particulate and colloidal substances are effectively removed by the MBR process. In the CAS process the particulate metals attached to the suspended solids that escape into the final effluent are not removed. Also colloidal substances may not settle and escspe in the effluent. Thus, it is expected that MBR processes will have higher performance concerning the removal of heavy metals from municipal wastewater compared to CAS.

Some research studies identify a 'small' superiority of MBR over CAS for removing heavy metals from domestic effluents. Santos and Judd (2010) summarize the findings of various studies in order to compare the performance of MBR and CAS for the removal of heavy metals from municipal wastewater and conclude that MBR achieve steady but not significantly higher metal removal than that of the CAS (64–92% instead of 51–87%). Similarly, Bolzonella *et al.* (2010) found that MBR improve heavy metal removal by 10–15% due to the more efficient retention of suspended solids. However, the performance of CAS and MBR in terms of metals removal wasnotcompared under the same operating conditions, since the CAS operated at lower *SRT* (12 d) and *MLSS* (2.7 g L^{-1}) compared to the MBR systems (*SRT* $\sim$200 d and $>$600 d and *MLSS* 5.8 g L^{-1} and 8.6 g L^{-1}). The relatively higher metal removal accomplished by MBR compared to CAS can be linked to the fact that they can reject completely the colloidal and particulate metal species. It is also associated with the operating conditions and not the technology per se, since MBRs usually operate at higher *SRT* and *MLSS* than CAS.

Battistoni *et al.* (2007) found that the metal removal in an MBR-like configuration was 40–50% higher compared to CAS. Furthermore the application of MBR was proved more effective than the application of UF membranes for the tertiary treatment of effluents containing metals, due to the formation of a cake layer in the surface of the membrane fibers increasing their selectivity. This effect is different depending on whether the membrane system is applied for the filtration of the secondary effluent or the activated sludge directly. The presence of activated sludge with *MLSS* concentration of 5–10 g L^{-1} can enhance the layer effect and increase the removal performances proportionally (18–69%). Fatone *et al.* (2007; 2008b) found that metals that present higher affinity with the cell surfaces are removed effectively from both the CAS and MBR systems.

Fatone *et al.* (2008b) found that Hg and Cd were effectively removed in CAS, while Cu, Cr, Ni can rely on an additional performance in membrane bioreactors. The further MBR effect is significant for Cu and Cr, while it is less significant for Ni. On the contrary, the removal of As, Cd and Pb is similar in CAS and MBR, since these metals present high affinity with biomass or biomass-bound ligands. Carletti *et al.* (2008) attributed the higher efficiency of the MBR for Al, Fe, Zn, Cu, Hg and Cr removal to the fact that MBR work at high *MLSS*, thus aiding the biosorption and bioaccumulation mechanisms.

The operation of the MBR at very high *SRT* could lead to lower metals removal compared to CAS, since very high *SRT*s may result in the generation of biological molecules that chelate metals, thereby retaining them in solution and preventing their removal (Crane *et al.*, 2010; Santos *et al.*, 2010).

Membrane bio/processes have also been used to remove inorganic anions within drinking water supplies Apart from the typical F^- removal by pressure-driven nanofiltration, dialytic membrane bio/processes by using ion exchange membranes have been employed to remove F^- (Velizarov *et al.*, 2004).

12.4 CONCLUSION

The findings reported in literature show that MBR processes have a small superiority compared to CAS processes in the removal of the majority of metals. The coupling of biochemical processes with membranes in MBR result in the retention of particulate and colloidal metal forms. Membranes in MBR are an absolute barrier to suspended solids and also reject colloidal matter; thus the metal species associated with these substances are removed. The removal of As by

MBR processes is usually low since the As species remain in soluble form. Few cases showed how major role was played by the problematic layers such as fouling and clogging layers. Consequently, other processes should be integrated if enhanced As removal is required. Fluoride removal in urban wastewater is variable depending on the operating conditions of the urban wastewater treatment plant. Research data concerning the fate and removal of trace U in urban wastewater is very limited. Selenium removal by MBR is moderate to low. Both U and Se are met in very low concentrations in municipal wastewater.

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CHAPTER 13

Membrane distillation for the treatment of waters contaminated by arsenic, fluoride and uranium

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13.1 INTRODUCTION

Nowadays, water is a limited natural resource and in many cases there is a lack of water with the desired quality for both industrial and domestic use. Population growth and industrialization have led to a reduction of surface water sources, forcing populations around the world to depend on groundwater sources. Both types of water are not suitable for direct consumption due to high salt concentrations and in some cases also to naturally occurring hazardous contaminants, such as arsenic (As), fluoride (F^-) and uranium (U) (US NRC, 1984). Therefore, extensive treatments are required prior to consumption. Another source of water is the one that can be obtained with appropriate treatments of both industrial and municipal wastewater.

This chapter begins with traditional techniques employed to treat water contaminated by As, F^- and U. Then, the basic principles of membrane distillation are described and the research works reported in literature on the application of this membrane process to treat the polluted water are reported and discussed, in terms of permeate flux and contaminants rejection.

13.2 TRADITIONAL TREATMENTS

The conventional physical-chemical processes used for As removal can be classified on the basis of the principles involved: (i) coagulation and filtration (Wickramasinghe *et al.*, 2004); (ii) adsorption; (iii) ion exchange; and (iv) membrane technology, that includes reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) (Choonga *et al.*, 2007). Other methods like ozone oxidation, bioremediation, electrochemical treatments (Choonga *et al.*, 2007) and natural zeolite (Baskan and Pal, 2011) are also used in the removal of As.

Many methods have been investigated to remove excessive F^- from water, i.e., adsorption (Raichur and Basu, 2001), ion exchange (Meenakshi and Maheshwari, 2006; Singh *et al.*, 1999), precipitation/coagulation (Reardon and Wang, 2000; Saha, 1993), Donnan dialysis and electrodialysis (Adhikari *et al.*, 1989; Durmaz *et al.*, 2005; Hichour *et al.*, 1999; 2000), membrane separation process as MF (Lu and Liu, 2010), NF and RO (Dolar *et al.*, 2011; Elazhar *et al.*, 2009; Hu and Dickson, 2006; Mnif *et al.*, 2010; Richards *et al.*, 2010); electrolytic defluoridation (Mameri *et al.*, 1998; 2001).

Only a few studies have been carried out to investigate the simultaneous removal of arsenic and fluoride. Among various methods used, attention has recently focused on the adsorption process (Bibi *et al.*, 2015; Kagne *et al.*, 2008; Mohapatra *et al.*, 2009; Yadav *et al.*, 2006) and the coagulation with Al (Ruiping *et al.*, 2015).

The water treatment techniques that have been used to reduce U concentration to the maximum admissible concentration are adsorption (Coleman *et al.*, 2003; Mellah *et al.*, 2006; Sprynskyy *et al.*, 2011), chemical coagulation-flocculation (Gafvert *et al.*, 2002), ion exchange (Barbette *et al.*, 2004; Barton *et al.*, 2004; Bryant *et al.*, 2003; Gu *et al.*, 2004; Vaaramaa *et al.*, 2000; Weihua *et al.*, 2009), UF, also assisted by complexation (Krivoruchko *et al.*, 2011;

Table 13.1. Main technologies for As (adapted from Wickramasinghe *et al.*, 2004) F (adapted from Meenakshi and Maheshwari, 2006) and U (adapted from Yarlagadda *et al.*, 2011) removal and theirs efficiency.

Element	Technology	Removal efficiency [%]
As	Coagulation/filtration	95
	Lime softening	90 at pH $>$ 10.5
	Ion exchange	95
	Reverse osmosis	$>$95
	Activated alumina	95
F	Adsorption	90
	Coagulation/precipitation	18–33
	Ion exchange	90–95
	Reverse osmosis	$>$95
U	Coagulation/filtration	80 to $>$95
	Lime softening	85–99
	Anion exchange	90–100
	Reverse osmosis	90–99
	Activated alumina	$\sim$90

Table 13.2. Main limitations of traditional technologies.

Traditional technologies	Main limitations
Pressure-driven membrane operations	– High operating pressures – Need of membranes with high resistance to compression – Membrane fouling
Precipitation; Coagulation/filtration; Adsorption; Ion exchange	– Chemical usage – Creation of sludge or solid wastes concentrated with contaminants – Adsorbents regeneration/replacement

Kryvoruchko *et al.*, 2004), RO (Lin *et al.*, 1987; Hsiue *et al.*, 1989; Huikuri *et al.*, 1998) and NF (Favre-Réguillon *et al.*, 2008; Raff and Wilken, 1999).

Table 13.1 summarizes the contaminant removal efficiencies of some of the technologies listed above.

Table 13.2 shows the main limitations of traditional technologies in treating contaminated water.

13.3 APPLICATION OF THE MEMBRANE DISTILLATION TECHNIQUE

Membrane distillation (MD) is a promising process that offers several benefits with respect to conventional distillation, like the much smaller equipment and the possibility of operating at temperatures as low as 30°C and, then, low-grade, waste and/or alternative energy sources such as solar and geothermal energy can be coupled with MD systems for an energy efficient process. When compared to pressure-driven membrane operations, as operating pressures are generally in the order of zero to a few hundred kPa, it is possible to use membranes with reduced mechanical characteristics and reduced fouling problems. Another benefit of MD lies in its efficiency in terms of solute rejection: 100% (theoretical) of ions, macromolecules, colloids, cells, and other non-volatile constituents are rejected (Alkhudhiri *et al.*, 2012; Camacho *et al.*, 2013; Khayet, 2011).

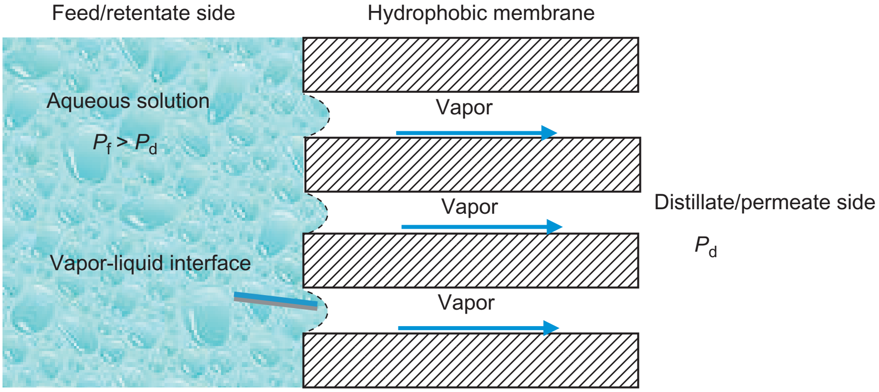

Figure 13.1. Vapor transfer in MD.

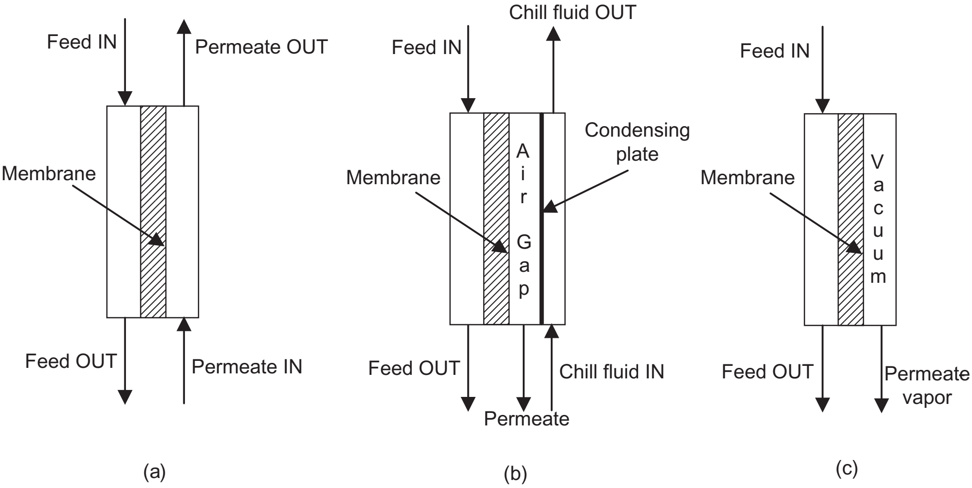

Figure 13.2. Different types of MD configurations: DCMD (a), AGMD (b) and VMD (c).

The membrane distillation process can be a feasible alternative to treat contaminated ground waters.

In MD, a hot aqueous feed solution is brought in contact with one side of a hydrophobic microporous membrane. After the evaporation of volatile molecules, to be separated from the feed, the transport of volatile molecules through dry pores of the hydrophobic membrane occurs thanks to a vapor pressure difference across the membrane ($P_f - P_d$), which is the driving force of the process. The Figure 13.1 shows the process.

Four configurations of the MD can be utilized to establish the required driving force: direct contact MD (DCMD), vacuum MD (VMD), air gap MD (AGMD), sweeping gas MD (SGMD). In particular, DCMD, AGMD and VMD configurations are reported in the literature as configurations used to treat contaminated solutions by As, F, and U. In DCMD, each side of the membrane (flat or capillary) is kept in contact with two liquid streams (the hot feed to be treated and the cold distillate); in AGMD the evaporated volatile molecules cross both the membrane pores and an air gap to finally condense over a cold surface inside the membrane module; in VMD, one side of the membrane is in contact with the feed stream while at the other side the vacuum is applied. Figure 13.2 illustrates the schemes of DCMD, AGMD and VMD configurations.

Table 13.3. Main properties of the membranes used (Macedonio and Drioli, 2008).

Material	Geometry	External diameter [mm]	Pore size [μm]
PP	Capillary	1.8	0.20

Table 13.4. Module characteristics (Macedonio and Drioli, 2008).

Shell diameter [cm]	Length [cm]	Number of membranes	Membrane area [m^2]
2.1	60	40	0.1

Membranes with pore sizes ranging from 0.01 μm to 1 μm can be generally used in MD. The polymers most used are polytetrafluoroethylene (PTFE), polypropylene (PP), polyvinylidenefluoride (PVDF) and polyethylene (PE) (Alkhudhiri *et al.*, 2012; Camacho *et al.*, 2013; Khayet, 2011).

Several works on the treatment of waters containing As, F^- and U with membrane distillation process, are presented in the literature. The main results are reported and discussed in the following sections.

13.3.1 *Arsenic removal*

There are different studies published in the literature on the use of membrane distillation for the treatment of waters contaminated by As, as reported in the following. Most of them deal with the DCMD configuration, although some experiments on the use of AGMD are also reported. Only recently, the potentialities of the vacuum configuration have been also explored.

An integrated membrane desalination system as a new and innovative technique for contaminant removal from water was investigated by Macedonio and Drioli (2008).

The proposed system consisted of a reverse osmosis step followed by a membrane distillation one. Seawater was treated with chemical agents and then fed to the RO unit; after this first step a fraction of the RO permeate was sent to the MD module. As feed water composition the standard seawater composition at which As(III) and As(V) were added, was considered.

The experimental set-up employed a MD020CP-2N membrane module (Enka Microdyn). The main membrane properties and the module characteristics are shown in Tables 13.3 and 13.4.

Experimental tests were carried out varying the operating parameters, like the concentration of As, the temperature (25–35°C) and the flow rate (100–250 $L\,h^{-1}$) of the feed solution. The distillate flow rate was fixed at 100 $L\,h^{-1}$. Experimental tests have demonstrated that the value of flux did not depend on the As concentration and slightly increased with the feed flow rate. Table 13.5 shows a comparison among the transmembrane fluxes at three different feed temperatures, when the concentration of As(V) in the feed was 339 $\mu g\,L^{-1}$ and feed flow rate was 100 $L\,h^{-1}$.

From Table 13.5, it can be noticed that the distillate flux increased with the feed temperature: the highest value (around 0.7 $kg\,m^{-2}\,h^{-1}$) was obtained at 34°C. Furthermore, all the analyzed samples have proven the absence of As(V) and As(III) in the permeate.

Qu *et al.* (2009) have studied the removal of As(III) (arsenite) and As(V) (arsenate) by DCMD with a self-made hydrophobic polyvinylidene fluoride (PVDF) capillary membrane. The main membrane properties and the characteristics of the module are reported in the Tables 13.6 and 13.7.

Table 13.5. Transmembrane flux at three different feed temperatures (Macedonio and Drioli, 2008).

T_{feed} [°C]	J [$\text{kg m}^{-2}\text{ h}^{-1}$]
25.3	0.36
29.7	0.47
34	0.72

Table 13.6. Main properties of the membranes used (adapted from Qu *et al.*, 2009).

Material	Geometry	Pore size [μm]	Porosity [%]
PVDF	Capillary	0.15	80

Table 13.7. Module characteristics (Qu *et al.*, 2009).

Diameter [m]	Length [m]	Number of membranes	Membrane area [m^2]
0.015	0.10	50	12.56×10^{-4}

Table 13.8. Operating conditions (Qu *et al.*, 2009).

Feed temperature [°C]	40–70
Solution pH [–]	5.0
Feed velocity [m s^{-1}]	0.23–0.96
Distillate velocity [m s^{-1}]	0.1
Arsenic concentration [$\mu\text{g L}^{-1}$]	200

Both the feed and the permeate were pumped from the bottom to the upper part of the module: the feed flowed inside the capillaries, whereas the permeate was fed at the shell side.

Arsenic removal experiments were carried out with aqueous As(III) and As(V) solutions at the operating conditions reported in Table 13.8.

The permeate flux, as a function of the feed temperature and at two feed velocities, is shown in Figures 13.3 and 13.4.

The experimental results showed that the permeate flux increased with the feed temperature and a maximum permeate flux of about 21 $\text{kg m}^{-2}\text{ h}^{-1}$ was obtained at 0.96 m s^{-1} when the feed temperature was 70°C.

The DCMD process also had high removal efficiency, above 99.95%, for both As(III) and As(V). In the permeate, the As(III) and As(V) contents were below the maximum contaminant limit (10 $\mu\text{g L}^{-1}$) when As(III) and As(V) increased up to 40 and 2000 $\mu\text{g L}^{-1}$, respectively. DCMD tests 250 h long on 500 $\mu\text{g L}^{-1}$ As(III), did not show changes in the permeate flux and the As(III) content in the permeate was always lower than the detection limit.

Pal and Manna (2010) have investigated a solar-driven membrane distillation (SDMD) system to remove As from contaminated groundwater. Three flat hydrophobic membranes (supplied by Membrane Solutions Shanghai, China) were used in a DCMD set-up equipped with a module

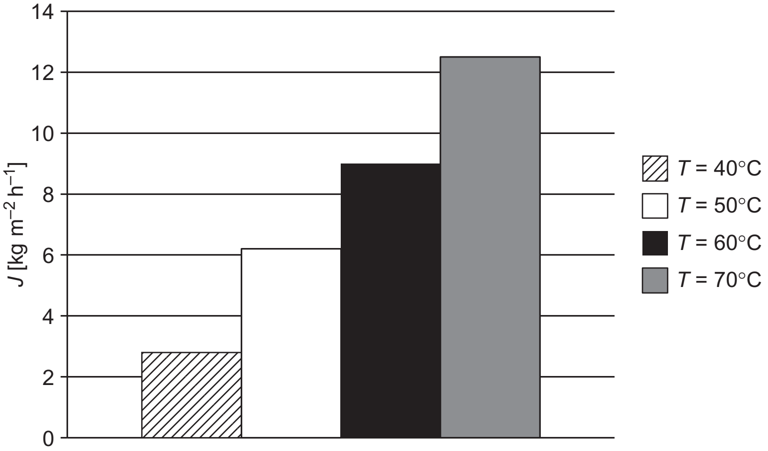

Figure 13.3. Trend of the permeate flux as function of feed temperature. $v_{\text{feed}} = 0.23\,\text{m}\,\text{s}^{-1}$ (adapted from Qu *et al.*, 2009).

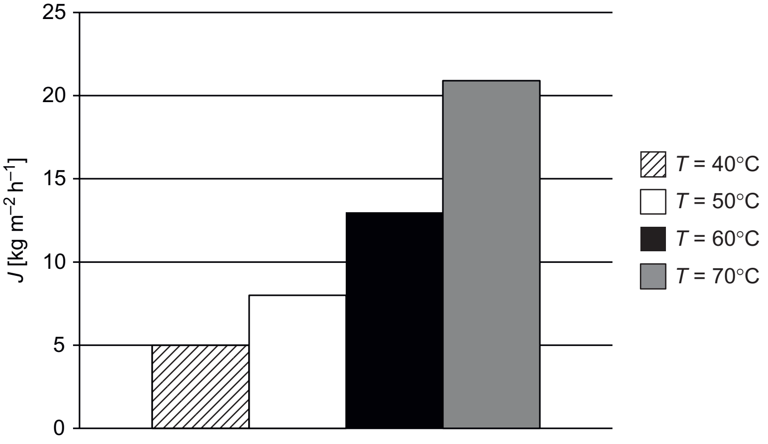

Figure 13.4. Trend of the permeate flux as function of the feed temperature. $v_{\text{feed}} = 0.96\,\text{m}\,\text{s}^{-1}$ (adapted from Qu *et al.*, 2009).

of 120 cm^2 membrane area. The module was made of polycarbonate, to ensure low heat losses to the surroundings. The hot stream was fed to the lower side of the membrane while the cold one flowed counter-currently over the upper surface of the membrane. Inside the module, the hot feed, coming from a small tube of 4 mm, flowed in a wide channel, so that, due to the lower pressure in the channel, it underwent flash vaporization. This particular design of the module led to a minimization of the temperature and concentration polarization during the process.

The main membrane properties are shown in Table 13.9.

In all the experiments with the composite membranes (MS3220 and MS3020) the support layer was in direct contact with the distillate. Tests were carried out on As-contaminated groundwater coming from Chakdah of South 24 Parganas of West Bengal (India) in which the concentration of As varied from 300 to 600 $\mu\text{g}\,\text{L}^{-1}$. Synthetic As solutions, containing both As forms, were also prepared and tested.

Table 13.9. Main properties of the membranes used (adapted from Pal and Manna, 2010).

Membrane	Material	Presence of support	Pore size [µm]	Thickness [µm]	Porosity [%]
MS3220	PTFE active layer with PP support sub-layer	YES	0.22	150	80
MS3020	PTFE active layer with PET support sub-layer	YES	0.22	175	80
MS7020	PP	NO	0.22	160	35

Table 13.10. Ranges of the operating conditions used (Pal and Manna, 2010).

Feed temperature [°C]	30–61
Distillate temperature [°C]	12–42
Feed velocity [$m\,s^{-1}$]	0.028–0.062
Distillate velocity [$m\,s^{-1}$]	0.026–0.08
Arsenic concentration [$\mu g\,L^{-1}$]	0–1200

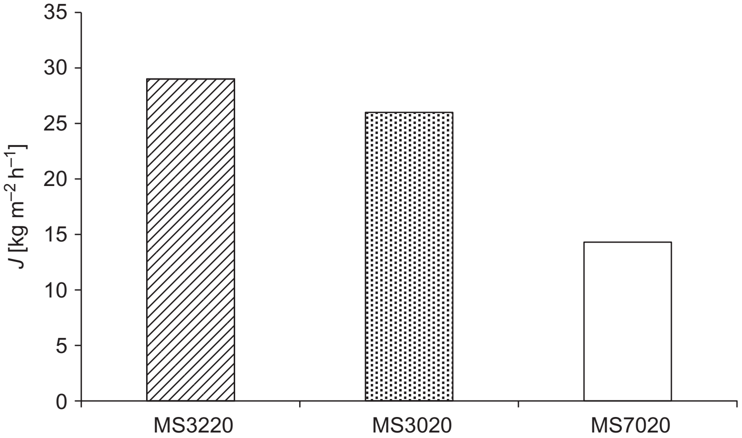

Figure 13.5. Trend of distillate fluxes. $T_{feed} = 60°C$; $T_{dist} = 21–23°C$; $c_{As} = 94\,\mu g\,L^{-1}$; $v_{feed} = 0.028\,m\,s^{-1}$; $v_{dist} = 0.052\,m\,s^{-1}$ (adapted from Pal and Manna, 2010).

Different operating parameters were varied, such as the feed and the distillate inlet temperatures, the feed and the distillate velocities, the feed concentration. Table 13.10 shows the ranges investigated.

The object of the study was to analyze the effect of feed and distillate inlet temperatures and flow velocities on flux and the effect of As concentration on flux and permeate quality.

Figure 13.5 reports a comparison, in terms of distillate fluxes, among the three membranes considered at a feed temperature of 60°C, at which the driving force of the process is higher.

The graph shows that the MS3220 membrane performed better than the others at the same operating conditions: the highest value of distillate flux was around 30 kg m^{-2} h^{-1}. By increasing the distillate temperature from 23 to 42°C, the flux decreased down to 22 kg m^{-2} h^{-1}, because of the lower driving force available for the transport. An increase of the distillate flux was obtained when the feed velocity was increased, due to a reduction of the heat and mass transfer resistances.

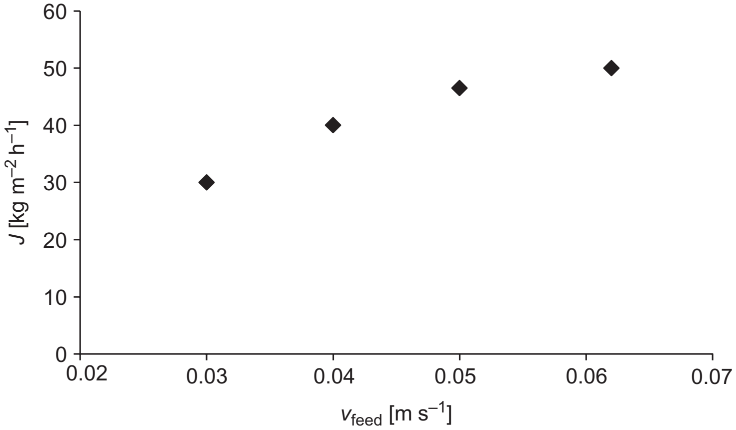

Figure 13.6. Trend of distillate flux with feed velocity. MS3220 membrane; $T_{\text{feed}} = 60°\text{C}$; $T_{\text{dist}} = 21°\text{C}$; $c_{\text{As}} = 394\,\mu\text{g L}^{-1}$; $v_{\text{dist}} = 0.052\,\text{m s}^{-1}$ (adapted from Pal and Manna, 2010).

In Figure 13.6, the trend of the distillate flux, for the MS3220 membrane, at various feed velocities, is reported.

The highest value of the distillate flux was around 50 kg m^{-2} h^{-1} at a feed temperature of 60°C and at a feed velocity of 0.062 m s^{-1}. The increase of flux observed at higher distillate velocities was lower than that obtained when operating at higher feed velocities.

The authors have also studied the effect of As feed concentration on flux. When increasing As level from 200 to 1200 μg L^{-1} an average of 12% flux decline was registered for the three membranes. Furthermore, for each membrane, the DCMD experiment was continuously run for 5 days: for a feed water with an As content of 394 μg L^{-1} at 60°C, the flux reduction was only about 2% for MS3220, 3% for MS3020 and 4.2% for MS7020, and no As was detected in the permeate.

Summarizing, the authors have demonstrated that by the DCMD process almost 100% As separation can be achieved. Moreover, the PTFE membrane led to high fluxes (49.80 kg m^{-2} h^{-1}), without wetting of membrane pores, even after 120 h of operation.

Manna *et al.* (2010), with the same solar driven DCMD configuration reported in Pal and Manna (2010), have investigated the performances of a hydrophobic flat sheet membrane (nominal pore size, 0.13 μm; thickness, 150 μm; porosity, 70–75%) to remove As from contaminated groundwater with an As content varying from 300 to 500 μg L^{-1}. An As removal of almost 100% from contaminated groundwater was achieved and no flux decline was registered during 4 days of operation. The PVDF membrane led to high fluxes (74 kg m^{-2} h^{-1} at 40°C and 95 kg m^{-2} h^{-1} at 60°C), by working with feed and distillate flow rates of 120 and 150 L h^{-1}, respectively, distillate inlet temperature of about 20–22°C and an As concentration in the feed of 396 μg L^{-1}.

The new flux-enhancing and solar-driven membrane distillation module was also theoretically studied by Pal *et al.* (2013) who developed a mathematical model that was successfully validated (relative error of only 0.042) with experimental results.

Islam (2005) wrote a masters thesis on the purification of water contaminated by As, using the HVR (house-hold water purifier) system developed by the Swedish HVR Water Purification AB Company. The system includes a heated feed tank, a membrane module equipped with two flat membranes (total membrane area, 0.2 m^2) and a water chiller. The membrane distillation configuration investigated was that with the air gap (1 mm thick) at the permeate side.

The main membrane properties are shown in Table 13.11.

Experimental tests were carried out on feeds coming from different sources (Högsby in Sweden and Bhashail Bhogh in Bangladesh) with As contents in the range of 240–330 μg L^{-1}. In both cases

Table 13.11. Main properties of the membranes used (Islam, 2005).

Material	Thickness [mm]	Porosity [%]	Size [cm × cm]
PTFE	0.2	80	42 × 24

Table 13.12. Main operating conditions (Islam, 2005).

Feed temperature [°C]	Chill water flow rate [L min^{-1}]	Chill water temperature [°C]
85	1.5	29

Table 13.13. Main properties of the flat membranes (adapted from Criscuoli *et al.*, 2013).

Membrane	Material and producer	Pore size [μm]	Thickness [μm]	Porosity [%]
M1	PP – (Membrana Germany)	0.20	91	70
M2	PP – (Membrana Germany)	0.45	170	75
M3	PVDF – (Lab-made by the phase inversion technique)	0.20	60	70
M4	PVDF – (Lab-made by the phase inversion technique)	0.20	35	70

Table 13.14. Operating conditions (Criscuoli *et al.*, 2013).

Feed temperature [°C]	20–40
Reynolds number [–]	700–1700
Arsenic content [μg L^{-1}]	200–500
Type of feed water	Distilled and tap water

a purified permeate (As <1 μg L^{-1}) was obtained. The main operating conditions are reported in Table 13.12.

The system is compact and portable, therefore, easy to transport, and allows and easy replacement of the membranes. Some disadvantages are, however, pointed out as well, such as the limited storage tank and the required restart after 40–60 minutes.

Criscuoli *et al.* (2013) investigated the potentialities of VMD, in terms of permeate flux and As rejection, by treating water containing As both in the trivalent and pentavalent form. The main aim was to produce a purified permeate working at low feed temperatures (20–40°C). Experimental tests were carried out on a commercial flat membrane module (GFT, GmbH, Germany) with a circular shape and a membrane area of 180 cm^2, by sending the feed to the upper part of the module and applying vacuum at the bottom side.

Four flat microporous hydrophobic membranes, supported (M3 and M4) and non-supported (M1 and M2), were used in the tests. Their main properties are reported in Table 13.13.

For each membrane, different parameters were varied, as shown in Table 13.14, while keeping the feed and the vacuum pressure at 100 kPa and 1.0 kPa, respectively.

For all membranes, the flux increased with feed temperature and Reynolds number and was not affected by either the As content nor the As speciation in water. In all investigated cases As was not detected in the permeate. Moreover, the membranes showed a constant performance in terms of both flux and As rejection, even after one month of continuous use.

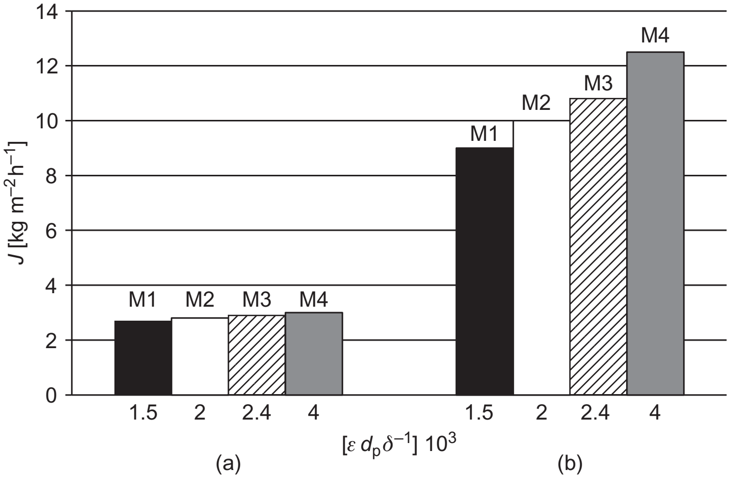

Figure 13.7. Comparison of the trans-membrane fluxes obtained with the different membranes at 20°C (a) and 40°C (b). Feed: distilled water; Reynolds number = 1700 (adapted from Criscuoli *et al.*, 2013).

Table 13.15. Main properties of the membranes used (adapted from Hou *et al.*, 2010).

Material	Geometry	Mean pore diameter [μm]	Thickness [mm]	Porosity [%]
PVDF	Hollow fiber	0.25	0.15	75.30

In Figure 13.7 a comparison of the trans-membrane fluxes obtained with the different membranes at two feed temperatures (20 and 40°C) is shown.

Figure 13.7 shows the effect of the porosity (ε), pore size (d_p) and thickness (δ) of the different membranes on the distillate flux: the trans-membrane flux increased with the $\varepsilon d_p \delta^{-1}$ ratio, due to the lower membrane resistance. The highest fluxes were obtained with the membrane M4 (around 3 kg m^{-2} h^{-1} at 20°C and 12.5 kg m^{-2} h^{-1} at 40°C), while the lowest values occurred with the M1 (2.3 and 9 kg m^{-2} h^{-1} at 20°C and 40°C, respectively).

In summary the authors have demonstrated that the VMD process is able to efficiently treat waters polluted by both As(III) and As(V) at low feed temperatures avoiding the need of the pre-oxidation step to convert As(III) into As(V). Lower feed temperatures mean lower thermal energy to be supplied, which is quite important for countries affected by As contaminated waters and where the sunny periods (for using solar energy) are limited.

13.3.2 *Fluoride and uranium removal*

The F^- and U removal from water by membrane distillation has not so far been much investigated. Few papers have, in fact, appeared in the literature on this topic.

Hou *et al.* (2010) applied the DCMD process to remove F^- from brackish groundwater. They used PVDF hollow fibers that were self-prepared by a dry/wet phase inversion process and assembled into a polyester tube. The main membrane properties and the module characteristics are reported in the Tables 13.15 and 13.16.

The hot salt solution was sent co-currently through the lumen side of the fibers while the cold distillate flowed through the shell side. The experimental tests were carried out varying many

Table 13.16. Module characteristics (Hou *et al.*, 2010).

Total length [mm]	Effective length [mm]	Packing fraction [%]	Membrane area [m^2]
240	100	32	0.014

Table 13.17. Operating conditions used (Hou *et al.* 2010).

Feed temperature [°C]	30–80
F concentration [$mg\,L^{-1}$]	5–5000
Feed velocity [$m\,s^{-1}$]	0.17–0.52

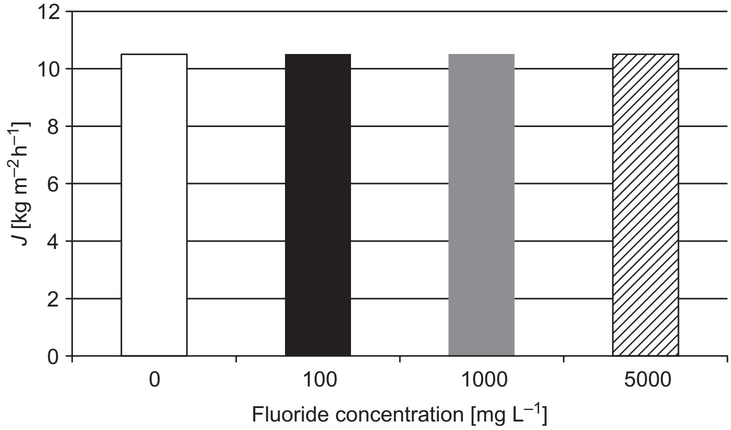

Figure 13.8. Variation of the permeate flux with fluoride concentrations. $v_{\text{feed}} = 0.52\,m\,s^{-1}$; $T_{\text{feed}} = 50°C$; $v_{\text{dist}} = 0.15\,m\,s^{-1}$; $T_{\text{dist}} = 20°C$ (adapted from Hou *et al.*, 2010).

parameters, as summarized in Table 13.17, keeping the distillate temperature and velocity fixed at 20°C and $0.15\,m\,s^{-1}$, respectively.

Furthermore, concentration experiments of natural brackish groundwater with or without the addition of $0.1\,mol\,L^{-1}$ HCl were performed. In this case, the inlet temperatures of the feed and cold distillate water were kept constant at 50 and 20°C, respectively; the feed velocity was $0.52\,m\,s^{-1}$, while that of the permeate stream was $0.15\,m\,s^{-1}$.

A significant increase of the permeate flux was registered by increasing the feed temperature: it increased from 2.9 to $35.6\,kg\,m^{-2}\,h^{-1}$ for feed temperatures of 30 and 80°C, respectively.

The effect of the feed concentration on the flux is shown in Figure 13.8.

It can be noticed that, when the F^- concentration increased up to $5000\,mg\,L^{-1}$, the permeate flux was stable at about $10.5\,kg\,m^{-2}\,h^{-1}$. This means that the influence of feed F^- concentration on the permeate flux was negligible.

Figure 13.9 reports the trend of the permeate conductivity with F^- concentrations.

Figure 13.9 shows that for F^- concentrations ranging from 5 to $1000\,mg\,L^{-1}$, there was no remarkable impact on the rejection and the permeate conductivity was constant and equal to $2\,\mu S\,cm^{-1}$. However, when the feed F^- concentration increased to $5000\,mg\,L^{-1}$, the permeate conductivity increased as well, reaching the value of $3\,\mu S\,cm^{-1}$. This result was attributed by authors to the partial wetting of larger pores present on the membrane surface.

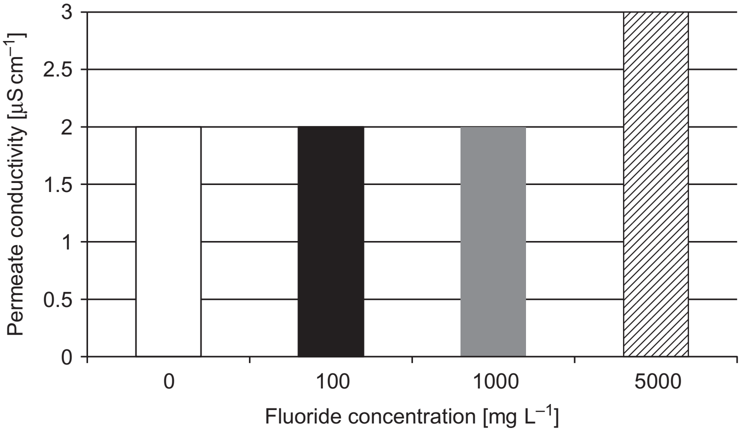

Figure 13.9. Variation of the permeate conductivity with fluoride concentrations. $v_{\text{feed}} = 0.52\,\text{m}\,\text{s}^{-1}$; $T_{\text{feed}} = 50°\text{C}$; $v_{\text{dist}} = 0.15\,\text{m}\,\text{s}^{-1}$; $T_{\text{dist}} = 20°\text{C}$ (adapted from Hou *et al.*, 2010).

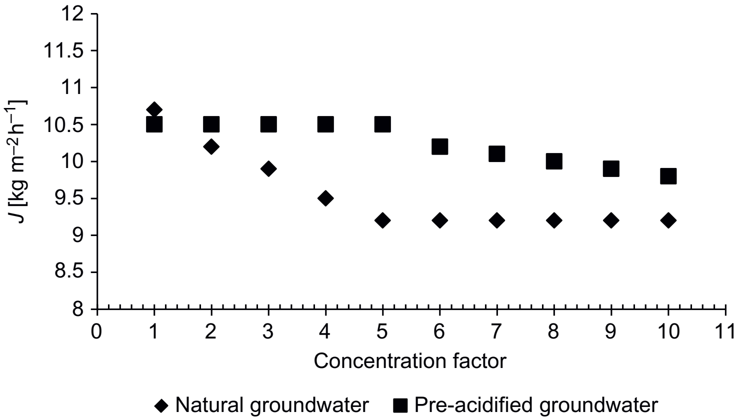

Figure 13.10. Comparison of the permeate flux obtained during the concentration of natural groundwater and of pre-acidified groundwater. $v_{\text{feed}} = 0.52\,\text{m}\,\text{s}^{-1}$; $T_{\text{feed}} = 50°\text{C}$; $v_{\text{dist}} = 0.15\,\text{m}\,\text{s}^{-1}$; $T_{\text{dist}} = 20°\text{C}$ (adapted from Hou *et al.*, 2010).

In the Figures 13.10 and 13.11, a comparison, in terms of permeate flux and permeate conductivity, between the gradual concentration of natural groundwater and pre-acidified groundwater is presented. When pre-acidified brackish groundwater was considered as feed, the tests were carried out at pH 4.0.

As can be seen, from Figures 13.10 and 13.11, the concentration factor had a significant influence on the DCMD performance.

In the case of natural groundwater, the permeate flux decreased until a concentration factor of 5.0, then the permeate flux was constant (around $9\,\text{kg}\,\text{m}^{-2}\,\text{h}^{-1}$). Concerning the pre-acidified groundwater, the acidification of the feed enhanced the stability of the process significantly. In fact, there was no decline of the permeate flux before the concentration factor reached 5.0, and only after this value the permeate flux began to decrease (from a concentration factor of 5.0 to 10.0, the permeate flux decreased from about 10.5 to $9.8\,\text{kg}\,\text{m}^{-2}\,\text{h}^{-1}$). The authors explained the flux decline observed in the two experiments by considering both the formation of deposits on the

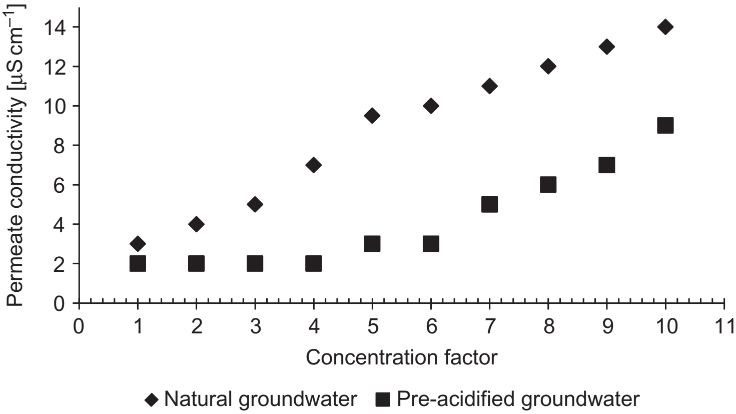

Figure 13.11. Comparison of the permeate conductivity measured during the concentration of natural groundwater and of pre-acidified groundwater. $v_{\text{feed}} = 0.52\,\text{m s}^{-1}$; $T_{\text{feed}} = 50°\text{C}$; $v_{\text{dist}} = 0.15\,\text{m s}^{-1}$; $T_{\text{dist}} = 20°\text{C}$ (adapted from Hou *et al.*, 2010).

Table 13.18. Operating conditions used in the long-term test and experimental results (Hou *et al.*, 2010).

Feed solution	pH	Conc. factor	v_{feed} [m s^{-1}]	T_{feed} [°C]	v_{dist} [m s^{-1}]	T_{dist} [°C]	J [kg m^{-2} h^{-1}]	Permeate conductivity [μ S cm^{-1}]
Pre-acidified brackish groundwater	4.0	4.0	0.52	50	0.15	20	11.4–11.6	2.0–4.0

membrane surface that clogged and wetted a fraction of the membrane pores, and the temperature and concentration polarization that increased with the concentration factor. With the pre-acidified feed, some of the bicarbonate ions responsible for the scale deposits were decomposed and the flux decay was reduced.

Figure 13.11 shows that there is a linear increase of the conductivity with the concentration factor, reaching a maximum value of about 15 μS cm^{-1}. After the acidification of the feed, the permeate conductivity stabilized at about 2.0 μS cm^{-1}, until concentration factors were lower than 5.0; when the concentration factor increased from 5.0 to 10.0 the permeate conductivity increased as well, from 3.0 to 8.0 μS cm^{-1}, respectively, because of deposit formation.

The authors performed also long-term experimental tests (300 h, concentration factor of 4.0) with the pre-acidified brackish groundwater as feed solution. The permeate flux was constant at about 11.5 kg m^{-2} h^{-1} during all the experiment and the permeate conductivity stabilized at about 3.0 μS cm^{-1} with a F^- content in the permeate below the detection limit.

The operating conditions used and the experimental results are summarized in Table 13.18.

Yarlagadda *et al.* (2011) studied the feasibility of the DCMD process to treat saline groundwater contaminated by As, U and F^-. Two types of microporous hydrophobic membranes supplied by General Electric were tested to compare the permeate fluxes and contaminant rejections. Their main properties are shown in Table 13.19.

Membranes were located in a module consisting of a circular acrylic case with an inside diameter of 8.75 cm and a membrane area of 60 cm^2. Experiments were carried out with different salt concentrations of As, F^- and U and at different operating conditions, as reported in Table 13.20.

Table 13.19. Main properties of the membranes used (adapted from Yarlagadda *et al.*, 2011).

Material	Nominal pore size [μm]	Thickness [μm]	Porosity [%]
PTFE	0.22	60	80
PP	0.22	110	70
PP	0.45	110	75

Table 13.20. Operating conditions (Yarlagadda *et al.*, 2011).

Feed temperature [°C]	50–80
Feed flow rate [L min^{-1}]	1–4
Salt concentrations [μg L^{-1}]	1000–10,000
As concentration [μg L^{-1}]	10–400
U concentration [μg L^{-1}]	10–400
F concentration [mg L^{-1}]	1–30

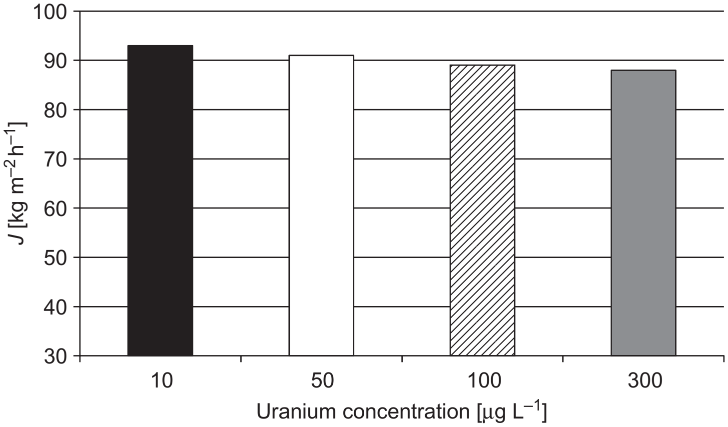

Figure 13.12. Effect of the uranium concentration on the permeate flux for the PTFE membrane. $T_{\text{feed}} = 80°C$; $T_{\text{dist}} = 20°C$; $Q_{\text{feed}} = Q_{\text{dist}} = 4\,\text{L}\,\text{min}^{-1}$ (adapted from Yarlagadda *et al.*, 2011).

The permeate flux for the PP membrane (0.22 μm pore size) was lower than for the PTFE membrane because of the higher mass transfer resistance of the PP membrane, due to the higher thickness and lower porosity.

The authors studied the effect of salts and contaminant concentration on both flux and rejection.

Figure 13.12 shows the effect of the uranium concentration on the permeate flux for the PTFE membrane.

The decrease in permeate flux rate was more evident when the contaminants concentration increased, probably because of the polarization effect. A similar trend was observed for waters containing salts, As and F^- and during tests carried out on PP membranes.

For the highest As, F^-, and U feed concentrations investigated, their content in the permeate were 0.17 μg L^{-1}, 0.56 mg L^{-1}, and 0.2 μg L^{-1}, respectively, with removal efficiencies for most of the tests in the range of 99–99.9%.

The pore size effect on the permeate flux, for the two PP membranes, is shown in Figure 13.13.

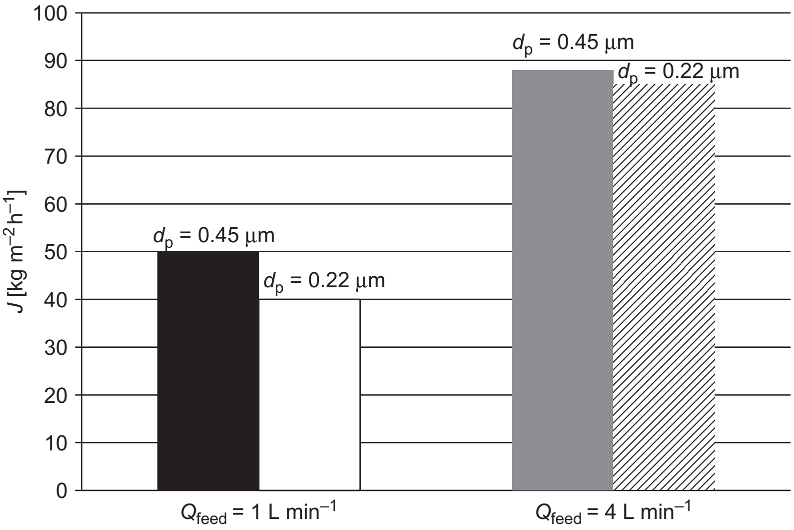

Figure 13.13. Effect of pore size on the permeate flux. PP membranes; $T_{\text{feed}} = 80°\text{C}$; $T_{\text{dist}} = 20°\text{C}$; $Q_{\text{dist}} = 4\,\text{L min}^{-1}$; Concentrations: salts = 6000 mg L^{-1}; U, As = 400 μg L^{-1}; F = 30 mg L^{-1} (adapted from Yarlagadda *et al.*, 2011).

The permeate flux increased with larger pore size, and at lower feed flow rates the difference between the two values was more evident: at higher feed flow rates the membrane with larger pores may get wetted causing resistance to the mass transfer.

From the study made by Yarlagadda *et al.* (2011), it can be concluded that the PTFE membrane produced a higher permeate flux than the PP membranes; however, the contaminant and salts rejections were comparable.

13.4 SYNTHESIS OF THE LITERATURE RESULTS

Table 13.21 summarizes the main results (in terms of rejection/permeate contaminant concentration and distillate flux) obtained in the literature works which are reported and discussed this chapter.

It has to be pointed out that it is possible to obtain values of rejection higher than 99% with all the investigated membrane distillation configurations (DCMD, VMD and AGMD). In many cases this value increases up to 100% for the As and F^- confirming the potential of membrane distillation as a very efficient technique for purifying contaminated waters. These rejection values are often also coupled to high distillate fluxes that range from 10 to 95 kg m^{-2} h^{-1}, depending on the membrane properties, module design and operating conditions used.

13.5 CONCLUSIONS AND REMARKS

The experimental tests carried out using DCMD, AGMD and VMD on different microporous hydrophobic membranes have proven that membrane distillation is a promising technology for the recovery of purified water from As, F^- and U contaminated sources. In fact, the content of the above species in the obtained permeates was always lower than the imposed limits. The permeate fluxes varied depending on the operating conditions used, the membrane properties and the module design. Although the DCMD is the simplest configuration, the use of VMD facilitates

Table 13.21. Summary of the main results obtained in the cited literature works.

Contaminant	MD configuration (Membrane geometry)	Membrane material	Main results	References
As	DCMD (Capillary)	PP	Rejection ≅ 100% $J \cong 0.7\,\mathrm{kg\,m^{-2}\,h^{-1}}$ ($Q_{\mathrm{feed}} = 100\,\mathrm{L\,h^{-1}}$; $Q_{\mathrm{dist}} = 100\,\mathrm{L\,h^{-1}}$; $T_{\mathrm{feed}} = 34°\mathrm{C}$; $c_{\mathrm{As}} = 339\,\mu\mathrm{g\,L^{-1}}$)	Macedonio and Drioli (2008)
As	DCMD (Capillary)	PVDF	Rejection ≅ 99.95% $J \cong 21\,\mathrm{kg\,m^{-2}\,h^{-1}}$ ($v_{\mathrm{feed}} = 0.96\,\mathrm{m\,s^{-1}}$; $v_{\mathrm{dist}} = 0.1\,\mathrm{ms^{-1}}$; $T_{\mathrm{feed}} = 70°\mathrm{C}$; $c_{\mathrm{As}} = 200\,\mu\mathrm{g\,L^{-1}}$)	Qu *et al.* (2009)
As	DCMD (Flat sheet)	PTFE active layer with PP support sub-layer	Rejection ≅ 100% $J \cong 50\,\mathrm{kg\,m^{-2}\,h^{-1}}$ ($v_{\mathrm{feed}} = 0.062\,\mathrm{m\,s^{-1}}$; $v_{\mathrm{dist}} = 0.052\,\mathrm{m\,s^{-1}}$; $T_{\mathrm{feed}} = 60°\mathrm{C}$; $T_{\mathrm{dist}} = 21°\mathrm{C}$; $c_{\mathrm{As}} = 394\,\mu\mathrm{g\,L^{-1}}$)	Pal and Manna (2010)
As	DCMD (Flat sheet)	PVDF	Rejection ≅ 100% $J \cong 95\,\mathrm{kg\,m^{-2}\,h^{-1}}$ ($Q_{\mathrm{feed}} = 120\,\mathrm{L\,h^{-1}}$; $Q_{\mathrm{dist}} = 150\,\mathrm{L\,h^{-1}}$; $T_{\mathrm{feed}} = 60°\mathrm{C}$; $T_{\mathrm{dist}} = 20$–$22°\mathrm{C}$; $c_{\mathrm{As}} = 396\,\mu\mathrm{g\,L^{-1}}$)	Manna *et al.* (2010)
As	AGMD (Flat)	PTFE	Permeate: $c_{\mathrm{As}} < 1\,\mu\mathrm{g\,L^{-1}}$ ($Q_{\mathrm{chillwater}} = 15\,\mathrm{L\,min^{-1}}$; $T_{\mathrm{feed}} = 85°\mathrm{C}$; $T_{\mathrm{chillwater}} = 29°\mathrm{C}$; $c_{\mathrm{As}} = 334\,\mu\mathrm{g\,L^{-1}}$)	Islam (2005)
As	VMD (Flat sheet)	PVDF	Rejection ≅ 100% $J \cong 13\,\mathrm{kg\,m^{-2}\,h^{-1}}$ ($Re = 1700$; $P_{\mathrm{vacuum}} = 1.0\,\mathrm{kPa}$; $T_{\mathrm{feed}} = 40°\mathrm{C}$; $c_{\mathrm{As}} = 200$–$5000\,\mu\mathrm{g\,L^{-1}}$)	Criscuoli *et al.* (2013)
F	DCMD (Hollow fibers)	PVDF	Rejection ≅ 100% $J \cong 11\,\mathrm{kg\,m^{-2}\,h^{-1}}$ Permeate conductivity: 2–3 $\mu\mathrm{S\,cm^{-1}}$ ($v_{\mathrm{feed}} = 0.52\,\mathrm{m\,s^{-1}}$; $v_{\mathrm{dist}} = 015\,\mathrm{m\,s^{-1}}$; $T_{\mathrm{feed}} = 50°\mathrm{C}$; $T_{\mathrm{dist}} = 20°\mathrm{C}$; $c_{\mathrm{F}} = 5$–$5000\,\mathrm{mg\,L^{-1}}$)	Hou *et al.* (2010)
F, As, U	DCMD (Flat sheet)	PTFE	Rejection ≅ 99–99.9% $J \cong 90\,\mathrm{kg\,m^{-2}\,h^{-1}}$ ($Q_{\mathrm{feed}} = Q_{\mathrm{dist}} = 4\,\mathrm{L\,min^{-1}}$; $T_{\mathrm{feed}} = 80°\mathrm{C}$; $T_{\mathrm{dist}} = 20°\mathrm{C}$; $c_{\mathrm{salts}} = 6000\,\mathrm{mg\,L^{-1}}$; $c_{\mathrm{U}} = c_{\mathrm{As}} = 400\,\mu\mathrm{g\,L^{-1}}$; $c_{\mathrm{F}} = 30\,\mathrm{mg\,L^{-1}}$)	Yarlagadda *et al.* (2011)

efficient working at low feed temperatures and hence at lower thermal energy consumptions. As a general remark, the capability of treating waters containing different types of pollutants by a single separation technique is one of the advantages of membrane distillation. Moreover, the process is able to reject both As(III) and As(V) and the pre-oxidation step usually required to convert the trivalent As into the pentavalent is not needed, with a consequent reduction of plant complexity and use of chemicals. Furthermore, this technology can be driven by waste/renewable heat sources and can be easily coupled to existing plants leading to hybrid systems. It has, however, to be pointed out that the studies conducted until now, are mostly at lab scale and, therefore, the performance of membrane distillation has still to be evaluated in long-term tests under real conditions, in terms of membrane properties (chemical, thermal and mechanical stability, wetting, fouling, etc.), of energy requirements and of the quantity and quality of the produced permeate. Only a final estimation of both capital and operating costs of the process will be at the basis of its implementation at a large scale.

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CHAPTER 14

Removal of inorganic and organic trace contaminants by forward osmosis membranes

Qianhong She & Chuyang Y. Tang

14.1 INTRODUCTION

Forward osmosis (FO) is an emerging membrane technology for water treatment and energy production. In an FO process, a semipermeable membrane is placed in between two solutions of different osmotic pressures. One is a less concentrated "feed solution (FS)" with lower osmotic pressure, while the other is a more concentrated "draw solution (DS)" with higher osmotic pressure. The water in the FS permeates through the membrane into the DS due to the osmotic pressure gradient across the membrane, but the solutes in the FS are selectively rejected by the membrane.

After the FO process, the concentration and volume of FS and DS are changed. The FS is concentrated and its volume is reduced, such that the useful components in FS can be recovered or the detrimental components can be retained for further post-treatment. The DS is diluted and volume-expanded, from which the desired freshwater can be extracted using a proper post-treatment method and meanwhile the original DS can be regenerated and recycled to the membrane to maintain the FO operation. The freshwater extraction and DS regeneration can be an energy-intensive step. However, specifically designed draw solutions can facilitate the regeneration in an otherwise low energy process (McGinnis and Elimelech, 2007). For example, when ammonia-carbon dioxide is used as DS for the seawater desalination, the low grade waste heat can be used as energy source for the DS regeneration through distillation (Elimelech and Phillip, 2011; McCutcheon *et al.*, 2005; McGinnis and Elimelech, 2007). In some cases, draw solutes may serve the dual function of osmotic draw agents and constituents of the final product. One example is the case of commercially available personal hydration packs, which use a sugar-and-nutrient DS to provide energy-boosting drinks from impaired natural waters (Cath *et al.*, 2006). Alternatively, when the interest is to recover or enrich the components in FS, an abundant and low value DS, such as seawater, can be used in a once-through fashion without the need for regeneration (Cath *et al.*, 2006; 2010; Hoover *et al.*, 2011).

Unlike pressure-driven membrane processes (such as RO and NF), FO relies on the osmotic pressure difference (or chemical potential difference) as the driving force. This can potentially reduce the prime energy (i.e., electricity) consumption and thus the cost for the FO operation, if suitable draw solutes and their regeneration methods can be economically and technically developed or the target application does not require the DS regeneration (Cath *et al.*, 2006; Elimelech and Phillip, 2011; Hoover *et al.*, 2011; McGinnis and Elimelech, 2007; 2008). Besides this, FO offers many other advantages. Because the only pressure involved in the FO process is due to flow resistance in the membrane module (max. a few bars), the equipment used is simple (Cath *et al.*, 2006). In addition, recent studies revealed that membrane fouling in FO has lower propensity (Achilli *et al.*, 2009; Lay *et al.*, 2010) and better reversibility (Mi and Elimelech, 2008; 2010), and can be more easily controlled compared to typical pressure-driven membrane processes (Arkhangelsky *et al.*, 2012; Lee *et al.*, 2010; Mi and Elimelech, 2010; Valladares Linares *et al.*, 2012). Furthermore, in the fields of liquid food and pharmaceutical processing, FO can well maintain the physical properties (e.g., color, taste, aroma and nutrition) of the feed as FO does not require high pressure or temperature in FS (Cath *et al.*, 2006; Zhao *et al.*, 2012).

Owing to the various advantages, FO has received increasing attention in a broad spectrum of applications. The major applications reported in the literature (Cath *et al.*, 2006; Zhao *et al.*, 2012) include (i) wastewater treatment and water purification, (ii) seawater desalination, (iii) food processing, (iv) pharmaceutical applications, and (v) osmotic power harvesting. As the FO is capable of achieving high rejection of a variety of solutes in the FS, a specific application among those aforementioned categories is to remove contaminants from impaired water. This chapter will review the FO technology for the removal of contaminants (both organics and inorganics) from impaired water, particularly for As removal.

14.2 FUNDAMENTALS OF MASS TRANSPORT AND SOLUTE REJECTION IN FO

The mass transport (both water and solute) in the FO processes is illustrated in Figure 14.1. The water in the FS of higher water chemical potential will permeate through the membrane into the DS of lower water chemical potential. Meanwhile, the draw solute in the DS will reversely diffuse into the FS due to the concentration gradient across the membrane. Solute diffusion in this fashion is referred to as reverse solute diffusion. Coupled with reverse solute diffusion, solute in the FS will forwardly diffuse into the DS if its concentration in FS is greater than that in DS. Solute diffusion in this fashion is referred to as forward solute diffusion. This section will introduce the fundamentals of the mass transport and solute rejection in FO processes.

14.2.1 *Internal concentration polarization (ICP)*

All the currently available FO membranes have asymmetric structures consisting of a dense rejection layer (i.e., active layer) and a porous support layer. The water flux in FO is strongly affected by the internal concentration polarization (ICP) inside the membrane support layer (Fig. 14.2). ICP gives rise to severe loss of the effective osmotic driving force and thus the water flux. This can be either due to the dilution of the draw solution within the support layer when the membrane is placed with its active layer towards the feed solution (AL-FS) or the concentration of feed solution within the support layer when the membrane is placed with its active layer towards the

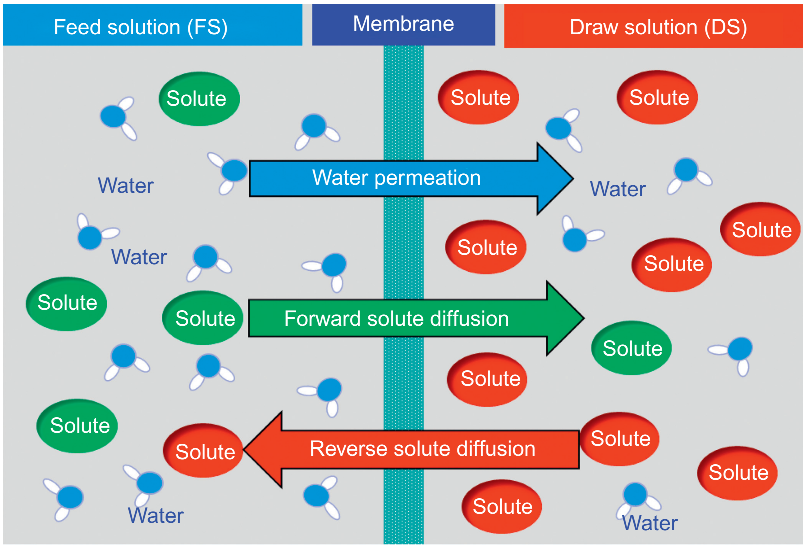

Figure 14.1. Schematic illustration of mass transport (both water and solute) in the FO processes.

draw solution (AL-DS). In addition to the ICP, external concentration polarization (ECP) that occurs near the membrane surface is another factor affecting the FO performance. While ECP can be well mitigated by improving the hydrodynamic conditions, the control of ICP is still a challenge for FO.

In the FO processes, the ICP can be modeled based on the solution-diffusion theory for the rejection layer coupled with the convection and diffusion of solute in the porous support layer. The modeling equations in AL-DS and AL-FS orientations can be expressed by Equations (14.1) and (14.2) (Tang *et al.*, 2010):

$$J_w = K_{m,s} \ln\left(\frac{\pi_d - \frac{J_w}{A} + \frac{B}{A}}{\pi_f + \frac{B}{A}}\right) \quad \text{(AL-DS orientation)} \tag{14.1}$$

and

$$J_w = K_{m,s} \ln\left(\frac{\pi_d + \frac{B}{A}}{\pi_f + \frac{J_w}{A} + \frac{B}{A}}\right) \quad \text{(AL-DS orientation)} \tag{14.2}$$

where J_w is the water flux, $K_{m,s}$ is the mass transfer coefficient; A and B are the water permeability coefficient and draw solute permeability coefficient, respectively; π_d and π_f are the osmotic pressure in the draw solution and feed solution, respectively. The mass transfer coefficient ($K_{m,s}$) in Equations (14.3) and (14.4) is the ratio of the solute diffusivity (D) over the structure parameter of membrane porous support layer (S):

$$K_{m,s} = \frac{D}{S} \tag{14.3}$$

The structure parameter (S) can be determined through:

$$S = \frac{\tau l}{\varepsilon} \tag{14.4}$$

where l is the thickness, τ is the tortuosity and ε is the porosity of the membrane porous support layer. Similar to the mass transfer coefficient ($K_{m,s}$) for external concentration polarization (ECP), $K_{m,s}$ can be used to determine the influence of ICP on water and solute flux. Also, analogous to the boundary layer thickness (δ) for ECP, S provides a length scale of ICP in the support layer.

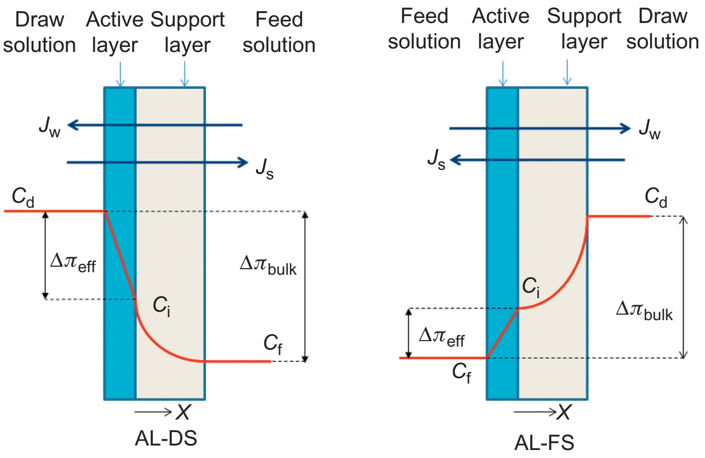

Figure 14.2. A schematic representation of the internal concentration polarization (ICP) in FO processes. Modified from Cath *et al.* (2006).

14.2.2 *Reverse solute diffusion*

Reverse solute diffusion is a unique phenomenon in the osmotically driven membrane processes (Hancock and Cath, 2009; Phillip *et al.*, 2010; She *et al.*, 2012b; Tang *et al.*, 2010). The reverse solute flux in FO can be expressed by a general equation for both orientations (Tang *et al.*, 2010):

$$J_s = \frac{B}{A\beta R_g T} J_w \qquad (14.5)$$

where J_s is the reverse solute flux, β is the van't Hoff coefficient, R_g is the universal gas constant, and T is absolute temperature. Equation (14.5) can well predict the solute flux in FO for a given membrane (whose A and B values are constant) simply using the experimentally measured water flux (J_w). Equation (14.5) also suggests that the specific reverse solute flux (J_s/J_w) is a constant for a given membrane, regardless of the FS concentration, DS concentration and membrane orientation used in the FO operation.

Severe reverse solute diffusion can influence the water transport behavior in FO and is undesirable for FO application. The draw solute reversely diffusing into the FS can elevate the FS concentration and may also enhance the concentrative concentration polarization near the membrane surface, which will lead to the reduction of the effective concentration difference (and thus osmotic driving force) across the membrane and thus the water flux (Phillip *et al.*, 2010; Tang *et al.*, 2010). This enhanced concentration polarization is much more pronounced in the AL-DS orientation (in terms of enhanced ICP), as the elevated solute accumulation within the support layer is much less susceptible to the cross-flow conditions compared to that near the active layer in the AL-FS orientation (Tang *et al.*, 2010). The accumulation of draw solute in the feed solution can also change the feed solution chemistry, such as ionic strength and ionic composition. If the draw solute can act as a fouling initiator, it can enhance the membrane fouling and thus cause more water flux reduction when it reversely diffuses into the FS (She *et al.*, 2012a).

14.2.3 *Forward solute diffusion*

To introduce the forward solute diffusion, boron, a contaminant of interest in the desalination industry, is selected as the representative feed solute following Jin's study (Jin *et al.*, 2011). A schematic of boron transport into DS in the FO processes is shown in Figure 14.3.

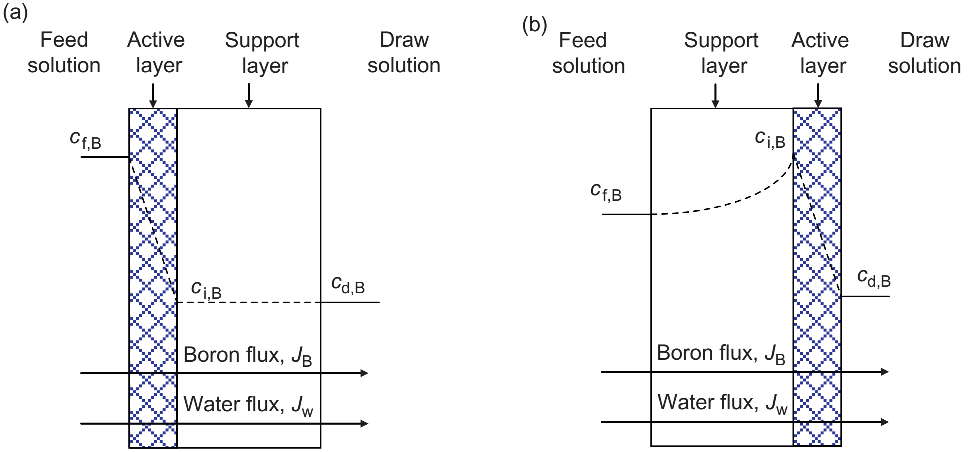

Figure 14.3. Schematic of boron transport into draw solution in the FO process: (a) in AL-FS orientation, and (b) in AL-DS orientation. Figure reproduced from Jin *et al.* (2011) with permission from American Chemical Society.

When the feed solution is placed against the active layer (AL-FS, Fig. 14.3a), forward boron flux (J_B) through FO membrane is expressed as:

$$J_B = B_B(c_{f,B} - c_{i,B}) \tag{14.6}$$

where B_B is the boron permeability coefficient, $c_{f,B}$ is boron concentration in feed solution, $c_{i,B}$ is boron concentration at the interface between FO support layer and active layer. In this membrane orientation, once boron permeates through the active layer, it is carried away from the membrane support layer by the water flux. Thus, boron does not experience ICP in this orientation. J_B and J_w are related via the boron concentration transported across the FO membrane:

$$c_{i,B} = \frac{J_B}{J_w} \tag{14.7}$$

Substituting Equation (14.7) for $c_{i,B}$ in Equation (14.6) yields an expression for the boron flux into the draw solution:

$$J_B = \frac{B_B}{1 + \frac{B_B}{J_w}} c_{f,B} \quad \text{(AL-FW)} \tag{14.8}$$

Equation (14.8) suggests the J_B increases with higher water flux J_w. This is because $c_{i,B}$ becomes more dilute at higher water flux, which enhances the driving force for boron transport across the membrane active layer.

When active layer is facing the draw solution (AL-DS), J_B through FO membrane is expressed as (Kedem and Katchalsky, 1958):

$$J_B = B_B(c_{i,B} - c_{d,B}) \tag{14.9}$$

where $c_{d,B}$ is the effective boron concentration in draw solution arising from the boron flux ($c_{d,B} = J_B/J_w$). In this membrane orientation, Boron entering the porous support layer experiences a concentration ICP due to the retention of boron by the active layer, i.e., the boron concentration at the support layer-active layer interface ($c_{i,B}$) is higher than that in bulk feed solution ($c_{f,B}$). $c_{i,B}$ can be derived from the film theory (Elimelech and Bhattacharjee, 1998) and described as:

$$\frac{c_{i,B} - c_{d,B}}{c_{f,B} - c_{d,B}} = \exp\left(\frac{J_w}{K_{m,B}}\right) \tag{14.10}$$

where $K_{m,B}$ is mass transfer coefficient of boron within membrane porous support layer, which is given by the ratio of boron diffusion coefficient (D_B) over the membrane structural parameter (S):

$$K_{m,B} = \frac{D_B}{S} \tag{14.11}$$

By substituting Equation (14.10) into Equation (14.9), boron flux through an asymmetric FO membrane in the AL-DS orientation can be predicted from:

$$J_B = \frac{B_B \exp(J_w/K_{m,B})}{1 + \dfrac{B_B \exp(J_w/K_{m,B})}{J_w}} c_{f,B} \quad \text{(AL-DS)} \tag{14.12}$$

The unknown parameter $K_{m,B}$ was estimated as follows. First, $K_{m,s}$ was determined according to Equation (14.1), where A and B_s were determined from RO experiments; J_w was determined from FO experiments; π_{draw} and π_{feed} were calculated using OLI Stream Analyzer 3.1 (Morris Plains, NJ). Since the structural characteristics of the membrane support layer t, τ and ε should be constant for membranes that are mechanically and chemically stable under the chosen experimental conditions (McCutcheon and Elimelech, 2006), $K_{m,B}$ was estimated from the measured $K_{m,s}$ using the following relationship by assuming equal S value:

$$\frac{K_{m,B}}{K_{m,s}} = \frac{D_B}{D_s} \tag{14.13}$$

14.2.4 *Feed solute rejection in FO*

Rejection of a pressure-driven membrane is typically defined as one minus the ratio of permeate concentration over feed concentration, where the permeate concentration is given by the ratio of permeate solute flux over the water flux (Baker, 2004). Consistent to this definition, the rejection of contaminants in FO processes is defined as:

$$R = 1 - \frac{c_{\mathrm{p,B}}}{c_{\mathrm{f,B}}} = 1 - \frac{J_{\mathrm{B}}}{J_{\mathrm{w}} \cdot c_{\mathrm{f,B}}} \tag{14.14}$$

By substituting Equations (14.8) and (14.12) into (14.14), rejection of boron by an FO membrane is expressed as follows:

$$R = 1 - \frac{B_{\mathrm{B}}}{B_{\mathrm{B}} + J_{\mathrm{w}}} \quad \text{(AL-FW)} \tag{14.15}$$

$$R = 1 - \frac{B_{\mathrm{B}} \exp(J_{\mathrm{w}}/K_{\mathrm{m,B}})}{B_{\mathrm{B}} \exp(J_{\mathrm{w}}/K_{\mathrm{m,B}}) + J_{\mathrm{w}}} \quad \text{(AL-DS)} \tag{14.16}$$

14.3 REMOVAL OF ORGANIC CONTAMINANTS BY FO MEMBRANES

Removal of trace organic contaminants such as endocrine disrupting chemicals (EDCs) and pharmaceuticals from the impaired water is essential to reduce the risk of the aquatic environment to humans and wildlife. Advanced treatment technologies such as membrane processes have been extensively used for trace organic removal. Although RO/NF can be powerful options to remove trace organic compounds from impaired water, these pressure-driven membrane processes are limited by membrane fouling and high energy consumption. Alternatively, FO technology, which has potentially low fouling tendency and low energy consumption, has been applied for the removal of trace organics recently (Alturki *et al.*, 2013; Hancock *et al.*, 2011; Jin *et al.*, 2012a; Xie *et al.*, 2012a; 2012b). This section will introduce the rejection of trace organics by FO and discuss the potential rejection mechanisms.

14.3.1 *FO rejection of trace organics*

In a recent study, Jin *et al.* (Jin *et al.*, 2012a) performed systematic research on the rejection of pharmaceuticals by FO. In this study, four types of flat-sheet FO membranes were used for removal of four different pharmaceuticals. The properties of the selected membranes and pharmaceuticals are summarized in Table 14.1 and Table 14.2, respectively. The selected membranes include: two commercial FO membranes (CTA-HW and CTA-W) that were made of cellulose triacetate (CTA) supported by polyester embedded woven mesh; two hand-cast thin film composite (TFC) FO membranes (TFC-1 and TFC-2) with a polyamide (PA) active layer and polysulfone

Table 14.1. Properties of the selected FO membranes. Reproduced from Jin *et al.* (2012a) with permission from Elsevier.

Membrane	Active layer material	Water permeability A [$\times 10^{-12}$ m s^{-1} Pa^{-1}]	NaCl permeability B_{s} [$\times 10^{-8}$ m s^{-1}]	Selectivity B_{s}/A [kPa]	Glucose rejection [%]	Contact angle [°]
CTA-HW	CTA	2.1 ± 0.4	7.2 ± 1.9	34	86.5 ± 3.9	63 ± 3
CTA-W	CTA	1.0 ± 0.1	5.2 ± 1.7	52	85.2 ± 1.2	73 ± 2
TFC-1	PA	3.4 ± 0.4	4.9 ± 0.5	15	90.9 ± 0.1	43 ± 4
TFC-2	PA	5.1 ± 0.2	9.4 ± 0.1	18	92.1 ± 0.4	45 ± 4

support layer. During all FO experiments, the membrane was oriented with its active layer facing the feed solution (i.e., AL-FS orientation). The selected pharmaceuticals were on the basis of environmental relevance.

The removal of the selected pharmaceuticals by FO membranes was first investigated with a feed water electrolyte background solution containing 10 mM NaCl and a draw solution containing 2 M NaCl. Under this condition, permeate water flux followed the order of CTA-W ($3.29 \pm 0.23\,\mu\text{m s}^{-1}$) < CTA-HW ($3.64 \pm 0.03\,\mu\text{m s}^{-1}$) < TFC-1 ($4.53 \pm 0.44\,\mu\text{m s}^{-1}$) < TFC-2 ($8.15 \pm 0.04\,\mu\text{m s}^{-1}$). Compared to CTA based membranes, the TFC polyamide membranes exhibited higher FO water flux. This is due to the higher water permeability A values and lower structure parameter S values of the TFC FO membranes. Figure 14.4 presents the rejection values of the pharmaceuticals by each FO membrane. For both TFC polyamide membranes, all compounds were efficiently removed with rejection ranging from 94 to 97%. The high removal efficiency of the TFC polyamide membranes can be attributed to the coupled effects of size exclusion, electrostatic repulsion and adsorption to the membrane surface, in a way similar to these mechanisms in reverse osmosis and nanofiltration (Bellona *et al.*, 2004; Nghiem *et al.*, 2005). Because of the nearly complete rejection, the influence of compound physicochemical properties on the rejection by TFC-1 and TFC-2 membranes was not observed.

For both CTA-HW and CTA-W membranes, the rejection of pharmaceuticals followed the order of decline: CMZ (95–96%) ≈ DCF (92–95%) > IBU (82–83%) > NPX (64–73%). As both

Table 14.2. Physico-chemical properties of selected pharmaceuticals. Reproduced from Jin *et al.* (2012a) with permission from Elsevier.

Compound	Acronym	Molecular weight MW [g mole^{-1}]	Dissociation constant pK_a	Partitioning coefficient log K_{ow}	Apparent partitioning coefficient log D		
					pH 3	pH 6	pH 8
Carbamazepine	CMZ	236	n.a.	2.45	2.45	2.45	2.45
Diclofenac	DCF	296	4.08	4.51	4.48	2.58	0.59
Ibuprofen	IBU	206	4.47	3.97	3.96	2.4	0.44
Naproxen	NPX	230	4.20	3.18	3.15	1.37	−0.62

n.a., not applicable.

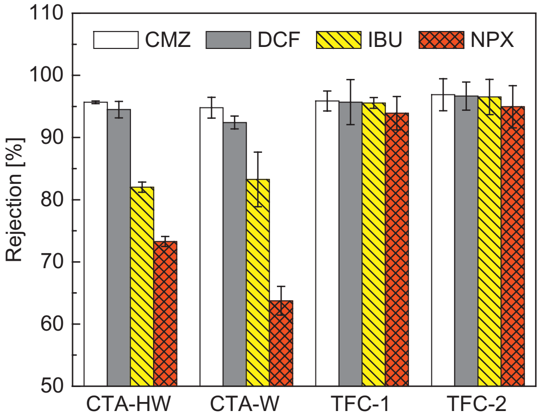

Figure 14.4. Pharmaceuticals rejection by selected FO membranes. The feed solution contained 250 μg L^{-1} of each pharmaceutical and 10 mM NaCl at pH 6. The draw solution contained 2 M NaCl. Figure reproduced from Jin *et al.* (2012a) with permission from Elsevier.

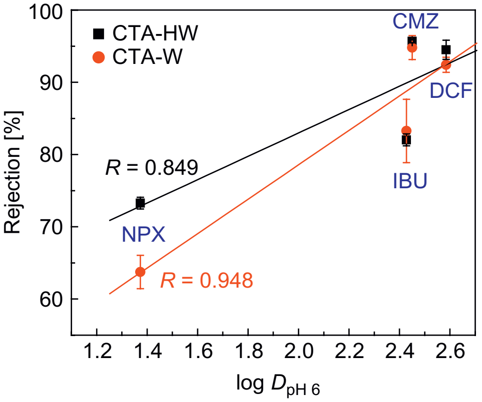

Figure 14.5. Pharmaceuticals rejection as a function of solute hydrophobicity (log *D*) with CTA-HW and CTA-W membranes. Figure reproduced from Jin *et al.* (2012a) with permission from Elsevier.

CTA-HW and CTA-W membranes had marginal negative charge (the absolute values were below 5 mV) in the feed water electrolyte background solution (10 mM NaCl at pH 6), the contribution of charge repulsion between negatively charged compounds and the CTA membranes to their rejection was unlikely important. Under this condition, the removal performance of the CTA membranes can be attributed to their adsorption capacities and size exclusion. The adsorption of pharmaceuticals onto the membranes is likely the result of hydrophobic interactions. In Figure 14.5, the pharmaceutical rejections are plotted as a function of their pH-dependent hydrophobicity (log *D* at pH 6) for both CTA-HW and CTA-W membranes. The hydrophobicity of the pharmaceuticals strongly influenced their rejection: increased rejection was observed for the pharmaceuticals with greater hydrophobicity. This phenomenon indicates that hydrophobic interaction between selected pharmaceuticals and CTA membranes may be the dominant short-term removal mechanism in FO process. Thus the poorest rejection of naproxen by CTA based FO membranes can be due to its lowest affinity to the membrane polymer, indicated by its smallest log *D* value. It is worth noting that the rejection of carbamazepine with relatively larger MW is significantly higher than that of ibuprofen, despite they have similar hydrophobicity (Table 14.2). This indicates that size exclusion also contributed to the initial pharmaceuticals rejection. However, initial adsorption of trace contaminants could not be considered a long-term removal mechanism since the amount adsorbed and rejected decreased with time.

In addition to their physicochemical characteristics, the pharmaceuticals rejection is also influenced by the membrane properties. For all selected pharmaceuticals, the TFC polyamide membranes exhibited higher rejection than the CTA membranes did (Fig. 14.4). It has been reported that solute rejection increased with increasing water flux in the AL-FS orientation (Jin *et al.*, 2011). Figure 14.6 presents the rejection of pharmaceuticals as a function of permeate water flux, where water flux was varied by changing NaCl concentration in the draw solution to isolate the effect of membrane physicochemical properties (zeta potential, hydrophobicity and pore size) from the effect of water flux. For carbamazepine and diclofenac, the effect of membrane property on their removal behavior is not noticeable. For naproxen and ibuprofen, rejection values were remarkably higher with TFC-1 and TFC-2 membranes than those with CTA-HW membrane considering the effect of water flux. The higher rejection by TFC-1 and TFC-2 membranes can be attributed to (i) the electrostatic repulsion between the deprotonated (negatively charged) naproxen/ibuprofen and the negatively charged surface of the TFC polyamide membranes at pH 6 and (ii) greater size exclusion effect indicated by the lower B_S/A values of TFC membranes (Table 14.2).

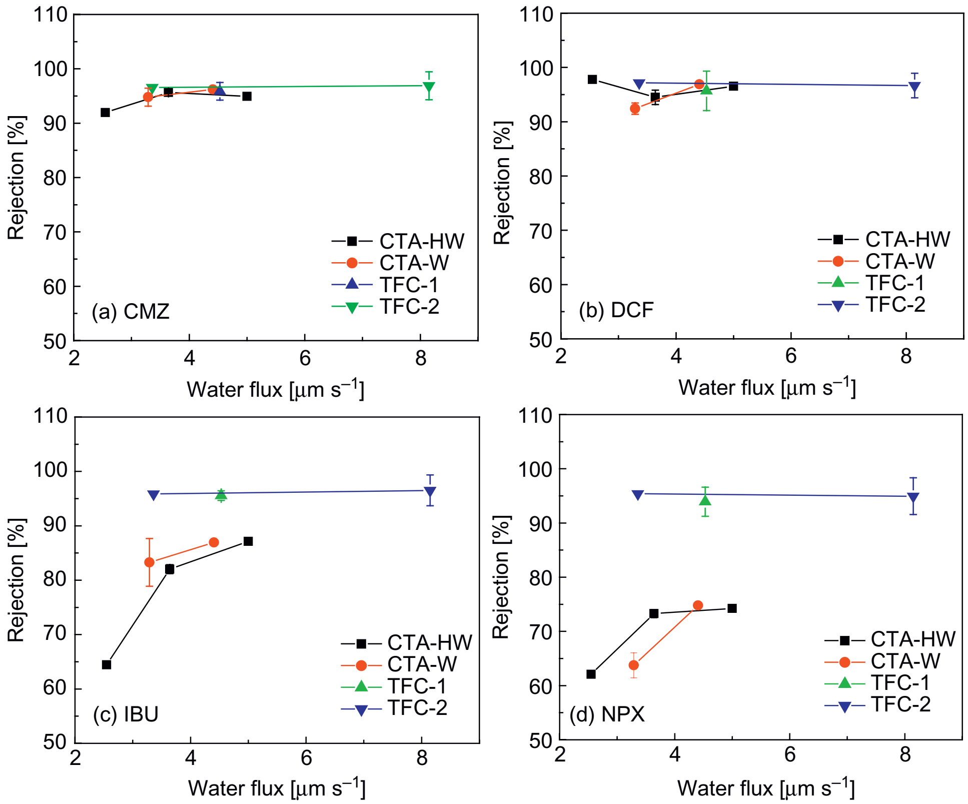

Figure 14.6. Rejection of (a) carbamazepine, (b) diclofenac, (c) ibuprofen, and (d) naproxen as a function of water flux. The feed solution contained 250 µg L^{-1} of each pharmaceutical and 10 mM NaCl at pH 6. The water flux was varied by changing NaCl concentration (1–4 M) in draw solution. Figures reproduced from Jin *et al.* (2012a) with permission from Elsevier.

14.3.2 *Effect of pH on trace organic rejection by FO*

As both membrane surface charge and pharmaceutical properties including hydrophobicity (log *D*) and charge vary with pH, the pharmaceuticals rejection can be pH dependent. To examine the effect of pH on the pharmaceuticals rejection, the experiments were conducted with feed solutions at different pH levels (3, 6 and 8). TFC-1 and CTA-HW membranes with different materials were used. For both membranes, feed water pH had no effect on the permeate water flux (data not shown). In Figure 14.7a, complete or almost complete rejection of all four pharmaceuticals by TFC-1 membrane was observed over the entire pH range tested. The pH effect on the pharmaceuticals rejection was not noticeable. This indicates that TFC-1 membrane performance is stable over pH 3–8 and that the size exclusion mechanism may dominate over than pH-dependent mechanisms (charge repulsion and adsorption).

For CTA-HW membrane, solution pH exhibited a remarkable influence on the rejection of naproxen and ibuprofen (Fig. 14.7b). As pH decreased from 6 to 3, naproxen rejection increased from 73 to 89% and ibuprofen rejection increased from 82% to 93%. At pH 3 (below their pK_a values), naproxen and ibuprofen exist predominantly as neutral species and their effective hydrophobicity (log *D*) is greatly higher than that at pH 6 (Table 14.2). This allows more compounds adsorption onto the CTA-HW membrane surface, which can be the cause for the enhanced rejection as the pH decreased from 6 to 3. As pH increased from 6 to 8, naproxen rejection

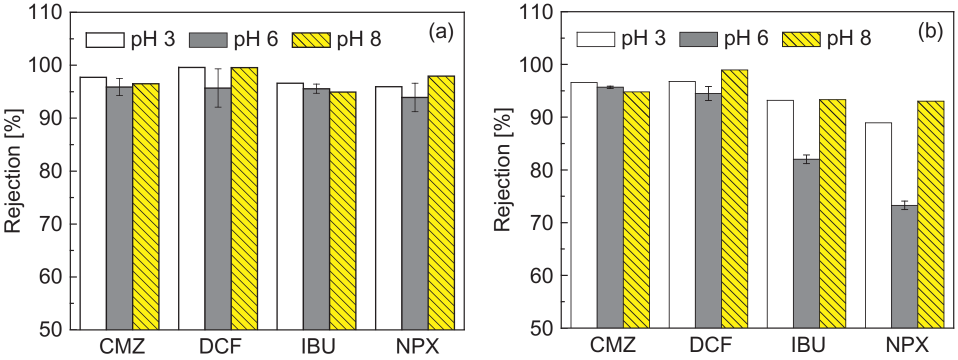

Figure 14.7. Effect of pH on pharmaceuticals rejection by (a) TFC-1 membrane and (b) CTA-HW membrane. The feed solution contained 250 $\mu g\,L^{-1}$ of each pharmaceutical and 10 mM NaCl. The draw solution contained 2 M NaCl. Figures reproduced from Jin *et al.* (2012a) with permission from Elsevier.

increased from 73 to 93% and ibuprofen rejection increased from 82 to 93%. This phenomenon can be attributed to an increase in the membrane surface negative charge as the solution pH increased (Fig. 14.1). The electrostatic repulsion between negatively charged naproxen/ibuprofen and membrane plays a dominant role in their rejection at pH 8. It is worth noting that although pH 3 and pH 8 are beyond the operating pH range (4–6) of the CTA membrane, this observation indicates that short-term application of the CTA based FO membrane under strongly acidic and weak alkaline conditions will not result in poor rejection of the pharmaceutical compounds investigated in this study.

14.3.3 *Comparison of trace organic rejection between FO and RO operations*

The removal behavior of the trace organics by FO and RO methods was compared by Xie *et al.* (Xie *et al.*, 2012a; 2012b). Figure 14.8 presents the bisphenol A (BPA) rejection in FO and RO modes. Bisphenol A is a hydrophobic compound with a distribution coefficient (log D) value of 3.64 at pH 7. The used CTA membrane was also moderately hydrophobic based on the contact angle values. Figure 14.8 shows that the feed concentration of the compound decreased as the filtration process progressed in both FO and RO modes, indicating that the adsorption of bisphenol A was adsorbed on the membrane. Despite this, the rejection behavior of bisphenol A in FO mode was remarkably different from that in RO modes when NaCl was used as the draw solution for FO. The adsorption process reached a quasi equilibrium state faster in the FO mode than that in the RO mode. In the FO mode, the BPA concentration in the feed solution decreased from 500 to 470 $mg\,L^{-1}$ within the first 100 min, and then slightly increased after 100 min of filtration due to the continuous reduction of the feed solution volume when water permeated through the membrane to the draw solution. In contrast, in the RO mode, it took almost 200 min for the feed BPA concentration to reach a stable value of approximately 420 mg^{-1}. Both mass balance calculation and extraction measurement consistently showed that the more amount of BPA adsorbed to the membrane in the RO mode compared to the FO mode.

Obviously, Figure 14.8 shows that the rejection of BPA in the FO mode was higher than that in the RO mode at the same permeate water flux. This observation in the FO mode in Figure 14.8 was comparable to that reported by Hancock *et al.* (2011) who examined the rejection of BPA by the same membrane using similar experimental conditions. The rejection value of BPA in the RO mode also agreed well with the estimated pore radius of the membrane, whose pore size is larger than that of the NF270 membrane and slightly smaller than that of the NF90 membrane. In the RO mode, the BPA rejection by the CTA FO membrane was 75%. In comparison, BPA rejection by

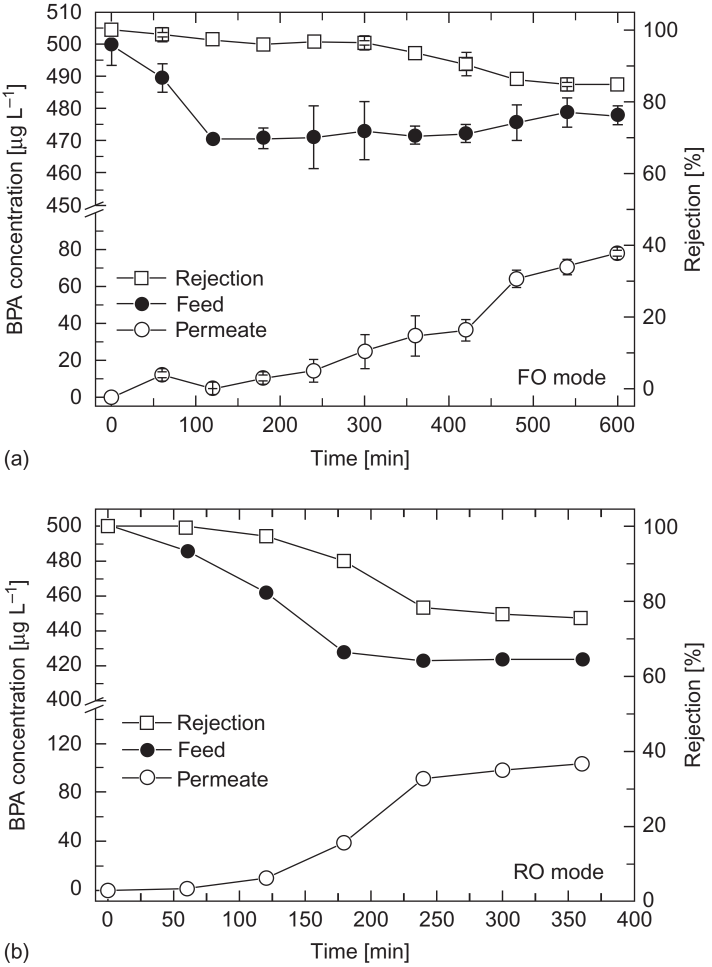

Figure 14.8. Bisphenol A (BPA) concentration in feed and permeate and rejection as a function of time in the (a) FO mode and (b) RO mode at the same permeate water flux of 5.4 $\mathrm{L\,m^{-2}\,h^{-1}}$ (or 1.5 $\mu\mathrm{m\,s^{-1}}$). The FO experimental conditions were as follows: the initial concentrations of BPA in the feed was 500 $\mathrm{mg\,L^{-1}}$, pH was 7, the background electrolyte contained 20 mM NaCl and 1 mM $NaHCO_3$, draw solution was 0.5 M NaCl, crossflow rate was 1 L $\mathrm{min^{-1}}$ for both sides, and crossflow velocity was 9 $\mathrm{cm\,s^{-1}}$. The temperature was 25 ± 1°C for both sides. The error bars represent standard deviation of data obtained from two independent experiments. The RO experimental conditions were as follows: the initial concentration of BPA in the feed was 500 $\mathrm{mg\,L^{-1}}$, pH was 7, the background electrolyte contained 20 mM NaCl and 1 mM $NaHCO_3$. Operating pressure 1.0 MPa, crossflow rate was 1 L $\mathrm{min^{-1}}$, crossflow velocity was 25 $\mathrm{cm\,s^{-1}}$, temperature was 25 ± 1°C. Figures reproduced from Xie *et al.* (2012a) with permission from Elsevier.

the NF270 and NF90 membranes in the RO mode was 30 and 90%, respectively (Nghiem *et al.*, 2008).

The higher BPA rejection in the FO mode compared to the RO mode when operated at the same permeate water flux may be due to the smaller adsorption of this compound to the membrane in the FO mode (i.e., 1.41 $\mu\mathrm{g\,cm^{-2}}$ in FO mode and 2.24 $\mu\mathrm{g\,cm^{-2}}$ in RO mode based on direct extraction measurement). The adsorption of hydrophobic trace organic contaminants to the membrane can subsequently facilitate their long-term transport by diffusion through the membrane polymeric matrix (Nghiem *et al.*, 2004). The molecular size of BPA is slightly smaller than the mean effective membrane pore size and diffusive transport of this compound through the membrane polymeric matrix is expected to be the dominant mechanism.

The relatively greater rejection of the trace organics by FO than that by RO could be attributed to the steric hindrance by the reverse draw solute diffusion through the membrane in the opposite direction in FO mode, i.e., the forward permeation of the feed solute within the membrane pores can be potentially retarded by the draw solute that reversely diffuses from the draw solution into the feed solution (Fig. 14.9). Significant reverse NaCl flux was observed when the NaCl was used as draw solution, (Table 14.3). It is also noted that the hydrated radii of Na^+ (~0.36 nm) and Cl^- (~0.33 nm) were comparable to that of the membrane pore radius (~0.37 nm) as well as the molecular dimensions of hydrophobic organic contaminants (i.e., height × length × width is ~0.38 nm × 1.07 nm × 0.59 nm) investigated in this study. Thus, the reverse solute diffusion could hinder the pore forward diffusion of the trace organic solute, leading to higher rejection in the FO mode than that in the RO mode. The "retarded forward diffusion" phenomenon was also observed by Hancock and Cath (2009), who reported that the permeation of dissolved silica (SiO_2) from the feed to the draw solution was lower when NH_4HCO_3 was used as the draw solute instead of NaCl or $MgCl_2$.

It is worthwhile to note that the retarded forward diffusion phenomenon would diminish when the reverse draw solute flux is negligible. This hypothesis is verified using glucose and $MgSO_4$ as the draw solutes for the FO experiments. Glucose has a low diffusion coefficient ($6.9 \times 10^{-10}\ m^2\ s^{-1}$) and a Stokes radius of 0.32 nm which is comparable to the membrane mean effective pore radius. $MgSO_4$ has a considerably low diffusion coefficient ($3.5 \times 10^{-10}\ m^2\ s^{-1}$)

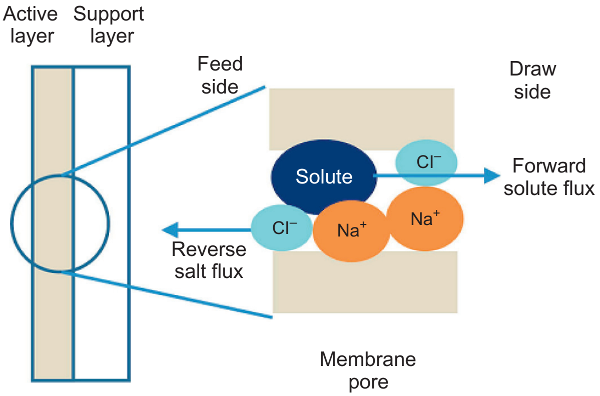

Figure 14.9. Schematic diagram representing the retarded forward diffusion of feed solutes in the FO process by the reverse draw solutes. Figure reproduced from Xie *et al.* (2012a) with permission from Elsevier.

Table 14.3. BPA mass balance in FO (NaCl, $MgSO_4$, and glucose draw solutions) and RO modes (permeate water flux = $5.4\ L\ m^{-2}\ h^{-1}$ (or $1.5\ \mu m\ s^{-1}$)). Reproduced from Xie *et al.* (2012a) with permission from Elsevier.

Operation mode	Draw solution	Reverse solute flux [$g\ m^{-2}\ h^{-1}$]	Normalized by membrane area [$\mu g\ cm^{-2}$]	
			Mass balance calculation	Direct extraction measurement
FO	NaCl	4.28	1.25	1.41
	$MgSO_4$	0.06	1.98	2.01
	Glucose	0.28	1.82	1.89
RO	n.a.	n.a.	2.07	2.24

n.a., not applicable.

and the hydration radii of Mg^{2+} (0.43 nm) and SO_4^{2-} (0.40 nm) are larger than the membrane pore radius (0.37 nm). As a result, the reverse fluxes of both glucose and $MgSO_4$ were negligible (Table 14.3). In the absence of substantial reverse flux of the draw solute, the pore transport and the adsorption of BPA to the membrane in both FO and RO modes were almost identical (Table 14.3). The rejections of BPA using glucose (77%) and $MgSO_4$ (76%) as the draw solutes in the FO mode were comparable to that in the RO mode (76%).

14.4 REMOVAL OF INORGANIC CONTAMINANTS BY FO MEMBRANES

In addition to the organic contaminants, a wide range of inorganic contaminants, such as boron and As, can be found in natural and engineered aquatic environments. The occurrence and fate of these contaminants is an important environmental and public concern. The removal of boron and As are important topics in groundwater treatment and seawater desalination, respectively, and their removal by RO/NF membranes has been studied extensively. At typical pH of natural water (pH 5–8), boron and arsenite mainly exist as uncharged species while arsenate exists as anion. RO/NF membranes are capable of removing 48–65% of boron, 22–75% of arsenite and 90–99% of arsenate (Figoli *et al*., 2010; Nguyen *et al*., 2009). Recently, Jin *et al*. (2011; 2012b) used FO membranes for boron and As removal and achieved boron rejection of 30–60% and As rejection of 60–95%. This section will introduce the study on the FO rejection of inorganic contaminants (i.e., boron and As) and discuss the underlying rejection mechanisms.

14.4.1 *FO rejection of inorganic contaminants: effect of membrane orientation*

In the experimental feed solution with pH 6, boron and arsenite mainly exist as uncharged species (H_3BO_3 and H_3AsO_3), which are not hydrated. In contrast, Ca^{2+} ions have a high hydration number and large hydrated radius, and thus diffuse less readily through the membrane than uncharged H_3BO_3 and H_3AsO_3 species. The measured permeability of the boron (B_B), arsenite (B_{As}) and calcium (B_{Ca}) through the selected CTA-HW FO membrane are $5.02 \pm 0.87 \times 10^{-6}\ \mathrm{m\,s^{-1}}$, $1.91 \pm 0.27 \times 10^{-6}\ \mathrm{m\,s^{-1}}$ and $137 \pm 0.33 \times 10^{-7}\ \mathrm{m\,s^{-1}}$, respectively. Figure 14.10 presents the rejection of inorganic compounds (boron, As and calcium) by FO membranes in different orientations. When the water flux increased from $\sim 1\ \mu\mathrm{m\,s^{-1}}$ to $\sim 7.2\ \mu\mathrm{m\,s^{-1}}$ in the AL-FW orientation,

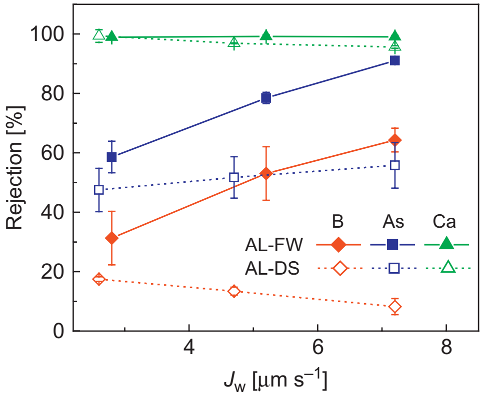

Figure 14.10. Effect of membrane orientation on solutes rejection by FO membrane. The feed solution contained 7 mM NaCl, 1 mM $CaCl_2$, 10 mg L^{-1} boron and 10 mg L^{-1} arsenite. The draw solution contained 0.5, 2, 5 M NaCl for AL-FW orientation and 0.25, 0.5, 1 M NaCl for AL-DS orientation. Other experimental conditions were as follows: cross-flow velocity = 23.2 cm s^{-1}, pH ≈ 6, and temperature = 24°C. Figure reproduced from Jin *et al.* (2012b) with permission from Elsevier.

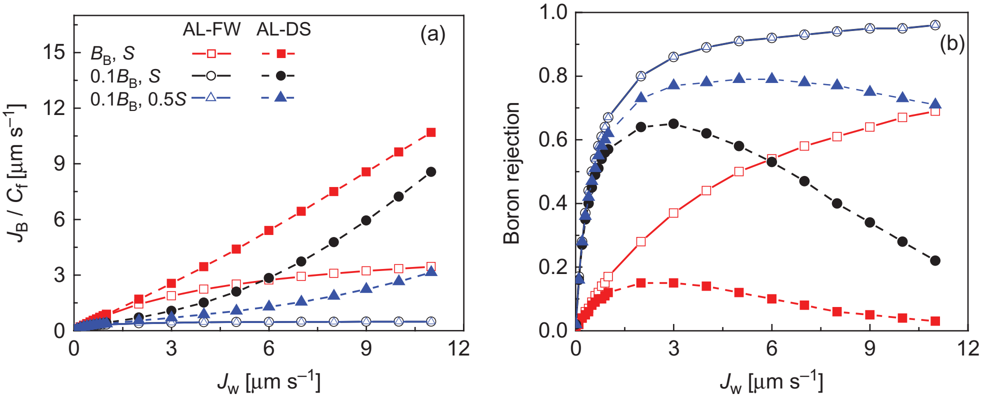

Figure 14.11. Influence of boron permeability (B_B) and membrane structural parameter (S) on predicted (a) boron flux and (b) rejection. Figures reproduced from Jin *et al.* (2011) with permission from Elsevier.

the boron rejection increased from 30 to 60%, the arsenite rejection increased from 60 to 90%, and the calcium was nearly completely rejected. In comparison, lower rejection of all three types of solutes was observed in the AL-DS orientation: ~9–18% boron rejection, ~46–55% arsenite rejection, and ~95–99% calcium rejection. The difference in rejection between the two FO membrane orientations became greater at higher water flux level. This behavior is attributed to the severe internal concentration polarization of the feed solutes in the AL-DS orientation (Jin *et al.*, 2011). In this orientation, solutes in the feed water can enter the membrane support layer but are retained by the rejection layer. The accumulation of solutes in the porous support layer leads to a higher solute concentration gradient across the membrane active layer and thus a lower solute rejection. It is worth noting that the difference in rejection between the two orientations followed the order of boron > arsenite >> calcium, which was consistent with the sequence in solute permeability B values. This observation is in agreement with the modeling results of the forward boron flux and boron rejection by FO membranes (Fig. 14.11), which suggests the role of ICP in solutes rejection by FO membrane becomes less important with decreasing solutes permeability.

Figure 14.11 illustrates the effect of boron permeability (B_B) and membrane structural parameter (S) on the normalized boron flux and boron rejection based on Equations (14.8), (14.12), (14.15) and (14.16). The lines labeled with "B_B, S" represent the performance of CTA-HW FO membrane. B_B was then decreased by 10 times to represent the typical boron permeability of a high boron rejection SWRO membrane or a BWRO membrane when operating at pH of 10.5. The S value was reduced to half of the value of CTA-HW FO membrane to simulate a membrane with less thickness, higher porosity and lower tortuosity. In both orientations, the decrease of B_B can significantly decrease the boron flux (Fig. 14.11a) and improve the boron rejection (Fig. 14.11b). This suggests that the solute with lower permeability through a membrane tends to better rejection in FO. A decreasing S value, which reduces ICP, can further reduce the boron flux and improve the boron rejection. The reduction effect is more significant at higher water flux. Moreover, water flux and boron concentration in the feed solution are important factors that must be considered. Higher water flux and feed concentration result in higher boron flux. It is worth noting that based on current FO membrane technology, the AL-DS orientation is not preferred due to its lower removal efficiency of contaminants in addition to its higher fouling propensity.

14.4.2 *Effect of FO membrane fouling on the rejection of inorganic contaminants*

Alginate, a major component of the effluent organic matter in wastewater, was selected as the model foulant to conduct the FO membrane fouling experiments. Each FO fouling experiment

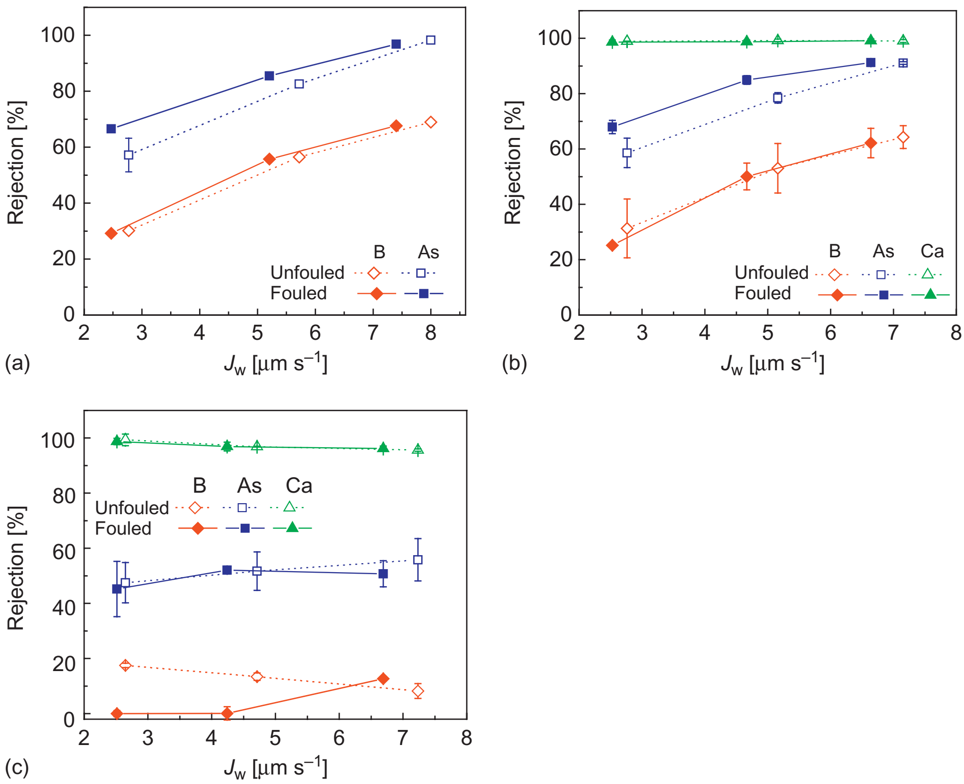

Figure 14.12. Effect of alginate fouling on rejection of inorganic solutes in FO experiments with (a) AL-FW and FW containing 10 mM NaCl, (b) AL-FW and FW containing 7 mM NaCl + 1 mM $CaCl_2$ and (c) AL-DS and FW containing 7 mM NaCl + 1 mM $CaCl_2$. Figures reproduced from Jin *et al.* (2012b) with permission from Elsevier.

was first conducted for 8 hours. Then the solutes rejection of both unfouled and fouled FO membranes was characterized to examine the influence of alginate fouling. Figure 14.12 illustrates the solutes rejection by both clean and fouled FO membranes. For both orientations, rejection of Ca^{2+} was not affected by alginate fouling and rejection remained above 95% (Figs. 14.12b and 14.12c). In contrast, alginate fouling had diverse influences on the rejection of boron and arsenite depending on membrane orientations. In the AL-FW orientation (Figs. 14.12a and 14.12b), fouled membranes were able to better reject the arsenite compared to clean membranes. Alginate fouling can change the effective pore size of the FO membrane through sealing the molecular-scale defects in the FO rejection layer and creating an additional barrier that restricts the passage of non-ionic inorganic compounds, resulting in an increased arsenite rejection. However, boron rejection was not significantly affected by membrane fouling. This could be ascribed to the much smaller MW of boric acid. The enhanced sieving effect caused by alginate deposition is not enough to increase boron rejection.

In the AL-DS orientation, arsenite rejection by the fouled membrane remained approximately equal to that by the clean membrane. When the support layer is facing the feed solution, membrane fouling can cause two opposite effects on the rejection of inorganic contaminants by FO membrane. On the one hand, foulant entrapment inside the porous support layer will likely reduce porosity of support layer, resulting in a greater structural parameter and thus a reduced mass transfer coefficient. Consequently, alginate fouling inside the membrane support layer can decrease the

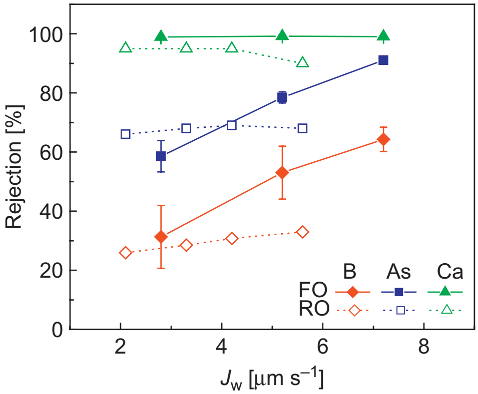

Figure 14.13. Comparison of solutes rejection between FO and RO operation with active layer facing the feed solution. The feed solution contained 7 mM NaCl, 1 mM $CaCl_2$, 10 mg L^{-1} boron and 10 mg L^{-1} arsenite. Other experimental conditions were as follows: cross-flow velocity = 23.2 cm s^{-1}, pH ≈ 6, and temperature = 24°C. The permeate flux was varied by changing the applied pressure (100–260 psi ≈ 687–1793 kPa) for RO operation and by changing NaCl concentration (0.5–5 M) in the draw solution for FO operation. Figure reproduced from Jin *et al.* (2012b) with permission from Elsevier.

arsenite rejection by exacerbating the ICP effect. On the other hand, alginate deposition can lead to pore clogging and thus improve the rejection. Owing to these two competing mechanisms with opposite effects, the effect of fouling on arsenite rejection was not observed. However, boron rejection was found to be negatively impacted by alginate fouling at water flux below 4.2 μm s^{-1}. The decline in boron rejection was from 17 ± 1% and 13 ± 1% to zero at the draw solution concentration of 0.25 M and 0.5 M, respectively. As discussed earlier, the enhanced sieving effect by limited alginate fouling is not enough to increase boron rejection by the FO membrane. Therefore, the membrane fouling-enhanced ICP effect can play a dominate role, resulting in the complete loss of boron rejection by the alginate-fouled FO membrane. The severe decline in boron rejection due to alginate fouling has important implications for seawater and brackish water desalination with FO.

14.4.3 *Comparison of inorganic contaminants rejection between FO and RO operations*

Figure 14.13 presents the rejection of boron, arsenite and calcium as a function of water flux determined from both RO and FO experiments with active layer facing the feed solution. For both operation modes, solutes rejection followed the order of calcium > arsenite > boron, which was in agreement with the order of their permeability. In FO operation, the rejection of calcium was relatively constant at 99% over the water flux investigated. In contrast, greater boron and arsenite rejection was observed at greater water flux. This is attributed to "dilution effect". In membrane filtration processes, the rejection of solutes that are present in the feed water is defined as Equation (14.14). The water flux increases at a greater rate than the flux of solutes permeating across the membrane. Thus, the solutes rejection increases with increasing water flux. It is worthwhile to note that FO rejection of all solutes was higher than RO rejection especially at higher water flux. This may be due to the deformation of polymer chains and thus the expansion of network pores under hydraulic pressure which allows solutes to penetrate through the membrane more readily in the RO operation mode. This has important technical implications that FO membranes can achieve higher solute rejection but require less mechanical stability than RO membranes.

14.5 CONCLUSIONS AND OUTLOOK

FO technology has shown great promise in water applications. This chapter presents the use of FO membranes for both organic and inorganic trace contaminants removal. The effects of membrane materials, membrane orientation, feed solution pH, and membrane fouling on the trace contaminants removal were reviewed. The rejection efficiency between FO operation and RO operation was also compared. Moreover, the underlying rejection mechanisms were discussed. Overall, FO can achieve more than 90% rejection of most trace organic contaminants under the normal operating conditions. For the charged trace organics, electrostatic repulsion and size exclusion are dominant rejection mechanisms. In addition, the rejection of both organic and inorganic contaminants in FO operation is greater than that in RO operation probably due to the retarded reverse draw solute diffusion in FO operation and the membrane instability at very high applied pressures in RO operation. Specifically, As removal by FO technology was systematically evaluated. In general, FO can remove 60–95% As from aquatic solutions, while the removal efficiency in RO operations is below 70%. Membrane fouling can also improve the As rejection through the sealing of the membrane pores.

Due to the high rejection of trace contaminants and low prime energy consumption, FO can be potentially applied for the removal of a wide range of contaminants not only limited to those introduced in this chapter. For example, the toxic U and F^- either in domestic or industrial waters can be potentially removed by FO technology, although there is no report of relevant studies in the existing literature. The future research can be warranted to systematically investigate the efficiency and mechanisms of U and F^- removal by FO. In addition, the advanced and efficient technology for draw-solute synthesis and draw-solution regeneration should be developed for the widespread application of FO technology, if the ultimate goal is to extract the clean water from the contaminated feed water.

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