

M.H. Fulekar
Bhawana Pathak
R.K. Kale *Editors*

Environment and Sustainable Development

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M.H. Fulekar
School of Environment
and Sustainable Development
Central University of Gujarat
Gandhinagar, Gujarat
India

Bhawana Pathak
School of Environment
and Sustainable Development
Central University of Gujarat
Gandhinagar, Gujarat
India

R.K. Kale
School of Life Sciences
Jawahar Lal Nehru University
New Delhi and Vice Chancellor
Central University of Gujarat
Gandhinagar, Gujarat
India

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About the Book

Global society in the 21st century is facing challenges of improving the quality of air, water, soil and the environment and maintaining the ecological balance. Environmental pollution, thus, has become a major global concern. The modern growth of industrialization, urbanization, modern agricultural development and energy generation has resulted in the indiscriminate exploitation of natural resources for fulfilling human desires and needs, which has contributed in disturbing the ecological balance on which the quality of our environment depends.

Human beings, in the truest sense, are the product of their environment. The man-environment relationship indicates that pollution and deterioration of the environment have a social origin. The modern technological advancements in chemical processes/operations have generated new products, resulting in new pollutants in such abundant levels that they are above the self-cleaning capacity of the environment. One of the major issues in recent times is the threat to human lives due to the progressive deterioration of the environment from various sources. The impact of the pollutants on the environment will be significant when the accumulated pollutants load will exceed the carrying capacity of the receiving environment.

Sustainable development envisages the use of natural resources, such as forests, land, water and fisheries, in a sustainable manner without causing changes in our natural world. The Rio de Janeiro-Earth Summit, held in Brazil in 1992, focused on sustainable development to encourage respect and concern for the use of natural resources in a sustainable manner for the protection of the environment.

This book will be beneficial as a source of educational material to post-graduate research scholars, teachers and industrial personnel for maintaining the balance in the use of natural sources for sustainable development.

About the Editors



Dr. M.H. Fulekar is Professor and Dean at the School of Environment and Sustainable Development, Central University of Gujarat. He was also Professor and Head, University Department of Life Sciences, University of Mumbai. He has in his credit more than 150 research papers and articles published in national and international journals of repute. He is also author of 10 books. He has supervised nine Ph.D. students. He has done extensive research in the area of Environmental Sciences under the following research projects: UGC, CSIR, BRNS, DBT (R&D) and industrial consultancy projects.



Dr. Bhawana Pathak is Assistant Professor at the School of Environment and Sustainable Development, Central University of Gujarat. Earlier she has worked as a Pool Officer in the Department of Life Sciences, University of Mumbai. She has done research in the area of Plant Ecology and Biodiversity Conservation from G. B. Pant Institute of Himalayan Environment and Development, Kosi Katarmal Almora, Uttaranchal. She was awarded gold medal in her postgraduate studies. Her research interests include Environmental Biotechnology and Biodiversity.



Professor R.K. Kale has been teaching at the School of Life Sciences, Jawaharlal Nehru University (JNU), New Delhi. He has published more than 120 research papers in national and international scientific journals. He supervised research work of 29 students leading to award of Ph.D. and also 6 students for M.Phil degree. His research areas include cancer and radiation biology. He has also greatly contributed to the area of higher education and society. He was awarded ICMR Prize for Biomedical Research – 1996, for his original contribution to radiation biology. He

has extensive experience in University Administration and Planning; and served the JNU in various capacities including Dean of the School of Life Sciences. Presently, he is Vice-Chancellor of the Central University of Gujarat, Gandhinagar, India.

Contents

1	Emergence of Green Technologies Towards Sustainable Growth	1
	Tapan Chakrabarti	
2	Sustainable Development: An Earnest Hope	23
	Sangeeta Singh	
3	Soil Seed Bank Dynamics: History and Ecological Significance in Sustainability of Different Ecosystems	31
	Upama Mall and Gopal S. Singh	
4	Challenges and Prospects in Exploring Marine Microbial Diversity	47
	K.B. Akondi and V.V. Lakshmi	
5	Bioprospecting of Plant Essential Oils for Medicinal Uses	59
	Jayant Shankar Raut and Sankunni Mohan Karuppayil	
6	Air Pollution Scenario over Delhi City	77
	Siddhartha Singh and S.K. Peshin	
7	Nanotechnology: Perspective for Environmental Sustainability	87
	M.H. Fulekar, Bhawana Pathak, and R.K. Kale	
8	An Overview of Environmental Remediation Using Photocatalyst	115
	Dimple P. Dutta	
9	Role of Biopolymers in Industries: Their Prospective Future Applications	133
	Ria Rautela and Swaranjit Singh Cameotra	
10	Green Federalism: A Historic Leap Towards Sustainable Human Development	143
	Indira Dutta and Jiya Shahani	
11	Economic Sustainability in Light of Consumer Behaviour: Gandhian Perspectives	159
	Nimisha Shukla and Sudarshan Iyengar	

12 Global Warming and Agriculture: Institutional Arrangement for Sustainable Development	173
A.K. Asthana	
13 Green Buildings: Opportunities and Challenges	177
R.R. Singh and Suhail Sharma	
14 Mathematical Models in Sustainable Development	185
R.N. Singh	
Index	195

Contributors

K.B. Akondi Department of Microbiology, Sri Padmavati Mahila Visvavidyalayam, (Women's University), Tirupati, Andhra Pradesh, India

A.K. Asthana Udaybhansinhji Regional Institute of Co-operative Management (Ministry of Agriculture, Govt. of India), Gandhinagar, Gujarat, India

Tapan Chakrabarti CSIR-National Environmental Engineering Research Institute, Nagpur, India

Dimple P. Dutta Chemistry Division, Bhabha Atomic Research Centre, Mumbai, Maharashtra, India

Indira Dutta Centre for Studies in Economics and Planning, School of Social Sciences, Central University of Gujarat, Gandhinagar, Gujarat, India

M.H. Fulekar School of Environment and Sustainable Development, Central University of Gujarat, Gandhinagar, Gujarat, India

Sudarshan Iyengar Gujarat Vidyapeeth, Ahmedabad, Gujarat, India

R.K. Kale School of Life Sciences, Jawahar Lal Nehru University, New Delhi and Vice Chancellor, Central University of Gujarat, Gandhinagar, India

Sankunny Mohan Karuppaiyl DST-FIST & UGC-SAP Sponsored School of Life Sciences, SRTM University, Nanded, MS, India

V.V. Lakshmi Department of Microbiology, Sri Padmavati Mahila Visvavidyalayam, (Women's University), Tirupati, Andhra Pradesh, India

Upama Mall Department of Botany, Banaras Hindu University, Varanasi, Uttar Pradesh, India

Bhawana Pathak School of Environment and Sustainable Development, Central University of Gujarat, Gandhinagar, Gujarat, India

S.K. Peshin India Meteorological Department, Environment Monitoring & Research Centre, New Delhi, India

Jayant Shankar Raut DST-FIST & UGC-SAP Sponsored School of Life Sciences, SRTM University, Nanded, India

Ria Rautela Institute of Microbial Technology, Mumbai, India

Jiya Shahani School of Social Sciences, Central University of Gujarat, Gandhinagar, Gujarat, India

Nimisha Shukla Rural Economics, Gujarat Vidyapeeth, Ahmedabad, Gujarat, India

Gopal S. Singh Institute of Environment and Sustainable Development, Banaras Hindu University, Varanasi, Uttar Pradesh, India

R.R. Singh PEC (DU), Chandigarh, India

R.N. Singh INSA Senior Scientist, CSIR-National Geophysical Research Institute, Hyderabad, India

Sangeeta Singh Department of Earth and Atmosphere Sciences, Metropolitan state University of Denver Auraria, Denver, CO, USA

Siddhartha Singh India Meteorological Department, Environment Monitoring & Research Centre, New Delhi, India

Swaranjit Singh Cameotra Institute of Microbial Technology, Chandigarh, India

Emergence of Green Technologies Towards Sustainable Growth

1

Tapan Chakrabarti

Abstract

Environmental technology (abbreviated as envirotech) or green technology (abbreviated as greentech) or clean technology (abbreviated as cleantech) is the application of the environmental science and green chemistry to conserve the natural environment and resources and to curb the negative impacts of human involvement. A growing wave of global environmentalism is forcing manufacturers to produce greener products through greener processes. Sustainable growth demands that market should take steps both to expand the number of green-oriented products they receive and to reduce heavy environmental footprint. For the technology industries at large, going green requires transformation along virtually every step of every value chain.

This chapter deals with the 4 principal requirements for sustainable development, 12 principles of green engineering, 5 major attributes of green technology and 9 Rs for waste minimisation and waste to wealth paradigm shift and addresses 'end-of-life' issues. Emphasis should be laid on ecosystem protection and reduction in the waste and greenhouse gas emission within the limits of the carrying capacity of the ecosystem. Under no circumstances, the biodiversity should be sacrificed in the name of development. Safety, health and environmental (SHE) issues must be given top priority in all developmental ventures so that sustainable development with environment and health security is ensured for all the time. Special emphasis is laid on adoption of environmental carrying capacity-based planning process. Policy and regulation based on scientific and economic tools (natural resource accounting, polluter pays, damage assessment, risk-based standards and remediation) are the key ingredients for sustainable consumption and development.

T. Chakrabarti (✉)
CSIR-National Environmental Engineering Research
Institute, Nehru Marg, Nagpur 440020, India
e-mail: tapan1249@gmail.com

Keywords

Green technology • Energy efficiency • Hazardous material • Recycle material • Sustainable design

Preamble

A growing wave of global environmentalism is forcing manufacturers to produce greener products through greener processes. Sustainable growth demands that market should take steps both to expand the number of green-oriented products they receive and to reduce heavy environmental footprint. Sustainable development is the core of green environmental technologies. Sustainable development is the development that meets the needs of the present without compromising the ability of future generations to meet their needs. Sustainable growth is a subset of sustainable development. For the technology industries at large, going green requires transformation along virtually every step of every value chain.

Environmental technology (abbreviated as envirotech) or green technology (abbreviated as greentech) or clean technology (abbreviated as cleantech) is the application of the environmental science and green chemistry to conserve the natural environment and resources and to curb the negative impacts of human involvement. The four principal requirements for sustainable development are:

- Green demand grows.
- Green requires industry collaboration.
- Taking proactive steps towards sustainability.
- Hardware and software opportunities and support.

The 12 principles of green engineering are:

- *Inherent rather than circumstantial*
Designers need to strive to ensure that all materials and energy inputs and outputs are as inherently nonhazardous as possible.
- *Prevention instead of treatment*
It is better to prevent waste than to treat or clean up waste after it is formed.

- *Design for separation*
Separation and purification operations should be designed to minimize energy consumption and material use.
- *Maximize efficiency*
Products, processes, and systems should be designed to maximize mass, energy, space, and time efficiency.
- *Output pulled versus input pushed*
Products, processes, and systems should be “output pulled” rather than “input pushed” through the use of energy and materials.
- *Conserve complexity*
Embedded entropy and complexity must be viewed as an investment when making design choices on recycle, reuse, or beneficial disposition.
- *Durability rather than immortality*
Targeted durability, not immortality, should be a design goal.
- *Meet need, minimize excess*
Design for unnecessary capacity or capability (e.g., “one size fits all”) solutions should be considered a design flaw.
- *Minimize material diversity*
Material diversity in multicomponent products should be minimized to promote disassembly and value retention.
- *Integrate material and energy flows*
Design of products, processes, and systems must include integration and interconnectivity with available energy and materials flows.
- *Design for commercial “afterlife”*
Products, processes, and systems should be designed for performance in a commercial “afterlife.”
- *Renewable rather than depleting*
Material and energy inputs should be renewable rather than depleting.

The 12 principles of green chemistry are:

- *Prevention*
It is better to prevent waste than to treat or clean up waste after it has been created.
- *Atom economy*
Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- *Less hazardous chemical syntheses*
Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
- *Designing safer chemicals*
Chemical products should be designed to effect their desired function while minimizing their toxicity.
- *Safer solvents and auxiliaries*
The use of auxiliary substances (e.g., solvents, separation agents) should be made unnecessary wherever possible and innocuous when used.
- *Design for energy efficiency*
Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
- *Use of renewable feedstocks*
A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
- *Reduce derivatives*
Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
- *Catalysis*
Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
- *Design for degradation*
Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

- *Real-time analysis for pollution prevention*
Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
- *Inherently safer chemistry for accident prevention*
Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Attributes of Green Technology

The five major attributes of green technology are:

- **Sustainability**
Meeting the needs of society in ways that can continue indefinitely into the future without damaging or depleting natural resources. In short, meeting present needs without compromising the ability of future generations to meet their own needs.
- “Cradle-to-cradle” design
Ending the “cradle-to-grave” cycle of manufactured products, by creating products that can be fully reclaimed or reused
- **Source reduction**
Reducing waste and pollution by changing patterns of production and consumption
- **Waste reduction plans focus on 9Rs:**
 - (i) Restore
 - (ii) Reduce
 - (iii) Renew
 - (iv) Recover
 - (v) Recycle
 - (vi) Reuse
 - (vii) Rethink
 - (viii) Replenish
 - (ix) Replace
- **Innovation**
Developing alternatives to technologies – whether fossil fuel or chemical intensive agriculture – that have been demonstrated to damage health and the environment
- **Viability**
Creating a center of economic activity around technologies and products that benefit the en-

vironment, speeding their implementation and creating new careers that truly protect the planet

The green design and manufacturing calls for

- Pursuance of energy efficiency
- Avoidance of using and manufacturing hazardous materials
- Use of recycled materials
- Use of recyclable materials
- Designing to last
- Waste to wealth
- Packaging to meet the global packaging standards
- Addressing “end-of-life” issues

Pursuance of Energy Efficiency

The improvement in the standard of living and ever-expanding population result is high consumption of nonrenewable resources. It is estimated that 20 % of population is consuming 80 % of nonrenewable resources. To manage with limited resources, new technology is currently being researched and manufactured to reduce the consumption of nonrenewable energy. Energy consumption is divided into four classifications: the residential, commercial, industrial, and transportation sectors of the economy. Of these four categories, industry consumes the most amount of energy. By 2050, oil production throughout the world will be only half of what it is today, and, therefore, alternate sources of energy need to be discovered and implemented soon. In fact, the production of renewable energy is one of the keys to energy conservation.

There are several ways of conserving energy: the first being efficient energy use, which refers to using existing forms of energy and making it last longer. A good example of this is a car that has a higher mileage per liter of petrol/diesel/gas. Adoption of green architecture is another way of energy conservation. In transportation sector, automobiles can have more advanced tires, which decrease the friction between the road and the car; changes in motor oil formulas, which decreases the internal friction in the engine; and also breakthroughs in the aerodynamics of the

vehicles. Car companies are developing new hybrid car models with better fuel efficiency and a heavier reliance on electric energy, which considerably reduces the oil consumed as fuel for a vehicle. In fact, electric cars reduce greenhouse gases emissions, decrease in air pollution, and lessen the dependence on oil. LED light bulbs supply light for televisions, computers, phones, lamps, flashlights, headlights, and other systems. Furthermore, devices are incorporating more effective power save modes. An Energy Star efficient washing machine reduces the amount of electricity and water used per wash cycle, greatly reducing the energy cost. Another vanguard of future green technology is an advancement of electrical infrastructure known as Smart Grid. Currently, the power distribution system is wasteful in its transportation of electricity to the general consumer. The term Smart Grid refers to a proposed technology where a network of information-based equipment cooperates with the already established power distribution infrastructure. With meters strategically placed to track the patterns of electrical flow, the information could be used by both the utility companies and the ultimate consumer. Utility companies could adjust the flow and distribution to be more efficient with the knowledge of where the electricity is being used. In addition, sources of other electrical energy such as solar and wind energy could be incorporated into the distribution system easily and put to use effectively. With more data to analyze, companies can find the optimal positioning for new towers and power lines that will fulfill the highest need or yield the largest profit.

There are several applications for green technology in industry. Cogeneration is a relatively new method of harnessing the heat dissipated off plants that are generating electricity.

Avoidance of Using and Manufacturing Hazardous Materials

From the use of nonrenewable resources for fuel and feedstock (e.g., gas and soil), through the

release of pollutants from factories during production, to the disposal of final products that contain hazardous waste, each stage of the life cycle of a product produced by the chemical industry (“cradle to grave”) can have negative impacts on man and his environment (OECD 2001). The reaction system in a process transforms the feeds from lower-value materials to higher-value products. Green chemistry is the design of chemical products and chemical processes that reduce or eliminate the use and/or generation of hazardous substances. This involves the definition of the feed materials, reaction pathways, products, and reactor conditions to minimize the impact of the reaction system on the environment, including the workers. The various aspects considered are:

- Use of nonhazardous, renewable feed materials
- Development of molecules that are not toxic, bioaccumulative, and persistent in the environment, yet still retain the desired functionality for which the product molecule was designed
- Development of reaction systems that use non-hazardous, environmentally friendly materials, media, and conditions (temperature, pressure, and energy requirements) to manufacture the desired molecules

As any material added to, or made in, a process will ultimately be emitted to the environment, the hazardous nature of the feedstock to a chemical process must be taken into consideration. If a toxic material is required, then only small amounts, at a time, should be used in the process of manufactured.

Green chemistry research is, therefore, focused on reducing the inherent toxicity of feedstock materials through structural modification or replacement and on the in situ manufacturing of toxic feedstock from nontoxic feed materials. The ideal would be to develop molecules that are not toxic, do not pass through a toxic state during metabolism, are not persistent, are not bioaccumulative, and have the desired efficacy for which the product is designed. Some examples include direct reaction of carbon dioxide with amines, instead of with phosgene, to produce isocyanates and urethanes. Use of polysaccharides

from biological/agricultural wastes to make new polymeric substances and development of a process for the in situ manufacture of methyl isocyanate in a small reactor, rather than purchasing and storing larger quantities of the material as a feedstock, are some of the other examples to check the hazardous impact of the process.

In contrast to feedstock and molecule development, green chemistry’s focus is on the reactor system which encompasses catalyst and solvents.

Catalysis can lead to the design and implementation of environmentally benign processes by developing reaction pathways that attain 100 % selectivity towards the desired product. Catalysis can also reduce the amount of energy required to transform feed materials into products, that is, allowing reactions to proceed rapidly at lower pressures and temperatures. The ability to run a system closer to ambient conditions is one of the basic principles of inherently safer processing.

The tragic release of methyl isocyanate (MIC) at Bhopal led to the development of a catalytic route for in situ manufacture of MIC. Within 6 months after the incident, an online small, catalytic pipeline reactor could be developed that produced MIC, resulting in only a few pounds being inventoried in the process at any one time.

Elimination of solvents not only eliminates waste generation, but it also reduces the cost of manufacture. A supercritical fluid, such as carbon dioxide, is an example of a very desirable solvent substitute. Studies showed that free-radical halogenations (bromination) in supercritical fluids were equal to, or superior to, those conducted in conventional solvents. Methyl methacrylate polymers could be produced in supercritical fluids, thus eliminating the need for halogenated organic solvents.

Use of Recycled Materials

Recycling is processing used materials (waste) into new products to prevent waste of potentially useful materials, reduce the consumption of fresh raw materials, reduce energy usage, reduce air pollution (from incineration) and water pollution

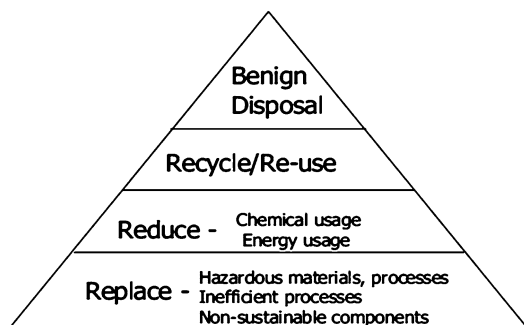


Fig. 1.1 Green chemistry priorities (Smith 2003)

(from landfilling) by reducing the need for “conventional” waste disposal, and lower greenhouse gas emissions as compared to virgin production (Wikipedia). Recycling is a key component of modern waste reduction and is the third component of the “Reduce, Reuse, Recycle” waste hierarchy. The recycling sector in India has been in operation since the 1960s, and while only a fraction of the total plastic waste is being recycled in most Western countries, around 75 % of the plastic wastes are recycled in India (Haque et al. 1997; Haque 1998). Ragpickers mainly carry out the recycling process in India, and they play a vital role in the economy of solid waste recycling process (Agarwal et al. 2005).

Recycling, being one of the green chemistry priorities, is shown in Fig. 1.1.

In the strictest sense, recycling of a material would produce a fresh supply of the same material – for example, used office paper would be converted into new office paper, or used foamed polystyrene into new polystyrene. Paper is a natural resource that can be recycled up to about five times. This substantially reduces the impact on the environment. By using recycled paper, unnecessary use of virgin materials can be avoided. Today the quality of paper containing recycled fiber (e.g., 51 % recycled fiber) has improved and is comparable with virgin paper. Similarly, one can think of recycling plastics, glass, metals, and wood derived from municipal solid wastes. However, this is often difficult or too expensive (compared with producing the same product from raw materials or other sources), so “recycling” of many products or materials involves their reuse in

producing different materials (e.g., paperboard) instead. There are some ISO standards relating to recycling such as ISO 15270:2008 for plastics waste and ISO 14001:2004 for environmental management control of recycling practice.

However, this is often difficult or too expensive for other materials (compared with producing the same product from raw materials or other sources). Therefore, “recycling” of many products or materials involves their reuse in producing different materials (e.g., paperboard) instead.

The two leading innovative mechanisms of waste disposal being adopted in India include composting (aerobic composting and vermicomposting) and waste to energy (WTE) (incineration, pelletization, biomethanation). WTE projects for disposal of MSW are a relatively new concept in India. Although these have been tried and tested in developed countries with positive results, these are yet to get off the ground in India largely because of the fact that financial viability and sustainability is still being tested.

Municipal solid waste (MSW) generally includes degradable (paper, textiles, food waste, straw, and yard waste), partially degradable (wood, disposable napkins, and sludge), and nondegradable materials (leather, plastics, rubbers, metals, glass, ash from fuel burning like coal, briquettes or woods, dust, and electronic waste). Composition-wise MSW has around 50 % of organic/biodegradable materials, around 10 % of the recyclables, and around 40 % of inert materials. Generally, MSW is managed as collection from streets and disposal at landfills. Aerobic composting is practiced by some of municipalities in the country. Most of the municipalities opt for uncontrolled landfilling. Anaerobic decomposition of MSW in landfills generates about 60 % methane (CH₄) and 40 % carbon dioxide (CO₂) together with other trace gases.

The major barriers to the recycling of hazardous waste are economic in nature. Although the technology may be available to recycle or recover chemicals from hazardous wastes, costs for disposal are lower than to recycle; investment risk is high, and payback is low for recycling

facilities. Further, the volume of available waste material and market for recycled materials are small.

Use of Recyclable Materials

Recyclable materials encompass raw or processed material that can be recovered from a waste stream for reuse and include many kinds of glass, paper, metal, plastic, textiles, and electronics. Although similar in effect, the composting or other reuse of biodegradable waste – such as food or garden waste – is not typically considered recycling. Materials to be recycled are either brought to a collection center or picked up from the curbside, then sorted, cleaned, and reprocessed into new materials bound for manufacturing.

Designing to Last

Waste minimization and resource maximization for manufactured products can most easily be done at the design stage. Reducing the number of components used in a product or making the product easier to take apart can make it easier to be repaired or recycled at the end of its useful life.

In some cases, it may be best not to minimize the volume of raw materials used to make a product but instead reduce the volume or toxicity of the waste created at the end of a product's life or the environmental impact of the product's use.

Waste to Wealth

Globally, the estimated quantity of annual wastes generation during 2010 is about 20 billion tons of which about 12 billion tons is industrial wastes and 4 billion tons is municipal solid wastes (MSW). Currently, out of 1 billion tons of waste produced annually in India, about 350 million tons is organic wastes arising from agricultural sources and about 390 million tons is inorganic waste from industrial and mining sectors. The rest of them are from different sources such as municipal, medical and biomedical/hospital, radioactive, hazardous, and electrical and electronic waste.

The sources for the nonhazardous inorganic wastes are coal combustion residues, overburden wastes from coal colliery, mine tailing, and wastes from aluminum, iron, copper, and zinc primary and secondary extraction processes. The major sources for agricultural waste are as follows: bagasse; biomass yield (except grain and edible yield) of crops, vegetables, and cereals; groundnut shell; wooden mill waste; coconut husk; and cotton stalk and residues from natural fiber extraction processes. The sources for the hazardous wastes are electroplating, metal extraction, galvanizing, refinery, petrochemical, pharmaceutical, leather, ship-breaking, paint, and coating industries.

Recycling is one of those activities which has taken off in India very well. However, environmentally sound technologies (ESTs) must be adopted to carry on with green recycling operations (Haque et al. 2000).

Packaging to Meet the Global Packaging Standards

Global packaging industry is growing swiftly and ready to meet the tomorrow's trends although the global recession of 2009 has also affected the sales of the packaging products and packaging films. During recession, a decline in the global packaging sales has been observed which is about 2.6 % in 2009. But the global packaging industry has regained its original growth in 2010 and expected to reach \$739.9 billion by 2014. The global market for packaging machinery is projected to reach US\$52.9 billion by the year 2018, the annual growth rate being 3.1 %. With such a high growth rate, the global packaging industry has become an integral part of product marketing, merchandising, food chain, and logistics. Seventy percent of the sales is estimated in the consumer market and rest of the 30 % in industrial market. In consumer market, the food industry is the biggest industry using the packaging films and material. After this comes the beverage industry.

Environmental concerns have led to governments throughout the world taking steps to deal with the issue of packaging waste and recycling.

Packaging directives from the European Commission, for example, have led to the imposition of challenging targets for recycling, and national governments are also examining new ways to discourage packaging waste. Landfill is a major political issue, with landfill taxes and ban on landfill of organic material being introduced by governments – in some cases before the necessary infrastructure is in place to provide alternatives to disposal.

In the light of climate change and environmental concerns, major retailers and brand owners have started to put pressure on suppliers, demanding carbon footprints and sustainable business practices. Also consumers have begun to desire all things natural, unaffected by “unnatural” processes, hence the suspicion of GM foods, etc. The packaging industry has taken steps to address the environmental question, but this has been more of a function of cooperation with government rather than a broader perspective. A broad collaboration throughout the value chain will be required in the future to address sustainability, avoiding suboptimization.

Addressing “End-of-Life” Issues

All products have a life cycle that covers a sequence of interrelated stages from the acquisition of raw materials until their end of life, when the product’s functionality no longer satisfies the requirements of the original owner (2). At the end of life, the product can be disposed of or its life cycle extended over time (2,4) (Fig. 1.1). There are five basic end-of-life strategies. In accordance with their potential economic and environmental efficiency, the strategies can be ranked as follows:

- Reuse
- Servicing
- Remanufacturing
- Recycling
- Disposal

Manufacturers can reduce the life-cycle environmental impacts of their products through their influence on product design, material choices, manufacturing processes, product delivery, and product system support.

From an economic perspective, extended producer responsibility (EPR) is a referential strategy to promote the integration of the environmental costs associated with product life cycles into the market prices of the products. This economic approach to EPR focuses on the role of producers and consequently of corporate organizations. The minimization and prevention of wastes, the increased use of recycled materials in production, and the internalization of environmental costs in product prices are fundamental while implementing an EPR program in companies.

Although all strategies follow the extended producer responsibility principle, in practice several logistic differences arise due to particular interpretations of the concept. In general, it was observed that a direct comparison is rather difficult since the strategies consider different legal frameworks, they cover different types and numbers of products, and the resultant mass flows and related operational costs are highly context-dependent variables. Therefore, it is not possible to indicate which strategy presents the highest overall efficiency. The study concludes that a little contribution is feasible if the advantages and weaknesses of the models depicted and discussed here are considered in further regulatory decisions.

Sustainable Design Principles

The main attributes of sustainable design principles are:

- Low-impact raw materials
Nontoxic, sustainably produced or recycled materials which require little energy to process.
- Energy efficiency
Manufacturing processes and products which require less energy.
- Quality and durability
Longer-lasting and better-functioning products to be used to avoid frequent replacement.
- Design for reuse and recycling
Reusable and recyclable products, processes, and systems to be adopted.
- Design impact measures

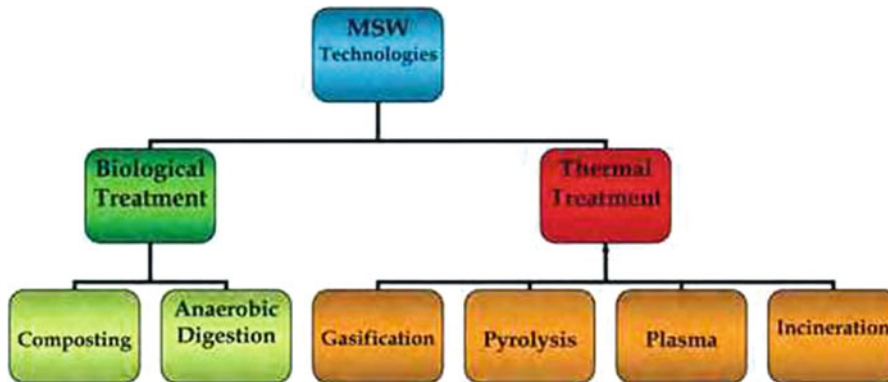


Fig. 1.2 Different biological and thermal methods for solid waste management

Calls for total carbon/ecological footprint measurement and life-cycle assessment for any resource used.

- Sustainable
Sustainable design standards and project design guides are to be adopted.
- Biomimicry
Redesigning industrial systems on biological lines enabling the constant reuse of materials in continuous closed cycles.
- Service substitution
Shifting the mode of consumption from personal ownership of products to provision of services which provide similar functions, e.g., from a private automobile to a car sharing service. Such a system promotes minimal resource use per unit of consumption.
- Renewability
Materials should come from nearby places (local or regional) and from sustainably managed renewable sources that can be disposed of in an environmentally friendly manner when their usefulness has been exhausted.
- Robust eco-design
Robust design principles are to be applied to reduce for treatment process
Some of the green technologies currently being practiced for MSW in India are:
 - Mechanical biological treatment (MBT)
 - Materials recovery facility (clean MRF)
 - Energy from waste
 - Moving grate incineration
 - Fluidized bed incineration

- Landfill gas recovery (LGR)
- Refuse-derived fuel plant

The effective management of solid waste (MSW) involves the application of various treatment methods, technologies, and practices. All applied technologies and systems must ensure the protection of the public health and the environment. Apart from sanitary landfill, mechanical recycling, and common recycling routes for different target materials, the technologies that are applied for the management of domestic solid waste include (Fig. 1.2) biological treatment (composting, anaerobic digestion) and thermal treatment technologies (incineration, pyrolysis, gasification, plasma technology).

Figure 1.2 shows different biological and thermal methods for solid waste management.

Mechanical Biological Treatment of MSW (Aerobic Composting)

Total MSW generated in urban India is around 68.8 million tons per year (TPY) or 188,500 t per day (TPD). The data collected indicate a 50 % increase in MSW generated within a decade since 2001. In a “business as usual scenario,” urban India will generate 160.5 million TPY (440,000 TPD) by 2041; in the next decade, urban India will generate a total of 920 million tons of municipal solid waste that needs to be properly managed in order to avoid further deterioration of public health, air, water and land

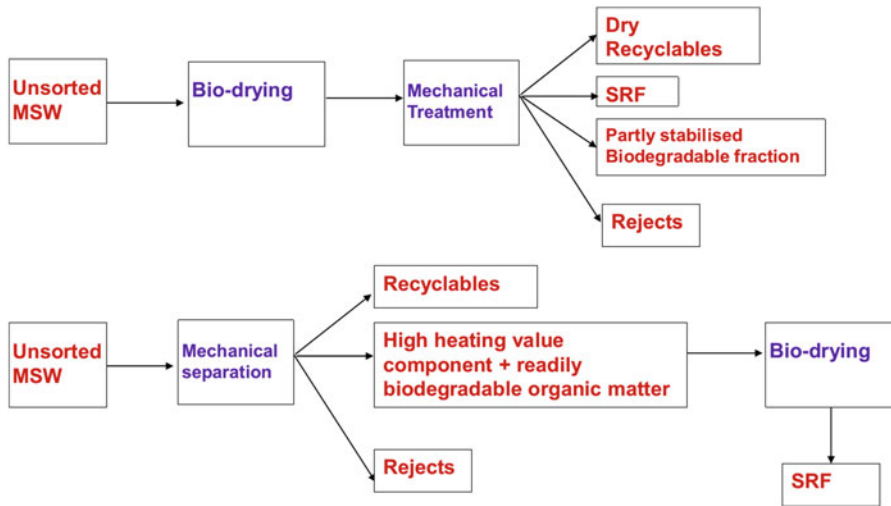


Fig. 1.3 Simplified configurations of MBT process (Source: Anurag Garg 2012)

resources, and the quality of life in Indian cities. The calorific value of the waste varied between 6.8 and 9.8 MJ/kg (1,620–2,340 kcal/kg). In a “business as usual” scenario, India will not be able to dispose these wastes properly.

Aerobic composting (or mechanical biological treatment) is the preferred option for the country’s solid waste management as determined by the Supreme Court of India in 1999 based on the Burman Committee Report.

The compost product from mixed wastes was found to be of very low quality and contaminated by heavy metals (Fig. 1.3). The majority of the mixed waste compost samples fell below the quality control standards for total potassium, total organic carbon, total phosphorus, and moisture content and exceeded the quality control limits for heavy metals (lead (Pb) and chromium (Cr)). If all MSW generated in India in the next decade were to be composted as mixed waste and used for agriculture, it would introduce 73,000 t of heavy metals into agricultural soils (Sustainable Solid Waste Management in India by Ranjith Kharvel Annepu submitted in partial fulfillment of the requirements for the degree of Master of Science in Earth Resources Engineering Department of Earth and Environmental Engineering Fu Foundation School of Engineering and Applied Science Columbia University in the City of New York

January 10, 2012). Use of compost product from mixed wastes for agriculture should be regulated in view of heavy metal contents. It should be used for gardening purposes only or as landfill cover.

This study also found that the calorific value (lower heating value) of some composting rejects (up to 60 % of the input MSW) is as high as 11.6 MJ/kg (2,770 kcal/kg). This value is much higher than the minimum calorific value of 7.5 MJ/kg (1,790 kcal/kg) recommended for economically feasible energy generation through grate combustion. Rejects from the composting facility should be combusted in a waste-to-energy facility to recover energy. Ash from WTE facilities should be used to make bricks or should be contained in a sanitary landfill facility. Such a system will divert 93.5 % of MSW from landfilling and increase the life span of a landfill from 20 to 300 years. It will also decrease disease, improve the quality of life of urban Indians, and avoid environmental pollution. Figure 1.3 depicts a simplified configuration of MBT process.

Materials Recovery Facility (Clean MRF)

Life-cycle impacts of extracting virgin raw materials and manufacturing make material recovery options like recycling and composting the most

environment-friendly methods to handle waste. They are positioned higher on the hierarchy compared to other beneficial waste handling options like energy recovery. Due to the limitations for source separation, wastes are collected in a mixed form which is referred to as municipal solid waste (MSW). Once the wastes are mixed, it becomes difficult to separate them. Recyclables can still be separated manually to some extent as is widely practiced in India. High-income countries use machines to do the same, but they would need the recyclables to be collected as a separate dry stream without mixing with organic food wastes.

The separated stocks of paper, plastic, glass and metal can then be recycled. A 100 % separation of these materials from MSW is highly energy and time intensive and is generally not carried out.

Energy from Waste

The overall power potential from MSW in India is estimated to be 3,650 MW and 5,200 MW by 2012 and 2017, respectively. Waste to energy (WTE) is the only technological solution which could recover the maximum energy and materials from mixed waste. WTE boilers are specifically designed to be flexible with feed in order to be able to handle highly heterogeneous mixed solid wastes. Electricity generation from WTE would require a steam turbine in addition to the combustion facility and therefore is more expensive compared to a facility which generates only steam. The capital cost of building such a WTE plant is USD 51,000 (INR 2,300,000) per ton of waste processed in comparison to windrow composting which costs only \$4,500 (INR 200,000) per ton of organic waste processed. Cost per kilowatt hour of electricity generated by MSW is slightly costlier than other biomass fuels, wind, and small hydro. It is very cheap compared to solar photovoltaic, which is currently highly subsidized by GOI.

WTE is recognized as a renewable energy technology by the Government of India (GOI). Australia, Denmark, Japan, Netherlands, and the USA are some countries which recognize WTE as a renewable energy technology (15). Due to the dominance of organic waste in MSW, it is considered as a biofuel which can be replenished

by agriculture. In India, urban MSW contains as much as 60 % organic fraction and 10 % paper. Therefore, potentially, 70 % of energy from WTE plants is renewable energy. Two WTE plants and two RDF-WTE plants were built in India until now. The latest one among them has finished construction on the Okhla landfill site, New Delhi, and is about to start operations. The first WTE incinerator in India was installed at Timarpur, Delhi, in 1985. It was designed to produce 3.75 MW of electricity, based on imported technology at the cost of \$9.1 million (INR 410 million). It failed to operate on a daily basis and was on a trial run until 1990 when it was closed.

Moving Grate Incineration

The incineration of MSW essentially involves combustion of waste leading to volume reduction and recovery of heat to produce steam that in turn produces power through steam turbines; basically, it is a furnace for burning waste and converts MSW into ash, gaseous and particulate emissions, and heat energy. The efficiency of the technology is linked to the waste characteristics and their properties such as moisture content and calorific values. When the waste is dry, it may not need any auxiliary fuel except for start-up, but when it is rich in inert and moisture content, supplementary fuel may be needed to sustain combustion, adversely affecting net energy recovery. The combustion process involves essentially drying, volatilization, and ignition and desirably elimination of odors and combustion of unburned furnace gases and carbon suspended in the gases. It requires high temperature of the order of 800–1,000 °C and sufficient air and mixing of gas stream. The minimum temperature for burning carbonaceous wastes to avoid release of smoke and prevent emissions of dioxins and furans is 850 °C. In order to ensure proper breakdown of organic toxins, this temperature should be maintained at least for 2 min. For steam generation and energy recovery, the combustion temperature should be 1,400 °C. This will also ensure degradation of all organic compounds. Depending on the nature of wastes and the op-

erating characteristics of combustion reactor, the gaseous products derived from the combustion of MSW may include carbon dioxide (CO₂), water (H₂O, flue gas), oxygen (O₂), nitrogen oxides (NO_x), sulfur dioxide (SO₂), and small amounts of hydrogen chloride, mercury, lead, arsenic, cadmium, dioxins and furans, and organic compounds. The combustion residues include bottom ash, fly ash, and noncombusted organic and inorganic materials. Modern incinerators include pollution mitigation equipment such as flue gas cleaning, and in such versions, sludge from scrubber and waste water adds to the contaminants in lieu of polluted emissions. There are various types of incinerator plant design: moving grate, fixed grate, rotary kiln, and fluidized bed. Proper design and operation of incinerators should achieve desired temperatures, residence times, and other conditions necessary to destroy pathogens, minimize emissions, avoid clinker formation and slagging of the ash (in the primary chamber), avoid refractory damage destruction, and minimize fuel consumption. Good combustion practice (GCP) elements also should be followed to control dioxin and furan emissions. Incinerators generally cannot meet modern emission standards without emission controls. For example, dioxin concentrations in combustion gas could be 100–700 times higher than the (EU) legal limit (0.1 ng TEQ/m³), depending on the waste composition. One new control approach appears very promising, namely, catalytic filter technology that removes dioxins and furans, along with particulate matter. This essentially passive technology can be retrofitted in existing baghouses, typically following water quenching and dry scrubbing, and it appears cost effective. However, it is not likely adaptable to small-scale units that do not have exhaust fans, any pollution controls, much less the needed infrastructure.

The typical incineration plant for municipal solid waste is a moving grate incinerator. The moving grate enables the movement of waste through the combustion chamber to be optimized to allow more efficient and complete combustion. A single moving grate boiler can handle up to 35 t of waste per hour and can operate 8,000 h per year with only one scheduled stop for inspection

and maintenance of about 1 month's duration. Moving grate incinerators are sometimes referred to as municipal solid waste incinerators.

Fluidized Bed Incineration

According to the technology that is applied for this type of incinerator, a strong airflow is forced through a sand bed. The air seeps through the sand until a point is reached where the sand particles separate to let the air through and mixing and churning occurs; thus a fluidized bed is created and fuel and waste can now be introduced

Landfill Gas Recovery

Landfill gas (LFG) recovery has been shown to be economically feasible at seven landfills located in four cities: Delhi, Mumbai, Kolkata, and Ahmadabad. Development of these seven LFG recovery projects will result in an overall GHG emissions reduction of 7.4 million tons of CO₂ equivalents. One of these landfills, the Gorai dumpsite in Mumbai, has already been capped in 2008 for capturing and flaring LFG. This project will result in an overall GHG emissions reduction of 2.2 million tons of CO₂ equivalents by 2028.

Refuse-Derived Fuel Plant

Refuse-derived fuels (RDFs) cover a wide range of waste materials including residues from MSW recycling, industrial/trade waste, sewage sludge, industrial hazardous waste, and biomass waste. High calorific fractions from processed municipal solid waste (MSW) and industrial wastes are being used both in dedicated energy-to-waste plants and as fuel substitutes in industrial processes. One of the less expensive and well-established technologies to produce RDF from MSW is mechanical biological pretreatment (MBT) as has been mentioned earlier. An MBT plant separates out metals and inert materials, screens out organic fractions (for stabilization using composting processes, either with or without a digestion phase), and separates out high calorific fractions for RDF. RDF can also result from a "dry stabilization

process” in which residual waste (after separating out metals and inert materials) is dried through a composting process leaving the residual mass with a higher calorific value.

A wide range of industrial wastes are also processed to be co-incinerated in industrial processes as secondary fuels. These wastes include plastics and paper/card from commercial and industrial activities (i.e., packaging waste or rejects from manufacturing), waste tires, biomass waste (i.e., straw, untreated waste wood, dried sewage sludge), waste textiles, residues from car dismantling operations (automotive shredder residues – ASR), and hazardous industrial wastes such as waste oils, industrial sludge, impregnated sawdust, and spent solvents. These wastes need to have a high calorific value to be consistent in quality and to be cheap. Secondary fuels processed from industrial waste are commonly co-incinerated in cement kilns. RDF can be suitably used in coal-based power plants, cement production, and waste incineration plants. Gasification and pyrolysis processes are generally promoted as “greener” alternatives to incineration or energy from waste. Via gasification, the energy content of the waste is transformed into a syngas which can be reused as chemical feedstock or to produce power. Pyrolysis produces from waste a biofuel and syngas which again can be used as chemical and/or for power production. However, the major negative factor about adopting gasification and pyrolysis for waste treatment is that they are less proven in operation than mass burn incineration.

India has a total of five RDF processing plants, located near Hyderabad, Vijayawada, Jaipur, Chandigarh, and Rajkot. The first two plants burn the RDF produced in WTE boilers, whereas the next two burn the RDF in cement kilns. All these facilities have encountered severe problems during operation. Problems mainly pertain to lack of proper financial and logistical planning and not due to the technology. Only two WTE combustion plants were built in India, both in New Delhi. The latest one among them has finished construction in Okhla landfill site and is about to begin operations. It is designed to generate 16 MW of electricity by combusting 1,350 TPD of MSW.

Technology to Be Based on Sound Ecological Principles

The green technology proposed to be adopted must also encompass certain sound ecological principles:

- Protection of ecosystem
- Adoption of clean(er) energy options
- Carbon capture and sequestration
- Environment and health security

Protection of Ecosystem

Protection of ecosystem can be ensured through:

- Adoption of carrying capacity–based planning process
- Avoidance of activities which may lead to irreversible ecological damage
- Maintaining environmental flow in rivers

Adoption of Carrying Capacity–Based Planning Process

The concept of carrying capacity implies that improvement of the quality of life is possible only when the pattern and level of production–consumption activities are compatible with the capacities of the natural environment as well as with social preference. The carrying capacity–based planning process thus involves the integration of social expectations and ecological capabilities and aims not only at environment harmony but also at long-term sustainability of the natural resource base and economic efficiency in resource utilization vital for ensuring sustainable development.

For human society, carrying capacity can be defined as the maximum rate of resource consumption and waste discharge that can be sustained indefinitely in a defined planning region without progressively impairing the bio-productivity and ecological integrity. Carrying capacity is ultimately determined by the single vital resource or function in least

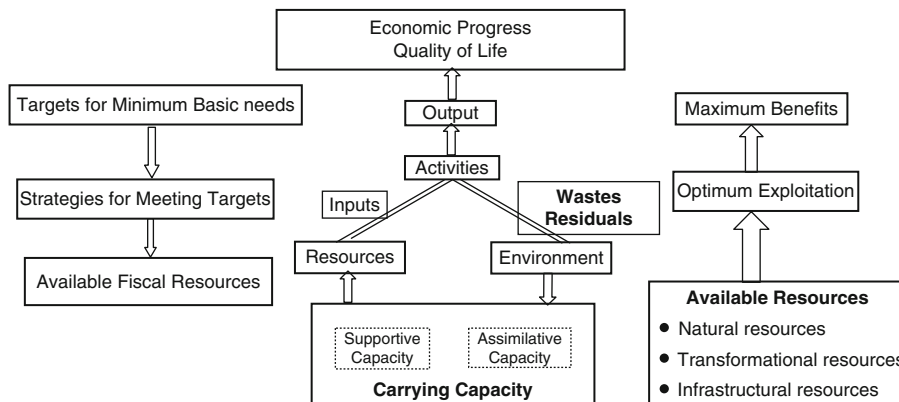


Fig. 1.4 Elements of carrying capacity

supply. Working within the limits of carrying capacity does not, however, preclude some unavoidable environmental damage in the course of development.

The carrying capacity–based planning process involves the integration of societal expectations and ecological capabilities by minimizing differentials between realized and desired supply/demand patterns, infrastructure congestion patterns, resource availability/resource use patterns, and assimilative capacity/residual patterns. Given certain flow of resources, the carrying capacity–based planning process uses various modeling and analytical techniques to estimate changes in carrying capacity indicators and makes trade-offs like changes in technology and pricing pattern, changes in environmental system structures, changes in socially acceptable capacity levels, and control of exogenous forcing functions.

Elements of carrying capacity are shown in Fig. 1.4.

Avoidance of Activities Which May Lead to Irreversible Ecological Damage

India is one of the mega diversity countries of the world with:

- Over 15,000 flowering plant species
- Totally over 45,000 species of plants
- Over 77,000 species of animals

- 1,178 bird species
- 10 recognized biogeographic zone

It is among the top 12 countries of the world in respect of the diversity and endemism of species and harbors 6.5 % of the world’s species. About a third of the flowering plants species and 18 % of the total species are endemic to India.

Since India is a party to the Convention on Biological Diversity (CBD) whose main objectives are: conservation of biological diversity, sustainable use of the components of biodiversity, and fair and equitable sharing of benefits arising out of the utilization of genetic resources, the country must take all necessary measures to maintain the unique biodiversity and avoid all activities leading to irreversible ecological damage. One of the major challenges before the country lies in adopting policy and legislative instruments which help realize the objectives of equitable benefit sharing enshrined in the convention. India has worked out biodiversity legislation. It aims at regulating access to and conserve as well as protect biological resources.

Maintaining Environmental Flow in Rivers

“An Environmental Flow is the water regime provided within a river, wetland or coastal zone to maintain ecosystems and their benefits” (adapted from Dyson et al. 2003). Environmental flow is defined as the flow that is necessary to ensure

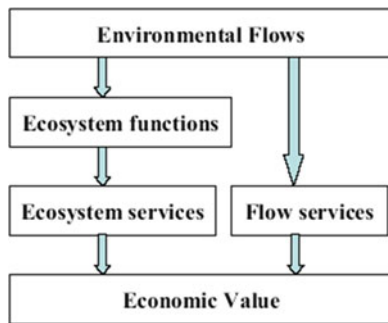


Fig. 1.5 Links between flows, functions, services, and economic value

the existence of habitats in a river. Environmental flows may comprise elements from the full range of flow conditions which describe long-term average flows, variability of flows including low flows and irregular flooding events (EFG 1999).

In this country, the Center (Parliament) legislated only with regard to interstate rivers (Entry 56 of List I Union-List of the Seventh Schedule and Article 262 of the Constitution) and not on waters of state rivers over which the concerned state alone had the full and final authority. Article 21 guarantees the right to life and state's river waters are the lifeline of its people. The riparian Indian states has its sovereign right over its rivers that cannot be taken away by any means though sharing of river waters can be possible only with co-riparian states. This riparian right has been acknowledged by the tribunal made under the Inter-State Water Disputes Act, 1956, in case of the Narmada that passes through MP, Maharashtra, and Gujarat.

Therefore, the minimum flow in all the rivers must be above the environmental flow applicable for individual rivers so that the river ecology as well as ecological services is maintained throughout all seasons. The links between flows, functions, services, and values are shown in Fig. 1.5.

Adoption of Cleaner Energy Options

The types of energy used in India are:

- Nonrenewable energy
Petroleum, natural gas and coal

- New and renewable energy
Solar energy, hydroelectric energy, wind energy, nuclear energy, tidal energy, hydrogen energy, wood energy, energy from biomass or biofuel, chemical energy, and geothermal energy

The country's energy policy states that the energy needs to be utilized not just from the conventional energy resources like the coal, petroleum, natural gas deposits, and burning of wood that is still a perishable source but also from other new and nonconventional renewable sources like wind, water, geothermal, and biomass. The India energy policy act clearly mentions development of newer energy sources that are more efficient and nonperishable.

About 70 % of India's energy generation is from fossil fuels, with coal accounting for 40 % of India's total energy consumption followed by crude oil and natural gas at 24 % and 6 %, respectively. India has a total hydro energy potential of about 1.5 lakh MW of which about 20 % is installed. Small hydro plant potential is about 15,000 MW, and most of it is in the northern and eastern hilly regions.

Indian geothermal provinces have the capacity to produce 10,600 MW of power – a figure which is five times greater than the combined power being produced from nonconventional energy sources such as wind, solar, and biomass. However, geothermal power projects have not been effectively implemented due to the availability of around 200 billion tons of recoverable coal reserves.

Wind energy will be the biggest beneficiary and will grow from its present position of around 7,500 MW of installations to 45,000 MW potential which is indeed a long way to go. In a short span, i.e., around next 5 years, it will be wind energy which will grow.

India's theoretical solar potential is about 5,000 T kWh per year (i.e., ~600 TW), far more than its current total consumption. Currently, solar power is prohibitive due to high initial costs of deployment. Out of the 6,00,000 km² of waste land that is available in India, over 3,00,000 km² is suitable for energy crop/algae cultivation. For algae, the input is none other than

carbon dioxide – the old foe of clean environment and light – which is aplenty. Just by using these two things, algae grow and could be used for extracting oil and then extracting biofuel from it. It will also act as a sink for carbon dioxide and seems to be the most attractive option. In a way, it should be called utilization of solar energy. Algae, if pursued and successful, will be the answer to the worries of energy. It will not only engulf the huge amounts of carbon dioxide but also give higher yields per unit area.

Carbon Capture and Sequestration

Climate change mitigation scenario calls for more than 2 gigatons of negative CO₂ emissions per year with bioenergy with carbon capture and storage (BECCS) in 2050. This could be realized with increasing use of new and renewable biofuels in the future.

The four generations of biofuels can be distinguished from each other by the feedstock used and the processing technology adopted.

“First-generation biofuels” use food-based feedstocks (like corn, sugar cane, or soybean) as raw material and utilize processing technologies like fermentation (for ethanol) and transesterification (for biodiesel).

“Second-generation biofuels” are produced from non-food feedstocks:

- Lignocellulosic plant biomass (switch grass, poplar)
- Nonedible oilseeds (Jatropha)

“Third-generation biofuels” uses specifically designed or “tailored” bioenergy crops (often by molecular biology techniques) to improve biomass-to-biofuel conversions. An example is the development of “low-lignin” trees, which reduce pretreatment costs and improve ethanol production, or corn with embedded cellulase enzymes.

Fourth-generation biofuels are thought to contribute better to reducing GHG (greenhouse gas) emissions, by being more carbon neutral or even carbon negative compared to the other

generation biofuels. Fourth-generation biofuels epitomize the concept of bioenergy with carbon storage (BECS).

Biodiesel Yield (L of oil/ha/yr)

Rapeseed	119
Soybeans	446
Mustard	1,300
Jatropha	1,892
Palm oil	5,950
Algae (low)	45,000
Algae (high)	137,000

Biofuel from algae looks quite promising. There are several aspects of algal biofuel production that have combined to capture the interest of researchers and entrepreneurs around the world. These include:

- High per-acre productivity
- Non-food-based feedstock resources
- Use of otherwise nonproductive, nonarable land
- Utilization of a wide variety of water sources (fresh, brackish, saline, marine, produced, and wastewater)
- Production of both biofuels and valuable co-products
- Potential recycling of CO₂ and other nutrient waste streams

The algae are harvested daily and their oil extracted to make biodiesel for transport use, leaving a green dry flake that can be further processed to ethanol, also a transport fuel. One key to success is to select an alga with a high oil density – about 50 % by weight. It is estimated that a 1,000 MW power plant using this system could produce more than 180 million liters of biodiesel and 225 million liters of ethanol a year which will require a 2,000 acre farm near the power plant. Out of the 6,00,000 km² of waste land that is available in India, over 3,00,000 km² is suitable for energy crop/algae cultivation.

Algae have been successfully used to clean up power plant exhaust, wherein the exhaust stacks of a 20 MW power plant were retrofitted with

rows of clear tubes with green algae soup inside. The algae grew and utilized 40 % of the carbon dioxide for photosynthesis and, as a bonus, 86 % of the nitrous oxide as well, resulting in a much cleaner exhaust.

Power plant flue gases have carbon dioxide levels ranging from 10 % to 20 %. At the typical carbon dioxide percentages, microalgae show no signs of significant growth inhibition. Furthermore, studies have shown that microalgae respond better to increased carbon dioxide concentrations, outgrowing (on a biomass basis) microalgae exposed to only ambient air. End uses for microalgae are not only limited to the production of biodiesel but also useful as food supplements for humans and animal feed.

Environment and Health Security

In industrialized countries, typical health and environmental problems include outdoor air pollution, radon in homes and schools, the “sick building” syndrome, toxic chemicals in drinking water, and non-ionizing electromagnetic radiation and pesticide residues in food. In developing countries, health and environmental problems are often related to poverty and arise largely as a result of such factors as rapid, uncontrolled urbanization and agricultural and land-use practices. In addition to hazards related to pollution, vector-borne environmental diseases may be prevalent as well as health and environmental problems associated with a lack of proper shelter, water, and sanitation or poor food hygiene.

Some of the issues related to environment and health security are:

- Impact of genetic regulation on the response to exposure to toxic agents
- Molecular mechanisms of action of toxic environmental pollutants
- Identification of cancer biomarkers
- Identification of EDCs and sex change chemicals in target organisms
- Redox imbalance
- Molecular mechanisms of heavy metal toxicity

Impact of Genetic Regulation and Predisposition on the Response to Exposure to Toxic Agents

Pharmaceuticals, pesticides, air pollutants, industrial chemicals, heavy metals, hormones, nutrition, and behavior can change gene expression through a broad array of gene regulatory mechanisms. Mechanisms include regulation of gene translocation, histone modifications, DNA methylation, DNA repair, transcription, RNA stability, alternative RNA splicing, protein degradation, gene copy number, and transposon activation. Furthermore, chemically induced changes in gene regulation are associated with serious and complex human diseases, including cancer, diabetes and obesity, infertility, respiratory diseases, allergies, and neurodegenerative disorders such as Parkinson and Alzheimer diseases. One of the best-studied areas of gene regulation is epigenetics, especially DNA methylation. Our examples of environmentally induced changes in DNA methylation are presented in the context of early development, when methylation patterns are initially laid down.

The focus is also laid to understand the interaction between genetics and the environment. Why do people, when exposed to the same dose of an environmental toxin, have different levels of disease. The estimated 30,000–60,000 genes of the human genome have been sequenced, and rapidly expanding knowledge in this area will lead to possibilities for new interventions with greater specificity about individual vulnerabilities to environmental and behavioral factors and later to alteration of genetic determinants of disease and disability. The single nuclear polymorphisms (SNPs) observed in different population may lead to the evolution of a new discipline termed toxicogenomics.

Molecular Mechanisms of Action of Toxic Environmental Pollutants

Epigenetics investigates heritable changes in gene expression that occur without changes in DNA sequence. Several epigenetic mechanisms,

including DNA methylation and histone modifications, can change genome function under exogenous influence results obtained from animal models indicate that in utero or early-life environmental exposures produce effects that can be inherited transgenerationally and are accompanied by epigenetic alterations. The search for human equivalents of the epigenetic mechanisms identified in animal models is underway. Recent investigations have identified a number of environmental toxicants that cause altered methylation of human repetitive elements or genes. Some exposures can alter epigenetic states, and the same and/or similar epigenetic alterations can be found in patients with the disease of concern. Several investigations have examined the relationship between exposure to environmental chemicals and epigenetics and have identified toxicants that modify epigenetic states. Whether environmental exposures have transgenerational epigenetic effects in humans remains to be elucidated. In spite of the current limitations, available evidence supports the concept that epigenetics holds substantial potential for furthering our understanding of the molecular mechanisms of environmental toxicants, as well as for predicting health-related risks due to conditions of environmental exposure and individual susceptibility.

Identification of Cancer Biomarkers

The majority of cancers have a complex etiology where one or more environmental risk factors interact with genetic background, age, sex, sociodemographic status, and other factors. However, the precise contribution of individual factors and their interaction, both with each other and with genotype, continues to be difficult to elucidate. This is partially due to the challenges inherent in accurately measuring exposure. Molecular cancer epidemiology promised to provide biomarkers to refine exposure assessment. Among the potential advantages of exposure biomarkers are the provision of a more objective measure at the individual level; a relevant measure in relation to events on, or related to, the causal pathway; and information relevant to the biological plausibility of an exposure-disease association and an ability

to detect low levels of exposure using sensitive laboratory technology.

A notable feature of much of the literature to date on exposure biomarkers in cancer epidemiology is the emphasis on compounds that damage DNA, with the associated measurement of DNA adducts and mutations. One of the most exciting future challenges for molecular epidemiology is the development of an analogous set of biomarkers for exposures acting through other mechanisms of carcinogenesis. This follows the recognition that environmental exposures can alter gene expression not only by mutation but also by epigenetic mechanisms. It is critical that the rapid advance in understanding of epigenetic mechanisms is matched by translation of this knowledge into biomarkers applicable to population-based studies of cancer etiology. This field is particularly compelling because of the recognition that a number of epigenetic events are reversible.

Some of the major epigenetic mechanisms relevant for biomarker development which are of interest include methylation of CpG promoter sequences, chromatin remodeling, receptor binding, and the modification of histones, which are common findings in human cancers. The measurement of CpG hypermethylation and global methylation in biological fluids and the observation that environmental exposures such as tobacco smoking are associated with altered methylation patterns offer an opportunity to molecular epidemiology in a similar way to the detection of mutated circulating DNA sequences in peripheral blood. The close mechanistic link between DNA methylation and histone modification, for example, through methyl-CpG-binding domain proteins, opens up a further important area of research where molecular epidemiologists have opportunities to consider the role of the environment in modifying these processes. In addition, the role of microRNAs, which inhibit expression of specific target genes, also merits consideration in terms of environmental exposures.

DNA and protein adducts have been widely measured in human biological samples, and these have been referred to as biomarkers of “biologically effective dose,” i.e., a measure of the amount of the carcinogen reaching the

critical cellular target. Adduct levels provide an integration of exposure, absorption, distribution, metabolism, and, in the case of DNA adducts, DNA repair. Some assays are chemical specific, while others, such as the ^{32}P post-labeling or the Comet assay, reflect general levels of DNA damage although chromatographic purification techniques or DNA repair enzymes can provide more specificity. Other markers of general DNA damage include chromosomal aberrations, micronuclei, and sister chromatid exchanges, which can be induced by a wide range of exposures, reflecting cumulative exposure to a variety of environmental factors.

The application of transcriptomics, proteomics, and metabolomics to cancer research may contribute not only to understanding mechanisms of carcinogenesis but also potentially to the development of a new generation of biomarkers of exposure and early effect.

Identification of EDCs and Sex Change Chemicals in Target Organisms

There is growing interest in the possible health threat posed by endocrine-disrupting chemicals (EDCs), which are substances in our environment, food, and consumer products that interfere with hormone biosynthesis, metabolism, or action resulting in a deviation from normal homeostatic control or reproduction. EDCs are chemicals that may interfere with the body's endocrine system and produce adverse developmental, reproductive, neurological, and immune effects in both humans and wildlife. Endocrine disruptors are naturally occurring or man-made substances that may mimic or interfere with the function of hormones in the body. Endocrine disruptors may turn on, shut off, or modify signals that hormones carry and thus affect the normal functions of tissues and organs.

A wide range of compounds that can bind steroid hormone receptors include industrial chemicals such as bisphenol A (BPA), certain alkylphenol ethoxylates, phthalates, parabens, benzophenones, and environmental contaminants like DDT, methoxychlor, some PCBs, dioxins, and furans. Endocrine disruptors may be found in many everyday products – including plastic

bottles, metal food cans, detergents, flame retardants, food, toys, cosmetics, and pesticides. Research shows that endocrine disruptors may pose the greatest risk during prenatal and early postnatal development when organ and neural systems are forming.

In Japan (1968) and Taiwan (1979), a few thousand women were exposed to PCBs and their pyrolysis products (PCDFs) following consumption of contaminated rice oil. The offspring of these mothers exposed to PCBs and PCDFs tended to be smaller at birth and exhibited delays in neurological development. Subsequent studies on PCB exposure at lower levels have alleged other adverse effects, although these data remain somewhat controversial.

Redox Imbalance

Toxic metals (lead, cadmium, mercury, and arsenic) are widely found in our environment. Humans are exposed to these metals from numerous sources, including contaminated air, water, soil, and food. Recent studies indicate that transition metals act as catalysts in the oxidative reactions of biological macromolecules; therefore, the toxicities associated with these metals might be due to oxidative tissue damage. Redox-active metals, such as iron, copper, and chromium, undergo redox cycling, whereas redox-inactive metals such as lead, cadmium, and mercury deplete cells' major antioxidants, particularly thiol-containing antioxidants and enzymes. Either redox-active or redox-inactive metals may cause an increase in production of reactive oxygen species (ROS) such as hydroxyl radical, superoxide radical, or hydrogen peroxide. Enhanced generation of ROS can overwhelm cells' intrinsic antioxidant defenses and result in a condition known as "oxidative stress." Cells under oxidative stress display various dysfunctions due to lesions caused by ROS to lipids, proteins, and DNA. Consequently, it is suggested that metal-induced oxidative stress in cells can be partially responsible for the toxic effects of heavy metals. Several studies are underway to determine the effect of antioxidant supplementation following heavy metal exposure. Data

suggest that antioxidants may play an important role in abating some hazards of heavy metals. In order to prove the importance of using antioxidants in heavy metal poisoning, pertinent biochemical mechanisms for metal-induced oxidative stress should be reviewed.

Molecular Mechanisms of Heavy Metal Toxicity

Over the past 200 years, emissions of toxic heavy metals have risen tremendously and significantly exceed those from natural sources for practically all metals. Uptake and accumulation by crop plants represents the main entry pathway for potentially health-threatening toxic metals into human and animal food. Of major concern are the metalloids arsenic (As) and selenium (Se) and the metals cadmium (Cd), mercury (Hg), and lead (Pb).

Heavy metal (HM) toxicity is one of the major abiotic stresses leading to hazardous effects in plants. A common consequence of HM toxicity is the excessive accumulation of reactive oxygen species (ROS) and methylglyoxal (MG), both of which can cause peroxidation of lipids, oxidation of protein, inactivation of enzymes, DNA damage, and/or interaction with other vital constituents of plant cells. Higher plants have evolved a sophisticated antioxidant defense system and a glyoxalase system to scavenge ROS and MG. In addition, HMs that enters the cell may be sequestered by amino acids, organic acids, glutathione (GSH), or by specific metal-binding ligands.

Vision for Environment 2020

The industries in India must carry out a thorough environmental audit to identify the scope for substituting their existing processes with greener and cleaner techno-economically feasible processes not entailing excessive cost. In doing this, all the 12 principles of green chemistry and technology must be followed to the extent possible

and feasible. Wherever possible, cleaner energy options must be adopted to make the endeavor sustainable in all respects.

Greater emphasis should be laid on ecosystem protection and reduction in the waste and greenhouse gases emission within the limits of the carrying capacity of the ecosystem. Under no circumstances, the biodiversity should be sacrificed in the name of development. Safety, health, and environmental (SHE) issues must be given top priority in all developmental ventures so that sustainable development with environment and health security is ensured for all the time.

Vision for environment 2020 and beyond therefore calls for

- Paradigm shifts in R&D:
 - Waste to wealth – lab-to-land initiative
 - Micro to macro waste management – common effluent treatment plants (CETPs) and treatment storage and disposal facilities (TSDFs) for hazardous wastes
 - Environmental impact assessment to life-cycle assessment
 - Command and control system to cash flow generation
 - Traditional environmental science to molecular environmental science
 - Chemical catalyst-based processes to enzyme-driven processes
 - Clinical biochemistry to toxicogenomic approach for health
 - Service provider to knowledge center
- Augmentation of quality water resources to ensure ecological flow in rivers
- Policy and regulation based on scientific and economic tools (natural resource accounting, polluter pays, damage assessment, risk-based standards and remediation)

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Sustainable Development: An Earnest Hope

2

Sangeeta Singh

“We do not inherit the land from our ancestors; we borrow it from our children”

- Native American proverb

Abstract

Sustainable development is a widely used and highly debatable concept leading to board acceptance with very diverse interpretations. The ambiguity pertaining to the definition of the term and its myriad approaches makes it even more complex and multidimensional in nature. However, no matter how we define it and what approach we adopt the essence of all the efforts towards sustainability or sustainable development is to reduce and lessen the wasteful consumption and inevitable impacts that led to the demise of great generations and summoned the present and future generations. Our technologically sound and advanced super generation has the wisdom to understand, learn from the past mistakes, and create alternatives to overcome the challenges. The mantra and passport to the sustainable development lie in rooting and inculcating new set of values, principles, and ethics for a bright and sustainable future of our generations and the mother earth. This chapter discusses the conceptual framework of sustainable development and addresses why sustainable development is inevitable.

Keywords

Development • Environment • Growth • Intergenerational equity • Paradigm • Sustainability

Introduction

The above ancient proverb reverberates that whatever we are reaping today was sown in the past and what we are sowing today will

be reaped by our children. It indicates the effects of our ancestors on our current situations and warns us about the impact of our actions on the coming generations. However, in the last two decades, a profound understanding of safeguarding the dynamic surroundings has been achieved with a realization that “Environment and development are inextricably linked” (Kofi Annan, former Secretary General of the United Nations, 2002) at every level. Still the complexity and cause-effect of man-environment

S. Singh (✉)
Department of Earth and Atmospheric Sciences,
Metropolitan State University of Denver, Auraria Higher
Education Campus, Downtown Denver, Colorado, USA
e-mail: ssingh7@msudenver.edu

relationship is incomprehensible and calls to restore balance at all levels to avert possible unsustainable and undesirable outcomes. In this regard, utopia of sustainable development has become an incantation offering arrays of possibilities and potential challenges for a sustainable future for earth and its inhabitants. Being an extremely popular, widely used, and highly debatable concept, it has attracted many disciplines with different definitions and various interpretations. The astonishing growth of literature, discussions, approaches, and criticism makes it an everyday reality and fundamental concept of twenty-first century. This chapter discusses the conceptual framework of sustainable development and addresses why sustainable development is a necessary yardstick to assess overall development.

Evolving Concept of Sustainable Development

It is imperative to know the concept of development in order to understand the necessity for sustainable development. Development is a highly dynamic and ever-changing process of socio-economic change. Some view it as a directed change, some equate it with the increase in gross national product (GNP) for economic development, and others include any number of socially desirable phenomena. Broadly, it involves purposeful changes for improving the quality of life. Some scholars claim that the end of the Second World War (1945) was a watershed in the evolution of development theory as it was realized that “development is a right of all the people.” During this era, two important models *Modernization* and *Dependency Theory* were dominant. Modernization theorist promoted the ideas of economic growth and development to be identical, advocating that development can be achieved through Western science and technology replacing consequently the traditional society by modern forms when the growth takes place. On the contrary, dependency theorist accentuated that model of modernization is an illusion. They proscribed the path of development followed by

rich countries and advised the third world countries to break their links from them. Further, dependency theorist alleged that the systematic exploitation of third world colonies made the first world develop.

From 1960 to 1980 various capitalistic models such as models of articulation, internationalization of capital, anti-moderation and grassroots development emanated. In early 1970, the *basic needs approach* paved its way to support food, housing, water supplies, health services, education, and employment. But the skyrocketed price of oil during this time stunned the world and forced attention back on to purely economic growth, resulting in the demise of the more welfare-oriented approach. Once again in the late 1970s, two schools of thought emerged: first regarded development as a multidimensional concept (*purely economic growth oriented*) and second supported purely the *human welfare approach*. The first school of thought acknowledged development as rapid gains in overall capita gross national product which would *trickle down* (Thirwall 1983) to masses in the form of jobs and other economic opportunities, or would create necessary conditions for the distribution of economic and social benefits of growth. In this regard, United Nations Development Program (UNDP) economist, Mahbub ul Haq, suggested measuring development in terms of gross domestic product (GDP), gross national income (GNP), and per capita income. This notion favored economic growth to achieve overall development. On the other hand, second school of thought linked economic development to the reduction and elimination of poverty, inequality, and unemployment within the context of a growing economy. In short, during this era, the concept of development became closely associated to the policies, strategies, and technologies formed by the government; and economists professed economic growth as a quantitative change, absolutely necessary for the development.

The late 1970s and early 1980s was a landmark era in the history of development theory, when for the first time *conservation* and

preservation of ecosystem and habitat planning were introduced under the banner of *ecodevelopment* by UNEP. The term “ecodevelopment” was coined in 1972 at the first International United Nations Conference on Human Environment in Stockholm. This conference emphasized that socioeconomic development could be achieved only by environmentally sound development (ecodevelopment). Additionally, it was realized that the poor in the society suffer the most from environmental degradation; therefore, persuasive approach of harmonic coexistence with nature would be the best option, which could be accomplished by developing resources to satisfy basic needs and satisfactory socioeconomic system for a long-term development. Based on similar notion, Redcliff (1987) believed that ecodevelopment would lead to economic *equity*, social *harmony*, and environmental *balance*. Further, former director of World Development Institute, Streeten (1992), defined development “as an attack on chief evils of the world today: malnutrition, disease, illiteracy, slums, and unemployment. Development has been a great success. But measured in terms of jobs and justice and the elimination of poverty, it has been a failure or a partial success.”

This renewed and redefined approach of development completely altered the aims and objectives in favor of *quantitative growth and qualitative improvement to measure the progress and quality of life*.

Under the purview of these objectives, many pilot studies were initiated targeting the use of alternative energy sources, development and use of eco-techniques, preparative education to create social awareness of socioeconomic values, and formation of a horizontal authority for ensuring population concern and prevention of plundering ecodevelopment results. Likewise many paradigms and new approaches of development were introduced such as *the new population paradigm*, leveling of the rates of demographic growth; *the social paradigm*, basic needs and a decent living for everyone; *the equity paradigm*, reduction of income and social differences at the international and national levels; *the clean technology paradigm*,

technology with a nonpolluting use of resources and recyclable products; *the managerial or entrepreneurial paradigm*, economic model based on fundamental market mechanism and free entrepreneurs with a social concern; *good governance paradigm*, regulatory, distributive, participatory, and activating role of the state; *the participation and human rights paradigm*, development in a democratic environment; *the cultural paradigm*, strengthening of cultural life, social ability, and *leisure* time activities; and *the sustainable development paradigm*, conservation of nonrenewable resources and prudent use of renewable resources.

The emergence of sustainable development in early and mid-1980s was an extension of the 1960s, 1970s, and early 1980s concepts in a more renewed form. But the original concept of sustainable development could be traced back to the environmental movements during the mid-1960s when two major ideas of *conservation* and *preservation* evolved. Along with this concept, the term sustainable society and sustainable future became popular. However, widespread adverse effects of anthropogenic activities on the environment led to the concept of sustainable development, but the primary intent was conservation of nonrenewable natural resources and prudent use of renewable resources to attain overall development for human beings. Brundtland Commission, through its report titled *Our Common Future* (1987), introduced sustainable development as “development that meets the needs of the present generation without compromising the ability of future generations to meet their own needs emphasizing on principle of equity contemplating two types of equity as intergenerational equity: justice to current and future generations in relation to resource and intragenerational equity: fairness in sharing of resources to the competing interests of contemporary time (Yosef, 2008).” The report emphasized fair share of natural resources and expected consensus from the present and future generations (Our common future, 1987). Sustainable development encompasses three fundamental approaches: economic, social, and environmental development, which is interrelated and complimentary to each

other. Thus, the paradigm of sustainable development emerged with three primary objectives: (1) *poverty reduction*, (2) *sustainability*, and (3) *participation*; this applies to a set of processes for improving health of not only the planet but of all the human beings across the world. Therefore, the discourse of sustainable development moved beyond the ecological/environmental concept to other issues, like food security, peace security, trade, heritage, housing shelter, and clean water. With these perceptions and analysis of various models of development, it is clear that development is no longer restricted to the question of growth but is a mega-paradigm composed of a set of sub-paradigms of a different nature that are interrelated and occasionally overlapping combining socioeconomic and environmental parameters. The quintessence of sustainable development is credited for creating consciousness and a change in people's attitude and willingness to participate in the process of making sustainable development a reality.

Currently, sustainable development is extensively used in diverse policy issues, making it an integral part of policy formulation and development not only for regional/national governments and international agencies but also for corporate and business organizations. The core values undoubtedly convey intergenerational equity by effectively integrating social, economic, and environmental aspects for a sustainable society. But many scholars perceive it as a complex conundrum and argue as to what is sustainable or unsustainable or how to evaluate what is socially sound, acceptable, and economically viable. The intricacies pertaining to definition, interpretation, and usage of term are addressed next.

Glitches of Sustainable Development

Sustainable development is now a widely used term but ambiguous pertaining to its definition, interpretation, and myriad approaches that make it complex, multidimensional, and debatable. From 1980 to 1994, there have been more than 80 different definitions and interpretations

fundamentally sharing the core concept of the World Commission on Environment and Development (WCED)'s definition, leading to a very broad acceptance with very diverse interpretations. Tolba (1992) argued that sustainable development is a fashionable phrase, its definition is not universally accepted, and nobody cares to define it. Many people use the phrase "sustainable development" interchangeably with "ecologically sustainable" or environmentally sound development and define it as "a process of change in which the exploitation of resources, direction of investments, orientation of technological development and institutional changes are all in harmony and enhance both current and future potential to meet human needs and aspirations." Heinen (1994) also indicated no unanimous single approach of sustainable development as different institutes, communities, and programs use variety of approaches to achieve it.

The word "needs" was criticized by Lee (2000) in the definition of sustainable development (meeting the needs of the present generation without compromising the ability of future generations to meet their own needs) as it expresses anthropocentric view. (Ciegis et al. 2009) also argued that definition by Brundtland did not provide a thorough explanation for actions and practices required to be called sustainable. The World Bank described sustainable development as a development that continues (World Development Report 1992), and the Rio declaration described it as a long-term continuous development of society to satisfy the needs of present generations via rational usage and replenishment of natural resources by preserving the earth for future generations to satisfy their needs (Rio Declaration on Environment and Development 1992). In 1991, the IUCN, UNEP, and WWF equate sustainable development, sustainable growth, and sustainable consumption as identical concepts; however, they all are essentially different in nature. Later, over a period of time, sustainable development initiated strong discussions and problems pertaining to its dual nature, casing development as well as sustainability (Ciegis et al. 2009).

As briefly mentioned, sustainability was originated in the context of renewable resources, such as forests and fisheries, but subsequently adopted as a broad slogan by the environmental movements (Lele 1991). In this regard, environmentalists suggested three types of sustainability (a) *economic sustainability*, (b) *ecological (environmental) sustainability*, and (c) *sociocultural sustainability*, which were criticized for impact analysis. The economic sustainability was accentuated to maximize income and investment for future resources, and ecological sustainability emphasized on stability of biophysical systems (Hollings 1986), and Maler (1990) stressed on the upkeep of biodiversity considering it a critical component of sustainability. The sociocultural sustainability aimed to reduce the vulnerability and maintenance of healthy sociocultural system (Chambers 1989) by resolving and sharing responsibilities of social, economic, and environmental problems (Berkes and Folke 1994). Pearce (1993) viewed sustainable development with an *ethical* component and stated that the cost of society's development should not be placed on future generations. This ethical approach created the possibility of achieving overall well-being for current and future generations within the acceptable limits of the environment. The component of ethics bequeathed one more dimension to sustainability. Later, *institutional sustainability* was added for proper function and effective execution of policies at state, regional, and municipal levels to accomplish sustainability (Helm 1998). Overall, an integrated approach became valuable along with the active participation of society for strategic planning and policy making of a region.

After citing various ways of defining and approaching sustainable development, the essence of the concept is adequately clear as we know what we are striving for and how we can to achieve it. Further, different interpretations are beneficial as they provide basis to debate the choices for people from both developed and developing countries. Besides, the spark and optimistic premises of sustainable development on one hand help to learn from past mistakes and on

the other hand ensure lives worth living even after knowing the extent of damage done to the mother earth.

Necessity of Sustainable Development

An earnest hope of a bright future vision reconciles the relationship of man-environment as a mobilizing force behind the concept of sustainable development. So far humans have viewed environment as a beneficial and inexhaustible resource with no long-term consequences. But over the years, growing population and unsustainable consumption of resources have mounted unprecedented stress in developed as well as in developing countries. Both have consequently compromised and threatened the actual capacity and delicate equilibrium of the earth, respectively. The environmental scientists Wackernagel and Rees (1990) quantify resource consumption using the concept of *ecological footprint*, by which all the direct and indirect impacts on productive land and resources are consumed, disposed, and recycled and the waste a person or population creates was measured. Wackernagel and his colleagues furthermore calculated the ecological footprint for whole humanity and concluded that humans have already exceeded earth's productive capacity by 30 %, ensuing a global debit, designated as an *overshoot*. WWF international (2008) stated that humans are consuming renewable resources 30 % faster than they can be replenished. The challenge before humanity is how to live within the earth's carrying capacity. History has substantial proof regarding the demise of great civilizations that crumbled due to human pressure and environmental degradation, leaving a devastating landscape behind. The realization about the wasteful consumption of resources and inevitable impacts has summoned the present generation; they do not want the same fate as our ancestors. In today's globalized world, stakes are higher than before as our actions have global impact and the societal collapse would lead to global collapse. Conversely, the technological advancement and

ability to create alternatives make us a super generation who has the wisdom to understand and learn from the past mistakes. Our transition from economic growth to sustainable development is a remarkable act which possibly would lead to a right direction.

In the words of United Nations Secretary General (1996) Maurice Strong, “the transition to sustainability means process of deep and profound change in the political, social economic, institutional and technological environment. This change requires a supportive international economic environment as a common heritage of mankind, which would integrate development and environment, together with disarmament. Government must take the lead to establish the basic policy framework, incentives and infrastructures required for sustainability.” In the recent past, new programs like Millennium Development Goal and many strategies have been developed to promote and achieve sustainable development. It is noteworthy that strategies for poverty reduction, decentralized planning, and consultation among different organizations, institutions, and governments are much sought alternative approaches for good governance at micro- and macrolevel planning.

For active participation of society, a four-level approach has been analyzed to obtain an integrated and coherent result for sustainable development of a region (Hinterberger et al. 1997). As summarized in a Johannesburg Summit in 2002 “a collective responsibility to advance and strengthen the interdependent and mutually reinforcing pillars of sustainable development-economic development, social development and environmental protection-at the local, national, regional and global levels,” these four levels are appropriate to initiate integrated and comprehensive projects. The four-level approach identified by Hinterberger (1997) is as follows: (1) the microlevel comprised of entrepreneurs and consumers; (2) the mesolevel included institutions and their networks; (3) the macrolevel incorporates fiscal, monetary, and distribution system and conditions; and

(4) the metalevel aims at the social aims. The participatory approach fosters confidence among various stakeholders and enables policy-makers to understand appropriately the local’s social, economic, and environmental conditions. The strategies of sustainable development follow a multistep integrated and participatory process: (1) identification of an area; (2) reliable baseline information about areas socioeconomic, environmental conditions (especially major stresses, pressures, and trends); (3) identification of all the stakeholders involved in the process (local, regional, and national government and NGOs); (4) identification of rules to promote accountability; (5) preparation of an action plan; (6) monitoring system (who, how, and by whom); (7) management system (what and which system to be used); (8) disclosure (have transparency among various stakeholder); and (9) meetings (to discuss and track progress and any negative responses). The strategies promoting sustainable development are like a passport to enter a future with a new set of principles, ethics, and moral values guiding human beings through the whole process.

Conclusion

The mantra of sustainable development emerged due to a profound disappointment about conventional development. The growing popularity of sustainable development has changed the mindsets globally from quantitative to qualitative development leading to a healthy, better and meaningful future. Thoughtful deliberations, resolutions, new approaches, and ethical ideas have created all together a new form of value-based social learning which entails coordinate, cooperate, recycle, reduce, and renew for the well-being of man and earth. These undertakings outline the possibilities of ways to tackle the problems and preferred outcomes for a more meaningful and fruitful path for a desired progress. In conclusion, the need of the hour is to have an integrated, holistic approach which values what is eloquently urged by Maurice

Strong that “Sustainable development cannot be imposed by external pressures; it must be rooted in the culture, the values, the interests and the priorities of the people concerned.”

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Soil Seed Bank Dynamics: History and Ecological Significance in Sustainability of Different Ecosystems

3

Upama Mall and Gopal S. Singh

History

The existence and potential importance of the soil seed bank have been recognized by ecologists and evolutionary biologists since the dawn of modern biology, from Darwin (1859) to Mall and Singh (2011) and Hong et al. (2012). The earlier studies of soil seed banks began in 1859 with Darwin, when he observed the emergence of seedlings using soil samples from the bottom of a lake. However, the first paper published as a scientific research report was written by Putersen in 1882, studying the occurrence of seeds at different soil depths (Roberts 1981). Very early ecologists started to investigate the nature and the density of living seeds in the soil and the soil seed bank (Darwin 1859; Chippindale and Milton 1934; Nordhagen 1937; Bannister 1966; Barclay-Estrup and Gimingham 1975), and in modern times to determine the significance of soil seeds in the regeneration of different plant communities (Thompson and Grime 1979; Roberts 1981; Mallik et al. 1984; Simpson et al. 1989; Thompson et al. 1997; Miller and Cummins 2001; Lemenih and Teketay 2006;

Tessema et al. 2011b; Mall and Singh 2001; Hong et al. 2012) and the similarity between the soil seed bank and aboveground vegetation (Tessema et al. 2011b). A soil seed bank, which begins at dispersal and ends with the germination or death of the seed (Walck et al. 2005), is a reserve of mature viable seeds located on the soil surface or buried in the soil (Roberts 1981) that provides a memory of past vegetation and represents the structure of future populations (Fisher et al. 2009). Seeds are a crucial and integral part of an ecosystem that show the past history of standing vegetation and its future deviation. An understanding of the population dynamics of buried viable seeds is of practical importance in conservation of different communities and weed management in agriculture (Fenner 1985; Fenner and Thompson 2005). The balance between trees and grasses, however, is often highly disturbed as a consequence of heavy grazing and poor management (Pugnaire and Lazaro 2000). This study aimed to gain a better understanding of soil seed bank dynamics in different ecosystems of the world. All plants establish themselves by the expansion and subsequent fragmentation of vegetative parts such as tillers, rhizomes, or runners by the successful establishment of a soil seed bank or bulbils (Freedman et al. 1982). During the past decade, there has been a rapid increase of the number of studies assessing seed density and species richness and the composition of soil seed banks in a wide range of plant communities (Thompson et al. 1997). In India, the soil seed bank has been estimated

U. Mall
Department of Botany, Banaras Hindu University,
Varanasi, Uttar Pradesh 221005, India

G.S. Singh (✉)
Institute of Environment and Sustainable Development,
Banaras Hindu University, Varanasi, Uttar Pradesh
221005, India
e-mail: gopalshs@yahoo.co.in

in humid tropical forest (Chandrashekara and Ramakrishnan 1993), grasslands, irrigated and dry land agro-ecosystems (Srivastava 2002), tropical dry forest (Khare 2006), jhum cultivation (Saxena and Ramakrishnan 1984; Sahoo 1996), Himalayan moist temperate forest (Viswanth et al. 2006), and wastelands and roadsides (Yadav and Tripathi 1981).

Dynamics of a Soil Seed Bank

The soil seed bank is defined as seeds at or beneath the soil surface that are capable of germinating. Soil seed banks are important in various ecosystems where grasses, forbs, and weeds account for a large part of the vegetation for both annual and perennial species. The soil seed bank describes the composition, diversity, and density of the seed bank. The study of the soil seed bank is important because the bank influences seed reserves in the soil for current, past, and future vegetation. It is the term for the viable seeds that are present in the topsoil (Roberts 1981). All the viable seeds present in soil or with soil debris constitute the soil seed bank (Simpson et al. 1989). Soil seed banks include all seeds buried in the soil and those on the soil surface. Seed banks are essential to maintaining life and growth in different habitats such as grasslands, agro-ecosystems, savannas, desert, wetland, sand dunes, ecotones, plantations, and forests. The seed bank of an agro-ecosystem would be less diverse than the seed bank of a forest. Studies of soil seed banks are of relatively recent origin considering their importance as a source of diversity and continued occupation. The seed banks are the source of genetic material or evolutionary memory (Harper 1977).

Soil seed banks have importance in all types of vegetation. Seed banks can reflect evolutionary changes in plant communities as a result of changes in land use: they provide knowledge of the size and composition of species and predict future vegetation. A seed bank may be defined as a buildup of viable but ungerminated seeds in or on the soil. It is “an aggregation of ungerminated seeds potentially capable of replacing adult plants

that may be annuals, dying a natural or unnatural death, or perennials, susceptible to death by disease, disturbances, or consumption by animals including man” (Baker 1989). The second part of this definition, that is, the potential for replacing adult plants, is essential. If seeds are permanently buried too deeply, they fail to be an effective seed bank; the same is true for some seeds in aerial portions of plants. It is the reservoir of viable seeds or of vegetative propagules that are present in the soil and that is able to recompose natural vegetation. The seeds of pioneer species are commonly present in tropical forest soils, particularly in secondary forests (Cao et al. 2000).

The work of Thompson and Grime (1979) reflects fall and spring germination periods and degree of persistence. They defined four types of soil seed banks for herbaceous species, which fell into transient and persistent categories. Tropical soil seed banks show even more diversified strategies. Garwood (1989) described five soil seed bank strategies from the tropics: transient, persistent, pseudo-persistent, seasonal transient, and delayed transient seed banks: these arise from the more complex reproductive phenology of tropical plants and germination patterns of tropical seeds. A diversity of alternative patterns is possible, such as the pseudo-persistent seed banks found in tropical forests and cold deserts where continued dispersal guarantees the presence of a soil seed bank. Many studies suggest that seed banks persist in disturbance regimes, but persistent seed banks are not able to maintain their populations and regenerate without the environmental changes that are caused by disturbances. Annuals generally have persistent seed banks more often than other life forms; in annuals, the persistent stage is the seed only, but even in harsh environments not all annuals produce a persistent seed bank. In some communities perennial woody species produce large seed banks. Generally, small seeds have greater longevity in the seed banks (Harper 1977). The soil seed bank is the cause of persistence of annual species, but for perennials, there is a bank of vegetative propagules such as tubers, rhizomes, and stolons (Fernandez-Quintanilla et al. 1991). The revegetation of plants in the standing vegetation of any

ecosystem after any disturbance to the vegetation often depends on the persistence of seeds in the soil (Bakker et al. 1996). The seed bank types in a plant community often determine how the plant community will react to disturbance. Thus, an understanding of persistent seed banks is the key to many aspects of the practical management of weeds in agricultural fields and in conservation of different ecosystems such as grassland, plantation, natural forests, and deserts. Seed banks are classified as temporary or persistent. Temporary seed banks are composed of seeds with a short life that do not enter dormancy and are dispersed for short periods of time during the year (Garwood 1989). Persistent seed banks are composed of seeds that have more than 1 year of age, and reserves of these seeds remain in the soil year after year, buried in the soil. Seeds of species that form seed banks must be viable for long periods of time. Seeds persist in the soil far longer at high altitudes, but this can be because low temperatures prevent seed germination, or perhaps conditions found at high altitudes may favor seed survival. Persistent seed banks are the product of large seed crops produced in particularly favorable years, and the spatial pattern of seeds reflects the spatial pattern of seed production.

A number of environmental conditions influence seed bank dynamics via influence on seed production or other stages of the life cycle. Variations in soil conditions also affect the development and size of seed banks. Different soil parameters according to season affect the germination of seeds from soil seed banks and influence species composition in aboveground vegetation. Annuals generally germinate in a soil seed bank because perennial grasses often propagate vegetatively (O'Connor 1996). This pattern is derived by differences in the phenology of perennial versus annual species resulting from late-season disturbances: 98 % of the native species in a plant community are perennial, so by managing perennial species, native species can be maintained. The seed bank reflects the historical process of the plant life cycle from its establishment in the environment to its distribution in time and space. The seed bank is the store of seeds buried in the soil, composed of seed produced on site and seed

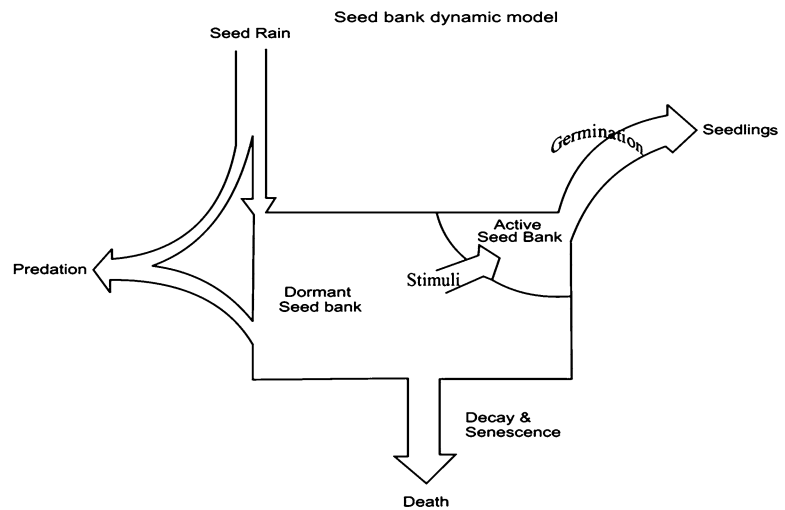
moved (dispersed) into the area. The dormant seed banks are seeds awaiting stimuli or the right conditions before germination. Active seed banks are seeds in a temporary stage, requiring only favorable temperature and moisture to germinate. Dispersed seed with simple germination whose stimulus requirements have already been met is seed recruited from the dormant seed bank. Different soil depths that provide favorable soil moisture or humidity for seed germination determine recruitment and plant community structure. Environmental variables as well as the standing vegetation of a site can induce or inhibit seed germination from the soil seed bank (Bueno and Baruch 2011). Canopy species modify understory conditions by altering water and nutrient availability, thus modifying the microclimate, and by determining the quality of the litter that covers the soil (Godefroid et al. 2006). Microenvironmental changes following gap creation allow seed germination, seedling establishment, and sapling recruitment (Cao et al. 2000). Graham and Hopkins (1990) predicted that any forest development tending to increase areas of persistent high light intensity would allow the invasion and reproduction of weeds.

Different fertilizers affect the size (Barberi et al. 1998), diversity (Boguzas et al. 2004), and community structure of a seed bank (Davis et al. 2005a). These changes in diversity are related to the productivity and stability of the ecosystem (Zhang et al. 2004a; Zhang et al. 2004b; Xiang et al. 2006). The increasing amounts of nitrogen and other different fertilizers in the soil may affect the composition and dynamics of the soil seed bank, leading to a decrease in species richness. In most seed bank studies a number of species were detected in the seed banks that were not seen in the vegetation (Fig. 3.1).

Vertical Distribution and Longevity of Seeds

Vertical distribution of seed banks shows that majority of seeds in grasslands (and probably no-till agricultural fields) are located in the upper 1 in. (2 cm) of the soil profile; nearly the entire

Fig. 3.1 Flow chart of soil seed bank dynamics (From Harper 1977)



seed bank is in the upper 10 cm. The majority of seeds in cultivated soils are in the upper 15 cm of the soil profile and can be found as deep as the soil is tilled; as the intensity of tillage declines, the seed bank moves closer to the soil surface. Many physical and biological factors affect the vertical distribution of seeds in the soil, as most seeds are found near the soil surface and deeply buried seeds rarely germinate from the soil. Long-lived seeds are characteristic of disturbed habitats. Most long-lived seeds are annuals or biennials; biennials are especially prevalent in soil samples taken from dated archaeological sites. Small seeds tend to have much longer soil lives than large ones; very large seeds have very short soil lives. Longevity depends on species, depth of seed burial, soil type, tillage, crop rotations, etc. Seed longevity increases with depth of burial. Many seeds in the soil decay or are lost because of pathogenic soil microflora and predation. Seedling germination is greater in cultivated fields than undisturbed soils; cultivation reduces the soil seed bank more rapidly than in undisturbed soil. Seedling germination increases with decreasing soil burial depth.

Seed Rain

Seed rain represents an historical record of the past vegetation that grew on or near the area. The

population dynamics of aboveground plants can be strongly influenced by vegetative reproduction (via rhizomes, new aboveground shoots, or other organs, e.g., bud bank) (Benson et al. 2004) and by sexual reproduction (seed rain and seed bank) (Bakker et al. 1996). Therefore, studies of the seed rain, seed bank, and bud bank are of crucial importance in understanding the regeneration of plant communities after disturbance events and the consequent increase of plant diversity. Seed dispersal can have an impact on species composition (Matthiessen and Hillebrand 2006), forest diversity (Janzen 1970), and the dynamics of plant communities (Nathan and Ne'eman 2004) and can determine spatial ranges of population regeneration (Levine and Murrell 2003). For seed rain study, seed traps are placed inside and outside the gaps. Late-season seed rain has a greater proportion of perennial species and native species in comparison to early-season seed rain. The term seed rain refers to the process by which seeds enter the seed bank. Seeds either generated and produced on site or carried to the site by a dispersal agent become incorporated into the soil. These patterns arise because species that successfully form persistent seed banks are the species with greatest seed longevity. It is one of the two contrasting strategies plants may employ to realize success in replacing themselves and ensuring maintenance of the species. A plant dispersing its seed is most successful, evolutionarily speaking,

if it can place its seed in an environment suitable for germination and growth. Such safe sites, as they are called, are generally rare in natural landscapes. To find them, seeds must be dispersed widely in space (to increase the probability of landing in a rare safe site) or widely in time (to increase the probability the seed will survive long enough for a safe site to materialize). Plants with high seed longevity have evolved the strategy of waiting patiently for the right time. If seeds can remain viable for many years, and new seeds continue to “rain” down, it is easy to see where the term seed bank comes from, as the seeds accumulate over time and form a reserve of seeds in the soil. Seed rain decreases with increasing altitude but seed bank density changes slightly. The establishment of target species will depend on seed dispersal (Bossuyt and Honnay 2008). Thus, seed rain or seed dispersal is important for restoration of an ecosystem.

Dynamics of a Weed Seed Bank in an Agro-Ecosystem

A soil seed bank present in an agro-ecosystem is related to weed studies of the so-called weed seed bank. Weed species resist in several adverse climatic conditions, tolerating high and low temperatures, dry and humid environments, and variations in oxygen supply (Christoffoleti and Caetano 1998). The weed seed bank has been studied more intensely than other seed banks because of its economical importance. In agro-ecosystems, the soil seed bank is closely related to weed studies. Its determination allows building models of population establishment through time, making possible the definition of weed control programs (Martins and Silva 1994). Knowledge of the emergence rate of the different species from a soil seed bank in these areas can be applied to soil and crop management programs, which can result in a rational use of herbicides (Voll et al. 1996). Weed seed banks are reserves of viable seeds present on the surface and in the soil. The seed bank consists of new seeds recently shed by a weed plant as well as older seeds that have persisted in the soil for several years. The

weed seed bank is the main source of weeds in agricultural fields. Most weeds start their life cycle from a single seed in the soil. If these weeds escape control, they grow and produce thousands of seeds, depending on the species. These seeds are returned to the soil seed bank and become the source of future weed populations. Therefore, knowledge of seed return and seed bank dynamics can help in future weed management. There are enormous numbers of viable weed seeds in the soil. Although a great number of the buried seeds die within a few years, seeds of some species can remain viable for decades. It has been estimated that only 1–9 % of the viable seeds produced in a given year develop into seedlings; the rest remain viable and will germinate in subsequent years, depending on the depth of their burial. Seeds are dispersed both horizontally and vertically in the soil profile. It has been reported that the majority (approximately 95 %) of the seeds entering the seed bank are from annual weeds; only about 4 % come from perennial weeds. Seed bank input is determined by seed rain from the weed plants. In other words, seed bank input is the number of seeds produced and shed by the plant. Although the horizontal distribution of weed seeds in the seed bank generally follows the direction of crop rows, the type of tillage is the main factor determining the vertical distribution of weed seeds within the soil profile.

The weed seed bank is the reserve of viable weed seeds present on the soil surface and scattered throughout the soil profile. It consists of both new weed seeds recently shed and older seeds that have persisted in the soil from previous years. In practice, a weed seed bank also includes the tubers, bulbs, rhizomes, and other vegetative structures through which some of our most serious perennial weeds propagate themselves. In the following discussion, the term “weed seed bank” is defined as the sum of viable weed seeds and vegetative propagules that are present in the soil and thus contribute to weed pressure in future crops. Agricultural soils can contain thousands of weed seeds and a dozen or more vegetative weed propagules per square foot. The weed seed bank serves as a physical history of the past successes

and failures of cropping systems, and knowledge of its content (size and species composition) can help producers both anticipate and ameliorate potential impacts of crop–weed competition on crop yield and quality. Eliminating “deposits” to the weed seed bank, which is also called seed rain, is the best approach to ease future weed management. During a 5-year period in Nebraska, broadleaf and grass weed seed banks were reduced to 5 % of their original density when weeds were not allowed to produce seeds. However, in the sixth year, weeds were not controlled and the seed bank density increased to 90 % of the original level (Burnside et al. 1986). Weed seeds can reach the soil surface and become part of the soil seed bank through several processes. The main source of weed seeds in the seed bank is from local matured weeds that set seed. Agricultural weeds can also enter a field on animals, wind, and water, as well as on machinery during activities such as cultivation and harvesting. Weed seeds can have numerous fates after they are dispersed into a field. Some seeds germinate, emerge, grow, and produce more seeds; others germinate and die, decay in the soil, or fall to predation. The seeds and other propagules of most weeds have evolved mechanisms that render a portion of propagules dormant (alive but not able to germinate) or conditionally dormant (depending on soil moisture, temperature, and light) for varying periods of time after they are shed. This adaptation helps the weed survive in a periodically disturbed, inhospitable, and unpredictable environment.

Weed seeds can change from a state of dormancy to nondormancy, in which they can then germinate over a wide range of environmental conditions. Because dormant weed seeds can create future weed problems, weed scientists think of dormancy as a dispersal mechanism through time. Maintaining excellent weed control for several consecutive seasons can eliminate a large majority of the weed seed bank, but a small percentage of viable, highly dormant seeds persist, which can be difficult to eliminate (Egley 1996). Researchers are seeking more effective means to flush out these dormant seeds through multiple stimuli (Egley 1996). Weed species also

differ in the seasonal timing of their germination and emergence. Germination of many species is governed by “growing degree-days” (GDD) or the summation of the number of degrees by which each day’s average temperature exceeds a base temperature. This initial or primary dormancy delays emergence until near the beginning of the next growing season – late spring for warm-season weeds (dormancy broken by the cold period over winter) and fall for winter annual weeds (dormancy broken by a hot period in summer) – when emerging weeds have the greatest likelihood of completing their life cycles and setting the next generation of seed.

Management of Weed Seed Bank

Several factors other than mean daily soil temperature have a major impact on the timing of weed germination and emergence in the field. Adequate soil moisture is critical for germination, and good seed–soil contact is also important in facilitating the moisture uptake that is required to initiate the process. In addition, many weed seeds are also stimulated to germinate by light (even the very brief flash occasioned by daytime soil disturbance), fluctuations in temperature and moisture, or increases in oxygen or nitrate nitrogen (N) levels in the soil. Tillage, which exposes seeds to these stimuli, is therefore a critical determinant of seed germination. The timing of N fertilizer applications can also influence the number of weeds germinating (Menalled and Schnobeck 2011). For example, many weed species can be stimulated by large increases in soluble N after incorporation of a legume cover crop or inhibited by delayed applications of N fertilizer (Menalled and Schnobeck 2011). Although the horizontal distribution of weed seeds in the seed bank generally follows the direction of crop rows, type of tillage is the main factor determining the vertical distribution of weed seeds within the soil profile. In plowed fields, the majority of weed seeds are buried 10.16–15.24 cm (below the surface (Cousens and Moss 1990)). Under reduced tillage systems such as chisel plowing, approximately 80–90 % of the weed seeds are distributed in the

top 4 in. In no-till fields, the majority of weed seeds remain at or near the soil surface. Clements et al. (1996) have shown that soil texture may influence weed seed distribution in the soil profile under these different tillage systems. Understanding the impact of management practices on the vertical distribution of seeds is important because it can help us predict weed emergence patterns. For example, in most soils small-seeded weeds germinate at very shallow depths (less than 0.5 in.). Large-seeded weeds such as the common sunflower have more seed reserves and may germinate from greater depths.

Effect of Tillage on Weed Seed Bank

In no-tillage fields, the majority of weed seeds remain at or near the soil surface. Soil texture may influence weed seed distribution in the soil profile under these different tillage systems. The horizontal distribution of the weed seeds in the seed bank generally follows the direction of crop rows whereas the vertical distribution is influenced by the type of tillage (Menalled and Schnobeck 2011). The greatest diversity of weed species has been observed on field edges and heathlands. In terms of vertical distribution, reports from several states have shown that the majority of weed seeds in a no-till system were located in the top 2 in. of the soil profile. In an annual plow system, seeds were distributed in the upper 12 in. of the soil profile with 25 % of the seed in the upper 0–3 in.. Under reduced tillage systems such as ridge till and chisel plow, 50 % of the weed seeds were located in the upper 3 in. of the soil profile. The size and composition of the seed bank reflects the past and present weed management systems applied in the field and determines the future weed populations. So, it is important to limit current contributions to the weed seed bank for future weed management (Menalled and Schnobeck 2011). The effect of tillage on the weed seed banks will vary by soil type. Understanding the processes that influence the weed seed bank allow us to manipulate and manage weed seed banks effectively by implementing more informed weed management strategies. One strategy is to shift weed seeds

from the dormant to the active part of the seed bank: keeping weed seeds on the soil surface and exposing them to harsh environmental conditions and predation can enhance the mortality of the seeds. Weeds can never be eradicated, only managed. The first step toward improving our weed control practices is to understand how tillage can influence the positioning of weed seeds in the soil. Actual seed longevity in the soil depends on an interaction of many factors, including intrinsic dormancy of the seed population, depth of seed burial, frequency of disturbance, environmental conditions (light, moisture, temperature), and biological processes such as predation, allelopathy, and microbial attack (Davis et al. 2005a; Liebman et al. 2001). Understanding how management practices or soil conditions can modify the residence time of viable seeds can help producers minimize future weed problems. For example, seeds of 20 weed species that were mixed into the top 6 in. of soil persisted longer in untilled soil than in soil tilled four times annually (Mohler 2001), which likely reflects greater germination losses in the disturbed treatment. On the other hand, a single tillage can enhance the longevity of recently shed weed seeds, because buried seeds are usually more persistent compared to those left at the surface where they are exposed to predators, certain pathogens, and wide fluctuations of temperature and moisture. However, soil-borne pathogens may also contribute to attrition of buried seeds, even in large-seeded species such as velvetleaf (Davis and Renner 2006) (Fig. 3.2).

Soil Seed Bank and Aboveground Vegetation

Several studies in the past have addressed similarities between soil seed banks and aboveground vegetation (Leck and Graveline 1979; Henderson et al. 1988; Levassor et al. 1991), although several studies showed poor similarities between species composition of the soil seed bank and the aboveground vegetation (Bakker and Berendse 1999; Lemenih and Teketay 2006). The similarity between seed bank and standing vegetation is expected to decrease with increasing community

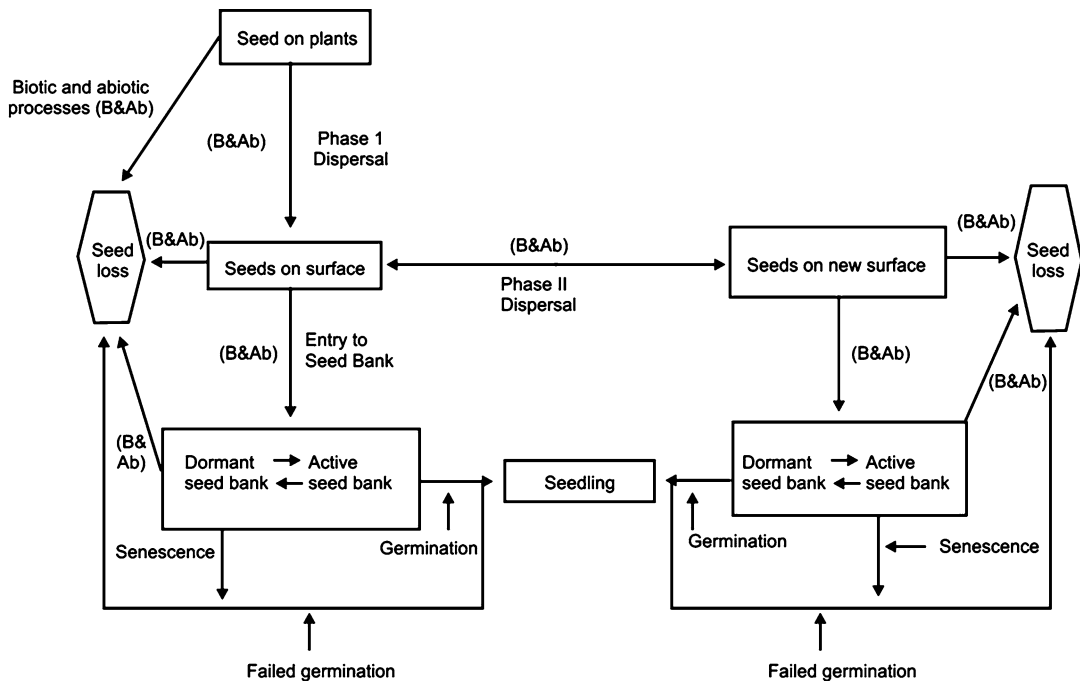


Fig. 3.2 A conceptual model of the movements and fates of seed. Phase I dispersal is movement of seed from parent to surface; phase II dispersal includes subsequent

horizontal or vertical movements (From Chambers and MacMohan 1994)

stability and stress because lack of disturbance creates sites for germination from the seed bank and there is a higher investment in clonal rather than sexual reproduction in stressful conditions (Bekker et al. 1997). Most species typical of stable habitats in contrast do not produce long-lived seeds (Lee 2004). This dissimilarity is the result of frequent occurrence of perennial grasses and woody species in aboveground vegetation (Tessema et al. 2011a) and more annual forbs in the soil seed bank (Solomon et al. 2006; Hopfensperger 2007). Such dissimilarities are caused by species differences in seed dormancy and germination rates (Baskin and Baskin 2004) that result from embryonic dormancy or an impermeable seed coat or both (Baskin and Baskin 2004). The differences in species composition, number of species, and germination success of the soil seed bank down the soil profile might be attributed to differences in soil texture and other soil quality parameters (Hopkins and Graham 1983) under the influence of grazing (Tessema

et al. 2011a). Heavy grazing reduces the soil buffer provided by the soil seed bank (Tessema et al. 2011b). The seeds in a tropical soil seed bank were generally near the surface. The similarity between seed bank and vegetation was greater at the site with the more recent history of grazing, and was more dissimilar at the site that had been in public ownership longer. The greatest similarity between seed bank and vegetation was in the ecotonal community, which forms at the interface between prairie and woodland. Similar patterns have been demonstrated for forests. In a study of seed banks in European forests varying in age from young (55–116 years old and established on formerly arable land) to old-growth forest (greater than 250 years), similarity between seed bank and vegetation decreased in the older forests. Species in the seed banks were mainly those typically found along forest edges, in earlier successional stages, or in small disturbances within the forest. This finding makes it clear that minimization of disturbances

is imperative for successful management of old-growth forests. Floristic dissimilarity has been observed between soil seed banks and above-ground vegetation generally in various ecosystems of the world (Kellman 1970; Thompson and Grime 1979). Environmental factors that are present around buried viable seeds in soil depths influence their germination and survival (Sakai et al. 2005). Forest and grasslands can be considered as long-term stable ecosystems with low disturbance destroying the vegetation, but in some moist tropical grasslands, a high similarity is found between the seed bank and standing vegetation as a consequence of high seed density, species richness, diversity, and evenness, which may be caused by moderate grazing that creates better soil texture and soil depth rotation. This high similarity may result from the presence of both transient and persistent seed banks, but low similarity is found in moist tropical forests because of high-level germination of weed seed, grasses, and forbs rather than shrubs and woody plants (Mall and Singh, unpublished data). High similarity between the seed bank and above-ground vegetation of any ecosystems of the world produces better recruitment for seed germination.

In tropical forests, there is often little correspondence between the composition of the vegetation and the seed bank (Guevara and Gomez-Pompa 1972; Hall and Swaine 1980; Saulei and Swaine 1988; Hopkins et al. 1990; Teketay and Granstrom 1995), or between the annual seed rain and the seed bank (Uhl and Clark 1983; Saulei and Swaine 1988). The same patterns are common in temperate forests (Livington and Allesio 1968; Enright and Cameron 1988; Matlack and Good 1990; Schiffman and Johnson 1992; Sem and Enright 1996).

Thus, we predict that soil seed banks and weed seed banks can be important tools for conservation: conservation of different ecosystems not only of India but of the world, with the help of vegetative propagation and seed rain, which also provide establishment and recruitment for germination, giving future diversity of standing vegetation and better management of weeds in agro-ecosystems.

Soil Seed Bank and Ecological Significance in Conservation of Different Plant Communities

Conservation ecology is a new paradigm of ecology that not only scientifically contributes to international social movements aiming at maintaining Earth's biodiversity (Primack 1995) but also is committed to adaptive ecosystem management indispensable to the intergenerational long-term sustainability of mankind (Christensen et al. 1996). Population ecology plays a central role in conservation biology because the decline of local, endemic, or rare species populations and biological invasion by invasive cosmopolitan species both constitute major aspects of local and global biodiversity degradation (Washitani 2001) (Table 3.1).

Soil seed bank studies are of great importance for the understanding of the secondary succession, considered as a necessary first step for the design of ecological restoration plans (Bossuyt and Honnay 2008). The seed bank represents the regeneration potential of the ecosystem and provides the memory of past vegetation, so it can be an important clue for conservation and restoration of plant species. In the near future there is a great role for the soil seed bank in the conservation of plant diversity and vegetation dynamics. At the community scale, seed banks can play a role in local diversity maintenance through temporal storage effects (Sletvold and Rydgren 2007). Because of their implications for population persistence and community resilience, seed banks have also been of interest for conservation research, but some studies conclude that they have little potential for restoration of natural ecosystems (Mitchell et al. 2008). Many studies found lesser species richness and a higher percentage of weed seeds and early-successional species in the seed bank relative to the standing vegetation (Bekker et al. 2000), concluding that seed banks should be a "spillover" of ungerminated seeds rather than an independent driver of population and community dynamics (Bekker et al. 2000). The soil seed bank of an ecosystem serves as an indicator of past and present weed populations: it is the primary source

Table 3.1 Soil seed bank and weed seed bank studies in various ecosystems of temperate and tropical regions of the world: seed banks were determined by the seedling emergence method for its significant role in conservation and restoration/management

References	Study location	Ecosystem	Seed bank (number of seeds m ⁻²)
Temperate region			
Davis et al. 2005b	USA	Agro-ecosystem	5,000–30,000
Benvenuti 2007	Italy	Agro-ecosystem	140–940
Clements et al. 1996	Canada	Agro-ecosystem	1,000–4,000
Sjursen et al. 2008	Norway	Agro-ecosystem	10,000–60,000
Kelton et al. 2011	USA	Agro-ecosystem	8,048–46,240
Kalamees et al. 2012	Northern Estonia	Grassland	20,145
Thompson 1986	England	Grassland	1,235
Kalamees and Zobel 2002	Estonia	Grassland	2,362
Matus et al. 2005	Hungary	Grassland	13,900–24,600
Bakker et al. 1996	Sweden	Grassland	13,400
Leckie et al. 2000	Quebec	Natural forest	475–16,700
Thompson and Grime 1979	South West England	Natural forest	2,937
Staff et al. 1987	South Sweden	Natural forest	1,757
Esmailzadeh et al. 2011	Northern Iran	Natural forest	28,931
Korb et al. 2005	USA	Natural forest	51–940
Decocq et al. 2004	France	Plantation	2,085–8,296
Dougall and Dodd 1997	East Kent	Plantation	5,847
Granstrom 1988	South Sweden	Plantation	30,085
Onaindia and Amezaga 2000	Northern Spain	Plantation	401
Erenler et al. 2010	England	Plantation	27,300
Landman et al. 2007	USA	Wetland	748–10,322
Assini 2001	Italy	Wetland	1,560
Amiaud and Touzard 2004	Western France	Wetland	1,191–27,340
Tu et al. 1998	USA	Wetland	800–38,000
Leck 2003	USA	Wetland	450–394,600
Tropical region			
Srivastava 2002	India	Agro-ecosystem	17,600–17,960
Li et al. 2012	China	Agro-ecosystem	20,417–220,831
Feng et al. 2008	China	Agro-ecosystem	116,812–294,761
Franke et al. 2007	India	Agro-ecosystem	100–1,000
Garcia 1995	Brazil	Agro-ecosystem	2,325
Srivastava 2002	India	Grassland	16,980–18,720
Zhao et al. 2011	China	Grassland	120–1,176
Kassahun et al. 2009	Pakistan	Grassland	320–676
Yan et al. 2012	China	Grassland	2,553–19,533
Weerasinghe et al. 2008	Japan	Grassland	12,220
Cao et al. 2000	South West China	Natural forest	4,585–65,665
Hopkins and Graham 1983	North Queensland Australia	Natural forest	588–1,068
Saulei and Swaine 1988	New Guinea	Natural forest	398
Metcalfe and Turner 1998	Singapore	Natural forest	Approximately 1,000
Dalling and Denslow 1998	Panama	Natural forest	55–243
Wang et al. 2009b	South China	Plantation	455–967
Bueno and Baruch 2011	Venezuela	Plantation	10–1,222
Senebeta and Teketay 2002	Ethiopia	Plantation	4,500–82,600
Senebeta et al. 2002	Ethiopia	Plantation	2,300–18,650
Mukhongo et al. 2011	Western Kenya	Plantation	1,550
Li et al. 2008	China	Wetland	40–2,600
Wang et al. 2009a	China	Wetland	2,000–12,500
Zhao et al. 2008	China	Wetland	Approximately 5,000–14,000
Hong et al. 2012	China	Wetland	11,575–24,831
Wang et al. 2011	China	Wetland	19,000

of future seed infestation as the soil seed bank may differ in species composition, richness, and diversity. There has been much work on this topic related to plant diversity conservation for endemic, invasive, and other plant species, whether herbs, shrubs, and trees, of different regions of the world. Restoration should be focused on self-regeneration of native species. The soil seed bank helps in documentation for conservation of different plant communities of the world. Soil seed bank study is more useful these days because it can help in conservation and restoration of vegetation and ecosystems. The soil seed bank is an important component of vegetation dynamics affecting both ecosystem resistance and resilience (Pugnaire and Lazaro 2000). It is a buildup of viable but ungerminated seeds present in or on soil and is essential to maintain life and growth in ecosystems (Baker 1989). It helps in population maintenance and provides information about the size, number, floristic composition, and dynamics of the seeds present in soil (Dalling et al. 1998).

The seed banks contain a generally high proportion of early-successional or invasive nontarget species. The understanding of the dynamics and functions of seed banks has become a great challenge to ecologists of plant communities because this understanding is necessary to determine the role of this community trait in ecosystem functioning and also to improve the integrated management of ecosystems (Luzuriaga et al. 2005). At high grazing pressures, perennial grasses are replaced by annual herbs, which could trigger a vegetation collapse from which recovery to the grassland state is extremely difficult even if grazing pressure is greatly reduced (Rietkerk et al. 1996). The recovery of species that have disappeared from the aboveground vegetation because of heavy grazing, however, can be facilitated by the soil seed banks (Baker 1989). Soil seed bank samples that were collected at the end of the growing season (October–November) after seed production can serve as an indicator of viable seeds that did not germinate in the field during the season. The ecosystem and habitat affect seed bank size. The seed bank of perennial grasses is often quite small because seed production is very small relative to that with

annual species. Annual weed species ecosystems have very large seed banks, especially where the land has been grazed: grazing increases seed bank size. Trampling may create conditions in which seeds retain greater viability in the soil. Soil disturbance affects seed bank size: one local or temporary disturbance that allows 1 year of annual weed growth and seed production can have profound impact on the seed bank.

The soil seed bank helps in understanding of the population dynamics of buried viable seeds and is of practical importance in conservation and agriculture (Fenner and Thompson 2005). Few species have seed banks in the tropical forest in general (Garwood 1989), and autochthonous seed banks rarely contribute to the regeneration of deforested tropical forest areas (Teketay and Granstrom 1995). Seeds are available in the soil at the end of the dry season. Collecting the transient seed bank (litter and soil) from the forested area at the end of the dry season and depositing it onto degraded areas seems to be a promising strategy for forest restoration (Sampaio and Scarriot, unpublished data). Generally, in plantations that are near harvest their soil seed bank influences the establishment of secondary succession after disturbances. Some of the persistent seeds in the soil and the seed rain (if any) may lead to restoration of the vegetation (Teketay 1998). The soil seed banks of plantations and natural forests are dominated by herbaceous species and mostly exhibit a persistent soil seed bank (Teketay and Granstrom 1995), but few woody species are also observed in a soil seed bank (Teketay and Granstrom 1995; Teketay 1998). A soil seed bank is a key factor for counteracting local extinction of plant species. The ecological implications of a soil seed bank in regeneration of different ecosystems need to be examined by monitoring the dynamics of the bank following cultivation activities (Cao et al. 2000).

In India, much research work has been accomplished in different ecosystems in both dry and moist topics. We compared grasslands and agroecosystems, finding a higher seedling emergence from a soil seed bank or weed seed bank in the moist tropics than in the dry tropics (Srivastava 2002).

In this review, in comparison between different ecosystems of temperate and tropical regions we observed that different ecosystems have more seed germination in the tropics than in temperate regions, which may be the result of environmental conditions and high diversity in both soil seed banks and aboveground vegetation. Agro-ecosystems of both regions have great weed seed bank density, so the present study concluded that the weed seed bank should be properly managed to control weeds for better crop yield. We observed that better emergence of seedlings (seed density m^{-2}) provides ideas about the conservation and restoration of grasslands and wetlands, which may be because of the high similarity between aboveground vegetation and the soil seed bank, which comprises grasses, forbs, weeds, shrubs, etc., because of seed rain or seed dispersal. Plantations and natural forest of both tropical and temperate regions have low germination of seeds from the soil seed bank in comparison with other ecosystems but have both high and low similarity, which occurs from the high germination rate of agricultural weeds, annual/perennial grasses, and forbs. Trees provide a low contribution of seed germination from the soil seed bank. Conservation of these ecosystems through the soil seed bank is limited and has less significance in these ecosystems. Thus, conservation and restoration of managed and natural forests should be accomplished by preservation of desirable seeds in situ and ex situ so that their biodiversity may exist in future generations.

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Challenges and Prospects in Exploring Marine Microbial Diversity

4

K.B. Akondi and V.V. Lakshmi

Abstract

The marine realm is one of the major habitats of the biosphere and covers around 70 % of the Earth's surface. Eighty to ninety percent of all life forms of the Earth are present only in the oceans. The microbial diversity is enormous in marine habitat. The knowledge of the oceanic biodiversity, as a whole, is limited, in spite of the advances in sampling techniques and use of in situ methods to study natural communities. Apart from natural variations in biodiversity, pollution of coastal waters and bio-invasions through human activity also alter the biodiversity drastically. Industrial effluents, discharges, land reclamation, and other anthropogenic effects are found to cause damage or create imbalance in coastal diversity and modify it significantly. This phenomenon is observed all around the world. Thus, better understanding of the relations between diversity at different topological levels as well as between biodiversity and ecosystem functioning is essential. This could have important implications in conservation management. Further it is being increasingly realized that the marine environment is an inexhaustible resource of biomolecules of commercial importance including antibiotics and enzymes. Marine diversity is also considered important to find solution for the expensive problem of bio-fouling, which is a serious impediment for maritime industries such as shipping, thermal and nuclear power plant maintenance. The potential of marine isolates against inhibition of primary foulers is opening a realm for the development of nontoxic, environmentally friendly natural product antifouling agents (NPAs).

Keywords

Marine biodiversity • Culture independent methods • Bioactive molecules • Antifouling • Natural product antifouling agents (NPA)

K.B. Akondi (✉) • V.V. Lakshmi
Dept of Microbiology, Sri Padmavati Mahila
Visvavidyalayam, (Women's University), Tirupati,
Andhra Pradesh 517502, India
e-mail: vedula_lak28@yahoo.co.in

Marine Environment and Its Complexity

Seventy percent of the Earth's surface is covered by the marine habitat which accounts for 80–90 % of all life forms on this planet. The realm of the marine biosphere can be categorized into coastal areas (neritic) and open ocean. The coasts are generally described as sandy or rocky types, and coastal habitats extend from the shore to the edge of the continental shelf. Sandy coasts are comparatively less stable with fewer organisms inhabiting them than rocky coasts. Rocky coasts, being stable, protective, and older, make home to diverse variety of organisms. Despite coast to the shelf area representing only less than ten percent of the total ocean area, majority of marine life forms are localized in this region. Sixty-five percent of the ocean is open water where the depth measures over 200 m and deep ocean habitats dwell in this region. The oceanic zone is also composed of a wide array of undersea terrain, including crevices of hydrothermal vents. Based on the depth and the penetration of light, the oceanic zones are categorized into the epipelagic, mesopelagic, and bathypelagic zones (Fig. 4.1). Epipelagic, also known as euphotic zone, extends from the surface to about 200 m deep. This zone

receives maximum penetration of sunlight and hence well supports the photosynthetic forms. A large variation in temperature between 40 °C and –3 °C is observed across the cross section of depth. On the surface as well as across the region, this zone supports both phytoplankton and zooplankton which in turn support larger organisms like fishes and marine mammals (Azam et al. 1983; Button 2004).

The next zone is defined as the mesopelagic or disphotic zone which appears deep blue to black in color. This zone has very little amount of light penetration and is sometimes referred to as the twilight zone. The temperature ranges from 4 °C to 5 °C, salinity goes up to 35ppt, and the amount of dissolved oxygen available in the water is also low compared to the first zone. Pressure is greatly elevated exceeding beyond 1,000 atm., increasing in direct proportion with depth. The depth of this zone is also influenced by the clarity/murkiness of the water. In clear waters, the disphotic zone begins from depths of 600 ft and extends up to about 1,000 m deep. However, in murky water it starts from 50 ft deep itself. As enough light does not penetrate beyond 200 m, photosynthetic organisms do not thrive in this zone. Thus in this sea zone, light is essentially the limiting factor. The food supply is extremely limiting in most areas of this zone except near hydrothermal vents. These

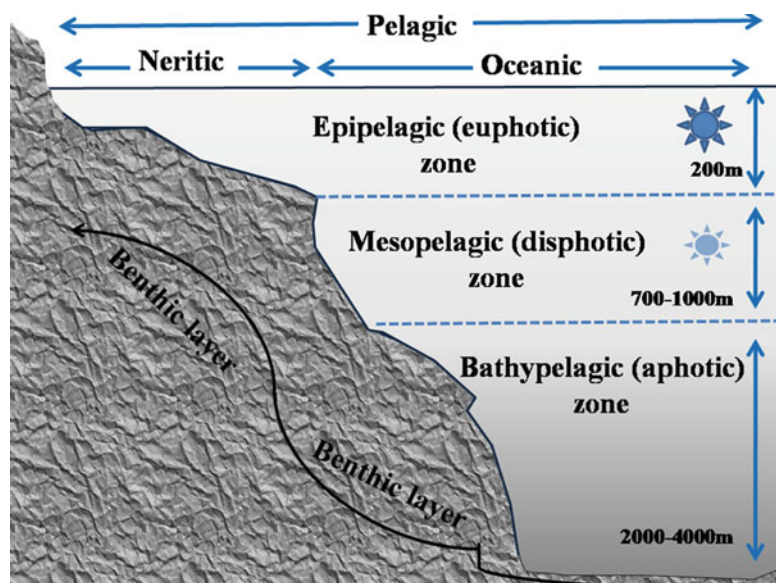


Fig. 4.1 Oceanic zones: the marine water column is categorized into distinct zones based on water depth and distance from shore

extreme factors are responsible for significantly lower distribution of micro- and macroflora in this zone (Chandramohan 1997; Karl 2007). The mesopelagic zone is followed by bathypelagic (aphotic) zone which constitutes majority portion of the ocean. This is also called the midnight zone as no light penetrates here. The temperatures are near freezing range with intense water pressure. This zone supports sparse life forms due to its harsh environment. The lowest zone of the ocean body is the benthic zone. This zone includes the sediment surface and some subsurface layers and is completely dark because no light penetrates here. The life surviving in this zone tolerates cold temperatures, very high pressure, and low oxygen levels (Azam et al. 1983; Meadows 1995; Aristegui et al. 2009). Because of high pressure and the lack of human interference, this zone does not change for long spans of time. This region is rich in life forms and the organisms living are called benthos. The zone supports diverse habitat of micro- and macroforms including bacteria, fungi, seaweeds, sponges, sea anemones, worms, sea stars, and fishes. Microbes are mainly chemosynthetic bacteria which utilize the abundant minerals. They generally live in close relationship with the substrate bottom and other life (Pawlik 1992; Gontang et al. 2007).

Biodiversity of Marine Environment

Marine forms account for 90 % of the world's biodiversity, many of which are yet to be characterized. Over 250,000 marine species identified live in sunlit surface seawaters, half of which are exclusive for marine environment. Nearly all terrestrial phyla of animals have their marine representative species. The distribution of different species is greatly influenced by the availability of food, ability to combat or avoid predation, and reproduce. Marine microbial biodiversity is enormous in both type and numbers and constitutes 80–90 % of life forms in ocean. They are found in all portions of the water column and sediment surface, as well as in sediments itself. High variation is observed in the biodiversity of these organisms in different strata of marine

bodies (Ventosa et al. 1998; Perez et al. 2006). Photosynthetic organisms such as phytoplanktons dominate epipelagic zone where light is available. These along with zooplanktons form the major contributors of food chain in the oceanic zones. Vast biodiversity is observed among phyto- and zooplanktons which exist as microscopic as well as macroscopic forms. These mainly include various types of algae, diatoms, euglenoids, and silicoflagellates. Zooplanktons are somewhat larger forms with not all microscopic forms and include protozoans, dinoflagellates, zooflagellates, foraminiferans, and radiolarians. Several larger animals begin their life as zooplankton before they become large enough to take their familiar forms (Meadows and Campbell 1995; Paerl 2000; Mcmanus and Woodson 2012).

Microorganisms persist deep into the aphotic zone where phytoplanktons are absent. Here they mediate the dynamics of organic material as they are the dominant forms. Typically, bacteria are most abundant in the sunlit upper layer, and their numbers decrease with depth. In euphotic region, both bacterial and archaeal counts range up to 10^7 ml⁻¹, whereas they are in the order of 10^4 – 10^5 ml⁻¹ at greater depths. Microorganisms also thrive well as benthic forms and around hydrothermal vents or geysers located on the mineral-rich ocean floor. Chemosynthetic bacteria use the superheated water and chemicals from the hydrothermal vents to generate energy in these light-impenetrable regions where photosynthesis is not possible (Amend et al. 2004). While most bacteria thrive as free-living forms, some live as symbionts with other organisms (Orcutt et al. 2011). Many deep-sea fish harbor symbiotic bacteria that emit light called bioluminescence. Bioluminescence causes water to glow, a phenomenon present at all depths which the fish use to signal other members of their species. Some marine bacteria can interact with diatoms, another type of marine microbe, in such a way that influences the cycling of silicon in the ocean. The viral counts are generally ten times higher than bacteria (Chandramohan 1997; Karl 2007). On average, the microbial biomass is estimated to be ~200 g (wet weight)/sq meter at the surface. It varies widely with depth ranging to less than

25 g (wet weight)/sq meter at 1,000–1,500 m and drops further to <0.3 (wet weight)/sq meter above 5,000 m of depth. Thus, the incredible numbers of the microorganisms make up a significant portion of the world oceanic biomass (Chandramohan 1997; Perez et al. 2006).

Halophiles and halotolerant microorganisms are adapted to grow in a wide range of salt concentrations and inhabit coastal and deep-sea waters and natural hypersaline brines in arid as well as in artificial salterns. Based on the salt requirement for growth, they are categorized as slight halophiles (grow at 2–5 % NaCl), moderate halophiles (grow at 5–20 % NaCl), and extreme halophiles (grow >20–30 % NaCl) (Sarma and Arora 2001; Bull 2004). Marine prokaryotes include Archaeobacteria, Eubacteria, and Cyanobacteria. Important members of halophilic Archaea include *Halobacterium*, *Halococcus*, *Natronobacterium*, and *Natronococcus* species. These thrive well in harsh environments with high osmolarity and very low temperature. The Eubacterial members comprise cyanobacteria; green and purple bacteria; sulfur-oxidizing bacteria; anaerobic, fermentative homoacetogenic bacteria; sulfate-reducing bacteria; and other aerobic heterotrophic gram-negative and gram-positive bacteria. The heterotrophic gram-positive bacteria in marine environment include species of the genera *Halobacillus*, *Bacillus*, *Mannococcus*, *Salinococcus*, *Nesterenkonia*, and *Tetragenococcus*. The gram-negative heterotrophic marine bacteria fall into two groups based on their capacity to ferment carbohydrates. The fermentative forms predominantly belong to the genera *Vibrio*, *Listonella*, *Photobacterium*, *Colwellia*, and *Aeromonas*. The non-fermentative forms belong to genera *Pseudomonas*, *Pseudalteromonas*, *Alteromonas*, *Alcaligenes*, *Halomonas*, *Shewanella*, and *Deleya* (Zobell 1994; Holmstrom et al. 1998; Bull 2004; Button 2004; Das et al. 2006).

Annual and seasonal cycles of microbial abundance are observed quite regularly in marine environment. Generally, bacteria are most abundant in summer and least in winter. Apart from natural variations in biodiversity, pollution of coastal waters through human activity is altering

the biodiversity drastically. Industrial effluents, discharges, land reclamation, and other anthropogenic effects are found to cause damage and create imbalance in coastal diversity. Losses in marine biodiversity are highest in coastal areas, and this phenomenon is observed all around the world. Improper use of coasts and increasing concern on destruction of marine habitats due to bioinvasion is making it necessary to investigate and manage coastal regions properly so as to minimize alterations to the natural biodiversity of various marine resources (De Sousa et al. 1996; Venkataraman and Wafar 2005).

Challenges in the Study of Microbial Diversity

It is being increasingly realized that microbial biodiversity is vastly underestimated. Until the 1990s, knowledge of microbial populations was determined using assays that relied on the growth of the microbe. Detection and identification of microbes based on their genetic material using molecular techniques have revealed much larger numbers and types of microbes in the ocean than what scientists had previously suspected. Knowledge of the diversity of microbial life in the oceans is rapidly growing with advances in sampling techniques and use of in situ methods to study natural communities. In 1987 marine biodiversity of bacteria was estimated at 12 divisions with cultured forms in all division and no uncultured representatives. However the scenario has changed since then in the post genomic era, with the use of culture-independent techniques. More than 100 divisions of bacteria are identified with 30 divisions having cultured representative and 70 with no cultured representatives (Achtman and Wagner 2008; Das et al. 2006; Heidelberg et al. 2010). Introduction of metagenomic approaches has further resulted in a rapid increase in candidates with no cultured representatives. Presently only 3,000–4,000 species of bacteria are described, whereas the worldwide species are predicted closer to three million using molecular tools (Curtis et al. 2002; Joint et al. 2010; Dionisi et al. 2012). A stark

variation is also observed among the predominant microbial forms when analyzed by culture and culture-independent methods. For instance, γ -Proteobacteria in general appear to be abundant in marine environment when using culturing techniques, whereas α -Proteobacteria appear as dominant forms when 16S clone libraries are analyzed by culture-independent methods (Gilbert et al. 2009). Archaea is another example of surprise to marine microbiologists as it is now perceived to make up to half the mass of life in the ocean in contrast to the previous notion that they predominantly inhabit hydrothermal vents in ocean floor (Sherr and Sherr 2000; Yu et al. 2005; Auguet et al. 2009).

Exploration of microbial diversity is thus clearly a topic of considerable interest, and this knowledge is essential to understand the importance of oceanic ecological processes. Assessing and understanding microbial diversity in marine environment still remains a daunting task as typically <1 % of bacteria can only be cultivated as axenic cultures (Connon and Giovannoni 2002; Joint et al. 2010). One of the major issues with the study of large microbial communities by culturing is the inability to detect and isolate underrepresented members of the community. This is because a few abundant taxa tend to dominate and mask detection of the rare community members. Hence surveys targeting only few hundred rRNA genes have limitations and cannot fully describe a microbial community. Introduction of tag sequencing facilitated the study of the marine microbial population structure by sequencing several short hypervariable regions in rRNAs. A further, significant reduction in the sequencing cost with pyrosequencing is making the survey of large microbial communities economically feasible. While it is possible to access the genetic information from uncultured organisms through genomics, the potential of the organism can be best harvested by obtaining the organisms in laboratory (Glöckner and Joint 2010; Heidelberg et al. 2010; Dionisi et al. 2012). In this direction efforts are being made to improve the methods of culturing the bacteria from marine environment. Novel culturing techniques are being actively

developed which mimic the natural habitat of the organism. Techniques like dilution to extinction, culturing in arrays, diffusion chambers, and micro-droplet encapsulation are being successfully applied to improve the cultivability of marine organisms in low-nutrient media (Joint et al. 2010; Dionisi et al. 2012). Thus, to get a more realistic assessment of the biodiversity of microbial community, integration of traditional/improved culture-based methods with culture-independent techniques and metagenomic approaches is important. This has resulted in isolation of several novel and previously uncultured marine bacteria and bacterioplanktons. Some of the newly described marine genera include *Salinispora*, *Demequina*, *Marinispora*, *Solwaraspora*, *Lamerjespora*, and several new species of *Actinobacteria* (Kaeberlein et al. 2002; Zengler et al. 2002, 2005; Nichols et al. 2008). With the aid of these novel techniques, the repertoire of cultivable marine microorganisms has increased significantly from 10 % to 25 % in the last decade alone (Connon and Giovannoni 2002; Lee et al. 2010; Dionisi et al. 2012).

As most of the organisms in marine habitat flourish as consortia, it is also important to understand bacterial community dynamics. Quorum sensing (QS) plays a major role in the interactions between different microorganisms. Acquiring information on cell attachment characteristics, cell signaling pathways, requirement of alternate electron acceptors, etc. can aid in optimization of culturing parameters (Daniels et al. 2004; Lee et al. 2009; Joint et al. 2010). It has been shown that some bacterial species selectively destroy signal molecules produced by other species. So it is not always easy to find the optimal conditions for QS to influence the isolation of novel clades. Co-culturing with a well-established N-acyl homoserine lactone (AHL)-producing bacterium can also be considered to optimize the QS response (Tait et al. 2009). Biodiversity studies are also significantly influenced by the sampling strategies adopted. Generally, the sampling procedures to be used are devised based on the scientific questions to be addressed, available resources, sampling density, etc. To get

a holistic view of the biodiversity, multiple-point sampling is required to take into consideration the temporal and spatial issues of the marine body. Though there are still no accepted global norms for these sampling procedures as of now, attempts are being made to come to consensus (Raghukumar and Anil 2003; Das et al. 2006). Establishing optimal measure of microbial diversity to determine the total and actual diversity of microbial forms and establishing levels of heterogeneity in terms of spatial and temporal parameters will help in correlating observed diversity to function in that ecosystem. Several of these issues can be addressed in the foreseeable future with the integration of culture dependent and culture independent methods.

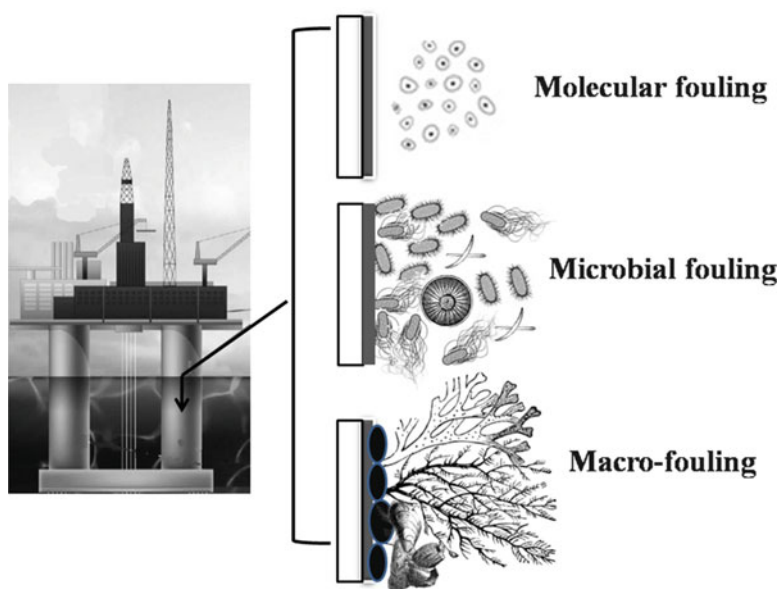
Microorganisms as Potential Bioresource

It is being increasingly realized that the marine environment is an inexhaustible resource of novel biomolecules of commercial importance. Since the 1970s, more than 15,000 structurally diverse natural products with an astounding array of bioactivities have been discovered from marine microbes, algae, and invertebrates. Bioactive molecules from the sea include phenols, lactones, sterols, terpenoids, phthalates, fatty acids, cyclic polysulfides, macrolides, antimicrobial peptides (AMPs), antibiotics, and enzymes (Newman et al. 2003; Salomon et al. 2004; Qian et al. 2010; Vignesh et al. 2011). The unique ability of the marine biomolecules to be capable of functioning under extreme conditions that lead to precipitation is appealing. The products are also safe as human therapeutics as the optimum environment for their activity is quite close to conditions of blood plasma. Interest in the development of marine compounds as potential drugs is thriving well with several marine drugs already available commercially. About 40 marine-derived natural products or their derivatives are in clinical or preclinical trials for the treatment of cancer, inflammation, and other diseases. Antibiotics isolated from marine bacteria in recent times include aplasmomycin, himalomyins, and

pelagiomycins and marinomycins C and D from actinomycetes (Snell 2003; Kalinovskaya et al. 2004; Qian et al. 2010). Marine bioprospecting has led to identification of several novel AMPs for development of new generation antibiotics. Unlike the majority of conventional antibiotics, AMPs also have the ability to enhance immunity by functioning as immunomodulators. AMPs are potent, broad-spectrum antibiotics which demonstrate potential as novel therapeutic agents. These AMPs have capabilities to inhibit and kill gram-negative and gram-positive bacteria (including strains that are resistant to conventional antibiotics), Mycobacteria, enveloped viruses, fungi, and even transformed or cancerous cells. These peptides have a variety of antimicrobial activities ranging from membrane permeabilization to action on a range of cytoplasmic targets (Brogden 2005; Tok 2005; Rahnamaeian 2011).

Another important ecological role of the halophilic bacteria is bioremediation. In marine environment they recycle nutrients and degrade and/or detoxify chemical substances including metals, petroleum products, aliphatic and aromatic hydrocarbons, industrial solvents, pesticides, and their metabolites. There has been a great interest in studying the diversity of indigenous halophilic organisms capable of degrading pollutants which are reviewed (Malik et al. 2008; Stenuit et al. 2008; Zhao and Poh 2008; Dinsdale et al. 2008). Tackling biological fouling is a serious and expensive impediment for maritime industries such as shipping, oil, petroleum and natural gas, thermal and nuclear power plants. All surfaces living or inanimate are susceptible to fouling in the marine environment, where there is intense competition for living space (Evans 1981; Pawlik 1992; Fusetani 2004). The phenomenon of the colonization and growth of sessile organisms, plants, or animals on the surfaces of man-made structures immersed in the sea is termed as biofouling. The major aquatic fouling organisms in the sea are microbes, protists, animals, and plants. These include bacteria, fungi, diatom, algae, and members of phyla Protozoa, Porifera, Coelenterata, Annelida, Tentaculata, Arthropoda, Echinodermata, and Chordata (Chambers et al. 2006; Dobretsov

Fig. 4.2 Process of biofouling: the different micro- and macroorganisms involved in distinct stages of biofouling



et al. 2007). These organisms cause extensive damage to commercially important marine structures by corroding their surfaces and thereby substantially decreasing the life of the structures. Settlement of invertebrate larvae on man-made surfaces also causes increased drag of marine surface and submarine vessels incurring increased fuel penalties. In addition to the direct costs, additional expenditures are incurred in the form of expenditure associated with continual inspections by divers, underwater cleaning for maintaining of the equipment, and cost of application of antifouling agents. Control of biofouling is a formidable problem in cooling circuits of power plants, ship hulls, oil rig platforms, and other marine structures also (Omae 2003; Yebra et al. 2004). Thus, dealing with biofouling alone costs the shipping and maritime industry over \$6.5 billion per year (Lodeiros and Himmelman 2000; Bhadury and Wright 2004). The vast economic loss due to fouling has instigated extensive investigations into the cause of biofouling, the exact sequence of events, the groups of organisms involved, etc. in order to develop practical methods for its prevention.

Solid surfaces exposed in seawater are subjected to a series of changes by numerous micro and macro marine fouling organisms. Biofouling

is a complex multistep process that could be distinguished into three distinct phases (Gunn et al. 1987; Rittschof 2000). Firstly, a biochemical conditioning film is formed, onto which primary foulers such as diatoms, bacteria, and protozoa colonize (Fig. 4.2). These microfoulers adhere firmly to the surfaces and avoid washing off. The composition of the primary bacterial fouling community is influenced by numerous environmental factors including the physicochemical properties of the surface, nutrient availability, seawater chemistry, temperature, and exposure time. The colonization by these organisms initiates the fouling process on a surface and makes it amenable for subsequent attachment of secondary foulers (Engel et al. 2002). Macroforms include various eukaryotic organisms like marine invertebrates, and algae which colonize as the secondary foulers. Thus the development of biofouling layers is a stepwise process, with each stage conditioning the surface for the next one (Daniel and Chamberlain 1981; Clare et al. 1992). Fouling varies spatially in its intensity and diversity and follows the distributional pattern of the marine epibenthos from which it is largely derived. In coastal or shallow waters, where temperatures as well as nutrient levels are generally higher, the intensity of fouling and species diversity is greater (Meadows and Campbell 1995;

Holm et al. 2000; Braithwaite and Mc Evoy 2005). Initially, around 2,000 marine species have been identified to be involved in fouling, but this number has since been revised and increased to more than 4,000 species (Callow and Callow 2002).

The principal protective method against fouling for ships, nets, and other installations has been the use of antifouling paints (Evans and Clarkson 1993; Douglas-Helders et al. 2003). The effectiveness of these paints against fouling organisms relies upon effective leaching of the toxic substance (Evans 1981). Prominent antifouling paints contain organotin compounds like tributyltin (TBT), tributyltin oxide (TBTO), tributyltin fluoride (TBTF), and triphenyltin acetate (TPTA). These organotin-based paints had devastating impact on the aquatic ecosystems, which brought about a complete worldwide ban on their use. As a tin-free alternative, copper has emerged as an important antifouling agent. The copper-based paints have been found to show significant antifouling against barnacles, tubeworms, and majority of algal fouling species (Omae 2003). However, algal species like *Enteromorpha* sp., *Ectocarpus* sp., and *Achnanthes* sp. exhibit marked physiological tolerance to copper (Chambers et al. 2006). Improved protection against the tolerant species is achieved by adding various organic biocides to the copper-based paints (Omae 2003). However, the increased residual concentrations of organic booster biocides in marinas and harbors are of concern as they adversely affect nontarget marine forms (Konstantinou and Albanis 2004). Silicone-based fouling-release coatings are also being developed as alternatives to the use of biocidal antifouling coating (Holm et al. 2000; Chambers et al. 2006). These provide nonstick coating, which prevents or reduces attachment of fouling organisms. The application of these toxic antifouling paints alone is not enough as regular cleaning and maintenance are still required for controlling/inhibiting fouling.

The major environmental concerns due to the use of antifouling paints and their impact on marine ecosystems have forced investigations into the development of environmentally friendly,

nontoxic or low-toxic natural product antifouling agents (NPAs). In nature, several benthic sponges, gorgonians, soft corals, algae, etc. use a variety of physical and chemical defenses to keep themselves free from biofouling (Egan et al. 2001; Dobrestov and Qian 2002; Harder et al. 2003). Both free-living and attached marine bacteria have been shown to produce surface-bound and/or soluble chemicals that inhibit adhesion of invertebrate larvae (Burgess et al. 2003; Longeon et al. 2004). Negative cues aid to repel foulers from the surface and inhibit larval settlement and metamorphosis (Pawlik 1992). Hence, a promising long term and environmental friendly solution to control the complex problem of biofouling is expected to arise from the marine environment itself. The use of naturally produced antifouling agents will be less expensive, eco-friendly, and offer longer durability (Burgess et al. 2003; Konstantinou and Albanis 2004). Thus, antifouling coatings prepared from marine bacteria and their biofilms are emerging as the primary candidates for the development of biological antifouling products. The use of bacteria as a source of naturally produced antifoulants also offers the advantages of easy culturability and amenability to cloning. The active metabolites produced by these organisms can be expressed in heterologous hosts for commercial production on large scale (Handelsman 2004).

Discovery of novel NPAs has been expedited by the continuous technological advancements and innovation in isolation and characterization of even minute quantities of marine samples (like NMR, MS, FT-MS, soft ionization). Studies on various marine organisms lead to isolation of around 200 NPAs with varying degrees of antifouling activity against a wide range of marine fouling organisms (Newman et al. 2003; Schroeder et al. 2007; Hellio et al. 2009; Qian et al. 2010). Among the NPAs tested, pyolipic acid, phenazine-1-carboxylic acid, and 2-alkylquinol-4-ones isolated from *Pseudomonas* sp. have been found to inhibit macrofouler settlement. The extracts incorporated into paints showed promising antifouling activity in both laboratory and field

experiments (Burgess et al. 2003; Eguía and Trueba 2007). 1-Hydroxymyristic acid and 9-Z-oleic acid, isolated from marine bacterium *Shewanella oneidensis*, completely inhibited the germination of spores of *Ulva pertusa* at 10 mg/ml concentrations (Bhattarai et al. 2006). The genus *Pseudoalteromonas* has attracted significant interest because of capability to produce diverse group of antifouling substances. These are effective specifically on marine fouling organisms by inhibiting and/or controlling their adaptive and behavioral responses (Holmstrom and Kjelleberg 1999; Egan et al. 2001; Dobretsov et al. 2007). Brominated compounds and furanones derived from *Pseudoalteromonas* sp. and seaweeds and alkylated butenolides and 12-methylmyristic acid (isolated from a deep-sea *Streptomyces* sp.) exhibited potent AF activity against the larvae of important fouling organisms (Penesyan et al. 2009; Xu et al. 2009). Diketopiperazines (DKPs), a common class of bacterial and fungal metabolites, have also been identified as novel AF compounds (Li et al. 2006). Apart from these, a variety of enzymes from microbial sources have been explored as nontoxic antifoulants (Olsen et al. 2007; Kristensen et al. 2008; Leroy et al. 2008). They offer the advantages of being readily available, nontoxic, and biodegradable. However, some crucial issues involving stability and control of release rates need to be addressed before the enzymes can emerge as effective AF paints. The enzymes showing the most promising antifouling activity include serine protease, Alcalase1, which have shown to degrade barnacle cyprid cement, thereby preventing larval attachment (Aldred et al. 2008). The active enzyme immobilized on a polymer matrix has been shown to reduce the attachment and adhesion strength of algal cells (Tasso et al. 2009).

Biofilms of the bacterium *P. tunicata* exhibited antifouling activity against invertebrate macrofoulers like *Balanus amphitrite* and *Ciona intestinalis*. Incorporating such natural products into antifouling paints has been tried, and the coatings are shown to exhibit good activity against marine bacteria, barnacle larvae, and algal spores, suggesting potential of their use in

antifouling paint (Fusetani 2004; Fusetani and Clare 2006; Hellio et al. 2009). These studies have opened up immense scope for the use of microbial biofilms or bacteria immobilized in hydrogels for controlling biofouling (Armstrong et al. 2000; Prochnow et al. 2004). An interesting NPA product called Biojelly[®] produced by microorganism of the *Alteromonas* genus has been patented in 2004 (Hayase et al. 2003). These bacteria when incorporated into cellulose acetate membrane polymer and immersed in seawater and harbors inhibited attachment of marine organisms such as algae and barnacles (Hayase et al. 2003; Marechal and Hellio 2009). Microencapsulation of the bioactive NPs is, so far, the best method developed to counter biofouling. Development of biological antifouling agents is a frontier area in the field of biotechnology. Though still in its infancy, natural antifouling compounds are emerging as the most promising candidates for controlling biofouling in years to come (Kalinovskaya et al. 2004; Braithwaite and McEvoy 2005; Qian et al. 2010).

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Jayant Shankar Raut and Sankunny Mohan Karuppaiyl

Abstract

Essential oils of plant origin have a long history of use by various civilizations in the world. They find place in almost all traditional systems of medicine like Ayurveda, Siddha, Unani, and Chinese traditional system of medicine. Essential oils extractable by steam distillation and various solvents from different parts of plants constitute complex mixtures of low molecular weight compounds. Terpenes and terpenoids form the major constituents of essential oils and determine the aroma as well as biological properties. Traditionally essential oils are prescribed by the healers for a variety of ailments ranging from skin infections to cancer. Many of these treatments have stood the test of time. As such essential oils offer tremendous scope for reverse pharmacological studies. With the use of HPTLC, HPLC, GC, NMR, GCMS, and the entry of phytochemists, the essential oil research has matured in to a science of its own. We are presenting an overview of the biological properties and potential applications of essential oils in medicine.

Keywords

Bioprospecting • Essential oil • Bioactive molecule • Plant molecule • Antimicrobial • Antibacterial • Antifungal • Anticancer • Antimutagenic • Antidiabetic • Anti-inflammatory • Antiviral • Antiprotozoal • Medicine

Introduction

Essential oils have been used by the humans for aroma, flavor, food preservation, as well as for medicinal purposes, since ancient times. Traditional systems of medicine like Ayurveda, Siddha, Unani, and Chinese traditional medicines prescribe the use of various aromatic essential

J.S. Raut • S.M. Karuppaiyl (✉)
DST-FIST & UGC-SAP Sponsored School of Life
Sciences, SRTM University, Nanded, MS 431 606, India
e-mail: rautjayant123@gmail.com;
prof.karuppaiyl@gmail.com

oils. Essential oils can be defined as “mixtures of compounds extractable by steam distillation, nonpolar solvents, supercritical carbon dioxide, and fluorocarbons.” Essential oils (EOs) can be extracted from different plant parts like flowers, leaves, stems, roots, fruits, and fruit peels. These are complex mixtures of various low molecular weight compounds (usually less than 500 Da), which may vary with the plant material and the extraction method used (Nakatsu et al. 2000). Terpenes and terpenoids form the major constituents of the essential oils, while aromatic as well as aliphatic constituents are also present in varying concentrations. Usually, one or two terpene molecules present in substantial quantity determine the aroma and biological properties of an essential oil (Bakkali et al. 2008). With the oncome of drug-resistant strains of pathogens, increase in the immunocompromised patients, and increased concerns on side effects of available drugs, people are looking for complementary and alternative therapies. Plants are rich in bioactive molecules with novel properties. Natural products and natural-product-derived molecules are still major sources of innovative therapeutic agents (Clardy and Walsh 2004). EOs constitute a major group of plant secondary metabolites involved in plant defense, which are synthesized in response to insect pest and herbivores attack. EOs as well as their constituent small molecules exhibit excellent medicinal properties and hence may be used against infectious and noninfectious diseases (Cowan 1999; Samy and Gopalakrishnakone 2010; Rajput and Karuppaiyl 2012).

Antibacterial Activities

Diseases caused by infectious agents are the leading cause of premature deaths worldwide. Emergence of drug-resistant strains of pathogenic bacteria has scaled up the severity of the infectious diseases (Ahmad and Beg 2001). Various studies have shown that EOs exhibit inhibitory activities against a wide spectrum of pathogenic bacteria (Table 5.1). Gram-positive as well as gram-negative bacteria are susceptible to plant

essential oils (Edris 2007; Lang and Buchbauer 2011). Efficacy of these molecules against both drug-sensitive as well as drug-resistant strains is of interest (May et al. 2000; Bozin et al. 2006). Moreover, oils of plant origin were found to be effective against drug-resistant biofilm growth of bacteria (Galvao et al. 2012). EOs are mainly acting through damage to the bacterial membrane (Edris 2007). They are lipophilic in nature and can easily pass through the cell wall and cell membrane. These compounds react with different layers of polysaccharides, fatty acids, and phospholipids, so that cell membrane becomes more permeable. Inactivation of bacterial enzymes is also proposed as a potential mechanism of action (Wendakoon and Sakaguchi 1995). Treatment with high concentrations of EOs results in loss of ions, inability to maintain homeostasis, interference in proton pump activity, loss of membrane integrity, leakage of cellular contents, and loss of viability (Cox et al. 2000; Lambert et al. 2001; Oussalah et al. 2006; Di Pasqua et al. 2007). EOs can disintegrate cytoplasmic proteins (Gustafson et al. 1998) as well as react with cellular lipids and proteins to cause denaturation leading to cell death (Burt 2004).

Antifungal Potential

Essential oils have been found to be effective against various plant and human pathogenic fungi, including yeasts (Table 5.2). It was proposed that EOs rich in phenylpropanoids like eugenol and the monocyclic sesquiterpene alcohols such as α -bisabolol exhibit strong inhibitory activity against dermatophytes growth and spore development (Bajpai et al. 2009; Maxia et al. 2009). Plant EOs were reported to prevent the growth as well as the mycotoxin production in molds like *Aspergillus flavus* (Rasooli et al. 2008; Kumar et al. 2010; Singh et al. 2010), by causing destruction of mycelia and the prevention of new mycelia development (Lang and Buchbauer 2011). Terpenoid-rich EOs have been found to be very effective against drug-sensitive as well as drug-resistant pathogenic yeasts, especially against, the major pathogen of humans, *Candida*

Table 5.1 Plant essential oils exhibiting activity against bacteria

Sr. no.	Essential oil	Susceptible bacteria	References
1.	<i>Anethum graveolens</i> (dill)	<i>Escherichia coli</i> , <i>Klebsiella pneumoniae</i>	Delaquis et al. (2002), Rafii and Shahverdi (2007)
2.	<i>Apium graveolens</i> (celery)	<i>E. coli</i> , <i>Pseudomonas aeruginosa</i> , <i>Staphylococcus aureus</i>	Baananou et al. (2012)
3.	<i>Artemisia dracunculul</i> (tarragon), <i>A. santonicum</i> (wormseed), <i>A. spicigera</i> (wormwood)	Fifteen different food bacteria and thirty-three different clinical bacteria	Kordali et al. (2005)
4.	<i>Carum nigrum</i> (black caraway)	<i>Bacillus cereus</i> , <i>P. aeruginosa</i>	Singh et al. (2006)
5.	<i>Coriandrum sativum</i> (coriander)	<i>Streptococcus hemolyticus</i> , <i>Salmonella typhimurium</i> , <i>Listeria monocytogenes</i>	Delaquis et al. (2002), Singh et al. (2002), Lo Cantore et al. (2004)
6.	<i>Croton cajucara</i>	<i>Lactobacillus casei</i> , <i>S. aureus</i> , <i>S. gingivalis</i> , <i>S. mutans</i>	Alviano et al. (2005)
7.	<i>Eucalyptus robusta</i> (swamp mahogany), <i>E. saligna</i> , <i>Eucalyptus globulus</i> (blue gum)	<i>Staphylococcus. aureus</i> , <i>E. coli</i> , <i>S. pyogenes</i> , <i>S. agalactiae</i> , <i>S. pneumoniae</i> , <i>K. pneumoniae</i> , <i>Haemophilus influenzae</i>	Sartorelli et al. (2007), Fabio et al. (2007), Galvao et al. (2012)
8.	<i>Eugenia caryophyllus</i> (clove)	<i>S. pyogenes</i> , <i>S. agalactiae</i> , <i>S. pneumoniae</i> , <i>K. pneumoniae</i> , <i>H. influenzae</i> , <i>S. aureus</i>	Fabio et al. (2007), Shan et al. (2007)
9.	<i>Juglans regia</i> (common walnut)	<i>S. epidermidis</i> , <i>B. subtilis</i> , <i>S. aureus</i> , <i>Proteus vulgaris</i> , <i>P. aeruginosa</i> , <i>S. typhi</i> , <i>Shigella dysenteriae</i> , <i>K. pneumoniae</i> , <i>E. coli</i>	Rather et al. (2012)
10.	<i>Lantana fucata</i> , <i>L. trifolia</i>	<i>Mycobacterium tuberculosis</i>	Juliao et al. (2009)
11.	<i>Lavandula angustifolia</i> (common lavender), <i>L. latifolia</i> , <i>L. luisieri</i>	MRSA, <i>E. coli</i> , <i>S. aureus</i>	Roller et al. (2009), Djenane et al. (2012)
12.	<i>Melaleuca alternifolia</i> (tea tree)	<i>Enterococcus faecalis</i> , <i>P. aeruginosa</i> , <i>S. aureus</i> , MRSA, <i>Mycobacterium avium</i> , <i>E. coli</i> , <i>H. influenzae</i> , <i>S. pyogenes</i> , <i>S. pneumoniae</i>	Dryden et al. (2004), Carson et al. (2006)
13.	<i>Melissa officinalis</i> (lemon balm)	<i>E. coli</i> , <i>S. typhimurium</i> , <i>S. aureus</i> , <i>Bacillus subtilis</i>	Mimica-Dukic et al. (2004)
14.	<i>Mentha longifolia</i> (wild mint), <i>M. piperita</i> (peppermint), <i>M. spicata</i> (spearmint)	<i>E. coli</i> , <i>Enterobacter aerogenes</i> , <i>Enterobacter cloacae</i> , <i>S. pyogenes</i> , <i>S. agalactiae</i> , <i>S. pneumoniae</i> , <i>K. pneumoniae</i> , <i>H. influenzae</i> , <i>S. aureus</i>	Fabio et al. (2007), Rafii and Shahverdi (2007), Djenane et al. (2012)
15.	<i>Myristica fragrans</i> (nutmeg)	<i>Acinetobacter calcoaceticus</i> , <i>Aeromonas hydrophila</i> , <i>Alcaligenes faecalis</i> , <i>B. subtilis</i> , <i>Brevibacterium linens</i> , <i>E. faecalis</i> , <i>E. coli</i> , <i>Flavobacterium suaveolens</i> , <i>K. pneumoniae</i> , <i>Micrococcus luteus</i> , <i>Moraxella</i> sp., <i>Proteus vulgaris</i> , <i>Salmonella pullorum</i> , <i>Serratia marcescens</i> , <i>S. aureus</i> , <i>Yersinia enterocolitica</i>	Dorman and Deans (2000)
16.	<i>Ocimum basilicum</i> (sweet basil) <i>O. gratissimum</i> (African basil)	13 different bacteria, various strains of <i>Shigella</i>	Iwalokun et al. (2003, 2008), Bozin et al. (2006)

(continued)

Table 5.1 (continued)

Sr. no.	Essential oil	Susceptible bacteria	References
17.	<i>Origanum vulgare</i> (oregano)	<i>A. alcoacetica</i> , <i>A. hydrophila</i> , <i>A. faecalis</i> , <i>B. subtilis</i> , <i>Clostridium sporogenes</i> , <i>E. faecalis</i> , <i>E. aerogenes</i> , <i>E. coli</i> , <i>F. suaveolens</i> , <i>K. pneumoniae</i> , <i>L. plantarum</i> , <i>M. luteus</i> , <i>Moraxella</i> sp., <i>P. vulgaris</i> , <i>P. aeruginosa</i> , drug-resistant <i>P. aeruginosa</i> , <i>Salmonella pullorum</i> , <i>S. marcescens</i> , <i>S. aureus</i> , <i>Y. enterocolitica</i>	Dorman and Deans (2000), Tepe et al. (2004), Bozin et al. (2006), Lopez et al. (2005, 2007), Rosato et al. (2007)
18.	<i>Pelargonium graveolens</i> (rose geranium)	<i>A. alcoacetica</i> , <i>B. subtilis</i> , <i>Brochothrix thermosphacta</i> , <i>Clostridium sporogenes</i> , <i>E. faecalis</i> ; <i>F. suaveolens</i> , <i>K. pneumoniae</i> , <i>L. cremoris</i> , <i>M. luteus</i> , <i>P. aeruginosa</i> , <i>S. pullorum</i> , <i>S. marcescens</i> , <i>S. aureus</i> , <i>Y. enterocolitica</i>	Dorman and Deans (2000)
19.	<i>Pimpinella anisum</i> (aniseed)	<i>E. coli</i>	Singh et al. (2002)
20.	<i>Pinus densiflora</i> (Japanese red pine), <i>Pinus koraiensis</i> (Korean pine)	<i>S. typhimurium</i> , <i>L. monocytogenes</i> , <i>E. coli</i> , <i>S. aureus</i> , <i>K. pneumoniae</i>	Hong et al. (2004)
21.	<i>Piper nigrum</i> (black pepper)	<i>A. calcoaceticus</i> , <i>A. hydrophila</i> , <i>A. faecalis</i> , <i>B. subtilis</i> , <i>B. linens</i> , <i>E. faecalis</i> , <i>E. coli</i> , <i>F. suaveolens</i> , <i>K. pneumoniae</i> , <i>M. luteus</i> , <i>Moraxella</i> sp., <i>P. vulgaris</i> , <i>S. pullorum</i> , <i>S. marcescens</i> , <i>S. aureus</i> , <i>Y. enterocolitica</i>	Dorman and Deans (2000)
22.	<i>Rosa</i> spp.	<i>E. coli</i> , <i>S. pneumoniae</i> , <i>S. typhimurium</i> , <i>E. aerogenes</i> , <i>P. vulgaris</i> , <i>S. aureus</i> , <i>S. epidermidis</i> , <i>B. subtilis</i> , <i>P. aeruginosa</i>	Hirulkar and Agrawal (2010)
23.	<i>Rosmarinus officinalis</i> (rosemary)	<i>Staphylococcus aureus</i>	Rota et al. (2004), Rosato et al. (2007)
24.	<i>Salvia sclarea</i> (sage clary), <i>S. officinalis</i> (sage), <i>S. lavandulifolia</i> , <i>S. rosifolia</i>	<i>S. typhimurium</i> , <i>S. pyogenes</i> , <i>S. agalactiae</i> , <i>S. pneumoniae</i> , <i>E. coli</i> , <i>K. pneumoniae</i> , <i>H. influenzae</i> , <i>S. aureus</i> , MRSA	Rota et al. (2004), Fabio et al. (2007), Roller et al. (2009)
25.	<i>Santolina rosmarinifolia</i> (cotton lavender)	<i>S. aureus</i> , <i>B. cereus</i> , <i>E. coli</i>	Ioannou et al. (2007)
26.	<i>Skimmia laureola</i>	MRSA and <i>S. epidermidis</i>	Shah et al. (2012)
27.	<i>Syzygium aromaticum</i> (clove)	<i>A. calcoaceticus</i> , <i>A. hydrophila</i> , <i>A. faecalis</i> , <i>B. subtilis</i> , <i>B. linens</i> , <i>E. faecalis</i> , <i>E. coli</i> , <i>F. suaveolens</i> , <i>K. pneumoniae</i> , <i>M. luteus</i> , <i>Moraxella</i> sp., <i>P. vulgaris</i> , <i>S. pullorum</i> , <i>S. marcescens</i> , <i>S. aureus</i> , <i>Y. enterocolitica</i>	Dorman and Deans (2000)
28.	<i>Tamarix boveana</i> (salt cedar)	<i>S. aureus</i> , <i>S. epidermidis</i> , <i>E. coli</i> , <i>P. aeruginosa</i> , <i>M. luteus</i> , <i>S. typhimurium</i>	Saidana et al. (2008)
29.	<i>Thymus vulgaris</i> (thyme), <i>Thymus</i> sp.	<i>S. pyogenes</i> , <i>S. agalactiae</i> , <i>S. pneumoniae</i> , <i>S. aureus</i> , MRSA, <i>P. aeruginosa</i> , <i>A. calcoaceticus</i> , <i>A. hydrophila</i> , <i>A. faecalis</i> , <i>B. subtilis</i> , <i>B. linens</i> , <i>E. faecalis</i> , <i>E. coli</i> , <i>F. suaveolens</i> , <i>K. pneumoniae</i> , <i>M. luteus</i> , <i>Moraxella</i> sp., <i>P. vulgaris</i> , <i>S. pullorum</i> , <i>S. marcescens</i> , <i>Y. enterocolitica</i>	Bozin et al. (2006), Lopez et al. (2005, 2007), Fabio et al. (2007), Dorman and Deans (2000), Tohidpour et al. (2010)
30.	<i>Ziziphora clinopodioides</i> (blue mint)	<i>S. epidermidis</i> , <i>S. aureus</i> , <i>E. coli</i> , <i>B. subtilis</i> , <i>E. faecalis</i> , <i>K. pneumoniae</i> , <i>P. aeruginosa</i>	Sonboli et al. (2006)

Table 5.2 Antifungal properties of selected essential oils of plant origin

Sr. no.	Essential oil	Susceptible fungi	References
1.	<i>Allium sativum</i> (garlic)	<i>Aspergillus niger</i> , <i>Penicillium cyclopium</i> , and <i>Fusarium oxysporum</i>	Benkeblia (2004)
2.	<i>Artemisia judaica</i> (wormwood), <i>A. absinthium</i> , <i>A. biennis</i> , other <i>Artemisia</i> spp.	<i>Botrytis fabae</i> , <i>F oxysporum</i> , <i>Pythium debaryanum</i> , <i>Rhizoctonia solani</i> , <i>Microsporium canis</i> , <i>Microsporium gypseum</i> , <i>Trichophyton rubrum</i> , <i>Fonsecaea pedrosoi</i> , <i>Geotrichum candidum</i> , <i>Aspergillus</i> and <i>Penicillium</i> species, <i>Cladosporium herbarum</i> , <i>Absidia repens</i> , <i>Trichothecium roseum</i> , etc.	Kordali et al. (2005), Lopes-Lutz et al. (2008), Cetin et al. (2009), Irkin and Korukluoglu (2009)
3.	<i>Carum nigrum</i> (black caraway)	<i>A. flavus</i> , <i>A. niger</i> , <i>Penicillium purpurogenum</i> , <i>Penicillium madriti</i> , <i>Penicillium viridicatum</i>	Singh et al. (2006)
4.	<i>Cedrus libani</i> (cedar wood oil)	<i>Alternaria alternata</i> , <i>A. flavus</i> , <i>A. fumigatus</i> , <i>A. niger</i> , <i>A. ruber</i> , <i>A. versicolor</i> , <i>Cladosporium cladosporioides</i> , <i>Curvularia lunata</i>	Dikshit et al. (1983)
5.	<i>Cinnamomum</i> sp.	<i>Candida albicans</i> , <i>Candida glabrata</i> , <i>Microsporium canis</i> , <i>Trichophyton mentagrophytes</i> , and <i>T. rubrum</i>	Mastura et al. (1999)
6.	<i>Chenopodium ambrosioides</i>	<i>A. niger</i> , <i>A. fumigatus</i> , <i>Botryodiplodia theobromae</i> , <i>F oxysporum</i> , <i>Sclerotium rolfsii</i> , <i>Macrophomina phaseolina</i>	Kumar et al. (2007)
7.	<i>Croton argyrophylloides</i> , <i>C. zehntneri</i> , <i>C. cajucara</i>	<i>M. canis</i> , <i>C. albicans</i>	Alviano et al. (2005), Fontenelle et al. (2008)
8.	<i>Cuminum cyminum</i> (cumin)	<i>A. flavus</i> , <i>A. fumigatus</i>	Khosravi et al. (2011)
9.	<i>Cymbopogon martinii</i> (ginger grass), <i>C. citrates</i> (lemon grass)	<i>A. alternata</i> , <i>A. niger</i> , <i>Penicillium roqueforti</i> , <i>F. oxysporum</i> , <i>C. albicans</i>	Saikia et al. (2001), Agarwal et al. (2008), Irkin and Korukluoglu (2009)
10.	<i>Daucus carota</i> (wild carrot)	<i>E. floccosum</i> , <i>M. canis</i> , <i>M. gypseum</i> , <i>T. mentagrophytes</i> , <i>T. rubrum</i>	Tavares et al. (2008)
11.	<i>Eucalyptus saligna</i> (saligna)	<i>C. albicans</i>	Sartorelli et al. (2007)
12.	<i>Eugenia caryophyllus</i> (clove)	<i>C. albicans</i> , <i>A. niger</i> , <i>A. fumigatus</i>	Devkatte et al. (2005), Bansod and Rai (2008)
13.	<i>Foeniculum vulgare</i> (fennel)	<i>A. alternata</i> , <i>A. niger</i> , <i>B. cinerea</i>	Mimica-Dukic et al. (2004), Peighami-Ashnaei et al. (2009)
14.	<i>Juniperi aetheroleum</i> (juniper)	Seven different fungi/three yeasts/four dermatophytes	Pepeljnjak et al. (2005)
15.	<i>Lavandula</i> sp.	<i>C. albicans</i> , <i>Cryptococcus neoformans</i>	Zuzarte et al. (2011, 2012)
16.	<i>Matricaria chamomilla</i> (chamomile)	<i>A. niger</i>	Tolouee et al. (2010)
17.	<i>Melaleuca alternifolia</i>	<i>C. albicans</i> , <i>C. glabrata</i> , <i>Saccharomyces cerevisiae</i> , different filamentous fungi/dermatophytes	Carson et al. (2006), Dryden et al. (2004), Devkatte et al. (2005)
18.	<i>Melissa officinalis</i>	<i>C. albicans</i>	Mimica-Dukic et al. (2004)
19.	<i>Mentha piperita</i> , <i>Mentha longifolia</i> , <i>M. viridis</i>	<i>C. albicans</i> , <i>Aspergillus ochraceus</i> , <i>Mucor ramannianus</i>	Agarwal et al. (2008), Mkaddem et al. (2009)
20.	<i>Nigella sativa</i> (black cumin)	<i>A. flavus</i> , <i>A. fumigatus</i>	Khosravi et al. (2011)

(continued)

Table 5.2 (continued)

Sr. no.	Essential oil	Susceptible fungi	References
21.	<i>Ocimum sanctum</i> (holy basil/tulsi), <i>Ocimum</i> sp.	<i>C. albicans</i> , <i>Aspergillus</i> sp.	Devkatte et al. (2005), Kumar et al. (2010)
22.	<i>Origanum vulgare</i>	Six different fungi	Bozin et al. (2006), Tepe et al. (2004), Rosato et al. (2007), Lopez et al. (2007), Dorman and Deans (2000)
23.	<i>Piper nigrum</i> (black pepper)	<i>C. albicans</i>	Rabadia et al. (2012)
24.	<i>Pimpinella anisum</i>	<i>C. albicans</i> , <i>C. parapsilosis</i> , <i>C. tropicalis</i> , <i>C. pseudotropicalis</i> , <i>C. krusei</i> , <i>C. glabrata</i>	Singh et al. (2002)
25.	<i>Rosmarinus officinalis</i> (rosemary)	<i>B. cinerea</i> , <i>A. parasiticus</i> , <i>A. alternata</i> , <i>F. oxysporum</i>	Rota et al. (2004), Rosato et al. (2007), Rasooli et al. (2008), Ozcan and Chalchat (2008)
26.	<i>Salvia fruticosa</i> , <i>S. officinalis</i> , <i>S. rosifolia</i>	<i>F. oxysporum</i> , <i>F. solani</i> ; <i>F. proliferatum</i> , <i>Colletotrichum</i> sp.	Rota et al. (2004), Fabio et al. (2007), Ozek et al. (2010)
27.	<i>Santolina rosmarinifolia</i>	<i>C. albicans</i>	Ioannou et al. (2007)
28.	<i>Satureja hortensis</i> (summer savory)	<i>A. flavus</i> , <i>A. parasiticus</i>	Razzaghi-Abyaneh et al. (2008)
29.	<i>Syzigium aromaticum</i>	<i>Epidermophyton floccosum</i> , <i>T. rubrum</i> , <i>T. mentagrophytes</i> , <i>M. canis</i> , <i>M. gypseum</i>	Pinto et al. (2009), Dorman and Deans (2000)
30.	<i>Tamarix boveana</i>	<i>F. oxysporum</i> , <i>A. niger</i> ; <i>Penicillium</i> sp., <i>Alternaria</i> sp.	Saidana et al. (2008)
31.	<i>Thymus algeriensis</i>	Two fungi, two yeasts	Dob et al. (2006)
32.	<i>Zingiber officinale</i> (ginger)	<i>A. flavus</i> , <i>A. niger</i> ; <i>Fusarium moniliforme</i>	Singh et al. (2008)
33.	<i>Ziziphora clinopodioides</i>	<i>C. albicans</i> , <i>Cryptococcus neoformans</i>	Khosravi et al. (2011)

albicans (Devkatte et al. 2005; Zore et al. 2011b). Activity of these compounds against drug-resistant biofilms of *C. albicans* is of importance (Agarwal et al. 2008; Raut et al. 2013). This may be mediated through inhibition of membrane ergosterol and inhibition of signaling pathways involved in yeast to hyphal filamentation (Raut et al. 2013). Components of EOs possess cell cycle inhibitory activities. For example, citral, citronellol, geraniol, and geranyl acetates which are major constituents of eucalyptus oil, tea tree oil, and geranium oil were reported to block *C. albicans* in the S phase of cell cycle (Zore et al. 2011a). Experiments in *S. cerevisiae* revealed that well-known EO components like eugenol, thymol, and carvacrol can affect Ca²⁺ and H⁺ homeostasis leading to loss of ions (Rao et al. 2010). Also, abnormalities in membrane fluidity

result in leakage of cytoplasmic contents and loss of viability. For example, tea tree oil has been shown to alter the permeability and also affect respiratory chain activity in *C. albicans* cells (Cox et al. 2000; Hammer et al. 2004; Carson et al. 2006). Mitochondrial membrane permeabilization leads to apoptosis and necrosis leading to cell death (Armstrong 2006). EOs and their components also interfere in TOR signaling pathway in *S. cerevisiae* resulting in loss of viability (Rao et al. 2010). Alterations in the structure of the plasma membrane, cytoplasm, and nucleus were observed in SEM and TEM analysis of *Phytophthora infestans* treated with plant EOs (Soylu et al. 2006). Based on various studies in *C. albicans*, a model for the action of phytochemicals against fungal cells was recently proposed (Zore et al. 2011a).

Anticancer Activities

Therapeutics and prevention of cancer growth is one of the biggest challenges in chemotherapy. Few of the plant molecules like taxol were found to be effective against malignant cell proliferation. In addition, EOs from plants have been reported to be useful in prevention and therapeutics of various types of cancerous growth including glioma, colon cancer, gastric cancer, human liver tumor, pulmonary tumors, breast cancer, leukemia, and others (Edris 2007; Kaefler and Milner 2008; Hamid et al. 2011) (Table 5.3). Geraniol, a terpenoid present in many plant oils (especially palmarosa oil, *Cymbopogon martinii*), was found to interfere in membrane functions, ion homeostasis, as well as cell signaling events. It also inhibits DNA synthesis and hence reduces the volume of colon tumors (Carnesecchi et al. 2004). Antiangiogenesis properties of β -eudesmol, a constituent of *Atractylodes lancea*, may be useful to prevent cancerous growth (Tsuneki et al. 2005). *Myristica fragrans* (nutmeg) oil was shown to possess significant hepatoprotective activity (Morita et al. 2003). Its main component myristicin induces apoptosis in human neuroblastoma cells (Lee et al. 2005). The high content of citral may be responsible for inhibitory effect of lemongrass oil on the early phase of hepatocarcinogenesis in rats (Puatanachokchai et al. 2002). *Allium sativum*, garlic essential oil, is recognized as a potential cancer chemopreventive agent due to its activity for modulating drug detoxifying enzymes (Milner 2001; Chen et al. 2004). The lemon balm (*Melissa officinalis* L.) oil was reported to be effective against a series of human cancer cell lines (De Sousa et al. 2004). *Melaleuca alternifolia* (Tea tree) oil and its major monoterpene alcohol, terpinen-4-ol, were found to induce apoptosis in human melanoma (Calcabrini et al. 2004). Tumor growth is associated with changes in increased cellular metabolism, mitochondrial overproduction, and permanent oxidative stress. EOs exhibit capacity to interfere with mitochondrial functions of mammalian cells and also act as antioxidants,

which may interfere in uncontrolled proliferation of tumor growth (Czarnecka et al. 2006). Terpenoids as well as polyphenol constituents of plant oils prevent tumor cell proliferation either by inducing apoptosis or causing necrosis (Dudai et al. 2005; Bakkali et al. 2008).

Antiviral Properties

Medicinal plants produce a variety of secondary metabolites which possess antiviral activities (Table 5.4). Phenylpropanoids, monoterpenes, and sesquiterpenes present in EOs contribute to their antiviral activity and inhibit viral replication (Astani et al. 2011). EOs of eucalyptus and thyme were reported to possess anti-herpesvirus activities (Schnitzler et al. 2007; Reichling et al. 2005). Recently, *Melaleuca alternifolia* oil was found to be effective in the treatment of recurrent herpesvirus infections (Carson et al. 2001). Various reports have suggested that it might interfere with viral envelope structures or mask viral structures, so that adsorption or entry of virus into the host cells is prevented. For example, dissolution of the HSV envelope is the mode of action for the activity of oregano essential oil (Siddiqui et al. 1996). A specific inhibition of early genes expression required for viral activation is proposed responsible for CMV (cytomegalovirus) inactivation by EO components (Pusztai et al. 2010). Eugenol, a clove oil constituent, was shown to interfere in the development of herpesvirus-induced keratitis in a mouse model (Benencia and Courreges 2000). Isoborneol, a monoterpene from several plant EOs, showed virucidal effect on HSV-1, through inhibition of glycosylation of viral proteins (Armaka et al. 1999).

Antimutagenic Activities

Molecules of plant origin were reported to prevent cellular mutagenesis (Odin 1997; De Flora et al. 1999; Dahanukar et al. 2000). *Matricaria chamomilla* oil has been shown to inhibit mutagenic errors induced by daunorubicin

Table 5.3 Essential oils of plant origin exhibiting antitumor and anticancer potential

Sr. no.	Essential oil	Antitumor/anticancer activities	References
1.	<i>Alpinia officinarum</i> (galangal/China root)	Inhibition of proliferation of murine leukemia and human mouth epidermal carcinoma cell lines	Manosroi et al. (2006)
2.	<i>Artemisia annua</i> L.	Induces apoptosis in cultured hepatocarcinoma cells	Li et al. (2004)
3.	<i>Atractylodes lancea</i>	Antiangiogenesis properties	Tsuneki et al. (2005)
4.	<i>Allium sativum</i>	Chemoprevention of various cancers	Milner (2001)
5.	<i>C. hystrix</i> (Thai lime) <i>C. paradise</i> (grapefruit tree)	Inhibition of proliferation of murine leukemia and human mouth epidermal carcinoma cell lines	Hata et al. (2003), Manosroi et al. (2006)
6.	<i>Curcuma longa</i> (turmeric)	Inhibition of proliferation of murine leukemia and human mouth epidermal carcinoma cell lines, primary liver cancer	Manosroi et al. (2006), Cheng et al. (2001)
7.	<i>Cymbopogon nardus</i> (citronella grass), <i>Cymbopogon martinii</i> (palmarosa)	Inhibition of proliferation of murine leukemia and human mouth epidermal carcinoma cell lines	Manosroi et al. (2006), Carnesecchi et al. (2004)
8.	<i>Elaeis guineensis</i> (palm oil)	Activity against a wide range of cancers	Luk et al. (2011)
9.	<i>Elettaria cardamomum</i> (cardamom)	Induces apoptosis in human leukemia cells	Moteki et al. (2002)
10.	<i>Eucalyptus globulus</i> (eucalyptus)	Induces apoptosis in human leukemia cells	Juergens et al. (1998)
11.	<i>Eugenia caryophyllata</i> (i.e., <i>Syzygium aromaticum</i>)	Inhibition of proliferation of cancerous cells	Yoo et al. (2005)
12.	<i>Foeniculum vulgare</i>	Hepatoprotective activity; inhibits growth of different human cancer cell lines including breast cancer and liver cancer	Ozbek et al. (2003)
13.	<i>Glycine max</i> (soybean oil)	Protective effect against colon cancer	Yoshiki et al. (1998)
14.	<i>Lavandula angustifolia</i>	Inhibition of proliferation of murine leukemia and human mouth epidermal carcinoma cell lines	Manosroi et al. (2006)
15.	<i>Matricaria chamomilla</i>	Inducer of apoptosis in highly malignant glioma cells	Cavaliere et al. (2004)
16.	<i>Melaleuca alternifolia</i>	Induces caspase-dependent apoptosis in human melanoma	Calcabrini et al. (2004)
17.	<i>Melissa officinalis</i> L.	Activity against a series of human cancer cell lines and a mouse cell line	De Sousa et al. (2004)
18.	<i>Mentha spicata</i>	Antiproliferative effect on human mouth epidermal carcinoma and murine leukemia cell lines	Manosroi et al. (2006)
19.	<i>Myrica gale</i> (myrtle/bayberry)	Activity against lung and colon cancer cell lines	Sylvestre et al. (2005, 2006)
20.	<i>Myristica fragrans</i>	Hepatoprotective activity; induces apoptosis in human neuroblastoma	Morita et al. (2003), Lee et al. (2005)
21.	<i>Nigella sativa</i>	Inhibition of cancer proliferation in rats	Salim and Fukushima (2003), Mansour et al. (2001)
22.	<i>Ocimum basilicum</i> , <i>Ocimum americanum</i> , <i>Ocimum sanctum</i>	Prevent proliferation of murine leukemia and human mouth epidermal carcinoma cell lines	Manosroi et al. (2006)
23.	<i>Olea europaea</i> (olive oil)	Protective activity against colorectal cancer	Gill et al. (2005)
24.	<i>Piper nigrum</i> , <i>Piper betle</i> (betle leaf)	Inhibit proliferation of murine leukemia and human mouth epidermal carcinoma cell lines	Manosroi et al. (2006)
25.	<i>Tetraclinis articulata</i> (conifer oil)	Preventive effect on human cancer cell lines including melanoma, breast cancer, and ovarian cancer	Buhagiar et al. (1999)
26.	<i>Vetiveria zizanioides</i> (khus)	Prevents proliferation of murine leukemia and human mouth epidermal carcinoma cell lines	Manosroi et al. (2006)
27.	<i>Zingiber montanum</i>	Prevents proliferation of murine leukemia and human mouth epidermal carcinoma cell lines	Manosroi et al. (2006)

Table 5.4 Examples of antiviral activities of essential oils

Sr. no.	Essential oil	Antiviral effect	References
1.	<i>Artemisia arborescens</i> , <i>A. vulgaris</i>	Activity against herpes simplex virus type 1 (HSV-1), inactivation of yellow fever virus	Sinico et al. (2005), Meneses et al. (2009)
2.	<i>Allium cepa</i> (onion), <i>A. sativum</i> (garlic)	Activity against herpes simplex virus type 1 (HSV-1)	Romeilah et al. (2010)
3.	<i>Eugenia caryophyllata</i> (i.e., <i>Syzygium aromaticum</i>)	Activity against HSV-1 and HSV-2	Siddiqui et al. (1996)
4.	<i>Coriandrum sativum</i> (cilantro/dhania)	Prevents herpes simplex virus type 1 (HSV-1)	Romeilah et al. (2010)
5.	<i>Cuminum cyminum</i>	Activity against herpes simplex virus type 1 (HSV-1)	Romeilah et al. (2010)
6.	<i>Eucalyptus globulus</i> (eucalyptus oil)	Inhibits HSV-1 and HSV-2, respiratory viruses	Schnitzler et al. (2001), Cermelli et al. (2008)
7.	<i>Glycyrrhiza glabra</i> (licorice)	Anti-HIV effect, prevents RNA and DNA viruses	Lalita (1994), Watanbe et al. (1996)
8.	<i>Houttuynia cordata</i> (fishwort/chameleon plant)	Virucidal effect on influenza virus and HSV-1	Hayashi et al. (1995)
9.	<i>Cymbopogon citrate</i> and other species	Inhibition of HSV-1 replication	Minami et al. (2003)
10.	<i>Leptospermum scoparium</i> (manuka oil)	Activity against HSV-1 and HSV-2	Reichling et al. (2005)
11.	<i>Lippia origanoides</i> (wild marjoram)	Inactivation of yellow fever virus	Meneses et al. (2009)
12.	<i>Melaleuca alternifolia</i> , <i>M. armillaris</i>	Activity against HSV-1 and HSV-2	Garozzo et al. (2009), Schnitzler et al. (2001), Bishop (1995)
13.	<i>Melissa officinalis</i> L.	Prevents replication of HSV-2	Allahverdiyev et al. (2004)
14.	<i>Mentha piperita</i>	Virucidal activity against HSV-1 and HSV-2	Schuhmacher et al. (2003)
15.	<i>Ocimum basilicum</i> , <i>O. americanum</i> , <i>O. sanctum</i>	Activity against herpes simplex virus type 1 (HSV-1)	Romeilah et al. (2010)
16.	<i>Origanum vulgare</i>	Activity against HSV-1 and HSV-2, inactivation of yellow fever virus	Siddiqui et al. (1996), Meneses et al. (2009)
17.	<i>Salvia fruticosa</i>	Antiviral activities	Sivropoulou et al. (1997)
18.	<i>Santalum</i> sp. (sandalwood)	Activity against HSV-1 and HSV-2	Benencia and Courreges (1999, 2000)
19.	<i>Santolina insularis</i>	Inactivation of viral particles of HSV-1 and HSV-2	De Logu et al. (2000)
20.	<i>Thymus</i> sp.	Inhibits replication of Epstein-Barr virus (EBV)	Hamid et al. (2011)

and methyl methane sulfonate, in mouse bone marrow cells (Hernandez-Ceruelos et al. 2002). Ames test confirmed the activity of α -bisabolol (a sesquiterpene in EOs) against aflatoxin B1-, benzopyrene-, and 2-aminofluorene-induced mutagenesis (Gomes-Carneiro et al. 2005). *Melaleuca alternifolia* and *Lavandula angustifolia* EOs strongly inhibit mutations induced by 2-nitrofluorene exposure in *E. coli* (Evandri et al. 2005). *Salvia officinalis* and its major compo-

nents were reported to provide protection from UV-induced mutations in *S. typhimurium*, *E. coli*, and *S. cerevisiae* (Vukovic-Gacic et al. 2006). *Helichrysum italicum*, *Ledum groenlandicum*, *Cinnamomum camphora*, and *Origanum compactum* EOs have activities against the urethane-induced mutations in *Drosophila melanogaster* (Idaomar et al. 2002; Mezzoug et al. 2007). Antimutagenic effects of EOs may be mediated through inhibition of penetration of mutagens

inside the cells, free radical scavenging activity, activation of antioxidant enzymes (Kada and Shimoi 1987; Sharma et al. 2001; Ipek et al. 2005), inhibition of P450-mediated formation of mutagens (Gomes-Carneiro et al. 2005), interference with mutation-inducing DNA repair systems (Vukovic-Gacic et al. 2006), or induction of necrosis and apoptosis leading to cellular death (Bakkali et al. 2008). *Curcuma longa*, *Piper betel*, and *Acacia catechu* extract mixture was reported to protect in vitro chromosomal damage in human lymphocytes (Ghaisas and Bhide 1994). Hastak et al. (1997) described the chemopreventive activity of *Curcuma longa* oil on cytogenetic damage to oral submucous cells. Components of *Terminalia arjuna* were found to exhibit antimutagenic potential in *S. typhimurium* (Kaur et al. 1997).

Antioxidant Potential

Free radicals and ROS species cause oxidative stress resulting in oxidative damage to cellular macromolecules (McCord 2000). This has been related to health problems such as aging, arteriosclerosis, cancer, Alzheimer's disease, Parkinson's disease, diabetes, and asthma (Edris 2007). Antioxidants perform the functions necessary to maintain balance of free radicals. EOs of herbs and spices contain flavonoids, terpenoids, and phenolic molecules responsible for antioxidant effect (Clarke and Armitage 2002; Ferguson et al. 2004; Collins 2005; Tomaino et al. 2005; Miguel 2010). Oils of *Origanum majorana*, *Tagetes filifolia*, *Bacopa monnieri*, and *Curcuma longa* have pronounced antioxidative activities (Maestri et al. 2006; Tripathi et al. 2007; Maheshwari et al. 2006). The EOs of *Salvia cryptantha* and *S. multicaulis* as well as *Achillea millefolium*, *Melissa officinalis*, *Melaleuca alternifolia*, *Curcuma zedoaria*, *Ocimum* sp., and *Mentha* sp. have been reported to possess antioxidant or free radical scavenging activity (Mau et al. 2003; Tepe et al. 2004; Kim et al. 2004; Gulluce et al. 2007; Politeo et al. 2007; Hussain et al. 2008). Thymol and carvacrol, the active ingredients of *Thymus* and

Origanum EOs, were found to exert strong antioxidant activities (Kulisic et al. 2004; Tepe et al. 2004; Miguel 2010). Moreover, in vitro analysis of free radical scavenging activity revealed effectiveness of *Coriandrum sativum*, *Allium sativum*, *A. cepa*, *Cuminum cyminum*, and *Petroselinum sativum* (Romeilah et al. 2010).

Antidiabetic Activities

Although antidiabetic potential of plant molecules has been studied by many workers (Marles and Farnsworth 1995; Dahanukar et al. 2000), only few EOs have been analyzed for their efficacy (Hamid et al. 2011). Inability to either produce insulin or use it to regulate normal glucose levels in the blood leads to hyperglycemic or hypoglycemic condition. EOs exhibit preventive effects on various health problems associated with diabetes. For example, rosemary oil was found to exhibit antidiabetic effects in hyperglycemic rabbits (Al-Hader et al. 1994; Broadhurst et al. 2000). A combination of EOs of cinnamon, cumin, fennel, oregano, and myrtle enhanced insulin sensitivity in type 2 diabetes and also lowered blood glucose in rat model (Talpur et al. 2005). *Satureja khuzestanica* EO resulted in significant decrease in fasting blood glucose levels in diabetic rats (Abdollahi et al. 2003). The mechanisms involved in these activities are not well elucidated.

Inflammation Preventive Properties

Plant EOs have been used traditionally for anti-inflammatory purposes. For example, for a long time, *Ocimum sanctum* is known to have activity against inflammatory reactions, which is also confirmed in laboratory (Singh and Majumdar 1997). *Baphia nitida* is another plant exhibiting activity against inflammatory reaction of the body (Onwukaeme 1995). EOs of *Lavandula angustifolia* and *Eucalyptus* were reported to exert anti-inflammatory activities (Hajhashemi et al. 2003; Silva et al. 2003). *Mentha* sp. was found

to possess anti-inflammatory attributes (Moreno et al. 2002; Gulluce et al. 2007). Eucalyptus, rosemary, lavender, pine, clove, and myrrh oils exerted potential activities against inflammation (Darshan and Doreswamy 2004). Reactive oxygen species are produced during the oxidative burst of inflammatory reaction. EOs mediate the anti-inflammatory responses through their free radical scavenging activity. However, other mechanisms are also known to be involved (Miguel 2010). Various EOs like aloe vera (*Aloe barbadensis*), anise star (*Illicium verum*), bergamot (*Citrus aurantium*), cinnamon leaf (*Cinnamomum zeylanicum*), eucalyptus (*Eucalyptus globulus*), juniper berry (*Juniperus communis*), lavender (*Lavandula officinalis*), thyme (*Thymus vulgaris*), and ylang-ylang (*Cananga odorata*) have shown anti-inflammatory effects. This activity is mediated through different mechanisms such as lipoxygenase inhibitory effects, inhibition of leukotriene synthesis, inhibition of COX-2 enzyme, inhibition of proinflammatory cytokines interleukin-1 β (IL-1 β) and tumor necrosis factor- α (TNF- α), as well as suppression of proinflammatory genes (Miguel 2010).

Antiprotozoal Efficacy

Diseases caused by protozoa which include Chagas disease (caused by *Trypanosoma cruzi*), amoebiasis (*Entamoeba histolytica*), leishmaniasis (*Leishmania amazonensis*, *L. infantum*, and other species), giardiasis (*Giardia lamblia*), trichomoniasis (*Trichomonas vaginalis*), and malaria (*Plasmodium falciparum*, *P. vivax*) are important public health problems. Drugs available against protozoal diseases are associated with drawbacks like side effects, emergence of drug resistance, and requirement of prolonged use (Setzer and Ogungbe 2012; Perez et al. 2012). Plant extracts and EOs have been used traditionally to cure protozoal diseases for a long time (Cowan 1999; Anthony et al. 2005; Sauter et al. 2012; Vunda et al. 2012). The oregano EO (*Origanum vulgare* L.) and oil from *Lippia alba* were found to inhibit the growth of trypanosomal

parasite by causing lysis of cells (Perez et al. 2012). *Thymus vulgaris* and its major component thymol were found to inhibit trypanosome through its effect on plasma membrane (Santoro et al. 2007). *Nepeta cataria* oil exhibited strong trypanocidal activities (Saeidnia et al. 2008). *Allium sativum* and *T. vulgaris* oils possess inhibitory activity against *E. histolytica*. Their antiamebic potential is attributed to the terpenoid components like thymol, carvacrol, and linalool (Behnia et al. 2008). *Thymbra capitata*, *Origanum virens*, *Thymus zygis* subsp. *sylvestris*, *Ocimum basilicum*, and *Lippia graveolens* prevent *Giardia lamblia* growth and adherence. Effect on viability was observed upon treatment with these oils through ultrastructure changes (Almeida et al. 2007; Machado et al. 2010). EOs of *Melaleuca alternifolia*, *Carum copticum*, and *Lavandula angustifolia* were reported to exhibit antiprotozoal effects, which are supposed to be due to phenolic constituents (Shahabi et al. 2008). The antiplasmodial activity of various EOs was reported by different workers (Milhau et al. 1997; Dell'Agli et al. 2012). It showed promising antimalarial potential of *Cymbopogon citrates*, *Origanum* spp., *Lippia multiflora*, *Ocimum gratissimum*, and *Satureja thymbra* oils (Tchoumboungang et al. 2005; El Babili et al. 2011). Anti-leishmania efficacy of oils extracted from *Achillea millefolium*, *Artemisia abrotanum*, *Chenopodium ambrosioides*, *Croton cajucara*, *Cymbopogon citrates*, *Ocimum gratissimum*, *Pinus caribaea* Morelet, *Piper aduncum*, and *Piper auritum* have been evaluated and discussed in various studies (Santos et al. 2010; Santin et al. 2009; Ahmed et al. 2011; Tariku et al. 2011; Perez et al. 2012).

Future Perspectives

Phytochemical studies using various analytical techniques have revealed the chemical diversity of essential oils. It has become possible to study the pharmacology of essential oil components and their combination in vitro, in model organisms, as well as in animal models. In addition, the essential oil components offer scaffolds

for building novel molecules for therapeutic research. Metabolic engineering is another area empowering the essential oil research. Tremendous opportunities exist for refining our knowledge on the therapeutic properties of essential oils, through reverse pharmacological studies.

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Siddhartha Singh and S.K. Peshin

Abstract

The rise in population and growth in economic activity have led to an increase in pollution in Delhi. About 55 % of Delhi's population live within 500 m of the roads with a high level of pollution which leads to higher exposure of population to air pollutants, thus resulting in health problems. In order to analyse the air pollution scenario in Delhi, a study has been conducted of the different criteria pollutants, e.g. NO₂, SO₂, CO, PM_{2.5} and PM₁₀, along with a study of surface ozone (O₃) for the period 2008–2011. The data of 10 stations of the air quality monitoring network of the India Meteorological Department along with the data collected by the Central Pollution Control Board have been analysed. The data of respirable suspended particulate matter (RSPM) shows that its concentration in Delhi's air is double that of the national limit. Significant changes have been noticed from year to year in concentrations of all pollutants in Delhi, which may be due to meteorological factors and changes in emissions from different sources of air pollutants. The level of surface ozone has been found rising due to high vehicular emissions in the city. The inverse relationship between surface ozone concentration and relative humidity indicates that the major photochemical paths for the removal of ozone become effective when humidity increases in Delhi. The study of CO/NO_x ratios in comparison to ratios of SO₂/NO_x reveals that CO/NO_x ratios are higher which indicates that vehicular emissions are the major sources of air pollution in Delhi.

Keywords

Air pollution • Particulate matter • Surface ozone • Respirable particulate matter

Introduction

Delhi is the largest metropolitan city by area covering 1,484 km² and the second largest by population in India. Delhi features an atypical

S. Singh (✉) • S.K. Peshin
India Meteorological Department, Environment
Monitoring & Research Centre, New Delhi, India
e-mail: siddhartha.singh74@gmail.com

version of the humid subtropical climate (Köppen Cwa, Köppen climate classification Cfa or Cwa). The high influx of population in Delhi, increase in consumption patterns and unplanned urban and industrial development have led to the problem of air pollution. About 55 % of Delhi's population live within 500 m of the roads with a high level of pollution which leads to higher exposure of population to air pollutants, thus resulting in health problems. The pollution levels in Delhi have been rising due to continuous increase in the number of motor vehicles (MoEF 1997) as well as increase in emissions from other sources, e.g. domestic sources, small-scale industries and non-road sources such as construction activities. The data generated over the years by the Central Pollution Control Board (CPCB) reveal that suspended particulate matter (SPM) and respirable suspended particulate matter (RSPM/PM₁₀) exceed permissible levels at many locations in Delhi. The air pollution problem becomes complex due to the multiplicity and complexity of air-polluting source mix (e.g. industries, automobiles, generator sets, domestic fuel burning, road side dusts, construction activities). Vehicular emissions are of particular concern since these are ground-level sources and thus have the maximum impact on the general population. Meteorological conditions play a significant role in spreading pollutants from roadways into residential areas (Srivastava and Jain 2005), causing widespread air pollution. To reduce vehicular pollution in Delhi, the government of Delhi has taken many measures, e.g. the use of heavy-duty compressed natural gas engines (CNG) and the development of metro railway. Goyal and Sidhartha (2003) have evaluated the impact of CNG implementation on air pollution and discovered a decrease in air pollutants due to a switch from diesel to CNG in Delhi's transport system. However, an increase in NO_x concentrations was observed after the switch, and no discernible impact on ambient PM₁₀ and CO concentrations was noted, stemming from CNG implementation (Mukherjee and Kathuria 2006).

In order to analyse the air pollution scenario in Delhi, a study has been made of the different

criteria pollutants, e.g. NO₂, SO₂, CO, PM_{2.5} and PM₁₀, along with a study of surface ozone (O₃) for the period 2008–2011.

Data Used

The data of the air quality monitoring network of the India Meteorological Department (IMD) along with the data collected by the Central Pollution Control Board have been analysed for the criteria pollutants, e.g. NO, NO₂, NO_x, SO₂, CO, PM_{2.5} and PM₁₀, along with a study of surface ozone (O₃) over the period 2006–2011. However, the data available vary from site to site and from pollutant to pollutant. The ambient air quality has been monitored by the CPCB at the Income Tax Office (ITO), one of the busiest traffic intersections, located on Bahadur Shah Zafar Marg in downtown, Delhi. The IMD's monitoring sites have been chosen near busy traffic intersections, residential areas, large-scale industrial areas, etc. which are representative of Delhi's scenario. The QA/QC procedures are explained in more detail in CPCB website. The location map of Delhi is shown in Fig. 6.1.

Results and Data Analysis

Variations of monthly averaged concentrations of NO₂, NO, NO_x and SO₂ have been shown in Figs. 6.2, 6.3, 6.4 and 6.5, respectively. The levels of oxides of nitrogen exceed the National Ambient Air Quality Standards of 80 µg/m³ at ITO. A decrease in NO₂, NO and NO_x concentrations at ITO after 2007 may be noticed. During the monsoon period (July–September), the concentrations of NO₂ and NO are lower in comparison to other seasons of the year. The concentrations of nitrogen oxides at ITO vary year to year and are affected by traffic flow patterns (Gokhale and Khare 2007).

The concentrations of SO₂ have been found below the CPCB standards as shown in Fig. 6.5. The main source of SO₂ emission is thermal power plants in Delhi. After the implementation

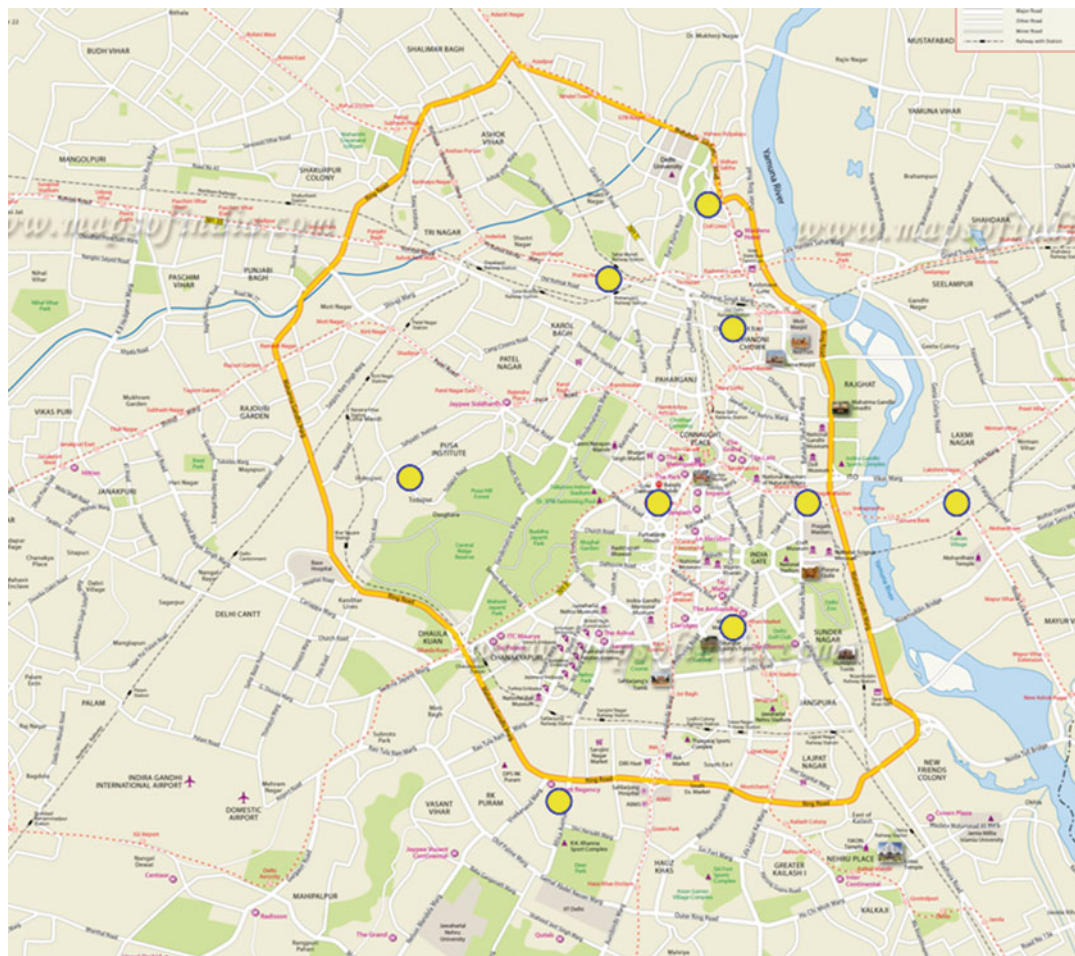


Fig. 6.1 Location of the air quality monitoring stations in Delhi

of rules and regulations for low-sulphur diesel for vehicles in Delhi, the contribution of vehicles to the concentration of SO_2 was very low.

An analysis of hourly concentrations of PM_{10} and $\text{PM}_{2.5}$ at Meteorological Complex, Lodi Road, New Delhi, during the period of October 2011–December 2011 as shown in Figs. 6.6 and 6.7 indicates that PM_{10} and $\text{PM}_{2.5}$ concentrations are far above CPCB standards. The two distinct peaks in PM_{10} and $\text{PM}_{2.5}$ represent the data of Diwali night, 2011. The PM values indicate that the stringent measures imposed on vehicular emissions are inadequate in controlling PM because vehicle exhaust, construction activity and roadside dust are significant sources for particulate matter.

Figure 6.8 shows that there is a decrease in CO concentrations at ITO after 2009, though concentrations crossed the CPCB standard of $2,000 \mu\text{g}/\text{m}^3$ during post-monsoon season. The decreasing trend may be due to the lowering of CO concentrations from vehicular sources because of newer, improved engines, advanced emission reduction technology and cheaper fuel like diesel and CNG replacing gasoline (Biswas et al. 2011).

Ozone is produced by the photooxidation of pollutants like CO and hydrocarbons in the presence of adequate amount of nitrogen oxides at low altitudes (Crutzen 1974). Chemical reactions involving O_3 production and removal occur within a time scale of few hours (Raj et al.

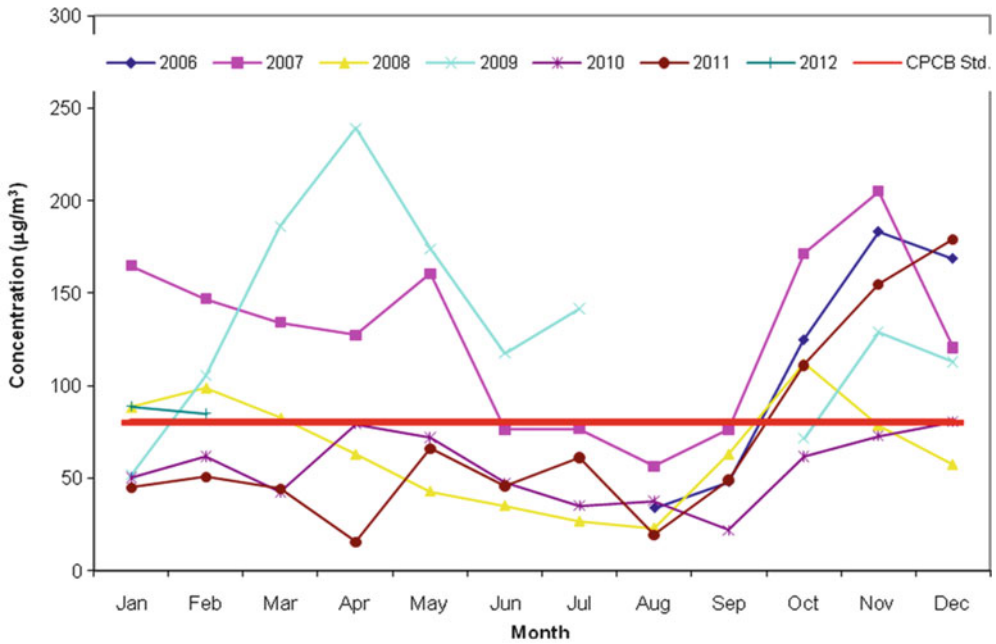


Fig. 6.2 Monthly averaged concentration of nitrogen dioxide (NO₂) at ITO cross section, Delhi

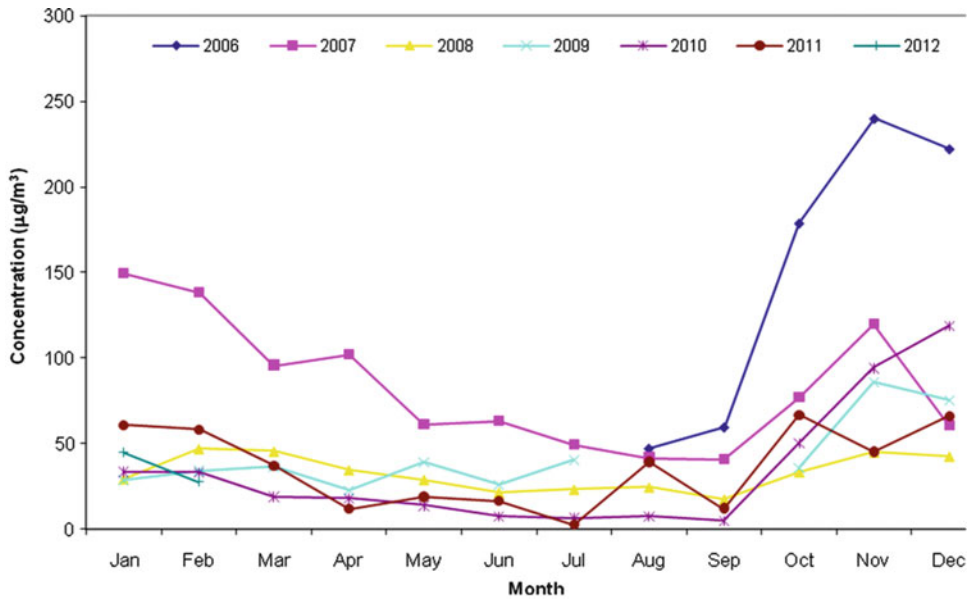


Fig. 6.3 Monthly averaged concentration of nitrogen monoxide (NO) at ITO cross section, Delhi

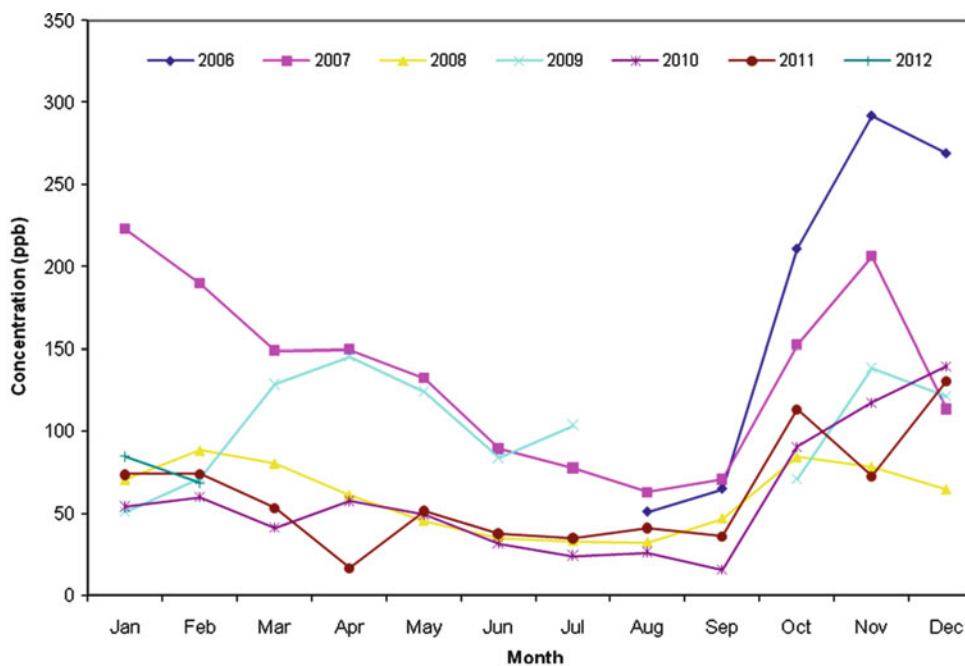


Fig. 6.4 Monthly averaged concentration of nitrogen oxide (NOx) at ITO cross section, Delhi

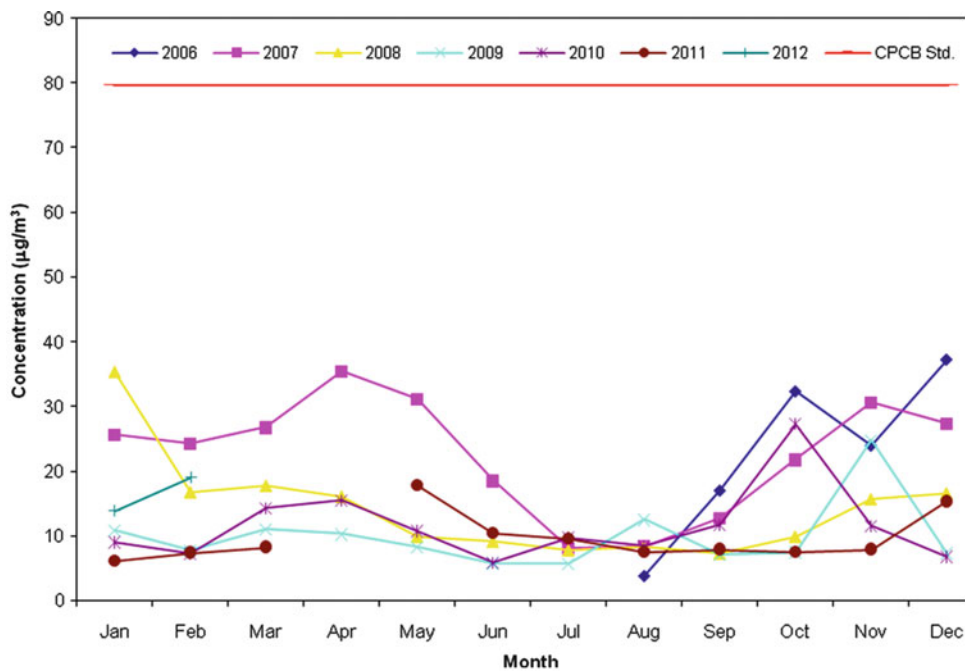


Fig. 6.5 Monthly averaged concentration of sulphur dioxide (SO₂) at ITO cross section, Delhi

Fig. 6.6 Variation of PM_{10} concentration at Meteorological Complex, Lodi Road, New Delhi, during the period of October 2011–December 2011

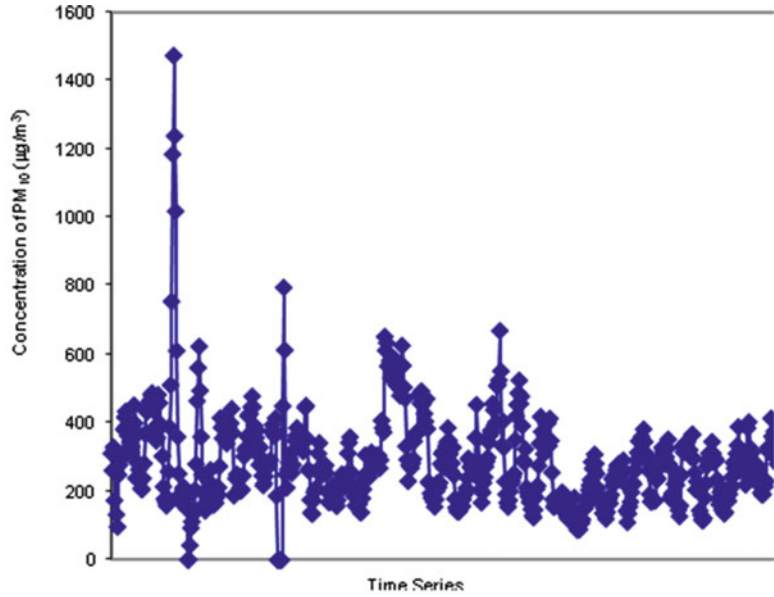
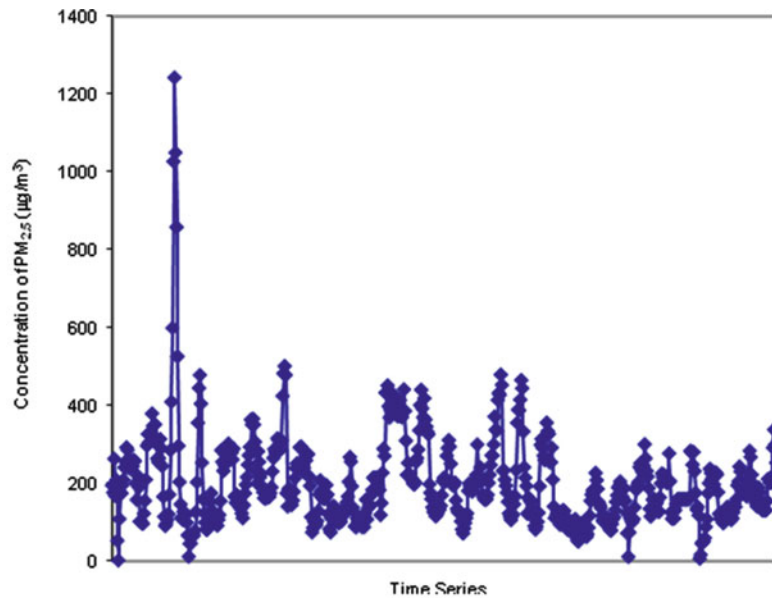


Fig. 6.7 Variation of $PM_{2.5}$ concentration at Meteorological Complex, Lodi Road, New Delhi, during the period of October 2011–December 2011



2003). ITO recorded high ozone concentrations (Fig. 6.9 (a)). The time series of ozone, CO and NOx (Fig. 6.9 (b)) shows that the levels of CO and NOx remained very high, resulting in higher levels of ozone at ITO. Fig. 6.10 indicates that the yearly averaged values of NOx are increasing continuously after the year 2009 which may be due to steady increase in the number

of vehicles registered in Delhi, which increases the production of surface ozone. To decrease NOx levels in Delhi, better planning of transport system is required. A considerable decrease in surface ozone concentrations is visible during winter season due to a decrease in solar radiation. A statistical study of 95 large urban communities in the United States found significant association

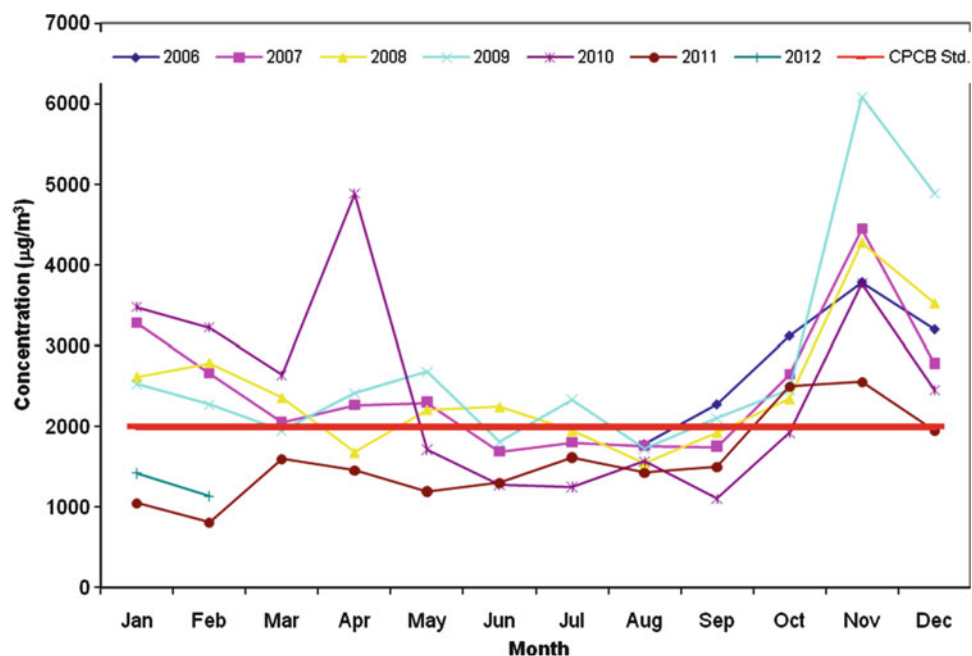


Fig. 6.8 Monthly averaged concentration of carbon monoxide (CO) at ITO cross section, Delhi

between ozone levels and premature death. The study estimated that a one-third reduction in urban ozone concentrations would save roughly 4,000 lives per year (Bell et al. 2004).

Figure 6.11 shows the comparison of CO/NO₂ ratios with SO₂/NO₂ ratios at ITO cross section with considerably higher ratios of CO/NO₂ than SO₂/NO₂ because impacts of mobile source emissions are associated with high CO/NO₂ ratios and low SO₂/NO₂ ratios, whereas impacts of point source are seen with lower CO/NO₂ ratios and higher SO₂/NO₂ ratios.

Conclusions

This study was conducted to examine the status of ambient air quality in Delhi. The observations for the years 2006–2012 have shown that Delhi has started losing the gains of its CNG programme as air is increasingly becoming more polluted, bringing back the pre-CNG days when diesel-driven buses and autos had made it one of the most polluted cities in India. Currently,

the maximum level of carbon monoxide (CO) is almost 6,000 µg/m³, which is way above the CPCB limit of 2,000 µg/m³, though the annual levels have registered a drop. The concentration of particulate matter (PM₁₀/PM_{2.5}) is three times higher than CPCB limits. If PM_{2.5} is not regulated, it will result in major health hazards. The number of asthma patients will rise, and in the future there may be a huge rise of lung cancer cases as well. Levels of nitrogen oxide (NO_x) have also been increasing after 2009. The high CO/NO_x ratios indicate that gasoline-powered vehicles are significant contributors of air pollution in Delhi, while low values of SO₂/NO_x indicate that point sources contribute mainly to SO₂ concentrations (Aneja et al. 2001). In the past 5 years, the Delhi Government has taken many initiatives to reduce air pollution, e.g. advanced emission norms of vehicles, restriction on the number of autorickshaws, conversion of buses from diesel to CNG and restricting commercial vehicles from entering the city, but pollution levels are on the rise due to the rise in the number of vehicles. At present, the city adds over 1,000

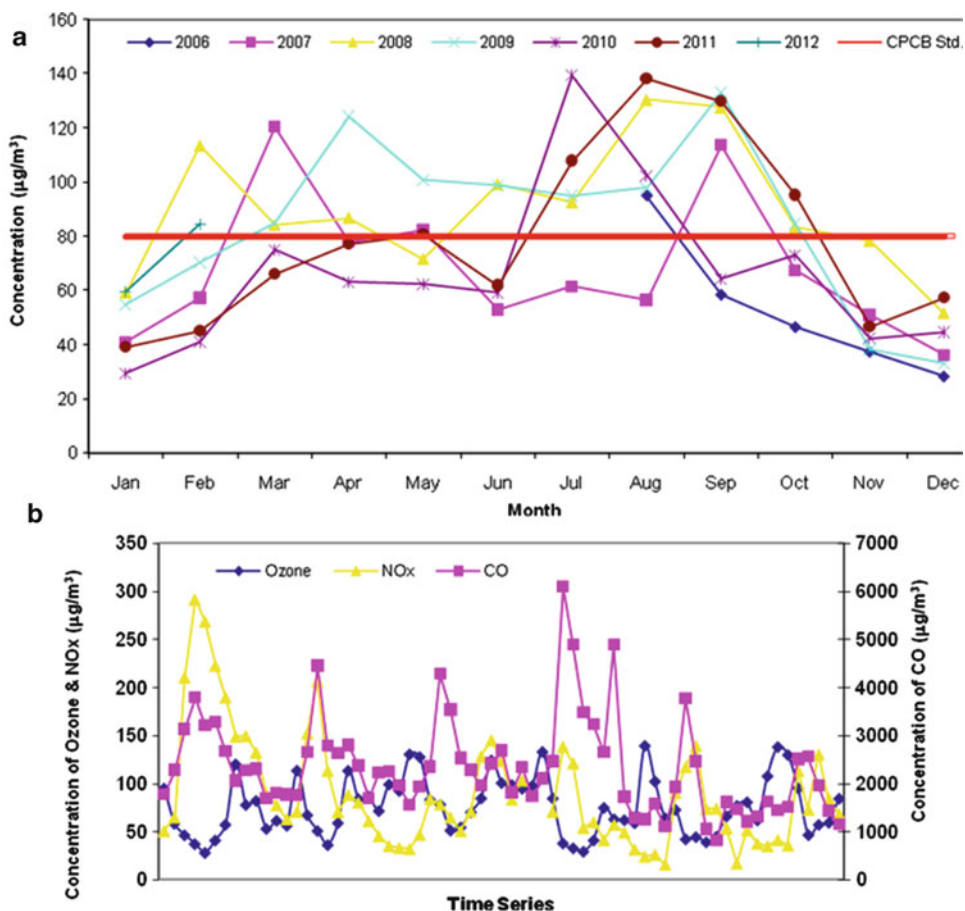


Fig. 6.9 (a) Monthly averaged concentration of ozone (O_3) at ITO cross section, Delhi. (b) Monthly averaged concentrations of ozone, NO_x and CO at ITO cross section, Delhi, during the period of August 2006–February 2012

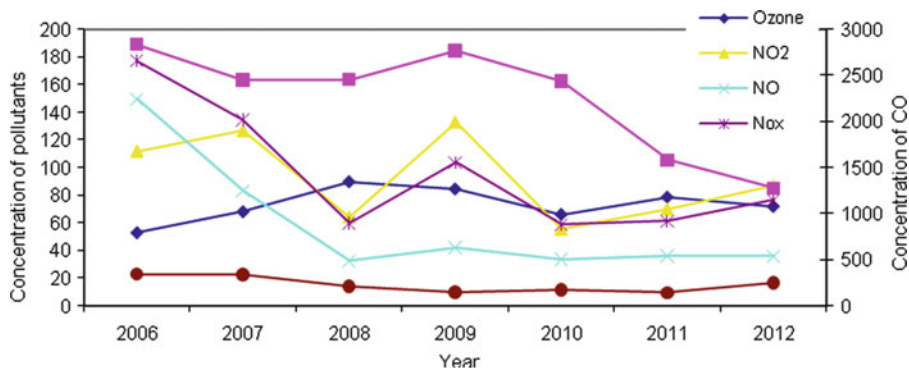


Fig. 6.10 Annual averaged concentration of air pollutants at ITO cross section, Delhi

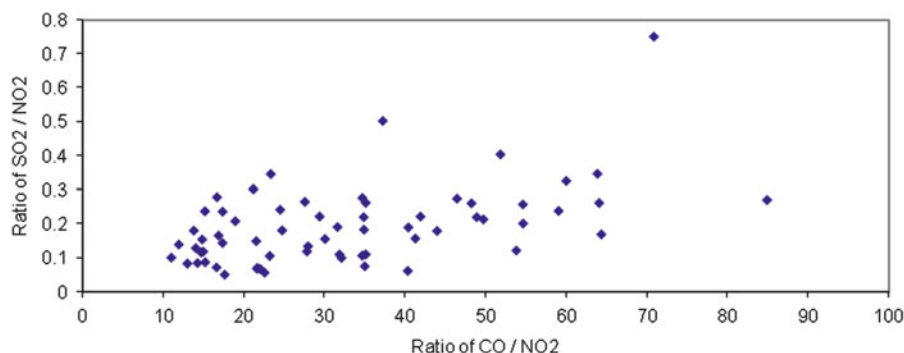


Fig. 6.11 Comparison of CO/NO₂ ratios with SO₂/NO₂ ratios at ITO cross section, Delhi, during the period of August 2006–February 2012

new personal vehicles (mostly diesel vehicles) each day, which is almost double of what was added in the city during pre-CNG days. Diesel vehicles emit more smoke, particles and NO_x than petrol vehicles. Along with a rising number of vehicles, Delhi is also dealing with massive dust due to construction activities and a failed effort to control burning of garbage and leaves. To keep Delhi's air environment healthy, more a comprehensive air pollution control policy is required.

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Nanotechnology: Perspective for Environmental Sustainability

7

M.H. Fulekar, Bhawana Pathak, and R.K. Kale

Abstract

“Environmental nanotechnology” is considered to play a key role in the shaping of current environmental engineering and science. The conventional environmental remedial techniques seem to be relatively ineffectual in the face of currently extensively expanding load of pollutants that permeate the air, water, and soil environment. Nanotechnology can provide a way to purify the air and water resources by utilizing nanoparticles as a catalyst and/or sensing systems. In the present research chapter, the potential of nanotechnological products and processes and their application to clean up the environment contaminants have been discussed. Water treatment and purification techniques based on nanotechnology have been highlighted. These also include the environmental and energy application of nanotechnology which focuses on clean technology, reducing global warming, eco-friendly and efficient energy-generating techniques, eco-friendly surface coating, remediation techniques, and environmental monitoring. Environmental nanoscience products, devices, and processes have an impact on socioeconomic aspects for maintaining a clean environment for sustainable development.

Keywords

Environmental nanotechnology • Nanoproducts • Clean technology • Eco-friendly coating • Environmental monitoring • Remediation

Introduction

Nanotechnology is a broad and interdisciplinary area of research and development activity that has been growing exponentially worldwide.

M.H. Fulekar (✉) • B. Pathak • R.K. Kale
School of Environment and Sustainable Development,
Central University of Gujarat, Sector 30, Gandhinagar,
Gujarat 382030, India
e-mail: mhfulekar@yahoo.com; bhawanasp@hotil.com

Nanotechnology will provide the capacity to create affordable products with dramatically improved performance. This will come through basic understanding of works to control and manipulate matter at the nanometer scale through the incorporation of nanostructures and nanoprocesses into technological innovations. A revolution has been occurring in science and technology, based on the recently developed ability to measure, manipulate, and organize matter on this scale. Nanotechnology is

fundamentally changing the way materials and devices will be produced in the future. The ability to synthesize nanoscale building blocks with precisely controlled size and composition and then to assemble them into large structure with unique properties and functions will revolutionize materials, manufacturing, and their applications.

Nanoscience and engineering could significantly affect molecular understanding of nanoscale processes that take place in the environment: the generation and remediation of environmental problems through control of emissions, the development of new “green” technology that minimize the production of undesirable by-products, and the remediation of existing waste sites and streams. Nanotechnology will also afford the removal of the smallest contaminants from water supplies and air and the continuous measurement and mitigation/prevention of pollution to clean up the environment.

New technologies offer interesting opportunities for sustainable solutions, depending on the area of application and the framework conditions given. The research results show that there are varying implications at different life-cycle stages and application levels concerning the resource consumption. Therefore, NT applications and their implications need to be carefully studied, taking a life-cycle-wide perspective as well as looking at different levels (e.g., the production of NT products, the use phase including systemic effects). Using the experience gained in investigating the sustainability impacts of emerging technologies, nano tech offer great promise for delivering new and improved Environment technology (Carvajal 2004). Nanotechnology can make a considerable contribution to sustainable development through its combination of economic, ecological, and social benefits. Sustainable development means balancing economic, ecological, and social requirements in order to meet present needs without restricting the opportunities available to future generation.

Potential of Nanotechnology

Nanoscience is associated with the intimate understanding and control of matter at dimensions

of roughly 1–100 nm and is intrinsically important because of the genuine expectation that the properties of materials at this scale will differ significantly from those of their bulk counterparts. Nanotechnology involves the imaging, measuring, modeling, and manipulation of materials at this length scale. The synthesis and fabrication of functional nanomaterials with predictive, rational strategies is a major focal point of research for many groups worldwide (Xia et al. 2008; Xu et al. 2009).

In practice, this effort has entailed the design, production, and characterization of a myriad of nanostructures including nanoparticles, nanocubes, nanorods, nanowires, and nanotubes, which maintain fundamentally interesting size-dependent electronic, optical, thermal, mechanical, magnetic, chemical, and other physical properties. From the perspective of applications, these structures have wide-ranging utility in areas as diverse as catalysis, energy storage, fiber engineering, fuel cells, biomedicine, computation, power generation, photonics, pollution remediation, and sensing. Tables 7.1 and 7.2 demonstrate nanomaterials and its properties and applications.

Nanotechnology: Multidisciplinary Aspects

Nanotechnology is the design, characterization, production, and application of structures, devices, and systems by controlling the shape and size at the nanometer scale; environmental nanotechnology (E-nano) products can be developed for a wide array of urgently needed environmental remediation. The nanoparticles/nanostructures made by mechanical and/or microbial action with fundamental building blocks are among the smallest human-made objects and exhibit novel physical, chemical, and biological properties, which has wider application for pollution prevention, detection, monitoring, and remediation of pollutants. Environmental nanotechnology would be the new innovation to remediate and treat the contaminants to acceptable levels. Environmental scientists and engineers are already working with

Table 7.1 Potential nanomaterial, materials, and manufacturing

Nanomaterials	Properties/application
<i>Nanotubes</i> (type of nanoparticulate with at least a roughly cylinder shape and a diameter that is nanometer scale)	Can be used both as raw materials and as products Multiwalled nanotubes are already going into composites Increased conductivity at much lower filler loads Carbon nanotubes are in commercial production and said to fit a wide range of applications
<i>Nanocatalysis</i>	Potentials for speeding up reactions Improving efficiency of many processes to many folds In controlling emissions in industrial processes and automobiles Wide applications in fossil fuel industries Other areas of applications like material production, reducing pollution, medicine production, and chemical industry
<i>Nanocomposites</i>	Mainly clay-based for structural application (increased strength) or with novel properties Developing nanospore composite materials, synthesis of polymeric optical display substrate materials, nanostructural surface components, polymer and clay organic–inorganic nanocomposites, embedding and filling technologies These are already penetrating the automotive and aerospace industries
<i>Nanopowders</i>	Nanoparticles of metals/compounds/ceramics Highly dense materials Potentials for magnetic, electronic, and structural applications
<i>Nanofilms</i>	They can be organic or inorganic Have a wide range of properties, like chemically active, wear resistant, high erosion resistance in hostile environments, ability to focus x-rays, and the prevention of the transmission of laser light Monolayers deposited on semiconducting substrates that emit electrons when sunlight fallson them form the basis of solar energy cell applications Can be deposited in multilayers, for example, specific magnetic properties useful in magnetic recording with high packaging

Table 7.2 Nanoengineered advanced materials and manufacturing

Advanced materials	Description
Super	Super materials are “nano-pure” or in other words every atom is exactly where it is supposed to be. ‘This type of developed material is free from defects and is super strong and could also be Nano engineered’ for enhancement of material properties, like diamond bolts and even wings for aircrafts
Smart	Smart materials have the ability to react to commands. They could change shape, color, density, and physical property. For example, smart paint has the ability to rearrange its atoms to refract the light differently
Active	Active materials are full of nanoscale sensors, computers, and actuators. Using these components the material can probe its environment, compute a response, and act
Swarms	Swarms consist of large numbers of simple nanomachines that work together to achieve complex goals. These are types of active materials

nanoscale structure to manipulate matter of the atomic or molecular scale that has cut across disciplines of chemistry, physics, biology, and even engineering (Fig. 7.1).

In research communities, there are statements that NT is still not well defined. Some defines it

on the basis of physical dimension of structures ranging from 0.1 to 100 nm; it means different for different disciplines of people. Definitions of NT are as the applications of it. The following table outlines the set of definitions related to its discipline (Table 7.3).

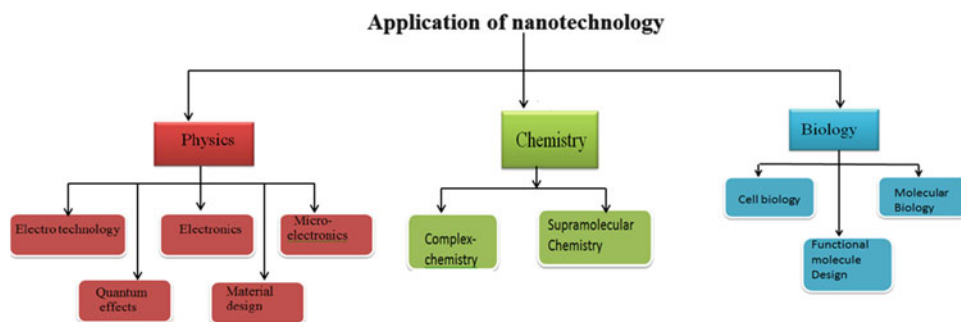


Fig. 7.1 Demonstration of nanotechnologies' multidisciplinary aspect

Table 7.3 The set of definitions related to its discipline

S. no.	Discipline	Definition of nanotechnology
1.	Physics	The ability to design and control the structure of an object at all length scales from the atom up to macroscale
2.	Biology	The core of nanotechnology consists of system in the size range of nanometers
3.	Chemistry	It is the assembly of molecules or atom to make use of their unique properties existing at nanoscale (Curtin University of Technology)
4.	Science fiction	Manipulation of individual atoms and molecules to form desired structures or patterns with novel functionality

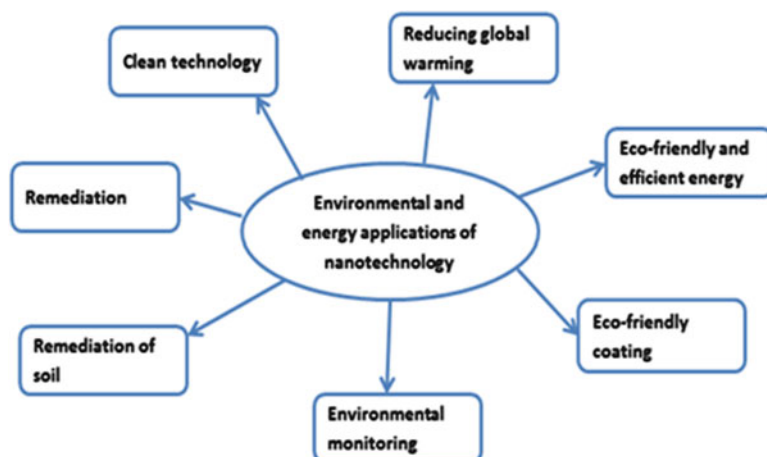
Nanotechnology is a result of convergence of traditional fields of physics, biology, and chemistry. It depends on the contribution from among these and other disciplines. The convergence of these traditional fields in the environment and energy is well illustrated in Fig. 7.2 which also shows the scales of the areas of interaction. There are considerable debates in the scientific community about the boundaries of the new disciplines emerging from this convergence, e.g., between microtechnology and nanotechnology, but it is becoming clear that in practice no clear division can be made. Thus, for example, sensors and biochips at nanoscale need to be packaged for commercial application using microtechnology.

Nanotechnology and Energy

Nanotechnology has been shown to directly contribute to the long-term energy sustainability through the development of energy-saving and renewable energy technologies. Nanoscience

accounts for the development of a vast variety of high-performance materials for thermal insulation as well as lighter and stronger materials for vehicle production and LEDs for application in energy-efficient lighting devices and displays. In the field of renewable energy, nanotechnology has contributed to the development of a variety of solar photovoltaic (PV) technologies for electricity production. PV nanotechnologies have lower production costs than the expensive, conventional silicon crystalline technology. The thin-film copper–indium–gallium diselenide (CIGS) technology is considered as the most promising PV nanotechnology. CIGS cells show very high conversion efficiency compared to the rest of the nano-PV technologies, and their manufacturing costs are relatively low. One of the promising areas of NT is under increased usage of renewable energies like hydrogen, solar, and cleaner fuels. Currently, conventional technologies provide hydrogen as energy carrier in fuel cells, but there are drawbacks in it, because unfortunately, a convenient hydrogen

Fig. 7.2 Environmental and energy applications of nanotechnology



storage system does not exist today. The current technologies include compressed gases (like natural gas, propane), which occupy larger volumes and metal hydrides, which are very heavy and therefore result in a reduced driving range for automobiles (National Renewable Energy Laboratory, n.d.). CNTs are essentially tiny, lightweight cylinders with diameters the size of several hydrogen molecules, and they can provide a solution to the storage problems.

Research carried showed that these CNTs are capable of adsorbing hydrogen (Dillon et al. 1999), and this indicates that CNTs are the ideal building blocks for constructing safe, efficient, and high-density adsorbents for hydrogen storage application like fuel cells and batteries in electronic and automobile applications. For example, these nanotubes have been reported to store up to 20 l of hydrogen per gram. This has significant implication for reducing costs – transporting and storing hydrogen (Khan et al. 2003). CNTs absorb trace quantities of CO₂ present in natural gas, so researchers are currently developing CNT membranes that could revolutionize natural gas purification technology. And also there are ongoing research to make use of CNTs for desalination and treatment of wastewater. These nanotubes can enhance water treatment and also out complete reverse osmosis or distillation processes using at least 10 times less energy than reverse osmosis and at least 1,000 times

less energy than distillation (Bruns 2000). It is envisaged that NT will show potentially significant impacts in environmental and energy applications. These include developing new green processing technologies that minimize the generation of undesirable by-products. It can be used to monitor and remediate existing waste sites and polluted wastewater resources. Nanotechnology, in particular nanofabrication, offers a variety of tools to contribute for solving the energy crisis, since creating materials and devices smaller than 100 nanometers (nm) offers new ways to capture, store, and transfer energy. The level of control that nanofabrication provides could help to solve many problems that the world is facing related to current energy generation technologies, including the array of alternative, renewable energy approaches. The conversion of primary energy sources, i.e., the sun into electricity, heat, and kinetic energy, can be made more efficient and environmentally friendly using nanotechnology. Producing electricity through the conversion of sunlight, known as solar photovoltaics (or solar cells), is a field where nanostructured materials and nanotechnology are contributing greatly. Successful research could result in a significant reduction of the manufacturing cost of these solar cells and also improve efficiency. Cell types being investigated include thin-layer solar cells, dye solar cells, or polymer solar cells. The use of a layer of quantum dots – tiny blobs of one semiconductor

grown on the surface of another, added behind the conventional multilayer compound – is also being investigated. It is anticipated that nanotechnology will help to develop the ideal solar cell, incorporating optimum structure and design.

Nanofabrication of materials is also being used in other energy conversion processes where specific, extreme conditions need to be withstood, such as heat-resistant turbine materials. Coal-fired power stations can also be made more environmentally friendly using nano-optimized membranes, which separate out and store the carbon dioxide. Thermoelectric energy conversion using nanostructured semiconductors promises increases in efficiency that could pave the way for a broad application in the utilization of waste heat, e.g., from car or human body heat for portable electronics in textiles. Hydrogen fuel cell technology is another area where nanotechnology can be applied to improve efficiency. Other renewable energy sources are also being “improved” using nanotechnology including wind energy, using lighter, more durable nano-based materials for rotor blades; geothermal, using nano-coatings and composites for wear-resistant drilling equipment; hydro-tidal power, using nano-coatings for corrosion protection; and biomass energy (“biofuels”), using nano-based precision farming to optimize yields.

Benefits of Nano-Energy

- Reduced energy consumption – By optimizing/increasing efficiency in energy storage, generation, and conservation, energy consumption will decrease through nanotechnology applications.
- Environmentally friendly – Nanotechnology can contribute to “cleaning” up and reducing the environmental impact throughout the value chain of the energy sector.
- Cheaper – The use of nanotechnology can reduce the cost of energy production, distribution, and storage, since it has the advantage of reducing the amount of power outputs.

Through miniaturization, nanotechnology also provides an opportunity to tailor-make solutions.

- Independent power sources – The application of nanotechnology in the energy sector could contribute to providing alternative sources of energy to the national grid.
- Facilitate transition to renewable – The application of nanotechnology in the energy sector could facilitate the transition from fossil fuels to renewable energy.

Clean Technology

Nanotechnology involves atom-by-atom construction; it will be able to create substances and finished objects without producing the dangerous and messy by-products that most current manufacturing processes produce. Nanodevices will operate in a liquid containing the necessary raw materials usually carbon or silicon, with trace amounts of other elements as needed, and will simply plug the appropriate atoms in the appropriate places to produce the desired end product. Such processes should produce few by-products, and those by-products can be purified readily by other nanodevices and recycled back into the feedstock (Reynolds 2001). Toxic waste generated during the various industrial processes consists of harmless atoms arranged into noxious molecule. With inexpensive energy and equipment able to work at the molecular level, these wastes can be converted into harmless forms (Drexler et al. 1991).

In addition, most products of NT and abundant elements like carbon in diamond or diamondoid form will be the basis of most nanomanufacturing. Products made of such materials will be strong, which uses smaller amounts of materials, and carbon is an abundant material, meaning that little in the way, exploration and extraction will be needed. As a greenhouse remediation measure, nanodevices could extract carbon dioxide (CO₂) form in the air, if desired (Reynolds 2001). Presently, the atom-by-atom-based manufacturing in the industries is achieving efficient, environment-friendly

processes by using some nanomaterials like nanocatalysts. The nanocatalysts are improving the efficiency and specificity of chemical reactions, which results in the design of light and strong materials that can lead to saving energy and raw materials (ION 2001). Apart from this, NT could contribute to cleaner industrial production process or products, mainly through the use of raw materials and energy. These trends includes miniaturization of devices design and new catalyst at the nanoscale level.

Nanomaterial could also help to develop greener technologies, hence reducing CO₂ emissions and energy consumption for buildings and transport. For example, US buildings account for about 40 % of the country's total energy consumption and are responsible for 39 % of CO₂ emissions. Transport's contribution amounts to another 33 %. By combining the use of light-emitting diodes (LEDs) and super-insulating and self-cleaning windows, together with the implementation of more powerful rooftop photovoltaic (PV) panels and nanosensors, monitoring energy usage, energy efficiency, and environmental sustainability of buildings would be enhanced. In particular, the improvement of solar photovoltaic (PV) is linked to the development of new materials with higher efficiency in solar energy conversion. Nanostructured organic photovoltaics can now reach a power efficiency of 8 %. Although still lower than traditional silicon-based PV, given their high flexibility and relatively cheap industrial production, these organic PV panels have found applications in many sectors, ranging from buildings to transport and electronic equipment. Improved recycling in industrial processes would enable the recovery of precious transition metal ions from aqueous solutions and mixtures, in parallel to a decrease in solid waste and greenhouse gas (GHG) emissions. Such recycling could be achieved through recovery and reuse of magnetic nanoparticles via magnetic separation.

Furthermore, highly porous nanomaterials encompassing metal organic and zeolitic imidazole frameworks capture large amounts of CO₂, in parallel to metallic iron nanoparticles which

degrade organic contaminants like chlorinated hydrocarbons. The development of new catalytic nanoparticles for transport technology, at lower cost than the currently used platinum-based catalytic converters, would guarantee cleaner emissions. New nanotechnologies based on carbon nanotubes (CNTs), leading to new materials between 10 and 56 times stronger than steel but significantly lighter, would reduce fuel consumption (PNNL 2002).

Nano-Enhanced Green Industry Technologies

Environmentally friendly catalysis is possible using cooperative catalytic systems incorporated in mesoporous silica nanoparticles (MSNs). Nano Scientists have described how catalyst work inside the pore of MSNs and tailored to perform a series of reactions – for instance, to synthesize biodiesel from free fatty acids in vegetable oils. These catalytic MSNs are environmentally benign and easy to recycle. It is possible to tailor the activity and stability of nanoparticle catalysts by modifying their pore structure. Researcher's goal is to make stable catalysts for use in removing poisonous carbon monoxide from the air in places such as mining shafts. Scientists have described a promising method for synthesizing nanogold and nanopalladium catalysis in an ordered mesoporous support structure with controllable pore sizes. The synthesis can be done at low temperatures using microwaves. A novel nonporous sorbent effectively removes mercury and other toxic heavy metals from wastewater generated during offshore oil and gas platform drilling. The material, which is called thiol-SAMs, removes 99 % of mercury from gas-condensate liquid containing 800 ppm of mercury.

Polymer nanospheres offer a new way to selectively detect hazardous materials in aquatic environment. Scientists have described how to prepare polymer nanospheres that change their shape and optical properties whenever a certain chemical is present. The change can be measured by surface plasma resonance, which enables

the detection of pollutants at the level of parts per billion (ppb). The nanospheres can be tailored to sense a specific chemical by molecular imprinting of the polymers. The method could prove particularly useful for detecting pharmaceuticals and other emerging pollutants in waterways that are currently difficult to detect.

Nano-Enhanced Cleanup Technologies

Magnetic nanoparticles could become an important green tool for removing arsenic from drinking water, particularly for point-of-use treatment in developing countries. Nanoparticles of iron oxide bind strongly and specifically to arsenic and can be separated out of solutions using magnets. Scientists determined that particles of 12 nm size removed 99.2 % of the arsenic in solution. Zerovalent nanoparticles of iron and magnesium more effectively degrade heavy metals and organic solvents in water sediments when they are combined with emulsion liquid membranes. The membranes increased the contact between these catalytic nanoparticles and the targeted pollutants. This is a promising remediation technology.

Eco-Friendly Coating: Pollution Prevention

Pollution prevention is reducing or eliminating waste at the source by modifying production processes, promoting the use of nontoxic or less-toxic substances, implementing conservation techniques, and reusing materials rather than putting them into the waste stream. The unique and potentially useful properties of nanomaterials have dramatically increased surface areas and reactivity that improved strength and weight ratios and increased electrical conductivity and changes in color and opacity. Materials designed to take advantage of these properties are finding application in a variety of areas, such as electronics, medicine, and environmental protection.

Nanoproducts

Examples of products with potential for preventing pollution include coatings that are free of volatile organic compounds and diisocyanates, safer surfactants, and self-cleaning surfaces. Nanotechnology and nanomaterials can help to create alternatives to light-emitting or absorbing applications that previously relied upon heavy metal-based semiconductors. Nanocomposites may be used in a variety of products, resulting in reduced need for addition of flame-retardant chemicals. In addition, products including a variety of tools, automobile and airplane components, and coatings can be made harder and more wear, erosion, and fatigue resistant than conventional counterparts. Examples are as follows:

- (a) *Alternatives to Chrome VI Coatings:* Chrome and cadmium plating provides very effective surface treatments for wear and corrosion reduction. Electrolytic hard chrome (EHC) is applied using the reduction of hexavalent chrome in a solution of chromic acid. The EHC plating process is a less efficient process which results in vigorous gas evolution at the electrode. This results in airborne mist which contains hexavalent chrome, a known carcinogen. Several alternative technologies exist to coat a substrate with metal without using electrolytic solutions or plating baths. These technologies do not eliminate the use of metal coatings, but they do eliminate the use of nonmetal toxic components such as cyanide from the plating process. They can also reduce the amount of metal-contaminated wastewater and sludge that is generated from plating. These alternative technologies include thermal spray coating, vapor deposition, and chemical vapor deposition and can be used to apply alternate materials.
 - Powdermet, Inc., has developed a combined top-down/bottom-up approach to this problem, utilizing a novel process for producing nano-featured feedstock materials for the alternative technologies mentioned above. This approach reduces both the amount of waste produced and

the amount of post-plating processing required resulting in a hard, corrosion-resistant coating.

(b) *Energetics, Including Safer Non-lead Primers to Prevent Pollution:* Researchers are currently developing nanoengineered thermites (nanothermite) with tailored properties that are expected to replace lead azide and lead styphnate primers in the near future. Nanothermites are comprised of a mixture of fuel and oxidizer nanostructures. Typically Al nanoparticles are used as fuel and metal oxides like CuO, MoO₃, and Bi₂O₃. Environmentally safe chemicals are utilized for the preparation of these materials. Nanothermites are self-assembled and coated with polymers or explosives in nanoscale for applications such as primers, reactive materials, and propellant initiators. These materials are also integrated with microdevices for various applications such as microthrusters, power generators, micro-shock generators for drug delivery, and microinitiators.

(c) *Nanoscale Thermoelectric Materials and Devices:* Increasingly, the ability to provide power and cooling is a major factor in how large-scale computer systems, as in Internet data centers, are designed and managed. This stems from the fact that advanced high-performance electronics in many situations are currently limited by the ability to remove heat from the operating chip. This heat is typically concentrated in hot spots in the chip, experiencing very high heat fluxes. Such thermal problems are also relevant to small-scale computationally intense, wireless, and communication devices that rely on advanced algorithms for voice, video, and error-free data operations. Component- and system-level heat flux densities are projected to increase as computers and other digital devices add increased functionality. Strategies to manage these problems will have a profound impact on future technology and economic growth. Concomitant with these technology issues are the emerging problems of rising energy costs that are demanding higher efficiency in automobiles to cooling

systems, as well as in other energy-intensive industries. It is worth noting that nearly 60 % of the world's useful energy is wasted as heat. Thus, it is worth considering the recovery of even a fraction of this heat by converting to useful electric power. Complicating this mix is the urgent need for limiting CO₂ levels in the atmosphere to contain global warming and minimizing ozone-depleting refrigerants. This shows how nanoscale thermoelectric materials and device technology can have an impact on such a broad spectrum of emerging technological, energy, and environmental issues.

Nanoprocesses

Processes that could prevent pollution include more efficient industrial chemical production through the use of nanoscale catalysts and the bottom-up self-assembly of materials, resulting in processing efficiency, reduction of waste in manufacturing, and stronger materials with fewer defects. In addition, the ability to enhance and tune chemical activity can result in catalysts that improve the efficiency of chemical reactions in automobile catalytic converters, power generation plants, and manufacturing facilities. Examples are as follows:

(a) *Nanoengineering Materials for Pollution Prevention: Concrete and Reduced CO₂ Emissions.* Protecting the built environment from the forces of the natural world with dams and seawalls is an important work, as is protecting the natural environment from the engineered world. But the twenty-first-century engineer should also look to the natural world as a powerful design partner and a source of sustainable solutions. A good place to begin is by studying the way natural materials are constructed at the nanoscale and drawing inspiration from them as we engineer our own materials. For example, the civil engineer's construction material of choice includes concrete, the oldest engineered building material and one of the most widely consumed materials on

earth. Each year, 2.1 billion tons of cement, the primary component of concrete, is manufactured, enough to produce one cubic meter of concrete for every person alive. Unfortunately, cement is a major source of atmospheric carbon dioxide largely because it is made by burning fossil fuel to heat a limestone and clay powder to 1,500°C, which changes its molecular structure. When the cement powder is later mixed with water and gravel, the invested energy is released into chemical bonds that form calcium silicate hydrates, the glue that binds the gravel to make concrete. The production of cement accounts for 7–8 % of all human-generated carbon dioxide emissions. If novel cement can be engineered, whose manufacture produces only half as much CO₂, a significant reduction in total CO₂ emissions will be achieved. The application of nanotechnology may make it possible for all this to happen.

- (b) *Stereoselective Green Chemistry Strategies Using Crystal-to-Crystal Reactions: The Advantages of Molecular Nanocrystals.* It has recently been shown that photochemical excitation of crystalline ketones bearing radical stabilizing substituents on their two α -positions leads to efficient photodecarbonylation reactions. Experiments with crystals of carefully designed carbonyl compounds can be used to accomplish the formation of sigma bonds between adjacent quaternary stereogenic centers in good chemical yields and with remarkable chemical control. The exceptional simplicity, chemoselectivity, and stereospecificity of the solid-state reactions have been combined with well-developed ketone chemistry for the preparation of several natural products, including the sesquiterpenes cuparenone, herbertenolide, and touchuinylnyl acetate. Simple scale-up strategies based on nanocrystals and the use of sunlight suggest a remarkable potential for specialty chemical applications for these crystal-to-crystal reactions.
- (c) *Nanotechnology as a Tool to Advance Pollution Prevention in the Semiconductor/IT*

Industry. Nanotechnology is not new to the semiconductor/IT (information technology) industry. Many features in semiconductors and integrated circuits have been at the nanoscale for decades. The International Technology Roadmap for Semiconductors identifies nanotechnology, both traditional semiconductor nanotechnology and novel nanomaterials, as a critical key to the future development of the industry, both in extending the current CMOS (complementary metal oxide semiconductor) scaling and in positioning beyond the current CMOS platform. The expanded use of nanotechnology and the incorporation of nanomaterials into semiconductor/IT processes and products not only provide potential solutions to many technical and business challenges facing the industry, but they also offer a tremendous opportunity to advance pollution prevention. Examples of nano-applications in semiconductor/IT processes and products that may result in energy and resource conservation, waste minimization, and energy-efficient products include bottom-up self-assembly, nanoarchitecture, and nanophotonics.

Environmental Monitoring

Environmental monitoring plays an important role in natural and resource conservation. It is crucial for environmental policy and research, because it provides policymakers, scientists, and the public with the data needed to understand and improve the environment.

- (a) *Air Monitoring:* Conventional air pollution monitoring employs large, fixed systems, which often fail to detect “hot spot” pollution peaks (Court et al. 2004). Solid-state gas sensors (SGSs), based on nanocrystalline metal oxide thin films, provide faster response with real-time analysis capability, higher resolution, simplified operation, and lower running costs compared to conventional methods, such as chemiluminescence and infrared spectrometry (Rickyerby and Morrison 2006).

- (b) *Water Monitoring*: When the EU Water Framework Directive was implemented in 2000, new regulations for water monitoring of organic substances were imposed and measurements had to be done down to microgram-per-liter (μgL^{-1}) levels. Such accuracy, however, was difficult to achieve with conventional water monitoring technologies, and a necessity for faster, more sensitive systems appeared. This is how the automated water analyzer computer-supported system (AWACSS) was created.
- (c) *Microbial Monitoring and Detection*: The use of QDs as a fluorescence labeling system in microbial detection has been successfully demonstrated. Thiolated CdSe-core QDs could be conjugated with wheat germ agglutinin (WGA), a lectin that is commonly found in gram-positive bacteria (Kloepfer et al. 2003). By reacting with bacterial cells, this QD-conjugated WGA can bind to sialic acid and *N*-acetylglucosaminyl residues on bacterial cell walls. QDs can also be bioconjugated with a substrate such as iron, which is essential for the growth of pathogenic organisms inside a human host. Pathogenic bacteria normally contain receptors for a human host's own shuttle protein transferrin and can harvest iron from transferrin (Modun et al. 2000). Using this metabolism-specific approach, transferrin-conjugated QDs can be transported through the membrane into metabolically active cells of iron-deprived *Staphylococcus aureus* and detected under fluorescence excitation. In contrast, no QD signal is observed in nonpathogenic bacteria. QDs can be further conjugated with specific antibodies to detect pathogenic microorganisms such as *Cryptosporidium parvum* and *Giardia lamblia* (Zhu et al. 2004).

The detection and monitoring of microorganisms can be further accelerated using nanoparticles in a fluorescence labeling system in microfluidic devices. Nanoparticle-based fluorescence reporting systems can be further developed to achieve rapid bacterial detection at the single-cell level (Zhao et al. 2004). To do so, the fluorescence intensity of individual nanoparticles

was greatly increased through the encapsulation of thousands of fluorescent dye molecules in a protective silica matrix. After modifying the surface of these silica nanoparticles, they were conjugated with antigens specific to *Escherichia coli* strain O157 and used in immunological assays. With the improvement in the fluorescence reporting system, the fluorescence intensity emitted by one *E. coli* O157 cell was sufficient to be detected using a normal spectrofluorometer in a conventional plate-based immunological assay or to be accurately enumerated using a laboratory-made flow cytometer within 60 s of sample preparation.

Nanoparticles can be further used to immobilize microbial cells that can degrade or biorecover specific chemicals (Shan et al. 2005). Unlike conventional cell immobilization on micron-sized media or a fixed surface, magnetic nanoparticles (i.e., Fe_3O_4) were functionalized with ammonium oleate and coated on the surface of *Pseudomonas delafieldii*. By applying an external magnetic field to these microbial cells, these magnetic nanoparticle-coated cells were concentrated at a specific location on the reactor wall, separated from the bulk solution, and recycled for the treatment of the same substrate. These microbial cells were added into a bioreactor at a high biomass concentration and were demonstrated to desulfurize organic sulfur from fossil fuel (i.e., dibenzothiophene) as effectively as non-nanoparticle-coated cells (Shan et al. 2005). In environmental research, these nanoparticles further enhance the detection sensitivity of microbial monitoring and the degradation and recovery efficiency of chemicals.

Water Treatment-Based Nanotechnologies

Water Treatment Technologies Involves the Following

- (a) *Filtration*: Filtration involves removing the pollutants through a straining mechanism. Nanoparticles enhance traditional filtration

methods because they are more strongly attracting the pollutants as they pass through the filter.

- (b) *Desalination*: Desalination is a very specific water treatment that focuses on creating freshwater from saltwater. Given that most of the Earth is covered with saltwater, desalination could be an important process to ensure that the world has enough drinking water. Desalination is often conducted using reverse osmosis.
- (c) *Disinfection*: Waterborne pathogens are the major cause of diseases and infection. A common disinfection technique uses powders or chlorine-based chemicals to kill bacteria in water. Nanotechnology can improve the disinfection capabilities of these chemicals, and new nanotechnology applications can kill organisms that are developing resistance to traditional disinfection techniques.
- (d) *Photocatalysis*: This application uses light to clean the water. As opposed to other techniques that simply collect pollutants from a dirty source, photocatalysis actually degrades the pollutants. In this process, a catalyst, often titanium dioxide, is placed into the dirty water. When UV light hits the particle, it begins a chemical reaction that degrades the pollutants in the system.
- (e) *Remediation*: In general remediation refers to removing heavy metals and other pollutants from water that was contaminated due to industrial processes. Remediation processes have to be quick and cheap in order to clean the effluent as it leaves industrial plants.
- (f) *Sensors*: It is important that pollutants be detected in water sources so that they can be treated. Nanosensors promise to be a cheap and easy method to detect whether a water source has been contaminated.

Water Purification

Water must be purified in order to remove harmful materials and make it suitable for human uses. Contaminants can include metals like cadmium, copper, mercury, lead, nickel, zinc, chromium,

and aluminum; nutrients include phosphate, ammonium, nitrate, nitrite, phosphorus, and nitrogen, and biological elements such as bacteria, viruses, parasites, and biological agents from weapons. UV light is an effective purifier, but it is energy intensive, and application in large-scale systems is sometimes considered cost prohibitive. Chlorine, also commonly used in water purification, is undesirable because its production is one of the world's most energy-intensive industrial processes, consuming about 1 % of the world's total electricity output. Nanotechnology is opening new doors to water decontamination, purification, and desalinization and providing improved detection of waterborne harmful substances.

For example, iron nanoparticles have high surface area and reactivity and can be used to detoxify carcinogenic chlorinated hydrocarbons in groundwater. They can also render heavy metals like lead and mercury insoluble, reducing their contaminations. Dendrimers, with their sponge-like molecular structure, can clean up heavy metals by trapping ions in their pores. Nanoscale filters have a charge membrane enabling them to treat both metallic and organic contaminant ions via both steric filtration based on the size of openings and Donnan filtration based on electrical charge. They can also be self-cleaning.

Gold nanoparticles coated with palladium have proven to be 2,200 times better than palladium for removing trichloroethylene from groundwater. In addition, photocatalytic nanomaterials enable ultraviolet light to destroy pesticides, industrial solvents, and germs. Titanium dioxide, for example, can be used to decontaminate bacteria-ridden water. When exposed to light, it breaks down bacterial cell membranes killing bacteria like *E. coli*. Purification and filtration of water can also be achieved through nanoscale membrane or using nanoscale polymer "brushes" coated with molecules that can capture and remove poisonous metals, proteins, and germs (Elvin 2007).

A new sterilizer, the RVK-NI, mixes ozone nanobubbles with oxygen microbubbles to produce, according to manufacturer Royal Electric, almost completely bacteria-free water for food processing. Ozone gas is a naturally occurring

type of oxygen that is formed as sunlight passes through the atmosphere; it can be generated artificially by passing high-voltage electricity through oxygenated air. Because ozone is an unstable highly reactive form of oxygen, it is 51 times more powerful than chlorine, the oxidizer used by most food processors. With it, manufacturers can forego the use of environmentally harmful chlorine or other chemicals used in conventional water disinfection process. The ozone process is also said to kill bacteria and other microbes 3,000 times faster than chlorine. Desalination is another critical area of water purification. Dais Analytic Corporation, for example, is currently preparing its nanoclear desalinization process for commercialization. Low-cost techniques for water purification, self-cleaning, evaporation, reduction, and desalination could have tremendous impact by providing adequate supplies of clean water.

Water Treatment

Conventional water treatment technologies include filtration, ultraviolet radiation, chemical treatment, and desalination, whereas the nano-enabled technologies include a variety of different types of membranes and filters based on carbon nanotubes, nanoporous ceramics, magnetic nanoparticles, and other nanomaterials.

In a recent study, several polymeric nanofiltration and reverse osmosis membranes were tested for the treatment of brackish groundwater (water that is salty, but less so than seawater). The tests showed that nanofiltration membranes can produce potable water from the brackish groundwater. As expected, the reverse osmosis membranes removed about 99 % of all the solutes, but the concentrations of essential nutrients, such as calcium and magnesium ions, were reduced to levels that were below the specifications of the World Health Organization standard for drinking water. The product water therefore had to be spiked with these nutrients to provide drinking water of the required quality.

These studies also underline the importance of making communities aware of the actual quality of their drinking water because it is not possible

to detect contaminants, for example, by simply observing the physical properties of the water (i.e., smell, taste, and color).

However, it is not enough to develop technical solutions to these problems; the technology must also be transferred to the country that needs it. To be effective, technology transfer must be accompanied by technology adaptation and technology adoption to take account of the technical capability, infrastructure, and market potential of the developing country that needs the technology.

Nanofiltration

Nanofiltration is a relatively recent membrane filtration process, which holds promise to deliver cost-effective water and air treatment solutions. Nanomembranes (NMs) are used not only to remove contaminants from polluted water and air but also for desalination of salty water. There are two types of NMs currently available on the market: nanofilters, using either carbon nanotubes (CNTs) or nanocapillary arrays to mechanically remove impurities, and reactive NMs, where functionalized NPs chemically convert the contaminants into safe by-products.

Ordered arrays of densely packed, vertically aligned CNTs are used as membranes to filter out water impurities while letting the water flow freely through the filter. Carbon nanotube membranes (CNMs) are able to remove almost all kinds of contaminants including bacteria, viruses, and organic pollutants. CNMs are also effective in desalinating salty water.

Until now, several NM types, which effectively remove CO₂ from industrial flue gases, were developed from both polymeric and inorganic materials (i.e., carbon-based membranes, mesoporous oxide membranes, and zeolite membranes). These membranes show better selectivity and higher removal capacity than their conventional alternatives, and they are often more cost-efficient (Fujiokya et al. 2007). The large-scale industrial application of the CO₂-removing NMs would contribute to the reduction of the anthropogenic CO₂ emissions in the atmosphere and impede climate change.

Recently, enzymatic quorum quenching (in the form of a free enzyme or an immobilized form on a bead) was successfully applied to a submerged membrane bioreactor with a microfiltration membrane for wastewater treatment as a novel approach to control membrane biofouling. In this study, a quorum-quenching enzyme (acylase) was directly immobilized onto a nanofiltration membrane to mitigate biofouling in a nanofiltration process. In a flow cell experiment, the acylase-immobilized membrane with quorum-quenching activity prohibited the formation of mushroom-shaped mature biofilm due to reduced secretion of extracellular polymeric substances (EPS). The acylase-immobilized membrane maintained more than 90 % of its initial enzyme activity for more than 20 iterative cycles of reaction and washing procedure. In the lab-scale continuous crossflow nanofiltration system operated at a constant pressure of two bar, the flux with the acylase-immobilized nanofiltration (NF) membrane was maintained at more than 90 % of its initial flux after a 38 h operation, whereas that with the raw NF membrane decreased to 60 % accompanied with severe biofouling. The quorum-quenching activity of the acylase-immobilized membrane was

also confirmed by visualizing the spatial distribution of cells and polysaccharides on the surface of each membrane using confocal laser scanning microscope (CLSM) image analysis technique.

Metal Ion Recovery from Solutions by Dendrimer Filtration

Diallo et al. (2005) have developed a dendrimer-enhanced ultrafiltration (DEF) system that can remove dissolved cations from aqueous solution ions using low-pressure membrane filtration (Fig. 7.3). DEF works by combining dendrimers with ultrafiltration or microfiltration membranes. Functionalized and water-soluble dendrimers with large molar mass are added to an incoming aqueous solution and bind with the target ions. For most metal ions, a change in solution acidity and/or salinity causes the dendrimers to bind or release the target metal ions. Thus, a two-stage filtration process can be used to recover and concentrate a variety of dissolved ions in water including Cu(II), Ag(I), and U(VI). A key feature of the DEF process is the combination of dendritic polymers with multiple chemical functionalities with the well-established

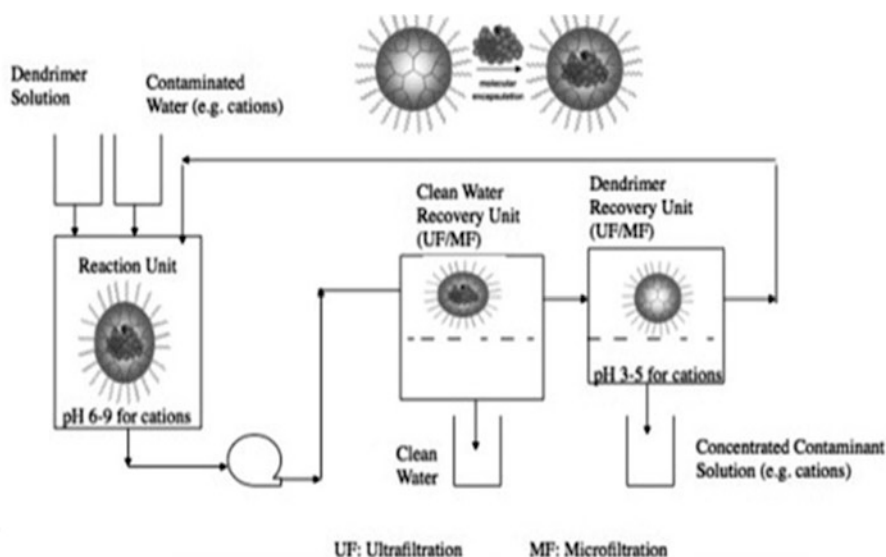


Fig. 7.3 Recovery of metal ions from aqueous solutions by dendrimer filtration (Adapted from Diallo 2008)

separation technologies of ultrafiltration (UF) and microfiltration (MF). This allows a new generation of metal ion separation processes to be developed that are flexible, reconfigurable, and scalable. The flexibility of DEF is illustrated by its modular design approach. DEF systems will be designed to be “hardware invariant” and thus reconfigurable in most cases by simply changing the “dendrimer formulation” and “dendrimer recovery system” for the targeted metal ions of interest. The DEF process has many applications including the recovery of valuable metal ions such as platinum group metals, rare-earth metals, and actinides from mineral/hydrometallurgical processing solutions, in situ leach mining solutions, and industrial wastewater solutions.

Research is under way to use advance nanotechnology in water purification for safe drinking. Nanotechnology, the deliberate manipulation of matter at size scales of less than 100 nm, holds the promise of creating new materials and devices which take advantage of unique phenomena realized at those length scales, because of their high reactivity due to the large surface to volume ratio (Ichinose et al. 1992). Nanoparticles are expected to play a crucial role in water purification (Stoimenov et al. 2002). The environmental fate and toxicity of a material are critical issues in material selection and design for water purification. No doubt that nanotechnology is better than other techniques used in water treatment, but today the knowledge about the environmental fate, transport, and toxicity of nanomaterials (Colvin 2003) is still in infancy. Advances in nano science and engineering suggest that many of the current problems involving water quality could be resolved or greatly diminished by using nonabsorbent, nanocatalysts, bioactive nanoparticles, nanostructured catalytic membranes, submicron, nanopowder, nanotubes, magnetic nanoparticles, granules, flake, high surface area metal particle supramolecular assemblies with characteristic length scales of 9–10 nm including clusters, micromolecules, nanoparticles, and colloids have a significant impact on water quality in natural environment (Mamadou and Savage 2005). Nano sensors are used for detection of pesticides (Nair

and Pradeep 2004) and biological agents including metals (e.g., cadmium, copper, lead, mercury, nickel, zinc), nutrients (e.g., phosphate, ammonia, nitrate, nitrite), cyanide organics, algae (e.g., cyanobacterial toxins) viruses, bacteria, parasites, antibiotics, and biological agents are used for terrorism. Innovations in the development of novel technologies to desalinate water are among the most exciting and seem to have promise (Diallo et al. 2005). Opportunities and challenges of using nanomaterials in the purification of surface water, groundwater, and industrial wastewater streams are a matter of continuing concern. A misconception and one of the many impressions that people have about the future of nanotechnology is the expectation that nanoparticles can be used to kill harmful organisms, to repair body tissue, to improve water quality, and to cure disease. Recent applications of nanoparticulate silver have included open wound and burn treatment, and preliminary studies have shown that a 20 ppm silver colloidal suspension (~30 nm diameter) in purified water has a 100 % cure rate for malaria. Titanium dioxide, especially as nanoparticulate anatase, is also an interesting antibacterial, with notable photocatalytic behavior. But ultrafine anatase has also been identified as cytotoxic and in vivo studies have shown that it can be severely toxic in the respiratory system (Oberdörste 2001; Ishibashi 2000). Nanocapsules and nanodevices may present new possibilities for drug delivery, gene therapy, medical diagnostics, antimicrobial activity, etc. The effect of particle size on the adsorption of dissolved heavy metals to iron oxide and titanium dioxide nanoparticles is a matter of laboratory-scale experiments. Iron oxide and titanium dioxide are good sorbents for metal contaminants. Spherical nanoparticle have a similar size and shape like resin beads that are used in water purification. Ligands, fulvic acids, humic acids, and their aggregates have a significant impact on contaminant mobility, reactivity, and bioavailability. Nanoparticles can also be designed and synthesized to act as either separation or reaction media for pollutants. The high surface area to mass ratios of nanoparticles can greatly enhance the adsorption capacities of sorbent materials. In addition to

having high specific surface areas, nanoparticles also have unique adsorption properties due to different distributions of reactive surface sites and disordered surface regions. Their extremely small feature size is of the same scale as the critical size for physical phenomena, for example, the radius of the tip of a crack in a material may be in the range 1–100 nm. The way a crack grows in a larger-scale, bulk material is likely to be different from crack propagation in a nanomaterial where crack and particle size are comparable. Fundamental electronic, magnetic, optical, chemical, and biological processes are also different at this level.

Environmental Nanotechnology: Perspectives

Biogenic Synthesis of Nanoparticles Using Microorganisms

Numerous microorganisms are reported to biosynthesize gold and silver nanoparticles by NADPH-dependent reductase enzymes that reduce metal salts to nanoparticles through electron shuttle enzymatic metal reduction process (Table 7.4). The pollution detection nanostructures and/or devices are being used for a variety of environmental applications.

Sensors

The characterization of environmental sensors is based primarily on the physics involved and their operating mechanisms. For example, chromatography relies on the separation of complex mixtures by percolation through a selectively adsorbing medium with subsequent detection of compounds of interest. Electrochemical sensors include sensors that detect signal changes (e.g., resistance) caused by an electric current being passed through electrodes that interact with chemicals. Mass sensors rely on disturbances and changes to the mass of the surface of the sensors during interaction with chemicals. Optical sensors detect changes in visible light or other

electromagnetic waves during interactions with chemicals. Within each of these categories, some sensors may exhibit characteristics that overlap with those of other categories. For example, some mass sensors may rely on electrical excitation or optical settings. The nanostructure material developed for detection of pollution monitoring and remediation is highlighted in Table 7.5.

Sensors: Biosensors, Electrochemical Sensors, Mass Sensors, Optical Sensors, Gas Sensors

Nanotechnology and Pollution Control

Pollution results from resource production and consumption, which in their current state are wasteful. Nanofabrication holds much potential for effective pollution control, but it currently faces many problems that prevent it from mass commercialization, particularly its high cost. Nanotechnology plays a vital role in air and water pollution control. Air pollution can be remediated using nanotechnology in several ways. One is through the use of nanocatalysts with increased surface area for gaseous reactions. Catalysts work by speeding up chemical reactions that transform harmful vapors from cars and industrial plants into harmless gases. Catalysts currently in use include a nanofiber catalyst made of manganese oxide that removes volatile organic compounds from industrial smokestacks. Other methods are still in development. Another approach uses nanostructured membranes that have pores small enough to separate methane or carbon dioxide from exhaust. John Zhu of the University of Queensland is researching carbon nanotubes (CNTs) for trapping greenhouse gas emissions caused by coal mining and power generation. CNT can trap gases up to a hundred times faster than other methods, allowing integration into large-scale industrial plants and power stations. This new technology both processes and separates large volumes of gas effectively, unlike conventional membranes that can only do one or the other effectively.

As with air pollution, harmful pollutants in water can be converted into harmless chemicals

Table 7.4 Biogenic synthesis of gold and silver nanoparticles by various microorganisms

Microbe	Location	Size range (nm)
Silver (Ag) nanoparticles		
Bacteria		
<i>Pseudomonas stutzeri</i>	Intracellular	200
<i>Morganella</i> sp.	Extracellular	20–30
<i>Lactobacillus</i> strains	Intracellular	
<i>Plectonema boryanum</i> (cyanobacteria)	Intracellular	1–10, 1–100
<i>Klebsiella pneumoniae</i>	Extracellular	5–32
Yeast		
MKY3	Extracellular	2–5
Fungi		
<i>Phoma</i> sp.3.2883	Extracellular	71.06–74.46
<i>Verticillium</i>	Intracellular	25±12
<i>Aspergillus fumigatus</i>	Extracellular	5–25
<i>Trichoderma asperellum</i>	Extracellular	13–18
<i>Phanerochaete chrysosporium</i>	Extracellular	50–200
Gold (Au) nanoparticles		
Bacteria		
<i>Lactobacillus</i> strains	Intracellular	
<i>Shewanella algae</i>	Intracellular, pH 7	10–20
Extracellular, pH 1		1–50
<i>Escherichia coli</i> DH5	Intracellular	25–33
<i>Thermomonospora</i> sp.	Extracellular	8
<i>Rhodococcus</i> sp.	Intracellular	5–15
Fungi		
<i>Fusarium oxysporum</i>	Extracellular	20–40
Algae		
<i>Sargassum wightii</i>	Extracellular	8–12
<i>Chlorella vulgaris</i>		9–20

Table 7.5 Pollution detection and sensing – nanostructure material

Nanostructure material	Function
Silver nanoparticle array membranes	Water quality monitoring
Carbon nanotubes (CNTs)	Electrochemical sensors
CNTs as a building block	Exposure to gases such as NO ₂ , NH ₃ , or O, the electrical resistance of CNTs changes dramatically, induced by charge transfer with the gas molecules or due to physical adsorption
CNTs with enzymes	Establish a fast electron transfer from the active site of the enzyme through the CNT to an electrode, in many cases enhancing the electrochemical activity of the biomolecules
CNT sensors	Developed for glucose, ethanol, sulfide, and sequence-specific DNA analysis
Magnetic nanoparticles coated with antibodies	Useful for the rapid detection of bacteria in complex matrices

through chemical reactions. Trichloroethene, a dangerous pollutant commonly found in industrial wastewater, can be catalyzed and treated by nanoparticles. Studies have shown that these materials should be highly suitable as hydrodehalogenation and reduction catalysts for the remediation of various organic and inorganic groundwater contaminants. Nanotechnology

eases the water-cleansing process because inserting nanoparticles into underground water sources is cheaper and more efficient than pumping water for treatment. The deionization method using nanosized fibers as an electrode is not only cheaper but also more energy efficient. Traditional water filtering systems use semipermeable membranes for electro dialysis

or reverse osmosis. Decreasing the pore size of the membrane to the nanometer range would increase the selectivity of the molecules allowed to pass through. Membranes that can even filter out viruses are now available. Also widely used in separation, purification, and decontamination processes are ion exchange resins, which are organic polymer substrate with nanosized pores on the surface where ions are trapped and exchanged for other ions (Alchin 2008). Ion exchange resins are mostly used for water softening and water purification. In water, poisonous elements like heavy metals are replaced by sodium or potassium. However, ion exchange resins are easily damaged or contaminated by iron, organic matter, bacteria, and chlorine.

Recent developments of nanowires made of potassium manganese oxide can clean up oil and other organic pollutants while making oil recovery possible (Yuan et al. 2008). These nanowires form a mesh that absorbs up to 20 times its weight in hydrophobic liquids while rejecting water with its water-repelling coating. Since the potassium manganese oxide is very stable even at high temperatures, the oil can be boiled off the nanowires and both the oil and the nanowires can then be reused (Yuan et al. 2008).

Removal of Pollutant by Adsorbent

The nanoparticles have been investigated as adsorbent for the removal of organic and inorganic contaminants. The nanosized metal oxides and natural nanosized clays have been investigated for the removal of metals and inorganic ions. Besides, oxidized and hydroxylated CNTs are good absorbers for metals such as Cu, Ni, Cd, and Pb. Pristine multiwalled CNTs have been found to be stronger adsorbent materials for organometallic compounds. CNTs have also been found as a powerful adsorbent for a wide variety of organic compounds from aquatic environment, which include dioxin, polynuclear aromatic hydrocarbons (PAHs), DDT and its metabolites, PBDEs, chlorobenzenes and chlorophenols, trihalomethanes, bisphenol A and

nonylphenol, phthalate esters, dyes, pesticides, and herbicides such as sulfuron derivatives, atrazine, and dicamba. Nanoporous polymers which have cross-linked and copolymerized with functionalized CNTs have been demonstrated for a high sorption capacity for a variety of organic compounds such as p-nitrophenol and trichloroethylene.

Nanoremediation Technologies

Environmental protection and pollution issues are frequently discussed worldwide as topics that need to be addressed sooner rather than later. Nanotechnology can strive to provide and fundamentally restructure the technologies currently used in environmental detection, sensing, and remediation for pollution control. Some nanotechnology applications that are near commercialization include nanosensors and nanoscale coatings to replace thicker, more wasteful polymer coating that prevent corrosion, nanosensors for detection of aquatic toxins, nanoscale biopolymers for improved decontamination and recycling of heavy metals, nanostructured metals that break down hazardous organics at room temperature, smart particles for environmental monitoring and purification, and nanoparticles as novel photocatalyst for environmental cleanup.

Environmental cleanup has promoted the development of highly efficient photocatalysts that can participate in detoxification reactions. Environmental remediation by photocatalysts comes with several advantages: direct conversion of pollutants to nontoxic by-products without the necessity for any other associated disposal steps, use of oxygen as oxidant and elimination of expensive oxidizing chemicals, potential for using free and abundant solar energy, self-regeneration and recycling of photocatalyst, etc. A significant amount of research on semiconductor-catalyzed photooxidation of organic chemicals has been carried out during the past 15 years. The ability to catalyze the destruction of a wide variety of organic chemicals and complete oxidation of organics to CO₂ and dilute mineral acids in many cases, the lack of inherent toxicity, and the resistance to

photodegradation at low cost render this process highly suitable for environmental remediation.

Degradation of Pollutants Using Semiconductors: TiO₂ and ZnO

The semiconductor TiO₂ nanoparticles have been extensively studied for oxidative transformation of organic and inorganic contaminants (Obare and Meyer 2004; Hoffmann et al. 1995). These are now used in a variety of products such as self-cleaning glass, disinfectant tiles, and filters for air purification (Fujishima et al. 1999). TiO₂ electrodes have the capacity to determine the chemical oxygen demand of water and are used as sensors for monitoring contaminated water (Kim et al. 2001). TiO₂ nanoparticles can be immobilized on different supports which are used for the solar detoxification of water and air. These engineered nanoparticles are known for their interaction with organic, inorganic, and biological contaminants such as heavy metals, organochlorine pesticide, arsenic, and phosphates in water, induced by ultraviolet light. TiO₂ leads to pollutant degradation through two everyday chemical reactions: reduction and oxidation. Once excited by UV and TiO₂ electron-hole pairs develop, these electrons have sufficient oxidizing potential to oxidize pollutants in wastewater (Bahnemann 2004). Interestingly, the combination of UV and TiO₂ generates bactericidal activity, which attacks several types of bacteria. This approach thus provides a comprehensive treatment procedure since chemical species and pathogens can be removed from wastewater simultaneously. Other nanoparticles with semiconducting properties, such as ZnO, ZnS, F₂O₃, and CdS, can be used for photocatalysis oxidation. TiO₂ is biologically and chemically inert and has demonstrated great resistance to corrosion along with the capacity to be used repetitively without substantial loss of catalytic activity, and it is therefore inexpensive to use. In light of these properties, TiO₂ is potentially more attractive for environmental applications than other oxidative nanoparticles (Pirkanniemi and Sillanpaa 2002). However, TiO₂ requires ultraviolet light and, consequently, is effective only for treatment of

transparent wastewater. Several research groups have attempted to overcome this limitation by extending the nanoparticle excitation into visible light with the doping of TiO₂ with transition metal ions or sensitizing dye such as Ru (II) polypyridyl complex, or investigated an approach involving a tube reactor production based on hollow glass tubes (Kamat and Meisel 2003). The tubes are extremely coated with TiO₂ and UV light passes through the hollow tubes. Preliminary results suggested that combining ultrasound processes such as sonolysis and photocatalysis improves pollutant oxidation and could be an effective approach. Several pilot projects are under way to evaluate the potential of solar reactors to generate the energy required for TiO₂ excitation and detoxification of polluted water. If these attempts are successful, sunlight could play an economic and eco-friendly role in the treatment of wastewater.

Nanoparticulate titanium dioxide (TiO₂) has been traditionally used in environmental remediation because of its low toxicity, high photoconductivity, high photostability, availability, and low cost (Wallington 2005). Novel technologies and improved processes, however, enabled the development of a variety of TiO₂ photocatalytic derivatives. Metals such as copper (Cu), silver (Ag), gold (Au), and platinum (Pt) have been tested for their ability to improve the decontamination activity of TiO₂ with Cu, for example, accelerates the reduction of hexavalent chromium (Cr⁺⁶) ions. The coupling of TiO₂ with Au or Ag results in similar reductive capabilities. The TiO₂-based p-n junction nanotubes (NTs) represent the most recent innovation in the field of nanophotocatalysts. The NTs contain platinum (Pt) (inside) and TiO₂ (on the outside). The TiO₂ coating of the tubes acts as an oxidizing surface, while the inside of the tube is reductive (Cheng and Cheng 2005). The ability of p-n junction on NTs to destroy toluene was tested by Chen et al., and the results showed that they exhibit much higher decontamination rates than non-nanotube materials (Cheng and Cheng 2005).

Unlike TiO₂, semiconductor nanoparticles such as ZnO are able to emit strongly in the visible region, and the visible emissions of ZnO

are usually very sensitive to whole scavengers such as phenols or iodide ions. ZnO particles thus seem good candidates for use as sensors for chemical compounds. It has been claimed that sensor system based on ZnO could reach a detection sensitivity of 1 ppm. Furthermore, ZnO has the ability to induce contaminant degradation under ultraviolet light (Kamat and Meisel 2003). Consequently, the use of ZnO can be considered as a promising way to simultaneously sense and destroy toxic chemicals. It has been reported that nanostructured ZnO films could simultaneously detect and degrade organic compounds in water. Such a catalyst system is useful to induce contaminant degradation where the system senses a targeted molecule, thus avoiding destruction of molecules present in the environment.

Degradation of Pollutants Using Iron Nanoparticles

Laboratory research has established that nanoscale metallic iron is very effective in destroying a wide variety of common contaminants such as chlorinated methanes, brominated methanes, trihalomethanes, chlorinated ethane, chlorinated benzenes, other polychlorinated hydrocarbons, pesticides, and dyes (Zhang 2003). The basis for the reaction is the corrosion of zerovalent iron in the environment. Contaminants such as tetrachloroethene can readily accept the electrons from iron oxidation and be reduced to ethane. However, nanoscale zerovalent iron (nZVI) can reduce not only organic contaminants but also the inorganic anions nitrate, which is reduced to ammonia (Sohn et al. 2006; Liou et al. 2006) perchlorate (plus chlorate or chlorite) and then reduced to chloride (Cao et al. 2005), selenate, arsenate (Kanel et al. 2006), arsenite (Jegadeesan et al. 2005), and chromate (Ponder et al. 2000; Manning et al. 2007). nZVI is also efficient in removing dissolved metals from solution, e.g., Pb and Ni (Li and Zhang 2006). The reaction rates for nZVI are at least 25–30 times faster and also sorption capacity is much higher compared with granular iron (Li et al. 2006). The metals are reduced to either zerovalent metals or lower oxidation states, e.g., Cr (III), and are surface complexed with the iron

oxides that are formed during the reaction. Some metal can increase the dechlorination rate of organics and also lead to more benign products, whereas other metals decrease the reactivity (Lien et al. 2007). Most of the research using nZVI has been devoted to groundwater and soil remediation. Nanoremediation methods entail the application of reactive nanomaterials for transformation and detoxification of pollutants. These nanomaterials have properties that enable both chemical reduction and catalysis to mitigate the pollutants of concern. For nanoremediation in situ, no groundwater is pumped out for aboveground treatment, and no soil is transported to other places for treatment and disposal (Otto et al. 2008).

Nanomaterials have highly desired properties for in situ applications. Because of their minute size and innovative surface coatings, nanoparticles may be able to pervade very small spaces in the subsurface and remain suspended in groundwater, allowing the particles to travel farther than larger, macro-sized particles and achieve wider distribution. However, in practice, current nanomaterials used for remediation do not move very far from their injection point (Tratnyek and Johnson 2006). Many different nanoscale materials have been explored for remediation, such as nanoscale zeolites, metal oxides, carbon nanotubes and fibers, enzymes, various noble metals [mainly as bimetallic nanoparticles (BNPs)], and titanium dioxide. Of these, nanoscale zerovalent iron (nZVI) is currently the most widely used. The different nanomaterials, along with the pollutants they could potentially remediate, are listed in Supplemental Material for a comprehensive overview of the chemistry and engineering of various nanotechnology applications addressed in Supplemental Material used for remediation (Theron et al. (2008) and Zhang (2003)). nZVI particles range from 10 to 100 nm in diameter, although some vendors sell micrometer-scale iron powders as “nanoparticles.” Typically, a noble metal (e.g., palladium, silver, copper) can be added as a catalyst. The second metal creates a catalytic synergy between itself and Fe and also aids in the nanoparticles’ distribution and

mobility once injected into the ground (Saleh et al. 2007; Tratnyek and Johnson 2006; U.S. EPA 2008). These BNPs may contain more than two different metals. The second metal is usually less reactive and is believed to promote Fe oxidation or electron transfer (U.S. EPA 2008). Some noble metals, particularly palladium, catalyze dechlorination and hydrogenation and can make the remediation more efficient (U.S. EPA 2008; Zhang and Elliott 2006).

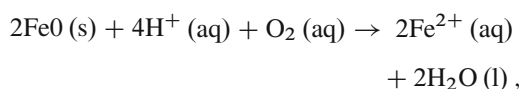
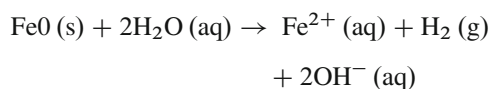
In the 1990s, Fe at the nanoscale was synthesized from Fe(II) and Fe(III) to produce particles ranging from 10 to 100 nm, initially using borohydride as the reductant, and examined in laboratory studies. Zhang (2003) tested nZVI for the transformation of a large number of pollutants, most notably halogenated organic compounds commonly detected in contaminated soil and groundwater. The author reported that nanoscale Fe particles are very effective for the transformation and detoxification of a variety of common environmental pollutants, including chlorinated organic solvents, organochlorine pesticides, and polychlorinated biphenyls (PCBs). According to Zhang (2003), Fe-mediated reactions should produce an increase in pH and a decrease in the solution redox potential created by the rapid consumption of oxygen, other potential oxidants, and the production of hydrogen. Although batch reactors produce pH increases of 2–3 and an oxidation–reduction potential (ORP) range of –500 to –900 mV, it is expected that the pH and ORP would be less dramatic in field applications where other mechanisms reduce the chemical changes (Zhang 2003). Previous work showing an increase of pH by 1 and an ORP in the range of –300 to –500 mV supports this assessment (Elliott and Zhang 2001; Glazier et al. 2003). Zhang (2003) also showed that modifying Fe nanoparticles could enhance the speed and efficiency of the remediation process.

The first field application was reported in 2000. Nanoparticles have been shown to remain reactive in soil and water for up to 8 weeks and can flow with the groundwater for >20 m. In one study, Zhang (2003) produced a 99 % reduction of TCE within a few days of injection.

Because nanoscale particles are so small, Brownian movement or random motion, rather than wall effects, dominates their physical movement or transport in water. The movement of micrometer-scale particles, especially microscale metal particles, is largely controlled by gravity-induced sedimentation because of their size and high density. In the absence of significant surface electrostatic forces, nanosized particles can be easily suspended in water during the design and manufacturing stages, thus providing a versatile remediation tool that allows direct injection as a liquid into the subsurface where contaminants are present. Coating the Fe particles to improve mobility and catalytic reaction rates is important. Some of the particles flow with the groundwater and remain in suspension for various amounts of time, whereas others are filtered out and bind to soil particles, providing an in situ treatment zone that could hold back emanating plumes (Henn and Waddill 2006).

The high reactivity of nZVI particles is in part a direct result of their high specific surface area. For example, nZVI produced by the borohydride method has surface areas in the range of 20–40 m²/g, which can yield 10–1,000 times greater reactivity compared with granular Fe, which has a surface area <1 m²/g (Wang and Zhang 1997). nZVI's small particle size also allows more of the material to penetrate into soil pores, and it can be more easily injected into shallow and deep aquifers.

Initially, Fe nanoparticles have a core of ZVI and an outer shell of Fe oxides, which suggest the following redox reactions:



where s is solid, aq is aqueous, g is gas, and l is liquid (Matheson and Tratnyek 1994).

Although Fe nanoparticles have been shown to have a strong tendency to form microscale

aggregates, possibly because of their weak surface charges, coatings can be applied to change the surface properties. These different forms of Fe could be useful for the separation and transformation of a variety of contaminants, such as chlorinated organic solvents, organochlorine pesticides, PCBs, organic dyes, various inorganic compounds, and the metals As(III) (trivalent arsenic), Pb(II) (bivalent lead), copper [Cu(II) (bivalent copper)], Ni(II) (bivalent nickel), and Cr(VI) (hexavalent chromium) (Sun et al. 2006).

Nanoremediation, particularly the use of nZVI, has site-specific requirements that must be met in order for it to be effective. Adequate site characterization is essential, including information about site location, geologic conditions, and the concentration and types of contaminants. Geologic, hydrogeologic, and subsurface conditions include composition of the soil matrix, porosity, hydraulic conductivity, groundwater gradient and flow velocity, depth to water table, and geochemical properties (pH, ionic strength, dissolved oxygen, ORP, and concentrations of nitrate, nitrite, and sulfate). All of these variables need to be evaluated before nanoparticles are injected to determine whether the particles can infiltrate the remediation source zone and whether the conditions are favorable for reductive transformation of contaminants. The sorption or attachment of nanoparticles to soil and aquifer materials depends on the surface chemistry (i.e., electrical charge) of soil and nanoparticles, groundwater chemistry (e.g., ionic strength, pH, and presence of natural organic matter), and hydrodynamic conditions (pore size, porosity, flow velocity, and degree of mixing or turbulence). The reactions between the contaminants and the nZVI depend on contact or probability of contact between the pollutant and nanoparticles (U.S. EPA 2007, 2008).

Degradation of Pollutants Using Bismuth Vanadate (BiVO₄) Photocatalyst

One of the promising non-titania-based visible-light-driven semiconductor photocatalyst is bismuth vanadate (BiVO₄). It was applied as catalyst in oxidative dehydrogenation of ethyl

benzene to styrene (Kudo et al. 1999) and as photocatalyst where O₂ was successfully evolved from aqueous silver nitrate solution under visible-light radiation (Kudo et al. 2001). There are exactly three main crystal forms of BiVO₄, known as tetragonal zircon-type structure, tetragonal scheelite structure, and monoclinic distorted scheelite structure (Gotic et al. 2005). The color of BiVO₄ varies from inhomogeneously yellow brown to homogeneously lemon yellow and depends on many factors including phase composition, stoichiometry, particle size, and morphology. The photocatalytic activity of BiVO₄ has also been reported to be strongly influenced by the crystal structure; monoclinic BiVO₄ showed better photoactivity than tetragonal (Kudo et al. 1999).

Several synthesis methods have been used to prepare monoclinic BiVO₄ such as sonochemical method (Zhou et al. 2006), solid-state reaction (Gotic et al. 2005), reflux (Zhou et al. 2007), solgel (Hirota et al. 1992), and hydrothermal method (Liu et al. 2003; Zhang and Zhang 2009; Zhang et al. 2006, 2009). The photocatalytic activities of BiVO₄ nanocrystals prepared by sonochemical methods, evaluated by decolorization of methyl orange under visible-light irradiation, showed better photodegradation rate (95 % in 30 min) than that of sample prepared by solid-state reaction (8 %).

The photocatalytic activities of BiVO₄ were evaluated by degrading methylene blue (MB) dye solution under visible-light irradiation. A 23 W light bulb was used as a visible-light source and the experiments were carried out at room temperature for 4 h. Prior to photocatalysis experiment, the amount of MB dye removed via photolysis and adsorption process was determined. Eleven percent of the dye was removed via photolysis after 4 h of irradiation time. However, under visible-light irradiation, significant increase in the percentage removal of MB was observed. Even though higher percentage of MB photodegraded by BiVO₄ has been reported, the authors have used a much higher intensity of light (200 W of Xe arc lamp) (Yu et al. 2009) compared to these studies (23 W). This indicates the potential

of the prepared BiVO_4 to be used as photocatalyst in photodegrading MB dye at low light intensity. The removal of MB dye by BiVO_4 is influenced by the surface area and the crystal structure of the catalyst. The higher the surface area of the catalyst, the higher is the removal by adsorption process. Removal of MB via photocatalytic processes is more dominant than adsorption process for a more distorted monoclinic scheelite BiVO_4 (Abdullah et al. 2009).

Degradation of Pollutants Using CdS

As an important II–IV compound semiconductor, CdS, with direct bandgap energy of 2.4 eV at room temperature, has attracted much attention because of its unique properties and potential application in light-emitting diodes, flat-panel displays, solar cells, photocatalysis, and thin-film transistors. Since a material's properties depend greatly on its morphological features, nanostructured CdS with different sizes, shapes, and dimensionalities has been fabricated and characterized. Extensive studies have prepared CdS nanostructures with various shapes, such as nanowires, nanobelts, and self-organized spheres on the scale of micro-/nanometers. The size, shape, and crystalline structure of semiconductor nanocrystallites, which lead to considerable changes in the recombination of electrons and holes trapped at spatially separated donors and acceptors, are important in determining their optical properties. For instance, Xu et al. reported the synthesis of nanostructured flower-like CdS by a solvothermal method using ethylenediamine as a structure-directing template. Qing Xia et al. successfully synthesized a wide range of cadmium sulfide (CdS) three-dimensional (3D) polycrystalline walnut-like nanocrystals by a solvothermal method with polyvinylpyrrolidone (PVP) as stabilizer. Lin et al. synthesized uniform-sized CdS hollow nanospheres via hydrothermal treatment of aqueous solutions of cadmium acetate and thiourea and reported that the spheres could be made solid or hollow by manipulating the precursor Cd/S molar ratio in the synthesis system. Li et al. synthesized CdS microspheres assembled from high-quality nanorods by a hydrothermal method using PVP

as a surfactant. Danjun Wang et al. synthesized novel 3D dendritic CdS nanoarchitectures via a facile template-free hydrothermal process using CdSO_4 and thiourea as precursors and cetylpyridinium chloride (CPC) as a capping reagent. Zhang et al. prepared CdS submicro- and microspheres by a convenient hydrothermal process through the reactions of CdCl_2 and $\text{Na}_2\text{S}_2\text{O}_3$ in aqueous solution at a relatively low temperature. The solution phase or hydrothermal or solvothermal technique has been demonstrated as an effective method for preparing low-dimensional nanomaterials from sulfides. Liu et al. (2012) have synthesized TiO_2 film coated on fiber glass cloth by solgel method and further sensitized by CdS nanoparticles using a sequential chemical bath deposition technique. Gaseous benzene was adopted as a model pollutant to evaluate the photocatalytic performances of the supported TiO_2 films sensitized with variable content of CdS nanoparticles, which are obtained by adjusting the concentration of Cd_2+ or S_2- precursor solution. Along with the increase of the CdS amount, the photocatalytic activity of these samples initially increases and then shows a downward trend. When the concentration of Cd_2+ or S_2- precursor solution achieved 0.005 M, the sample performs the best photocatalytic property and the degradation efficiency reaches 92.8 % and 32.7 % under uv–vis and visible-light irradiation, respectively. The enhancement of the photocatalytic activity could be attributed to the formation of micro-heterojunction. However, a thick CdS sheath-covered catalyst surface will form when a high concentration of Cd_2+ or S_2- solution is used. The low photogenerated electron–hole pairs' separation efficiency and the photo corrosion process of CdS decrease the photocatalytic activity gradually.

Single-crystalline CdS nanoparticles were synthesized for the first time by the composite-molten-salt (CMS) method, which had numerous advantages including one step, ambient pressure, low temperature, template free, and low cost. The influence of temperature, growth time, and amount of salts on the morphology of CdS nanoparticles was systematically investigated.

It shows that a smaller size of CdS nanoparticles can be obtained under lower temperature, less growth time, and more composite salts. UV–vis reflection spectrum of the nanoparticles reveals that the nanoparticles have a bandgap of 2.34 eV. Photoluminescence spectrum was also carried out to explore its optical property. Photocatalytic degradation of rhodamine B (RhB) and methylene blue (MB) in the presence of the CdS nanoparticles was compared with that in the presence of the commercial TiO₂ nanoparticles under the simulated sunlight (Li et al. 2012).

Doping of Photocatalysts for Effective Degradation

Doping of TiO₂ has been an important approach in bandgap engineering to change the optical response of semiconductor photocatalysts. The main objective of doping is to induce a bathochromic shift, i.e., a decrease of the bandgap or introduction of intra-bandgap states, which results in the absorption of more visible light. Doping may lead to photocatalytic systems that exhibit enhanced efficiency (Carp et al. 2004). There are three different main opinions regarding modification mechanism of TiO₂ doped with nonmetals:

1. Bandgap narrowing: Asahi et al. (2001) found N 2p state hybrids with O 2p states in anatase TiO₂ doped with nitrogen because their energies are very close, and thus, the bandgap of N-TiO₂ is narrowed and able to absorb visible light.
2. Impurity energy level: Hiroshi et al. (2003) stated that TiO₂ oxygen sites substituted by the nitrogen atom form isolated impurity energy levels above the valence band. Irradiation with UV light excites electrons in both the VB and the impurity energy levels, but illumination with visible light only excites electrons in the impurity energy level.
3. Oxygen vacancies: Ihara et al. (2003) concluded that oxygen-deficient sites formed in the grain boundaries are important to emerge vis-activity, and nitrogen doped in part of oxygen-deficient sites is important as a blocker for reoxidation.

Noble metals including Pt, Ag, Au, Pd, Ni, Rh, and Cu have been reported to be very effective at enhancing photocatalysis by TiO₂ (Rupa et al. 2009; Adachi et al. 1994; Wu and Lee 2004). Because the Fermi levels of these noble metals are lower than that of TiO₂, photoexcited electrons can be transferred from the conduction band of TiO₂ to metal particles deposited on the surface of TiO₂, while photogenerated holes in the valence band remain on TiO₂. This greatly reduces the possibility of electron–hole recombination, resulting in efficient separation and higher photocatalytic activity.

Sustaining a Clean Environment

Mitigating Ultimate Climate Change Impact

Nanoscale metal organic frameworks (MOFs) and zeolite imidazole frameworks (ZIFs) are promising CO₂ sorbents with high adsorption capacity, selectivity, and reversibility. However, the first generation of nanoscale MOFs and ZIFs can only perform a single function, i.e., CO₂ separation. Thus, their use alone might not lead to the revolutionary advances needed to significantly decrease the atmospheric release of greenhouse gases by capturing CO₂ and converting it to useable products (e.g., fuels and chemicals). The vision for the 5–10 year time frame is that convergence between nanotechnology, chemical separations, catalysis, and systems engineering will lead to revolutionary advances in CO₂ capture and conversion technologies, including:

- Nanoscale sorbents containing functionalized size- and shape-selective molecular cages that can capture CO₂ and convert it to useable products
- Nanoporous fibers and/or membranes containing functionalized size- and shape-selective molecular cages that can capture CO₂ and convert it to useable products

In addition to CO₂ capture, transformation, and storage, geoengineering is being considered

as a potential climate mitigation technology. The ultimate goal of geoengineering is to reduce global warming by developing and deploying large-scale “cooling” systems in the stratosphere.

- Cost-effective and environmentally acceptable solutions to the global sustainability challenges, including energy, water, environment, and climate change

Reducing Global Warming

As explained, clean nanotechnologies have the potential to produce plentiful consumer goods with much lower throughput of materials and much less production of waste and to reduce sources of chemical pollution. According to the vision of Drexler, the natural feedstock will be the input materials; using them will emit the same materials, which can be reused again. With NT, energy through solar cells and clean fuels from solar energy, air, and water can be made. With cheap solar and fuel energy, coal and petroleum can be replaced, ignored, and left in the ground. Like this many sources, pollution can be step by step eliminated.

The release of other gases, such as chlorofluorocarbons (CFCs) used in foaming plastics, is often a side of primitive manufacturing processes. Foaming plastics will hardly be used during molecular manufacturing. These materials can be replaced or controlled, and they include the gases most responsible for ozone depletion. Nanotechnology based devices/systems also absorb CO₂ that could help mitigation of global warming and bring the planet’s ecosystem back into balance.

Sustaining Biodiversity

In the next 10+ years, it is expected that nanotechnology will contribute significantly to the preservation of biodiversity through the development and implementation of:

- Advanced sensors and devices for monitoring ecosystem health (e.g., soil/water composition, nutrient/pollutant loads, microbial metabolism, and plant health)
- Advanced sensors and devices for monitoring and tracking animal migration in terrestrial and marine ecosystems

Socioeconomic Aspects for Sustainable Development

Nanoscience is at the unexplored frontiers of science and engineering, and it offers one of the most exciting opportunities for innovation in technology. It is important to have social scientists study the processes by which nanoscience is conducted and nanotechnology is developed even at this early stage. The knowledge gained will help policymakers and the public understand how nanoscience and nanotechnology are advancing, how those advances are being diffused, and how to make necessary course corrections. Insight into innovation process will also grow. Social scientists and scholars possess many effective ways of studying the development of new technology and its implications for society. Applications of a scientific idea to a technical problem, technology transfer, and an introduction of products into the marketplace can be tracked through statistics on research and development investments, patent applications, and new products and services. The societal impacts of nanotechnology may be of great scope and variety. The domains and measures of potential social impacts include economic growth, employment statistics, social transformations, and medical statistics.

Nanoscience may also enable new materials and technologies that reduce economic dependence on other kinds of natural resources. As the global economy continues to be transformed by new technology, a keen competition will develop for talent, intellectual property, capital, and technical expertise. Technical innovations will increasingly shape economies and market robustness. Technology will continue to drive global and domestic GDP. In the economic environment, nanotechnology comprehensively integrated into the economy due to high readiness, effective strategic planning, and widespread investments

by business, education, labor, and government. The study of socioeconomic aspects of nanoscale science and technology (NST) will provide green nanoproducts, nanoprocesses, and their applications in science, engineering, and technology for sustainable development.

Priorities for Promoting Nanotechnology

Educate and train a new generation of scientists and workers skilled in nanoscience and nanotechnology at all levels. Develop scientific curricula and programs designed to:

- (a) Introduce nanoscale concepts into mathematics, science, engineering, and technological education
- (b) Include societal implications and ethical sensitivity in the training of nanotechnologist
- (c) Produce sufficient number and variety of well-trained social and economic scientists prepared to work in the nanotechnology area
- (d) Develop effective means for giving nanotechnology students an interdisciplinary perspective while strengthening the disciplinary expertise they will need to make maximum professional contributions
- (e) Establish fruitful partnerships between industry educational institutions to provide nanotechnology students adequate experience with nanoscale fabrication, manipulation, and characterization techniques

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An Overview of Environmental Remediation Using Photocatalyst

8

Dimple P. Dutta

Abstract

In recent years a lot of emphasis has been placed on the role of photocatalytic oxidation in environmental remediation. In the presence of appropriate photocatalysts, harmful organic and inorganic compounds can be degraded and mineralized. The introduction of nanoparticulate photocatalysts has tremendously enhanced the catalytic efficiency of specific materials. In this chapter, the different synthetic techniques for generation of nanoparticulate photocatalysts have been discussed. An attempt has been made to explain the mechanism of photocatalysis. The different photocatalyst materials available and their suitability for various environmental remediation purposes have also been highlighted.

Keywords

Photocatalyst • Environmental remediation • Nanoparticles • TiO_2 • Bi_2O_3

Introduction

The alarming rate at which the level of environmental pollution is increasing in the world is a matter of great concern. Both developed and developing nations are struggling to combat this monumental problem. The imbalance to the ecosystem brought about by air, soil, and water pollution by anthropogenic sources needs constant remediation. Common pollutants like sulfur oxides (SO_x), nitrogen oxides (NO_x),

volatile organic compounds (VOCs), carbon monoxide (CO), ammonia (NH_3), and toxic chemicals like benzene, polycyclic aromatic hydrocarbons (PAHs), heavy metals, chlorinated organic compounds, dyes, detergents, surfactants, and harmful agro wastes are being released indiscriminately into the environment every day. With the advent of science and technology, it is expected that harmony in the global environment will be restored, and to make this possible, “photocatalyst” is expected to play a major role.

The word photocatalyst is composed of two parts, “photo” and “catalyst.” Catalyst is a substance which increases the rate of a reaction by reducing the activation energy, without being altered or consumed in the end. In a broad sense, photocatalysis is a reaction which uses light to

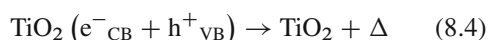
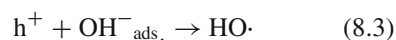
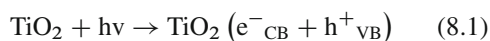
D.P. Dutta (✉)
Chemistry Division, Bhabha Atomic Research Centre,
Mumbai, Maharashtra, India
e-mail: dimpled@barc.gov.in

activate a substance which modifies the rate of a chemical reaction without being involved itself. Thus, photocatalyst is a substance which can modify the rate of chemical reaction using light irradiation. This process shows a lot of similarity with photosynthesis. Chlorophyll of plants is a typical natural photocatalyst. The difference between chlorophyll and any man-made photocatalyst is that usually chlorophyll captures sunlight to turn water and carbon dioxide into oxygen and glucose, but on the contrary photocatalyst creates strong oxidation agent and electronic holes to break down the organic matter to carbon dioxide and water in the presence of photocatalyst, light, and water. Thus, using light energy, water, and oxygen from air, the photocatalysts generate very reactive molecules (called free radicals) which are then able to break down substances into relatively harmless products. Photocatalysis is widely employed in water and air purification, self-cleaning surfaces, self-sterilizing surfaces, antifogging surfaces, anticorrosive surface treatments, lithography, photochromic materials, microchemical systems, selective and green synthesis of organic compounds, and the generation of hydrogen.

In recent years, applications to environmental cleanup have been one of the most active areas in heterogeneous photocatalysis. This is inspired by the potential application of semiconductor-based photocatalysts for the total destruction of organic compounds in polluted air and wastewater. In a heterogeneous photocatalytic system, photoinduced molecular transformations or reactions take place at the surface of a catalyst. Depending on where the initial excitation occurs, photocatalysis can be generally divided into two classes of processes. When the initial photoexcitation occurs in an adsorbate molecule which then interacts with the ground state catalyst substrate, the process is referred to as a catalyzed photoreaction. When the initial photoexcitation takes place in the catalyst substrate and the photoexcited catalyst then transfers an electron or energy into a ground state molecule, the process is referred to as a sensitized photoreaction.

Photocatalysis using semiconductors under irradiation has been extensively studied for about three decades. In 1972, Fujishima and Honda

discovered the photocatalytic splitting of water on TiO_2 electrodes (Fujishima and Honda 1972). This remarkable discovery marked the onset of photoinduced redox reactions on semiconductor surfaces. The utility of these redox reactions for environmental cleanup was demonstrated in 1977 by the photochemical oxidation of CN^- and SO_3^- using various semiconductor materials (Frank and Bard 1977). Photocatalyzed degradation of chlorinated organic compounds and photochemical sterilization of microorganism by TiO_2 established the versatility of such materials (Pruden and Ollis 1983; Hsiao et al. 1983; Matsunaga et al. 1985). Usually, semiconductors like TiO_2 are selected as photocatalysts, because semiconductors have a narrow gap between the valence and conduction bands. For photocatalysis to occur, the semiconductors need to absorb energy equal to or more than its energy gap. This movement of electrons forms e^-/h^+ or negatively charged electron/positively charged hole pairs. These holes have pH-dependent and strongly positive electrochemical potentials, in the range between +2.0 and +3.5 V, which is sufficiently positive to generate hydroxyl radicals (HO^\bullet) from water molecules adsorbed on the surface of the semiconductor (Eqs. 8.1, 8.2, 8.3). The hole can oxidize donor molecules. The electrons transferred to the conduction band are responsible for reducing reactions. The photocatalytic efficiency depends on the rate of formation of e^-/h^+ pairs in semiconductor surface and the recombination of these pairs (Eq. 8.4).



In case of TiO_2 , the band gap (E_g) is generally found to be between 3 and 3.2 eV (Hoffmann et al. 1995; Palmisano et al. 2007; Jin et al. 2010; Kumar and Devi 2011). However, the production of reactive species and the extent of photocatalysis depend on several factors like

pH of the reaction medium, surface acidity, morphology, porosity, interfacial electron transfer rate, and recombination probability of charge carriers (Hoffmann et al. 1995; Kumar and Devi 2011; Furube et al. 2001; Diebold 2003; Carp et al. 2004). Once the active species have been generated, the reactants are adsorbed onto the surface of the photocatalyst. This is followed by the oxidation of the reductant and the concomitant reduction of the oxidant by the attack of the hydroxyl radicals and conduction band electrons, respectively. The typical timescale for the processes are 100 ns and milliseconds, respectively. This means that the oxidizing power of the VB hole is always higher than that of the reducing power of the CB electrons. Moreover, there is also competition from the electron-hole recombination reaction (10 ns), and hence, the practical efficiency or quantum yield is always lesser than that of the theoretical yield.

Common Materials Used as Photocatalysts

In addition to TiO₂, many different semiconductors are able to trigger the heterogeneous photocatalytic processes. Notable among them are various metal oxides like ZnO, MoO₃, ZrO₂, WO₃, α -Fe₂O₃, SnO₂, and SrTiO₃ and metal chalcogenides like ZnS, CdS, CdSe, WS₂, and MoS₂. Materials like TiO₂, ZnO, SrTiO₃, and ZrO₂ are suitable for oxidation of organics due to their convenient band gaps. According to thermodynamic requirement, the oxidation potential of the hydroxyl radicals (2.8 V vs. NHE) and the reduction potential of the superoxide radicals (-0.28 V vs. NHE) should lie within the band gap of the photocatalyst material. The positions are derived from the flat-band potentials in a contact solution of aqueous electrolyte at pH = 1. The pH of the electrolyte solution influences the band edge positions of the various semiconductors compared to the redox potentials for the adsorbate. Thus, the redox potential of the VB hole and CB electron of these materials are sufficiently positive and sufficiently negative to generate hydroxyl radicals and superoxide radicals, respectively. Stability of the material toward photocorrosion is another

important factor. Materials like ZnO and CdS which have only one stable oxidation state are prone to decomposition by VB holes. TiO₂ has the capability to reversibly change its oxidation state from +4 to +3 and hence is more robust in this respect. Apart from this, its abundance, low toxicity, good chemical stability over a wide pH range, photosensitivity, photostability, insolubility in water, low cost, and biological and chemical inertness make it one of the forerunners among photocatalyst materials. TiO₂ exists in nature in three different polymorphic forms, anatase, rutile, and brookite. Anatase phase TiO₂ ($E_g = 3.2$ eV) is more active for photocatalysis applications, even though rutile phase TiO₂ ($E_g = 3.0$ eV) possesses a smaller band gap, indicating the possibility of absorption of long wavelength radiation. This is because, the CB position of anatase TiO₂ is more negative compared to rutile, which results in the higher reducing power of anatase.

Strong light absorption and suitable redox potential are prerequisites for photocatalytic reactions. The radiation from the sun consists of approximately 5 % UV, 43 % visible, and 52 % harvesting infrared. Hence, for efficient photocatalysis, it is better to have materials that absorb in the visible region as sun's radiation has a much greater visible component compared to UV. Size of the material also plays a major role in the rate of photocatalysis. Greater surface area enhances the rate of reaction. It is due to these factors that nanomaterials are being preferred as photocatalyst materials. Nanomaterials have typical dimensions in the range of 1–100 nm, and this restriction in dimension leads to changes in the chemical and physical properties compared to that of the bulk material. The properties of nanomaterials which make it superior compared to bulk materials in their application in photocatalysis are the enhanced surface-to-volume ratio and the quantum confinement effects. Nanostructured semiconductors are expected to display enhanced performances thanks to their extremely high surface-to-volume ratio which immensely increase the density of active sites available for adsorption and catalysis. When the crystallite dimension of a semiconductor particle falls below a critical radius related to the bulk exciton diameter,

the charge carriers appear to behave quantum mechanically as a simple particle in a box (Kamat 1993; Brus 1991; Weller 1993; Weller et al. 1993; Gratzel 1991; Steigerwald and Brus 1989; Bawendi et al. 1992). As a result of this confinement, the band gap increases and the band edges shift yielding larger redox potentials. The solvent reorganization free energy for charge transfer to a substrate, however, remains unchanged. The increased driving force and the unchanged solvent reorganization free energy in size-quantized systems are expected to increase the rate constant of charge transfer in the normal Marcus region (Marcus and Sutin 1985; Marcus 1990; Lewis 1991). Thus, the use of size-quantized semiconductors may result in increased photo-efficiencies for systems in which the rate-limiting step is charge transfer (Hoffman et al. 1992a, b). Furthermore, the size-dependent band gap allows tuning of the electron-hole redox potentials to achieve selective photochemical reactions. An effective photocatalytic process requires highly crystalline nanosized semiconductors with low defect concentration to increase the efficiency of the electron-hole pair separation (Hoffmann et al. 1995; Mills and Le Hunte 1997; Beydoun et al. 1999), whereas a narrow-size distribution allows to successfully modulate the size-dependent redox properties.

In the recent years, a lot of efforts have been made to increase the efficiency of the electron-hole pair separation. In fact, two critical processes determine the overall catalytic efficiency. These are the competition between the recombination and the trapping of the charge carriers, followed by the competition between the recombination of the trapped carriers and the interfacial charge transfer. Improved charge separation and inhibition of charge carrier recombination is essential in enhancing the overall quantum efficiency for interfacial charge transfer (Bedja and Kamat 1995). This can be achieved by modifying the properties of the particles by selective surface treatment. Several approaches have been explored. These have included surface modification of the semiconductor particles with redox couples or noble metals (Aruna and Patil 1996).

Another approach has involved the coupling of two semiconductor particles with different electronic energy levels (Bedja and Kamat 1995).

In order to extend the photocatalytic activity in the region of visible light, and in order to achieve a better use of solar radiation, tuning the band gap response of titania to the visible region has been tried out using various methods. Doping trace impurities in the structure of TiO_2 in order to obtain materials with photocatalytic activity maximized in the visible region are strategies that have been widely used (Ohno et al. 2003; Li et al. 2005; Zaleska et al. 2010). These strategies include doping with transition metals and non-metals and the inclusion of low-valence ions on the surface of the semiconductor (Nogueira and Jardim 1998; Yamashita et al. 2001; Cavaleiro et al. 2008). Certain metals, when incorporated to titanium dioxide, are able to decrease the band gap, making possible in some cases its application in solar photocatalysis. Furthermore, they can contribute to minimize the electron-hole recombination, increasing the photocatalytic efficiency of the semiconductor.

Coupled semiconductor photocatalysts provide an interesting way to increase the efficiency of a photocatalytic process by increasing the charge separation and extending the energy range of photoexcitation for the system. In case of the composite (coupled) semiconductor-semiconductor photocatalyst CdS-TiO_2 , the energy of visible light is too small to directly excite the TiO_2 portion of the photocatalyst, but it is large enough to excite an electron from the valence band across the band gap of CdS ($E_g = 2.5$ eV) to the conduction band. The hole produced in the CdS valence band from the excitation process remains in the CdS particle while the electron transfers to the conduction band of the TiO_2 particle. The electron transfer from CdS to TiO_2 increases the charge separation and efficiency of the photocatalytic process. The separated electron and hole are then free to undergo electron transfer with adsorbates on the surface. Nanosized coupled CdS-TiO_2 semiconductor would enhance the electron transfer rate exploiting the high surface-to-volume ratio. Moreover, in a very small

cluster, the photogenerated charges readily reach the surface limiting the recombination process (Linsebigler et al. 1995).

Metal nanoparticles highly dispersed on an active oxide are a classical example of bifunctional catalysts. Here chemisorptive activation of substrate on the metal is enhanced by charge transfer between the two different materials, while the oxide promotes oxygen atom transfer. Interestingly, small noble metals exhibit a considerable shift of their redox potential toward negative values in the nanosized regime, thus serving as efficient electron transfer mediators as well as reductants themselves. Furthermore, due to the size dependence of semiconductor nanocrystal band gap, the redox potentials of photogenerated holes and electrons can be eventually tuned, allowing redox process that are forbidden for extended solids.

Synthesis and Characterization

Among all the photocatalyst materials discussed above, oxide materials like TiO_2 is the most promising and is expected to play a major role in tackling serious environmental and pollution challenges. These materials can be synthesized by solution or gas-phase routes. The most popular method of synthesis of metal oxides including TiO_2 is their precipitation from the solutions of the corresponding salts with ammonia, alkalis, and alkali-metal carbonates. Titanium dioxide with different phase compositions, namely, amorphous TiO_2 , anatase, brookite, or rutile, can be synthesized by varying the temperature, the synthesis time, and pH of the medium. Hydrolysis of alkoxides and halides of titanium at low pH of 2–6 yields basic salts, whereas higher pH results in the formation of hydrates like $\text{TiO}_2 \cdot n\text{H}_2\text{O}$, where n depends on the ageing and drying conditions (Dzis'ko et al. 1978). Other solution-phase techniques include sol–gel method, sol method (nonhydrolytic sol–gel), hydrothermal synthesis, solvothermal synthesis, micelle and inverse micelle method, combustion synthesis, electrochemical synthesis, sonochemical synthesis, and microwave synthesis methodologies.

The sol–gel process normally proceeds via an acid-catalyzed hydrolysis step of titanium(IV)

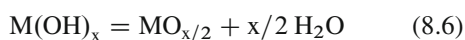
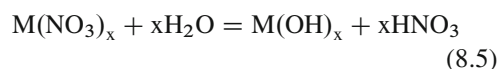
alkoxide followed by condensation (Bessekhouad et al. 2003; Chemseddine and Moritz 1999; Kim and Kim 2001, 2002; Kuznetsova et al. 2005; Lee and Yang 2005a, b; Li et al. 2004b; Liu et al. 2002; Reddy et al. 2001; Manorama et al. 2001; Moritz et al. 1997; Oskam et al. 2003; Pottier et al. 2001, 2003; Sugimoto et al. 1997, 2002; Sugimoto and Zhou 2002; Zhang and Banfield 1998, 2000, 2002, 2005; Zhang et al. 2001). In a typical sol–gel process, a colloidal suspension, or a sol, is formed from the hydrolysis and polymerization reactions of the precursors, which are usually inorganic metal salts or metal organic compounds such as metal alkoxides. Loss of solvent then converts the liquid sol into solid gel. The sol can be spun or dip coated onto substrates to give thin films. Heating of the polymerized product, to remove solvent, yields dense xerogel. Supercritical extraction of the solvent yields a highly porous and extremely low-density material called aerogel. Generally the development of Ti–O–Ti chains is favored with low content of water, low hydrolysis rates, and excess titanium alkoxide in the reaction mixture. With medium water content and high rate of hydrolysis, $\text{Ti}(\text{OH})_4$ is the main product. Highly crystalline anatase TiO_2 nanoparticles with different sizes and shapes could be obtained with the polycondensation of titanium alkoxide in the presence of tetramethylammonium hydroxide (Chemseddine and Moritz 1999; Moritz et al. 1997). Various amines like TEOA, diethylenetriamine, ethylenediamine, trimethylenediamine, and triethylenetetramine are also used as the shape controllers of the TiO_2 nanomaterials and act as surfactants. The shape control is attributed to the tuning of the growth rate of the different crystal planes of TiO_2 nanoparticles by the specific adsorption of shape controllers to these planes under different pH conditions.

Sometimes titanium halides are reacted with different oxygen donor molecules, viz., metal alkoxides or organic ethers. The condensation between Ti–Cl and Ti–OR leads to the formation of Ti–O–Ti bridges. This is known as the sol method. The reaction rate can be altered changing the R group on the metal alkoxides, and the size of the resultant TiO_2 nanoparticles depend on the X group of the halide used. Surfactants have

been widely used in the preparation of a variety of nanoparticles with good size distribution and dispersity (Burda et al. 2005; Murray et al. 2000). Adding different surfactants as capping agents results in the formation of monodispersed TiO₂ nanoparticles (Scolan and Sanchez 1998; Cozzoli et al. 2003). With the aid of surfactants, different sized and shaped TiO₂ nanorods can be synthesized (Cozzoli et al. 2003, 2004a, b, 2005a, b; Joo et al. 2005; Jun et al. 2003; Zhang et al. 2005; Buonsanti et al. 2006). The concentration of surfactant also plays a role in determining the shape of the nanoparticle.

A microemulsion is a thermodynamically stable dispersion of two immiscible fluids; the system is stabilized by added surfactant(s). Aggregates of surfactant molecules dispersed in a liquid colloid are called micelles when the surfactant concentration exceeds the critical micelle concentration (CMC). In micelles, the hydrophobic hydrocarbon chains of the surfactants are oriented toward the interior of the micelle, and the hydrophilic groups of the surfactants are oriented toward the surrounding aqueous medium. Reverse micelles are formed in nonaqueous media, and the hydrophilic headgroups are directed toward the core of the micelles while the hydrophobic groups are directed outward toward the nonaqueous media. The micelles are dynamic in nature and collide frequently due to Brownian motion. They coalesce and break apart resulting in exchange of materials between them. This exchange process is fundamental to nanoparticle synthesis inside reversed micellar “templates,” allowing different reactants solubilized in separate micellar solutions to react upon mixing. TiO₂ and various other oxide materials can be synthesized using micelle or inverse micelle synthesis technique (Hong et al. 2003; Kim et al. 2005; Li and Wang 1999; Li et al. 2004a, b; Lim et al. 2004a, b; Lin et al. 2002; Yu et al. 2001; Zhang et al. 2002). Particle growth has shown to be strongly dependent on intermicellar exchange rates. The resultant particle size appears to be dependent on type of solvent, type of surfactant/cosurfactant, concentration of the reagents, ionic additives, and composition, i.e., water-to-surfactant ratio. The as-prepared material is generally amorphous in nature, and some

heat treatment is required to induce high crystallinity. Hydrothermal synthesis is generally defined as crystal synthesis or crystal growth under high temperature and high pressure in aqueous conditions from substances which are insoluble in water at ordinary temperature and pressure (<100 °C, <1 atm). Since ionic product (K_w) has a maximum value of around 250–300°C, hydrothermal synthesis is usually carried out below 300 °C. The critical temperature and pressure of water are 374 °C and 22.1 MPa, respectively. Hydrothermal synthesis is normally conducted in steel pressure vessels called autoclaves with or without Teflon liners under controlled temperature and/or pressure with the reaction in aqueous solutions. The temperature and the amount of solution added to the autoclave largely determine the internal pressure produced. The formation mechanism of metal oxide particles from metal nitrate solution proceeds in two steps. First, hydrated metal ions are hydrolyzed to metal hydroxide. Then, metal hydroxides proceed to precipitate as metal oxides through dehydration (Adschiri et al. 2000a, b):



Hydrothermal synthesis in supercritical water has advantages for synthesis of multi-metal oxide compounds because the reaction rate is enhanced more than ten times that under the conventional hydrothermal conditions owing to the low dielectric constant (<10). Also products with high crystallinity are obtained. The particle size of metal oxide depends on the hydrolysis rate and solubility of the metal oxide. TiO₂ particles synthesized hydrothermally under supercritical conditions have high crystallinity and large surface areas which are responsible for good photocatalytic performance (Hayashi and Torii 2002). There are numerous reports on synthesis of TiO₂ nanomaterials using hydrothermal technique (Chae et al. 2003; Cot et al. 1998; Yang et al. 2000, 2001a, b, 2002, 2003, 2004a, b).

Solvothermal synthesis is also frequently used for synthesis of oxide materials (Li et al. 2006; Xu et al. 2006; Wang et al. 2005; Wen et al. 2005a, b, c; Yang and Gao 2006). The process is quite similar to hydrothermal synthesis and involves the use of a nonaqueous solvent under moderate to high pressure (1–10,000 atm) and temperature (100–1,000 °C) that facilitates the interaction of precursors during synthesis. The solvent plays an important role in determining the crystal morphology. Solvents with different physical and chemical properties can influence the solubility, reactivity, and diffusion behavior of the reactants. The polarity and coordinating ability of the solvent can influence the morphology and the crystallization behavior of the final products. In a typical synthetic method, titanium isopropoxide is dissolved in toluene (or any other suitable solvent) and kept in autoclave for 3 h at 250 °C. Adding various surfactants to the reaction mixture yields nanomaterials of various shapes.

Solution combustion synthesis (SCS) process involves a self-sustained reaction in homogeneous solution of different oxidizers (e.g., metal nitrates) and fuels (e.g., urea, glycine, hydrazides). It is a simple and rapid technique to synthesize nanomaterials. Depending on the type of the precursors, as well as on conditions used for the process organization, the SCS may occur as either volume or layer-by-layer propagating combustion modes. This process not only yields oxide nanomaterials but also allows uniform (homogeneous) doping of trace amounts of impurity ions in a single step. Noble metal-doped ceria and titania, which are used as catalysts for air and water remediation, have better catalytic properties when synthesized using SCS process. This is attributed to the ionic substitution, which is not possible in any other chemical route including sol-gel process. SC synthesized nanoTiO₂ (10 nm) has shown higher rate for carcinogenic hexavalent chromium Cr(VI) reduction compared to commercial Degussa P-25 TiO₂ (Aarthi and Madras 2008). This may immensely benefit the metal plating and metal finishing industries. Also, SCS-derived porous nanocrystalline MgO has proved to be

an eco-friendly and nontoxic adsorbent which could remove 97 % of fluoride present in water as compared to 76 % by regenerated MgO and 17 % by commercial grade MgO (Nagappa and Chandrappa 2007).

Electrochemical synthesis is another technique which is widely used for generating self-assembled vertically oriented TiO₂ nanotube arrays on Ti surface. It is generally done using anodization of titanium foil in a fluoride-based electrochemical bath (Mor et al. 2006; Raja et al. 2005; Kitano et al. 2006; Mohapatra et al. 2007). These nanotubes have remarkable properties since (1) the effective surface area is increased many folds, (2) the diffusion of photogenerated holes across the wall of the nanotubes can be made efficient by making the wall thickness comparable to the diffusion length of the holes, (3) the electron mobility is improved since the conduction path is one dimensional with minimal recombination loss as compared to the electron conduction in nanoparticles, and (4) the dimensions (length, wall thickness, and internal diameter) of the nanotubes can be easily tuned to meet the specific needs. The tube length can be controlled by varying the anodization time, the diameter of the tubes is adjusted by changing the applied anodization voltage, and the growth rate of the nanotubes is varied by ultrasonic excitation of the electrochemical bath. TiO₂ nanowires can also be obtained via electrodeposition by using an anodic alumina membrane (AAM) template (Lei et al. 2001; Liu and Huang 2004). In a typical process, the pulsed electrodeposition is carried out in 0.2 M TiCl₃ solution (pH ~2), and titanium and/or its compound is deposited into the pores of the AAM. By heating the above deposited template at 500 °C for 4 h and removing the template, pure anatase TiO₂ nanowires can be obtained.

Ultrasound is considered to be an important tool for the synthesis of a variety of nanomaterials including high-surface-area transition metals, alloys, carbides, oxides, and colloids. When liquids are irradiated with ultrasonic irradiation, it leads to cavitation. Ultrasonic cavitation is concerned with the formation, growth, and implosive collapse of bubbles. Ultrasonic cavitation

produces a variety of physical and chemical effects, such as high temperature ($>5,000$ K), pressure (>20 MPa), and cooling rate ($>10^{10}$ K s $^{-1}$), which provide a unique environment for chemical reactions under extreme conditions. Various groups have synthesized TiO₂ nanoparticles using sonochemical technique (Blesic et al. 2002; Guo et al. 2003; Huang et al. 2000; Jokanovic et al. 2004; Meskin et al. 2006; Xia and Wang 2002; Yun et al. 2004; Zhu et al. 2001). Depending on the precursor and solvent medium used for the reaction, different morphologies of the products were obtained. In a typical reaction process, an aqueous solution of titanium isopropoxide is made basic by adding ammonia solution, and the resultant mixture is sonicated for an hour with high-intensity (100 W/cm²) ultrasonic radiation operating at 20 kHz, under air for 2 h. After sonication, the precipitate is washed with water and centrifuged. Final washing is done with ethanol, and the residue is heated in furnace under air at ~ 500 °C. The powder XRD pattern and corresponding TEM image for nanoTiO₂ obtained from sonochemical synthesis is shown in Fig. 8.1a and b, respectively. Pure anatase phase of TiO₂ is obtained, and the size of the spherical nanoparticles range between 20 and 25 nm.

Microwave synthesis of photocatalyst material is also gaining popularity. Microwave radiation is known to have a faster heating rate than the conventional heating through conduction and convection. The microwave radiation heats up a material through its dielectric loss, which converts the radiation energy into thermal energy. The major advantages of using microwaves include rapid heat transfer and also volumetric and selective heating. It is also a well-recognized green chemistry technique. Various TiO₂ nano-materials have been synthesized using microwave radiation (Gressel-Michel et al. 2005; Ma et al. 2005; Szabo et al. 2001; Wu et al. 2005a, b, c; Yamamoto et al. 2002). In microwave synthesis, the growth rate of products is very high for small particle sizes, and, nearly always, the product exhibits a narrow particle-size distribution as a consequence of fast homogeneous nucleation.

Apart from solution-phase techniques discussed above, gas-phase techniques are also used

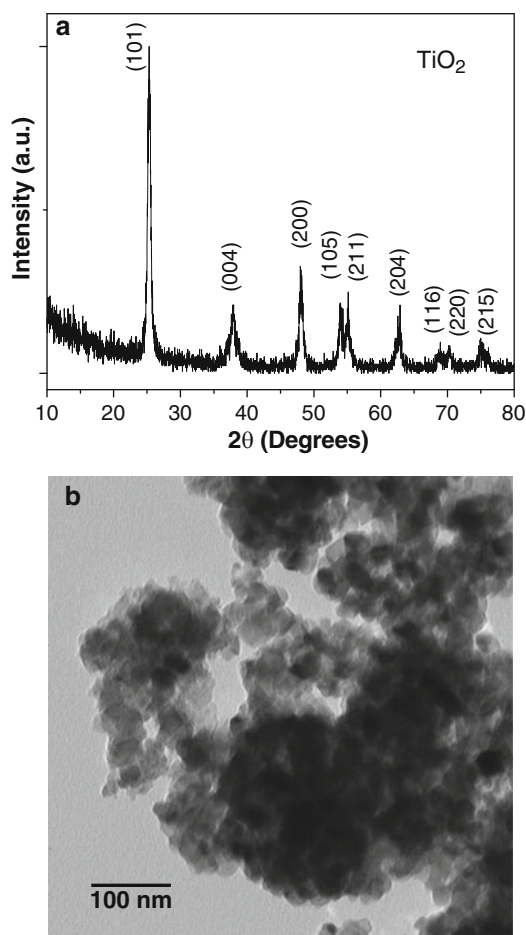


Fig. 8.1 (a) Powder XRD pattern. (b) TEM image of TiO₂ nanoparticles

for synthesis of photocatalyst materials. Some of the gas-phase techniques include chemical vapor deposition (CVD), physical vapor deposition, and spray pyrolysis deposition. Vapor deposition refers to any process in which materials in a vapor state are condensed to form a solid-phase material. Vapor deposition processes usually take place within a vacuum chamber. If there is no chemical reaction, the process is called physical vapor deposition (PVD). CVD occurs only when there is a chemical reaction. In PVD, materials are first evaporated and then condensed to form a solid material. Thus to form TiO₂, Ti metal powder is generally placed in a quartz boat and heated in a partially evacuated furnace pumped with argon gas. TiO₂ layer gets coated on the substrate

(Wu et al. 2005c; Xiang et al. 2005). In case of CVD, precursors like titanium isopropoxide and titanium acetylacetonate are used. These precursors are pyrolyzed in a mixed helium/oxygen or N_2/O_2 atmosphere, using liquid precursor delivery (Seifried et al. 2000; Ayllon et al. 1999; Pradhan et al. 2003; Wu and Yu 2004).

Photocatalytic Degradation of Organic Compounds Under UV and Visible Radiation

For environmental remediation, the major classes of compounds under scrutiny include dyes, pesticides, pharmaceutical wastes, heavy metal ions and anions from industries, and phenolic and organochlorine compounds. Dyes are mostly used in textile industries, and the residues from dye fixation treatment pose a major challenge for treatment of water effluents. The dyes are classified based on their functional groups into azoic, anthraquinonic, heteropolycyclic, aryl methane, xanthene, indigo, acridine, nitro, nitroso, cyanine, and stilbene groups. Dyes are the most widely used organic substrates to test the photocatalytic activity of nanosized catalysts. Decolorization of the dye is not the absolute test for photocatalytic degradation since it does not refer to the complete removal of the organic carbon content. It is the mineralization of the dyes in terms of the total organic carbon (TOC) content that is paramount. The mechanism of CO_2 evolution follows the photo-Kolbe decarboxylation where the photocatalytic degradation leads to the formation of a radical intermediate which can undergo further transformation to yield other intermediates with smaller size (Houas et al. 2001). The order of degradation among the different dyes followed the order: indigo \approx phenanthrene > triphenyl methane > azo \approx quinoline > xanthenes \approx thiazine > anthraquinone. The heteroatoms also undergo transformation, and the sulfonate groups transform to sulfate ions, primary and secondary amines to ammonium ions, azo group to nitrogen, and halogens to their corresponding anion. The rate of decomposition in this case follows the classical

Langmuir–Hinshelwood kinetics (Ollis et al. 1991). Pesticides are rampantly used in agro-industries and contain nitrogen, phosphorous, sulfur, chlorine, and heterocyclic nitrogen atoms in their molecule. They are classified as organochlorine and organophosphorous compounds. TiO_2 is used extensively to degrade these common pesticide compounds under UV light (Konstantinou et al. 2001; Zhu et al. 2005; Moctezuma et al. 2007; Wei et al. 2009; Aungpradit et al. 2007; Yu et al. 2007). Pharmaceutical compounds are also degraded by photocatalytic decomposition under UV irradiation using TiO_2 . The time taken for mineralization is more in this case, and generally the intermediates formed are stable and more toxic compared to the parent compound. TiO_2 has been reported to mineralize pharmaceuticals like antibiotics, analgesics, antipyretics, anti-inflammatory drugs, beta blockers, and anticholesteremics (Molinari et al. 2006; Chatzidakis et al. 2008; An et al. 2010).

Presence of anions and metal ions affects the photocatalytic degradation rate of organic compounds. Generally sulfate, halide, bicarbonate, nitrate, carbonate, and oxalate anions retard the rate of decomposition of dyes by scavenging the hydroxyl radicals to form the respective anion radicals. However, oxidizing agents like persulfate and hydrogen peroxide generate more hydroxyl radicals in the reaction and hence enhance the degradation rate of the organic compounds. Metal ions like Ag^+ , Hg^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , Ni^{2+} , and Cr^{6+} are toxic, and TiO_2 is quite effective in photocatalytic reduction of these ions. Metal ion reduction occurs primarily through the formation of conduction band electrons, and hence, the presence of electron scavengers like dissolved O_2 in the system results in retardation of the reduction rate. Simultaneous oxidation of organic compound and reduction of metal ions is also an active field of research. Presence of metal ions has been found to enhance the degradation rate of certain organic compounds. It depends on a large number of factors like pH of the medium, concentration of metal ion and organic compounds, electronic state of metal ion, and competition of the reactants and products for the active photocatalyst site.

Phenolic compounds are widely used as intermediates in the synthesis of various chemicals. Photocatalytic degradation of these compounds starts with attack of hydroxyl radicals in their para-position, which consequently on further oxidation leads to the fragmentation of benzene ring to form aliphatic carboxylic acids and aldehydes. With longer exposure, shorter-chain compounds are formed which finally lead to mineralization with evolution of CO₂ and water (Sivalingam et al. 2004; Priya and Madras 2006; Li et al. 1999).

Undoped TiO₂ has a band gap of ~3.2 eV which makes it an efficient photocatalyst in the UV region. However, the efficiency of any photocatalyst increases manifold if it can be activated with visible radiation. This makes it more suitable for practical applications using solar radiation as the light source. Consequently, various methodologies have been adopted over the years to modify the band gap of TiO₂ photocatalyst. Doping of TiO₂ with various cationic/anionic substituents is one such approach (Choi et al. 1994; Serpone et al. 1994; Shah et al. 2002; Dvoranova et al. 2002; Nagaveni et al. 2004; Vinu and Madras 2008, 2009). The metal ions form inter-band energy levels above the valence band or below the conduction band, which result in the lower band gap of the doped TiO₂ materials. The efficiency of a metal ion-doped TiO₂ photocatalyst depends on whether the metal ion energy levels aid in the interfacial charge transfer or act as recombination centers. Consequently, it can lead to either increase or decrease in photocatalytic activity, and hence a generalization of the activity of metal-doped TiO₂ compared to the undoped TiO₂ is not possible for a wide class of reactions. However, anion doping in TiO₂ is more successful in reducing the band gap. It results in the creation of a new valence band by the mixing of the anion dopant and O 2p orbitals. It has been suggested that in order to elevate the valence band, the electronegativity of the nonmetal dopant should be lesser than that of oxygen, and the radius of the dopant should be comparable to that of oxygen for a more uniform distribution (Liu et al. 2010). Another school of thought suggests that the enhanced visible

light activity in anion-doped TiO₂ is due to the formation of color centers which are essentially a single or a pair of electrons associated with an oxygen vacancy (Serpone 2006).

Heterostructuring of undoped TiO₂ is another way of enhancing its photocatalytic activity in the visible region. This is done by adding narrow band gap semiconductor dopants (like CdS, PbS, CdSe, Bi₂S₃), dyes as sensitizers, and cocatalysts (Liu et al. 2010). The main idea is to restrict the recombination process of the charge carriers by isolating the oxidation reaction due to the holes and the reduction reaction due to the electrons at different sites. CdS/TiO₂, Bi₂S₃/TiO₂, Cu₂O/TiO₂, and Bi₂O₃/TiO₂ heterojunction photocatalysts have shown enhanced degradation of organic compounds under visible light irradiation compared to pure TiO₂ (Brahimi et al. 2008). Dye-sensitized degradation is also another hugely popular technique to enhance the photodegradation reaction rate under visible light (Kim et al. 2008; Georgekutty et al. 2008; Qiu et al. 2008; Ru et al. 2009; Muruganandham and Kusumoto 2009). It should be noted that the generation of electrons in the conduction band is through electron injection from the excited state of the dye in dye-sensitized system, while it is through direct band gap excitation in UV photocatalysis. Since valence band holes, which are strong oxidizing agents, are not involved in dye-sensitized systems, its degradation efficiency is expected to be lower than that in UV photocatalysis.

Apart from the very common TiO₂ photocatalyst, there are reports on various polyoxometalates, perovskites, conjugated polymers, mesoporous materials, and Bi-based oxides which exhibit comparable or better photocatalytic activity for degradation of organic compounds.

Study of Photocatalytic Activity of Sonochemically Synthesized Bi₂O₃

Bi₂O₃ has been reported to be a good candidate for heterogenous photocatalysis. Bi₂O₃ has been synthesized sonochemically using the

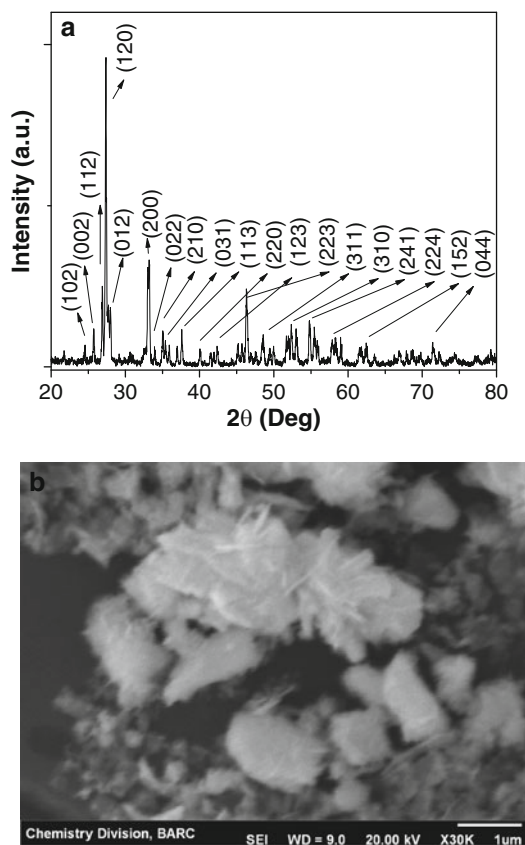


Fig. 8.2 (a) XRD pattern and (b) SEM image of sonochemically synthesized Bi_2O_3

following procedure. To an aqueous solution of $\text{Bi}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 2 ml of PEG was added. The solution was made basic by adding NH_4OH , and the pH of the solution was adjusted to 10. The system was then irradiated with high-intensity (100 W/cm^2) ultrasonic radiation operating at 20 kHz, under air for 1 h. The yellowish white powder obtained was dried at 80°C for 1 h in an oven. Powder XRD of residue obtained confirmed the formation of bismuth oxide. All the peaks in the XRD pattern (Fig. 8.2a) corresponded to the monoclinic structure of Bi_2O_3 with $P2_1/c$ space group. SEM image shows the formation of Bi_2O_3 nanorods (Fig. 8.2b). Statistical analysis of many SEM images shows that the 1D nanomaterials have diameters ranging from 80 to 100 nm and lengths up to $1 \mu\text{m}$.

The Bi_2O_3 nanorods exhibit a band gap of 3.81 eV. In order to study the photocatalytic effect of the undoped Bi_2O_3 nanorods, Rhodamine B (RhB) was chosen as the model pollutant for the photodegradation studies. The photocatalytic activity was observed by degradation of RhB in aqueous solution under UV light (310 nm). In each experiment, 0.2 g of the photocatalyst was added to 25 ml of RhB solution (0.01 mM). It was then stirred magnetically in the dark to make sure that absorption–desorption equilibrium was established between RhB and the nano Bi_2O_3 photocatalysts. It was observed that RhB is not degraded in the dark in the presence of nano Bi_2O_3 . However, negligible degradation was observed when RhB solution was exposed to UV light even in the absence of the photocatalyst. Figure 8.3 shows UV–vis spectra collected at intervals of 15 min over an exposure period of 1 h and 15 min with undoped nano Bi_2O_3 . Photodecomposition is clearly observed, and the maximum absorbance wavelength at 554 nm gradually decreased without any shift in its position. This kind of degradation of RhB can be accounted for by the breakdown of its conjugated structure brought about by the photocatalytic process. The photocatalytic results for RhB degradation show that Bi_2O_3 can effectively degrade 86 % RhB, within 75 min under UV irradiation of $\sim 310 \text{ nm}$.

Environmental Benefit of Photocatalytic Degradation

Techniques considered for environmental remediation include the general categories of biological, chemical, and physical treatments as well as the more specific extraction, immobilization, and thermal methods. Biological oxidation requires longer retention time and is not suitable for high concentrations of pollutants or for persistent pollutants. Many organic chemicals, especially which are toxic or refractory, are not amendable to microbial degradation. Biological treatment requires a

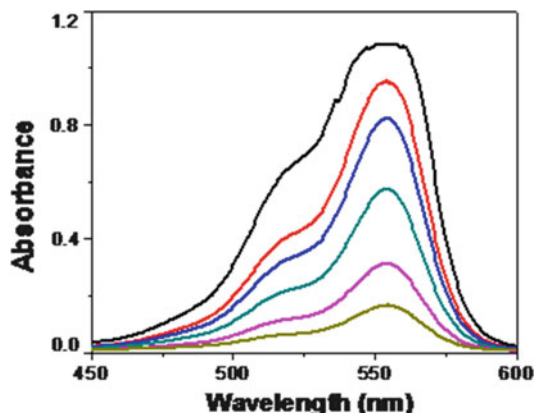


Fig. 8.3 Photodegradation of RhB collected at intervals of 15 min over an exposure period of 75 min with nano Bi_2O_3

large land area and is constrained by sensitivity toward diurnal variation, as well as toxicity of some chemicals, and less flexibility in design and operation. In particular, due to their xenobiotic nature, azo dyes are not totally degraded. Chemical methods include coagulation or flocculation combined with flotation and filtration, electroflotation, electrokinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation, or electrochemical processes. These chemical techniques are often expensive, and although the pollutants are removed, accumulation of concentrated sludge creates a disposal problem. There is also the possibility that a secondary pollution problem will arise because of excessive chemical use. Different physical methods are also widely used, such as membrane filtration processes (nanofiltration, reverse osmosis, electrodialysis) and adsorption techniques. The major disadvantages of the membrane processes is that they have a limited lifetime before membrane fouling occurs and the cost of periodic replacement must thus be included in any analysis of their economic viability. Adsorption processes do not always lead to complete mineralization and hence are not efficient for environmental remediation. Heterogeneous photocatalytic oxidation has received vast interest as a potential efficient method in

the degradation of harmful environmental contaminants. One of the major advantages of photocatalytic process over other technologies is that there is no further requirement for secondary disposal methods. Photocatalytic oxidation leads to an efficient, inexpensive, and green chemical degradation process for various persistent organic chemicals, thus making it a highly favored process. Photocatalytic surfaces have the potential to act against a variety of air pollutants and odors such as microbes, volatile organic carbons (VOC), formaldehyde, ammonia, and inorganic gaseous substances such as nitrogen oxide or sulfur oxide (NO_x , SO_x). The advantages are manifold as there is no consumption of expensive oxidizing chemicals, the oxidant is atmospheric oxygen, and the catalyst is nonhazardous. The light required to activate the catalyst may be long wavelength UV transmitted by glass. Also the photocatalytic reaction may be driven by the natural UV component of sunlight. With the advent of second- and third-generation photocatalysts, which are excited by visible light, the process is getting wider acceptance. The oxidation is powerful and indiscriminate leading to the mineralization of the majority of organic pollutants.

Conclusion

In the above discussion, the importance of photocatalytic degradation in environmental remediation has been discussed. It can be clearly inferred that TiO_2 plays a major role in this and lot of research work has been devoted on modified TiO_2 structures which can have better efficiency under visible radiation. Apart from TiO_2 , bismuth-based oxides are also showing promise as good photocatalytic material, and in the future modified Bi_2O_3 nanostructures might show better degradation capabilities than the commercially available TiO_2 photocatalysts. With heightened awareness for a cleaner environment, the role of photocatalytic degradation will witness a phenomenal growth in the future.

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Role of Biopolymers in Industries: Their Prospective Future Applications

9

Ria Rautela and Swaranjit Singh Cameotra

Abstract

Surfactants are surface-active compounds capable of reducing surface and interfacial tension at interfaces between liquids, solids, and gases, thereby allowing them to mix or disperse readily as emulsions in water or other liquids. The demand for eco-friendly products is high; therefore, an increasing interest in biosurfactants has resulted. Biosurfactants are amphiphilic compounds of microbial origin having advantages in biodegradability and effectiveness at extreme temperatures or pH and in having lower toxicity. These molecules are very effective in various fields nowadays. At present biosurfactants are mainly used in studies on enhanced oil recovery and hydrocarbon bioremediation. The solubilization and emulsification of toxic chemicals by biosurfactants have also been reported. Biosurfactants also have potential applications in agriculture, cosmetics, pharmaceuticals, detergents, personal care products, food processing, textile manufacturing, laundry supplies, and the metal treatment and processing, pulp and paper processing, and paint industries.

Introduction

With increase in global industrialization, concern regarding the preservation of the natural environment has arisen. Environmentalists are now working toward better biotechnological approaches, keeping in mind the present environment scenario. Surfactants form an important class of industrial chemicals widely

used in almost every sector of modern industry (Greek 1990). Many of the commercially available surfactants are chemically synthesized, resulting in serious consideration for biological surfactants as possible alternatives to the existing products. Owing to their microbial origin, biological surfactants are biodegradable, nontoxic, high foaming, with specific activity at extreme conditions (Kretschmer et al. 1982; Velikonja and Kosaric 1993), can be synthesized from renewable feed stocks, and, also, are more effective in their application in comparison to chemically synthesized surfactants. Their range of potential applications has led to an increase in demand and their commercialization by industry.

R. Rautela • S.S. Cameotra (✉)
Institute of Microbial Technology, Sector 39A,
Chandigarh 160036, India
e-mail: ssc@imtech.res.in

Screening of Biosurfactant-Producing Microorganisms

Many methods are being reported to screen biosurfactant-producing microorganisms. In the rapid drop-collapsing test, a drop of cell suspension is placed on an oil-coated surface, and drops containing biosurfactants collapse, whereas non-surfactant-containing drops remain stable (Jain et al. 1991). In the thin-layer chromatographic technique for characterization of biosurfactant-producing bacterial colonies (Matsuyama et al. 1991), biosurfactant activities can be determined by measuring the changes in surface and interfacial tensions, stabilization or destabilization of emulsions, and hydrophilic–lipophilic balance. The surface tension can be measured by a tensiometer. When a surfactant is added to air–water or oil–water systems at an increasing concentration, reduction of surface tension is observed up to a critical level, above which amphiphilic molecules associate readily to form supramolecular structure such as micelles, bilayers, and vesicles. This value is known as the critical micelle concentration (CMC). Emulsification index value (E-24) is estimated by vigorously shaking culture broth samples with an equal volume of kerosene and measuring the percent emulsification after 24 h (Cooper and Goldenberg 1987). The hydrophilic–lipophilic balance (HLB) value indicates whether a surfactant will promote water-in-oil or oil-in-water emulsion by comparing it with surfactants with known HLB values and properties. Emulsifiers with HLB values less than 6 favor stabilization of water-in-oil emulsification, whereas emulsifiers with HLB values between 10 and 18 have the opposite effect and favor oil-in-water emulsification.

Classification of Biosurfactants

The biosurfactants are classified mainly on the basis of their chemical composition and their

microbial origin. Their chemical structure includes a hydrophilic moiety consisting of amino acids or peptides; anions or cations; monosaccharides, disaccharides, or polysaccharides; and a hydrophobic moiety consisting of saturated, unsaturated, or fatty acids. Accordingly, the major classes of biosurfactant include glycolipids, lipopeptides, lipoproteins, phospholipids, fatty acids, and polymeric surfactants. These biosurfactants can be produced from hydrocarbon-degrading microorganisms as well as on water-soluble carbohydrates such as glucose, sucrose, glycerol, or ethanol (Cooper and Goldenberg 1987; Guerra-Santos et al. 1986; Hommel et al. 1994; Palejwala and Desai 1989; Passeri 1992). Different types of biosurfactant and the microorganisms related to them are shown in Table 9.1 (Desai and Banat 1997). The major groups of biosurfactant are described in detail.

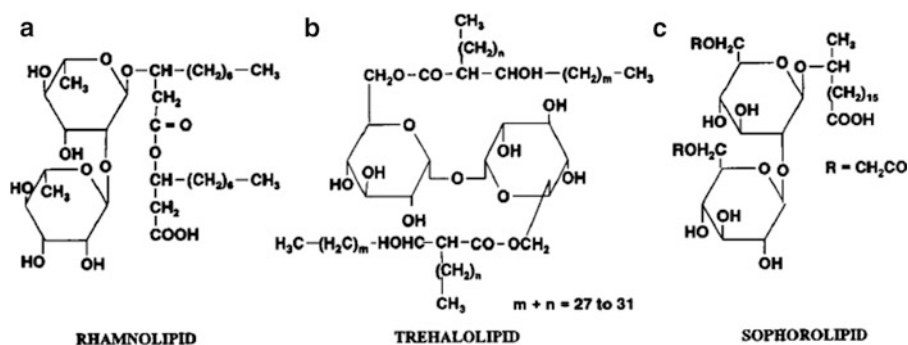
Glycolipids

Most of the known biosurfactants are glycolipids, which are carbohydrates in combination with long-chain aliphatic acids or hydroxyaliphatic acids. However, the best known are rhamnolipids, trehalolipids, and sophorolipids.

Rhamnolipids: One or two molecules of rhamnose are linked to one or two molecules of β -hydroxydecanoic acid. L-Rhamnosyl-L-rhamnosyl- β -hydroxydecanoate (Fig. 9.1a) and L-rhamnosyl- β -hydroxydecanoyl- β -hydroxydecanoate, referred to as rhamnolipids 1 and 2, are principal glycolipids produced by *Pseudomonas aeruginosa* (Edward and Hayashi 1965; Hisatsuka et al. 1971; Itoh and Suzuki 1972; Itoh et al. 1971). Rhamnolipid types 3 and 4 contain one β -hydroxydecanoic acid with one and two rhamnose units, respectively (Syldatk et al. 1985). Rhamnolipid is reported to lower the interfacial tension to 1 mN/m against *n*-hexadecane and surface tension to 25–30 mN/m and also emulsify alkanes (Guerra-Santos et al. 1986; Lang and Wagner 1987; Parra et al. 1989).

Table 9.1 Types and microbial species of origin of biosurfactants

Biosurfactant	Microorganisms
Trehalose	<i>Arthrobacter paraffineus</i> , <i>Corynebacterium</i> spp., <i>Mycobacterium</i> spp., <i>Rhodococcus erythropolis</i>
Rhamnolipids	<i>Pseudomonas aeruginosa</i> , <i>Pseudomonas</i> spp.
Sophorose lipids	<i>Candida apicola</i> , <i>Candida bombicola</i> , <i>Candida lipolytica</i> , <i>Candida bogoriensis</i>
Glucose, fructose, saccharose lipids	<i>Arthrobacter</i> sp., <i>Corynebacterium</i> spp., <i>Rhodococcus erythropolis</i>
Cellobiose lipids	<i>Ustilago maydis</i>
Polyol lipids	<i>Rhodotorula glutinis</i> , <i>Rhodotorula graminis</i>
Diglycosyl diglycerides	<i>Lactobacillus fermentii</i>
Lipopolysaccharides	<i>Acinetobacter calcoaceticus</i> , <i>Pseudomonas</i> spp., <i>Candida lipolytica</i>
Lipopptides	<i>Arthrobacter</i> sp., <i>Bacillus pumilus</i> , <i>Bacillus licheniformis</i>
Surfactin	<i>Bacillus subtilis</i>
Viscosin	<i>Pseudomonas fluorescens</i>
Ornithine, lysine peptides	<i>Thiobacillus thiooxidans</i> , <i>Streptomyces sioyaensis</i> , <i>Gluconobacter cerinus</i>
Phospholipids	<i>Acinetobacter</i> sp.
Sulfonylipids	<i>Thiobacillus thiooxidans</i> , <i>Corynebacterium alkanolyticum</i>
Fatty acids (corynomycolic acids, spiculisporic acids, etc.)	<i>Capnocytophaga</i> sp., <i>Penicillium spiculisporum</i> , <i>Corynebacterium lepus</i> , <i>Arthrobacter paraffineus</i> , <i>Talaromyces trachyspermus</i> , <i>Nocardia erythropolis</i>

**Fig. 9.1** Structures of rhamnolipid (a), trehalolipid (b), and sophorolipid (c)

Trehalolipids: Disaccharide trehalose linked at C-6 and C-6' to mycolic acids is associated with most species of *Mycobacterium*, *Nocardia*, and *Corynebacterium*. Trehalolipids are obtained from *Rhodococcus erythropolis*, lowering the surface tension to 25–40 mN/m (Lang and Wagner 1987) (Fig. 9.1b).

Sophorolipids: Produced by yeasts such as *Torulopsis bombicola*, *T. petrophilum*, and *T. apicola*, these consist of a dimeric carbohydrate sophorose linked to a long-chain hydroxyl fatty acid. These biosurfactants are a mixture of at least six to nine different hydrophobic sophorosides. Sophorolipids can lower surface and interfacial tension between *n*-hexadecane and water from

40 to 5 mN/m but are not effective emulsifying agents (Cooper and Paddock 1983; Lang and Wagner 1987) (Fig. 9.1c).

Lipopptides and Lipoproteins

Many microorganisms produce a large number of cyclic lipopeptides including decapeptide antibiotics (gramicidins) and lipopeptide antibiotics (polymyxins), produced by *Bacillus brevis* (Marahiel et al. 1977) and *Bacillus polymyxa* (Suzuki et al. 1965), respectively. *Serratia marcescens* produces serratamolide (Mutsuyama et al. 1985), an aminolipid biosurfactant. One of the powerful biosurfactants is cyclic

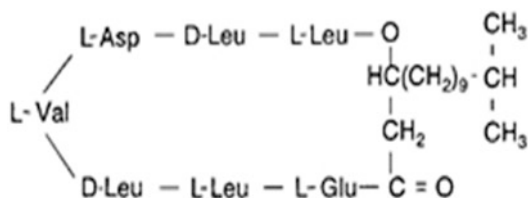


Fig. 9.2 Structure of cyclic lipopeptide by *Bacillus subtilis*

lipopeptide, surfactin (Fig. 9.2), produced from *Bacillus subtilis*, lowering surface tension from 72 to 27–28 mN/m at concentrations as low as 0.005 % (Arima et al. 1968). Several biosurfactants are stable at extremes of pH, temperature, and salinity. Biosurfactant from *Bacillus licheniformis* is also reported to reduce the surface tension of water to 27 mN/m. Each molecule contains seven amino acids and a lipid portion that is composed of eight to nine methylene groups and a mixture of linear and branched tails (Horowitz and Griffin 1991). Surfactin has an additional characteristic of lysing mammalian erythrocytes. Lichenysin A obtained from *B. licheniformis* contains a long chain of β -hydroxy fatty acids. It reduces surface tension to 28 mN/m with CMC of 12 μ M. In lichenysin A, isoleucine is the C-terminal amino acid instead of leucine, and an asparagine residue is present instead of aspartic acid as in surfactin peptide (Yakimov et al. 1996).

Fatty Acids, Phospholipids, and Neutral Lipids

These biosurfactants are produced by some bacteria and yeasts during their growth on *n*-alkanes. *Acinetobacter* sp. produce *N*-phosphatidylethanolamine-rich vesicles forming clear microemulsions of alkanes in water. The production of phospholipids has also been detected in some species of *Aspergillus* and in *Thiobacillus thiooxidans*. Phosphatidylethanolamine produced by *R. erythropolis* grown on *n*-alkane caused lowering of interfacial tension to less than 1 mN/m between water and hexadecane (Kretschmer et al. 1982) (Fig. 9.3).

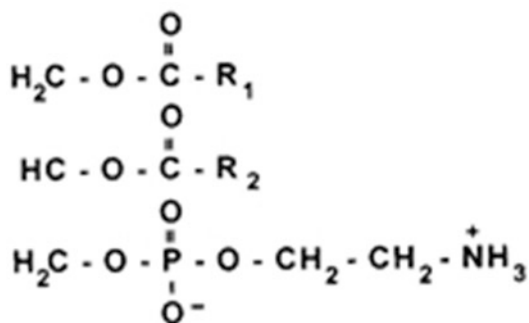


Fig. 9.3 Structure of phosphatidylethanolamine produced by *Acinetobacter* sp. R_1 and R_2 are hydrocarbon chains of fatty acids

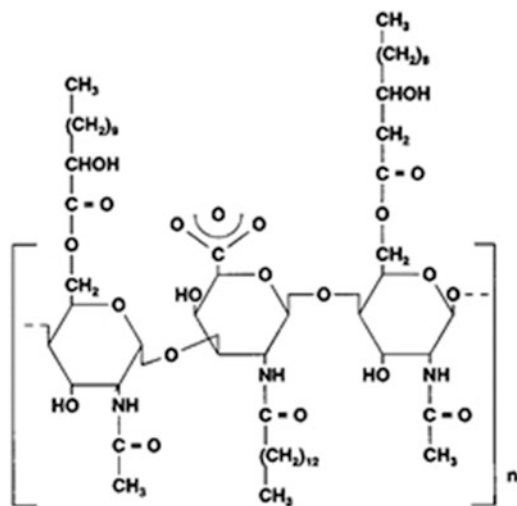


Fig. 9.4 Structure of emulsan, produced by *Acinetobacter calcoaceticus*, in which fatty acids are linked to a heteropolysaccharide backbone

Polymeric Biosurfactants

The most studied polymeric biosurfactants are emulsan, liposan, mannoprotein, and other polysaccharide–protein complexes. *Acinetobacter calcoaceticus* produces a polyanionic amphipathic heteropolysaccharide bioemulsifier called emulsan (Fig. 9.4) (Rosenberg et al. 1979). The heteropolysaccharide backbone contains the trisaccharide of *N*-acetyl-D-galactosamine, *N*-acetylgalactosamine, uronic acid, and an unidentified *N*-acetyl amino sugar. Fatty acids are covalently linked to the polysaccharide through

O-ester bonds. Emulsan is a very effective emulsifying agent even at concentrations of 0.001–0.01 %. Other polymeric biosurfactants produced by *Acinetobacter calcoaceticus*, that is, biodispersan and alasan, have also been reported.

Liposan, an extracellular water-soluble emulsifier synthesized by *Candida lipolytica*, is composed of 83 % carbohydrate and 17 % protein. The carbohydrate portion consists of glucose, galactose, galactosamine, and galacturonic acid. Production of mannoprotein by *Saccharomyces cerevisiae* showed excellent emulsifier activity toward oils, alkanes, and organic solvents. Mannoprotein contains 44 % mannose and 17 % protein. *Schizonella malanogramma* and *Ustilago maydis* produce a biosurfactant characterized as erythritol and mannose-containing lipid (Fautz et al. 1986). Desai et al. (Desai et al. 1988) demonstrated the production of bioemulsifier by *Pseudomonas fluorescens* during growth on gasoline, which is composed of 50 % carbohydrate, 19.6 % protein, and 10 % lipid. Trehalose and lipid-*o*-dialkyl monoglycerides were the major components of the carbohydrate and lipid, respectively.

Particulate Biosurfactants

These biosurfactants are extracellular vesicles that partition hydrocarbons to form a microemulsion, playing an important role in the uptake of alkane. Vesicles produced by *Acinetobacter* sp. are composed of protein, lipopolysaccharide, and phospholipid (Kappeli and Finnerty 1979). Several cell-surface components such as M protein and lipoteichoic acid of streptococci group A and prodigiosin in *Serratia* spp. are attributed for surfactant activity (Desai 1987).

Applications of Biosurfactants

With the increase in demand for eco-friendly products, researchers and industries are now searching for microorganisms that are capable of surviving and stabilizing under harsh conditions and producing surfactants. Their main benefits

toward the environment are putting them far ahead of chemically synthesized surfactants. Being ecologically safe, they can be applied in bioremediation and wastewater treatment. Some of the prospective applications related to the environment are enhanced oil recovery, solubilization and emulsification of toxic compounds, and removal of heavy metals from contaminated soil. In this review we discuss the future applications of biosurfactants on bioremediation, the food industry, the cosmetic industry, and biomedical science (Table 9.2).

Biosurfactants and Bioremediation

The microbes present in contaminated soil play an important role in hydrocarbon degradation from soil. Even partially purified biosurfactants can be used in bioreactors or in situ for emulsifying and increasing the solubility of hydrophobic contaminants. Addition of biosurfactants to the soil can enhance the growth of indigenous microorganisms capable of producing biosurfactants (Lang and Wagner 1993). With the input of biosurfactants, degradation of up to 90 % of hydrocarbon was possible in 79 h, whereas without biosurfactants degradation time required as long as 114 h. In another study, emulsan has been found to stimulate aromatic mineralization by pure cultures. Jain et al. (1992) were able to show that the addition of biosurfactant from *P. aeruginosa* enhanced biodegradation of tetradecane, pristene, and hexadecane in a silt loam with 2.1 % organic matter. An experiment performed by Falatko and Novak (1992) showed that removal of gasoline overlaid on the top of a coarse-grain sand-packed column, when facilitated with biosurfactant, led to a 15-fold increase in the effluent concentration of four gasoline constituents: toluene, *m*-xylene, 1,2,4-trimethylbenzene, and naphthalene. A study to check the ability of biosurfactant from *P. aeruginosa* in removing oil from Alaskan gravel samples under various conditions reported about two- to threefold oil displacement. These results demonstrated the capacity of biosurfactant removing oil from a naturally occurring substrate (Harvey et al. 1990). Evaluation showed that

Table 9.2 Industrial applications of biosurfactants

Industry	Application	Role of biosurfactants
Environmental	Bioremediation	Lowering of interfacial tension, emulsification of hydrocarbons, metal sequestration, soil flushing
Petroleum	Enhanced oil recovery	Improving of oil drainage into well bores, viscosity reduction, and demulsification of oil emulsions
Food	Emulsification and food ingredient	Emulsifier, interaction with lipids, proteins, and carbohydrates, protective agent
Biological	Microbiological	Physiological behavior such as cell mobility, cell communications, plant and animal physiology
	Pharmaceuticals and therapeutics	Antiviral, antifungal, antitumor, immunomodulatory molecules, vaccine
Cosmetics	Health and beauty products	Foaming agent, solubilizers, antimicrobial agents, cleansers
Agriculture	Biocontrol	Assist in controlling fungal pathogens, induced systemic resistance, and hypovirulence
Bioprocessing	Downstream processing	Enhanced extracellular enzyme production and fermentation products, biotransformation, recovery of intracellular products
Biomedical science	Antimicrobial activity	Rhamnolipid, surfactin, iturin mannosylerythritol lipids have shown antimicrobial activity against pathogenic organisms
	Antiviral activity	Surfactin, pumilacidin, trehalose lipid against human immunodeficiency virus (HIV)-1 and herpes simplex virus (HSV)-1, respectively
	Antiadhesive activity	Rhamnolipid and surfactin against several pathogens
	Antitumor activity	Surfactin against Ehrlich's ascites, carcinoma cells

pentachlorophenol (PCP) could be removed by rhamnolipid in the form of foam (Mulligan and Eftekhari 2001). When the foam was injected into contaminated soil with a 1,000 mg/kg level of PCP, 60 % and 61 % of PCP was removed from fine sand and sandy-silt soil, respectively. The major advantage of foam is the injecting of fluid in soil at low pressures. Because of their complexation ability, biosurfactants are able to remove metals and ions such as cadmium, copper, lanthanum, zinc, and lead. Metal extraction from mining ores is also possible with the addition of biosurfactant. Robinson et al. (Robinson et al. 1996) evaluated the impact of biosurfactant on microbial utilization of PCBs and concluded that addition of biosurfactants is a promising approach for the treatment of nonaqueous phase and soil-bound PCBs. These biosurface-active agents have been tested in enhanced oil recovery and transportation of crude oils. *Bacillus licheniformis* is stated to be well suited for in situ studies for enhanced oil recovery (Javaheri et al. 1985). Study on degradation of

n-hexadecane by species of *Pseudomonas* and *Rhodococcus* has been reported by S. Mishra and S.N. Singh (Mishra and Singh 2012). *Bacillus amyloliquefaciens* has shown to be an efficient organism for maximum oil recovery from oily sludge (Liu et al. 2012). Chlorinated pesticides are difficult to degrade because of their low solubility and sorption to the soil surface. To solve this problem, rhamnolipid and sophorolipid have shown maximum solubilization of HCH isomers by three- to ninefold at 40 μ g/ml CMC (Manickam et al. 2012).

Biosurfactants and Food Industry

Biosurfactants have now found application in the food industry. Biosurfactants, along with their role as agents decreasing surface and interfacial tension, are now being looked upon as food formulation ingredients and antiadhesive agents. They can have many functions in the food industry such as controlling agglomeration of fat

globules, stabilizing aerated systems, improving the texture and shelf-life of starch-containing products, modifying rheological properties of wheat dough, and improving the consistency and texture of fat-based products (Guerra-Santos et al. 1984). They accomplish these functions by maintaining consistency, retarding staling, and solubilizing flavor oils. They act as fat stabilizers and antispattering agents during cooking of oil and fat. L-Rhamnose is favored in industries as a high-quality flavor component. Also, the use of rhamnolipid has improved the properties of frozen confectionary products, butter cream, and croissants (Guerra-Santos et al. 1986). In meat products, the biosurfactants emulsify the partially broken-down fat tissue. Most common emulsifiers available in the market are lecithin and its derivatives (Bloomberg 1991). *Candida utilis* bioemulsifier has been used in salad dressings (Shepherd et al. 1995). A biofilm is formed by the colonization of a group of bacteria on the surface. This biofilm consists of extracellular material and any material trapped inside the matrix. These bacterial biofilms are potential sources of food spoilage and disease transmission. Hence, a checkpoint is needed to control adherence of microorganisms to food-contact surfaces to provide safe and quality products to consumers. Therefore, biosurfactants play a vital role in curbing the biofilm formation. The surfactant released by *Streptococcus thermophilus* is used to control fouling of heat exchanger plates in pasteurizers, retarding the growth of other organisms and agents of fouling. A new strategy of reducing surface adhesion is the bioconditioning of surfaces with the use of biosurfactants. Similarly, a biosurfactant obtained from *Pseudomonas fluorescens* inhibits adhesion of the *Listeria monocytogenes* L028 strain.

Biosurfactants and Cosmetic Industry

The properties of biosurfactants have paved their way through the life of the common man, holding a niche in the cosmetic industry because

of the moisturizing properties and skin compatibility (Brown 1991). A commercially available skin moisturizer contains 1 mol sophorolipid and 12 mol propylene glycol and is compatible to skin (Yamane 1987). Recently, higher concentrations of sophorolipids, up to 300 g/l (Davila et al. 1997) and 422 g/l (Daniel et al. 1998), have been reported using *Candida bombicola* on rapeseed oil as the main carbon source.

Biosurfactants and Biomedical Science

Owing to their diversity and environment-friendly nature, biosurfactants are mostly focused on environmental applications. Because of their antimicrobial activities and mechanism of action, however, they could be exploited for developing alternative drugs or biomaterials in the medical field. Because of the amphiphilic nature of biosurfactants, hydrophobic actions as well as a range of interactions are involved with interfaces. Some of the biologically active compounds have roles in the medical field. Lipopeptides act as antibiotics, antiviral and antitumor agents, and enzyme inhibitors. Iturin A was first reported as a potent antifungal lipopeptide (Ahimou et al. 2001). Along with antifungal and antimicrobial activities, surfactin has inhibited fibrin clot formation, cyclic adenosine monophosphate, platelet and spleen cytosolic phospholipase A₂, and antiviral and antitumor activities (Kim et al. 1998). Antiviral activity against enveloped virus has been studied by Vollenbroich and coworkers, showing disruption of viral lipid membrane and capsid, partially the result of the physiochemical interaction of membrane-active surfactant with a lipid membrane (Vollenbroich et al. 1997). Growing antimicrobial resistance is a matter of great concern nowadays. Nosocomial infections related to biomaterials such as urinary catheters, prosthetic heart valves, and central venous catheters are associated with biofilm formation. The bacteria in a biofilm not only evade host defenses but also withstand chemotherapy. *Serratia marcescens* produces a glycolipid biosurfactant capable

of degrading biofilm formation (Dusane et al. 2011). Apart from this, biosurfactants have shown antiadhesive activity in which pathogenic organisms are unable to adhere to solid surfaces, thus combating colonization of organisms. The biosurfactant rufisan from *Candida lipolytica* showed antiadhesive activity against a broad range of microorganisms (Rufino et al. 2011). By application of rhamnolipid, a 96 % detachment rate of microorganisms adhering on silicone rubber was shown (Rodrigues et al. 2006).

Conclusion

In the past few years, a wide variety of microorganisms have been reported to produce numerous types of biosurfactants. Their biodegradability and lower toxicity give them extra advantages in comparison to chemically synthesized surfactants. But, up to the present, biosurfactants have not been able to compete with their counterparts because of high production costs and lack of comprehensive toxicity testing. Fermentation processes can improve the overall process economics in biosurfactant production. Generally, the biosurfactants are produced during growth on hydrocarbons, which are expensive and in return increase the production cost. This problem can be avoided by using cheaper sources such as glucose, ethanol, olive oil mill effluent, and molasses and potato processing industrial residues. Another way to improve productivity of biosurfactants is to manipulate physiological conditions and medium composition as well as genetic manipulations. Mutants capable of several fold-higher biosurfactant production will be more cost-effective. To combat the high costs of downstream recovery processes, other alternatives such as recovery by foam fractionation, membrane ultrafiltration, and tangential flow filtration can be used. In recent years, new developments have taken place with sequencing of the full genomes of *Pseudomonas aeruginosa* and *Bacillus subtilis*, and many more are under way. This step will lead to the production of potent biosurfactants from genetically engineered bacteria in the near future.

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Green Federalism: A Historic Leap Towards Sustainable Human Development

10

Indira Dutta and Jiya Shahani

Abstract

India is engaged with the international community to collectively and cooperatively address the challenge of sustaining accelerated economic growth while dealing with the common threat of climate change. The ecological, ideological and political disruption accompanying the rapid economic growth has pushed welfare indicators to remain firmly in red, as nations have compromised environmental and social standards in order to gain high economic standards. The current growth model being intrinsically deleterious uses vast resources and generates enormous waste. In spite of investing huge amounts of money towards mitigation, the world remains many steps behind the adversity it creates. As a result, there are growing concerns about the economic growth patterns and the risk of causing irreversible damages to environmental base, needed to sustain life and economic prosperity. Natural capital, which powers the economy, is rarely reflected in the national accounts, and economic speculations of econometricians have always superseded the laws of ecology. This indicates that environmental idealism is honored more in the word than in the deed, resulting in current climate crisis; and global warming, the dire outcome of greenhouse gas emissions, is the price, world pays for over ambitious growth. India does not have legally binding commitments towards greenhouse gas mitigation. However, as a responsible and enlightened member of the international community, India has made or is in the process of making positive policy interventions in order to improve its domestic capacity towards attaining inevitable green transitions. The cost of not adopting green growth path would be high, in terms of foregone greener development.

I. Dutta (✉) • J. Shahani, Ph.D. Economics
School of Social Sciences, Central University of Gujarat,
Sector 30, Gandhinagar, Gujarat 382030, India
e-mail: indirabdutta@gmail.com;
jiyakshahani@gmail.com

Recognizing that the opportunity cost for green investment is currently low with a potential to grow exponentially, India's investment in climate change is ramping up. Reduction of greenhouse gas emissions is as much a part of its climate change strategy as adaptation efforts. The policy interventions which would result in emission cuts include increasing the proportion of renewable component in the country's energy mix, introducing fuel efficiency standards for vehicles and appliances, reducing energy intensity, adopting market-based mechanisms to trade energy-efficiency certificates, afforestation, sustainable land use practices and bringing in a new building code. The benefits accruing out of these vindicate that India is doing much more than the countries, which are bound by international law to take targeted emission cuts. Thus India's constructive approach and proactive contribution towards the issue demonstrates that country's commitment to actions shall improve its accountability and transparency. Additionally, India has also launched eight missions as part of the National Action Plan on Climate Change (NAPCC) in specific areas, which involve assessment of the impact of climate change and actions needed to address the issue. However, there are gaps impeding the progress on the green growth path.

In this study, we propose an improved economic configuration based on the robust index, which helps confront the contemporary development processes. Such a restructuring of present development context through the concept of Green Federalism would possibly rebuild the natural capital, and steer the economic growth towards sustainability by shifting production and consumption from destructive to regenerative forms. It would potentially close: a) the Green Economy price-gap by internalizing the costs of environmental externalities; b) the time-gap for achieving green growth by investing in the Green Economy today; and c) the political-gap by enabling government investment in initiatives that reward environmental conservation. The proposed index advocates rethinking the foundations of modern consumerism that paradoxically undermine nature and jeopardize human prosperity. It will enable rewriting the rules for business, investors as well as consumers and create more sustainable and equitable future economies. The framework so devised would focus on the economic-environmental interface that enables efficient mobilization of financial, technological and human capital to meet Green Economy goals. By unpacking the links between different strands of green economy and the MDGs (Millennium Development Goals), the paper demonstrates that the green federalism is in effect an opportunity for India, rather than a burden. And, pursuit towards green economy will involve a paradigm shift, wherein the generation of wealth will not increase social disparities, environmental risks and ecological scarcities, thereby unfolding into the desired human development and inclusive growth.

Keywords

Sustainability • Federalism • Green Economy • Human development

Introduction

Federalism describes a system of government in which sovereignty is constitutionally divided between a central governing authority and constituent political units such as states or provinces. These units are better situated than national governments to confront difficult developmental challenges including climate change. Both India and the world are reviewing such challenges ahead, climate change being the most crucial one. The climate problem arises from the joint evolution of economic growth and greenhouse gas emissions and plunges the world into more disorder. The ensuing ecological, ideological, and political disruption has pushed welfare indicators to remain firmly in red, as nations have compromised environmental and social standards in order to gain high economic standards. The current growth model being intrinsically deleterious uses vast resources and generates enormous waste. Today over one billion people are malnourished, and fossil fuels provide about 95 percent of the commercial energy used in the world economy. The world is facing a wide variety of critical environmental threats: degradation of soil, water, and resources, essential to increase food production; widespread health-threatening pollution; stratospheric ozone depletion; global climate change; and loss of biodiversity. Furthermore, it faces enormous human problems in the form of widespread persistent poverty and human misery. Growth in population and economic activities are creating multiple stresses on planet as well as human health. These stresses alter today's yields, earnings, health, physical safety, and ultimately the paths and levels of future development. This is evident from the fact that in spite of investing huge amounts of money towards mitigation, the world remains many steps behind the adversity it creates. The core of the issue lies in current infrastructures and production practices that are engineered to be robust only to previously experienced variations in weather conditions. However, when weather events do not remain within the envelope of past variations and

consistently exceed these boundaries, it is even harder to adapt and/or mitigate due to reduced capacity. Moreover, declining Living Planet Index and rising Ecological Footprint emphasize the need for more sustainable policies (WWF 2012).

Environmental issues range from local to cross jurisdictions, and so their impacts can be regional or global in scale. Consequently, the challenge to achieve sustainable human development requires a much greater engagement with distributed governance. Also, crafting meaningful climate policies requires fighting environmental problems on a war footing basis, with cooperation between union government and the states. Although federal systems are well placed to do so within the context of national policy making, federal structures do add an element of complexity, as constitutionally entrenched subnational entities may have policy priorities that do not align with that of higher-order governments. Therefore, the key challenge of climate change in a federal context is the necessity to think beyond spatial borders and yet be local. To this effect, the present work intends to impel planning and policy work to identify the merits of green federalism. The principle of green federalism points to a regulatory structure in which decentralized levels of government take responsibility for dimensions of environmental quality that fall within their jurisdictional boundaries. As a result of this structure, local governments will be in charge of implementing national policies in sectors key to mitigation (transportation, construction, public service provision, local advocacy) and adaptation (social protection, disaster risk reduction, natural resource management). Since these governments are closer to citizens, they can raise public awareness and mobilize non-state actors. In addition, the overall accountability of the government will be based on the appropriate responses and effectiveness of all the local governments. Consequently, there will be incentives for measures to improve the natural resource base in the respective regions, which will largely contribute towards the country performance. In order to develop policies that enable assessment of country performance, we propose a "Pooled

Federalism” model and a robust instrument in the form of PPFI, wherein the approach is focused on a triple bottom line, economic, environmental, and social, as against past narrow one, stressing only on economic and financial element. This approach develops an underlying platform of strong governance for pursuing the intended outcomes.

Political Dimension of Climate Policy

The national economy comprises of state economies, which are maintained and overseen by respective state legislatures. As a result, states retain the greatest power over the maintenance and sustenance of their own economies. Federal government has the capability to preempt subnational regulations and limit the scope and impact of their programs or schemes. However, an action by second and third tier of governance has the potential to shift the federal government towards further regulation by providing a pretested set of initiatives which could be scaled up to the higher level. The Federal government and national policy can support the interdependent network of state economies, but for the execution of any policy change, state economies are largely looked upon. The same should be followed between state and substate levels, so that climate policy goals can be successfully achieved. This can be brought about through multilevel governance framework. Such a framework provides a starting point for understanding how central governments and other public and private actors interface to design and implement policies from international to national and local levels of action (Liesbet and Marks 2003). Action on climate change must be along two broad fronts: adaptation and mitigation. The sooner we mitigate, the more cost-effective our actions will be. Consequently, we will be able to better protect the climate and limit the risk of dangerous climate change over the medium and long term. Equally, the earlier we adapt, the more we can cost-effectively protect people and infrastructure from dangerous impacts of inevitable climate change (IPCC 2007a; Stern

2007; OECD 2008; Nicholls et al. 2008). Thus, any political decision to deal with climate change certainly involves balance and the tension among a range of choices: the balance of effort to adapt “now versus later” to a range of uncertain climate changes and tension between different types of efforts, such as to “mitigate and/or adapt” in any particular regional setting (Corfee-Morlot et al. 2009). In this way, regardless of the constitutional form of government, multilevel governance helps to bridge the policy “gaps” among levels of government through adoption of tools for cooperation along vertical and horizontal dimensions.

The vertical dimension recognizes that national governments cannot effectively implement national climate strategies without working closely with regional and local governments as agents of change. It also recognizes that local governmental authority to act in areas related to climate change is often “nested” in legal and institutional frameworks at higher scales (Dietz et al. 2003; Liesbet and Marks 2003). While local policies determine the specific details of land use, human settlement patterns, and transportation planning, the space for action and potential for change is usually limited by national development paths, national policies and technical standards, and national budgets and funding priorities (Sathaye et al. 2007). This suggests that a two-way relationship exists between local and national action on climate change as each can enable or constrain the other. On the horizontal axis, there are multilevel patterns of governance and transnational networks on climate change and other global environmental issues, where entities work across organizational boundaries to influence outcomes. Within the multilevel regulatory framework, learning, information transmission, and cooperation can occur horizontally at each level. Horizontal coordination is not just about international associations of local authorities; it also concerns coordination among local jurisdictions that belong to the same urban metropolitan area or the same rural area or between urban and rural areas. Moreover, it should be associated with the improved

coordination across line ministries at the central level, for dealing with crosscutting policies, (particularly climate change), so that policy mixes that result in counter-productive overlaps of instruments should be avoided (de Serres et al. 2010). On issues of climate change, cities and other local governments hold the unique potential to work closely with local constituencies to develop visions of the future that match the needs of these constituencies while also addressing climate change (Brunner 1996; Cash & Moser 2000). However, lessons and experiences with adaptation at the local level must feed into higher levels of decision making to make sure that local strategies remain relevant and appropriate and provide a basis for transferring knowledge to other sectors and communities. Thus, challenge for the future is to pursue growth within environmental limits, so that it leads to sustainable human development.

Growth, Human Development, and Environmental Sustainability

The global economic growth over the past 15 years has been accompanied by accelerated environmental decline: the global GDP has more than doubled while 60 percent of the world ecosystems are degraded and used in an unsustainable manner. The environment interacts with development aspects through three functions – a source of resources for consumption, supply of basic life-supporting services, and assimilation of waste. Therefore, environmental sustainability is recognized as a crucial pillar of human development, along with social progress and economic growth. Without the strong support of environmental services, the system would be unstable and will collapse. The Istanbul declaration: towards an equitable and sustainable future for all was the starting point of sustainable human development. It stressed the relevance of human development thinking, to chart a course for a fairer and more sustainable world. Therefore, we need to have a globally adopted vision that combines equitable growth with environmental sustainability, rooted

in universal value and global justice. It should include a strong emphasis on social inclusion, protection, and equity in recognition of the fact that economic development has too often gone hand in hand with environmental degradation and increased inequality. The Istanbul declaration reflects the human development principles for building coherent policies, where development goals are based on measurable indicators and are relevant to all the nations. Thus, overall development is principally an element of climate problem as well as climate solution, depending upon the choice of a policy mix. The right choice of policies would ensure that the infrastructure can endure the expected increase in climate hazards while simultaneously improving the energy and emission performance of the built environment (Hallegatte et al. 2008; Saitherwaite 2008; McEvoy et al. 2006). However, any policy change generally faces resistance, particularly when it involves visible costs to large and diverse entities. Climate policy is a perfect example, because its costs are clearly visible to various economic groups and the population at large, while benefits are perceived as distant and uncertain. As a result, there is lack of concern towards environment conservation and prevention efforts. This has pushed humanity into ecological overshoot since the 1970s. Before that, humanity's consumption of the natural resources was outweighed by the Earth's ability to regenerate them.

The New Economics Foundation (NEF) marked Ecological Debt Day/Earth Overshoot Day for the first time on December 19, 1987. Since then, every year NEF calculates the calendar date of Ecological Debt Day for the subsequent year. When viewed through an economic perspective, Ecological Debt Day/Earth Overshoot Day represents the day on which humanity enters deficit spending, scientifically termed as "overshoot." From 1987 to the early 1990s, overshoot date fell in the month of December, followed by November till 2000. From 2001 to 2007, it appeared in October and is now appearing in September post 2007. Ecological Debt Day has, on average, fallen on an earlier date than the previous year, constituting a negative trend in which humanity is falling

deep into ecological debt. When viewed in terms of monetary debt, it demonstrates compounding interest on an unpaid loan. Thus, humanity's overconsumption of the natural resources seems unsustainable, should this behavior continue. To alter this behavior, climate reforms are necessary. In this regard, the world is aiming for "Global Green New Deal" which talks about environmentally focused investment having potential to be a historic opportunity for twenty-first-century prosperity and job generation. The call was made by UNEP and leading economists as they launched green economy initiatives aimed at bringing tomorrow's economy today.

Carrying these initiatives forward through green federalism ensures enormous economic, social, and environmental benefits. It orients both the center and the state towards climate policy with its prime focus on:

- Clean energy and clean technology including recycling
- Renewable energy and sustainable biomass
- Sustainable agriculture including organic agriculture
- Green infrastructure
- Reduced emission from deforestation and forest degradation (REDD)
- Sustainable cities including planning, transportation, and green building

Building public support for such a policy involves resolving tensions among conflicting objectives. Indeed, perceptions and conceptual frameworks across high-income (right to emit/pollute) and developing countries (right to develop) prove to be the strong political barrier to integrating climate change and development. Since current infrastructure and economic production are built on the assumption of costless carbon, building economies and societies around costly carbon will impose considerable adjustment costs. The politics around climate is closely tied to the burden-sharing assumption, because environment and equity constructions of the problem imply very different ways of sharing a burden and therefore different political costs. However, the split can be dealt by advocating and developing the counter-narrative of climate mitigation as an opportunity to be seized rather

than a burden to be shared. Even if climate mitigation imposes costs in aggregate, there are relative advantages to first movers. However, subnational jurisdictions in federalist systems can have varying degrees of success in terms of efficiency and effectiveness of green federalism policies based on their commercial appeal.

Commercial Appeal for Inclusive Growth Through Green Federalism

The social and ethical rationale of investing in environmental management is not adequate to change the status quo. However, the prospect of a silver lining of economic opportunity to the climate cloud could tip the political balance towards beginning the hard task of turning economies and societies close to a low-carbon future. Beginning is important, because it creates constituencies with a stake in a low-carbon future, starts the process of experimentation, and increases the costs to others of being left behind, creating a pull effect. Business-as-usual can only deliver development gains at an unaffordable price (UNEP 2011). Moreover, there is no reason to think that a low-carbon path will necessarily slow economic growth: many environmental regulations were preceded by warnings of massive job losses and industry collapse, few of which materialized. In fact, low-carbon economy being more labor intensive than a conventional one will have a positive employment effect. Investments in clean technology development and deployment will also create ample jobs, further increasing the demand for workers. Support for green transitions through climate policy is strong among groups that see a low-carbon economy as a business opportunity, but legacy industries remain opposed. Obtaining the prior agreement of the main stakeholders on specific measures can reduce political damage, and highlighting the co-benefits of green transitions can win over opposing vested interests. In addition to identifying co-benefits, developing consensus policies will involve setting up consultative systems and voluntary schemes that are able to bind key players (such as industry groups) to the principles

of climate policy. However, it is important to develop a climate policy that is able to draw a large pool of stakeholders towards intended purpose without unduly favoring any particular group.

Reaping the benefits of green transitions will require significant changes in human and organizational behavior, as well as a host of innovative supportive policies to reduce human vulnerability and manage natural resources. Mobilizing technology and fostering innovation on an adequate scale will demand that countries not only cooperate and pool their resources but also craft domestic policies that promote a supportive knowledge infrastructure and business environment. Most developing countries, particularly low-income countries, having small market sizes, taken individually, may be unattractive to entrepreneurs aspiring to introduce new technologies. However, contiguous countries have the potential to achieve a critical mass through greater regional economic integration. Moreover, developing an integrated financial accounting system will be encouraging, which demonstrates key stakeholders that investing in environment gives financial returns in the health sector, leading to greater economic activity and growth. Although, it may not be possible to change the course overnight from vulnerability to sustainability, a series of gradual steps in the right direction would lead to the desired path of sustainability.

India's Proactive Redress to Climate Change

India is a large country characterized by cultural, regional, linguistic, and geographical diversities. Democracy and federalism are essential features of our constitution and are part of its basic structure. But both democracy and federalism have got absolutely no meaning, if we do not follow green federalism. Indian states have diverse political, economic, and ecological characteristics. There are states such as Jharkhand and Chhattisgarh that have low-carbon footprint due to relative industrial backwardness. In contrast, there are

states such as Gujarat, Maharashtra, and Tamil Nadu that are bound to have heaviest emissions. The big constraint for most states is financial. Most of them exhaust revenues, almost totally in meeting government expenditure, leaving precious little for anything else. Most climate change control options have serious cost-benefit trade-offs. No doubt, the thirteenth Finance Commission of India has stressed on the need to manage ecology, environment, and climate change consistent with sustainable development; the critical burden, both in policy and implementation terms, is however to be shouldered by the states. The central government primarily plays the role of limiting environmental "spillover effects" of externalities across jurisdictional boundaries. While India has a comprehensive legislative framework for environmental regulation, in several instances, its impact has been diluted due to its shortcomings in design or ambiguities in jurisdictional responsibilities, including the lack of credible, incentive-based, pollution deterrence strategies (TERI 2010). In the context of environmental federalism, a general bias exists in environmental decision-making and management towards higher levels of governance in the country, as is evident in the distribution of legislative, administrative, and fiscal powers. This bias is evident both at the centre–state and state–local levels. Efforts towards greater decentralized environmental management need to first address the issues of capacity and accountability of local level institutions.

In Indian policy and planning, sustainable development in terms of environmental concerns has been a recurring theme. A dedicated and independent Ministry of Environment and Forests has been functioning with increasing responsibilities since 1985. The Constitution of India has incorporated relevant amendments over the years to reinforce the policy and legal basis of sustainable development in India. This journey towards sustainable development has been marked by reasons both for celebration and introspection. The National Environment Policy of 2006 attempted to mainstream environmental concerns in all developmental activities. The Government of India, through its various policies,

has been factoring ecological concerns into the development process to achieve economic development without permanently damaging the environment. Nevertheless, the challenges ahead are large. The Ministry of Statistics and Programme Implementation too has initiated the process in 2010 by putting in place a green national accounting system. The new system takes into account the environmental costs of development and reflects the depletion of natural resources in generating national income numbers. Comprehensive environmental statistics are being published since 1997 by the Central Statistics Office (CSO). It is expected that the depletion of stocks of natural resources will be incorporated into the standard national accounts to estimate a green GDP at state as well as country level in the current decade. Pilot projects have already been initiated at the level of states, and a high-level advisory group has been formed. The information will further integrate sustainable development into the development process. More careful measurements of inclusion and sustainability together will enhance development choices and decisions.

Voluntary Actions by India Towards Mitigation and Adaptation

Although India ranks among top five countries in terms of GHG emissions, its per capita emissions are much lower than those of the developed countries, even if historical emissions are excluded. The per capita emissions of carbon dioxide in India is 1.02 metric tons, which is well below the world average of 4.25 and that of China at 3.60 (NAPCC 2008). Its high level of emissions is due to its large population, geographical size, and economy. India has already taken a number of actions on voluntary basis in pursuance of a sustainable development strategy. As per India's GHG Emissions Profile, even two decades from now, India's per capita GHG emissions would be well below the global average of 25 years earlier (Economic Survey 2011–2012). Among important measures, India has adopted the National Action Plan on Climate Change (NAPCC) in

2008 which has both mitigation and adaptation measures. The eight National Missions¹, which form the core of the NAPCC, represent multi-pronged, long-term, and integrated strategies for achieving key goals in the context of climate change. Though adaptation is the focus of the NAPCC, missions on solar energy and energy efficiency are geared to mitigation. Moreover, India has announced a domestic goal of reducing the emission intensity of its GDP by 20–25 percent of the 2005 level by 2020. This will be achieved through a multi-sector low-carbon development strategy. Apart from the NAPCC, all the states are required to prepare state-level action plans. These plans are envisioned as extensions of the NAPCC at various levels of governance, aligned with the eight National Missions. Delhi launched a climate change action plan for 2009–2012 formulated on the lines of the NAPCC.

The major policies and actions for climate change mitigation and adaptation cut across different sectors and areas of the economy. The initiatives taken by India cover almost all major areas including energy efficiency, power plants, renewable energy, nuclear energy, transport, agriculture and forestry, marine and coastal environment, enhancing adaptive capacity, and initiatives for enhancing knowledge and scientific findings. However, all actions to address climate change ultimately involve costs. Currently, India is mostly utilizing and relying on domestic sources of finance, which are budgetary allocations for various sectors and the National Clean Energy Fund (NCEF) fed by a cess on coal at Rs. 50 per ton introduced in 2010. The NCEF finances innovative projects in clean energy technologies and harnesses renewable energy sources to reduce dependence on fossil fuels. It helps to pay for schemes, which protect and regenerate forests and clean up polluted sites. It is estimated that by 2015, an amount of Rs. 10,000 crore will be generated from the clean energy cess on coal.

¹National Solar Mission, National Mission for Enhanced Energy Efficiency, National Mission on Sustainable Habitat, National Water Mission, National Mission for Sustaining the Himalayan Ecosystem, National Mission for a Green India, National Mission for Sustainable Agriculture, National Mission on Strategic Knowledge for Climate Change.

Other fiscal incentives include exemption of some parts of hybrid vehicles from customs and imposition of a concessional 5 percent rate of excise duty to increase their domestic production, lower customs duty on light-emitting diodes (LEDs) and solar lanterns, and subsidies to renewable energy projects. The NAPCC outlines a number of steps to be taken in critical sectors along with financial outlays. State Action Plans also estimated costs that are significant by any standard for implementation of its various missions. Given the magnitude of the task and requirement of funds, domestic finances fall short of the current and projected needs. Global funding through the multilateral mechanisms will enhance domestic capacity to finance climate-related efforts.

Moreover, thirteenth Finance Commission (FC-XIII) recognizes that for achieving a greener and more inclusive growth path, we need a fiscally strong center, fiscally strong states, and fiscally strong local bodies or the third tier of government. Therefore, commission proposes the strategy of “expansionary fiscal consolidation” with no compression of development expenditures. Such a fiscal strategy will provide a more encouraging environment for increasing both public and private investments, as well as for better handling of adverse economic shocks. The important challenges identified by FC-XIII include a historically high degree of vertical imbalance, recent increase in the size of the non-shareable portion of central revenue receipts, spatial inequality in the fiscal capacity and fiscal needs of different states, and increase in the fiscal obligations of the local governments due to decentralization initiatives, without devolution of human and financial resources to discharge these obligations. Moreover, traditional theology that funds and functionaries will follow functions was largely missing. Since decentralization is not fiscally neutral, more funds devolved to local bodies along with transfer of functions and functionaries would accelerate decentralization efforts. In this connection, commission has made a number of sector-specific recommendations. It has recommended three grants under environment category of Rs. 5,000 crore each, aggregating to Rs. 15,000 crores. The first grant of Rs. 5,000

crore is a forest grant, the second is for promotion of renewable energy, and the third is for water sector. The eligibility of each state for availing these grants has been decided, based on various criteria. The commission has also recommended grants to incentivize state and local governments to demonstrably improve outcomes, which are vital for achieving the ultimate development goal of improving governance and effectiveness of public institutions. The government has accepted these recommendations. An important feature of the thirteenth Finance Commission’s recommendations is a plethora of conditions imposed on both central and state governments. There are economic reasons for giving conditional transfers, and stipulating conditions is a part of providing incentives to ensure provision of normative minimum standards of the specified service (Rao Govinda 2010). The president of India has declared the next 10 years as the “decade of innovation,” but innovation happens not just in the laboratories, universities, and cutting-edge research institutions of our nation, it also happens in the districts, villages, and towns of India, where people innovate to perform and deliver better in their day-to-day activities. These innovations are the essence of the continual effort to improve governance and, therefore, need to be recognized, rewarded, and shared. To this end, FC-XIII has recommended the creation of a district innovation fund to incentivize and recognize these practices, at the levels of government closest to the ordinary citizen, and a grant for the establishment of a national Centre for Innovations in Public Systems (CIPS). This would spur a virtuous cycle of improvements in governance in every sphere of public activity by demonstrating that such improvements are within the power of every civil servant and public agent, irrespective of their location and the challenges and constraints within which they work.

Global Challenges and Indian Outlook

Sustainable development is a difficult balancing act across the globe. Nations have to simultaneously accomplish three goals with

trade-offs: (a) improve economic well-being with social justice for the present generation; (b) carefully manage use of land, forest, energy, and water resources; and (c) protect future generations. The choices are difficult in developing countries, where livelihoods are affected more harshly by climate change. Resolving the threat of climate change to human well-being thus not only depends on climate-smart development, increasing incomes and resilience while reducing emissions relative to projected increases. It also requires climate-smart prosperity in the developed countries with greater resilience and absolute reductions in emissions (WDR 2010). Over the past decades, India has mostly done well on such counts of stewardship. However, new institutional challenges are being posed by more intense pressures on land and agriculture, rapid urbanization, quality of public services, public environmental health, and deteriorating air and water. To this effect, differential prices, incentives, regulations, and taxes will need to be supportive, especially on energy, to help shift to a more efficient and equitable development path. New non-carbon, renewable energy sources and technologies will be crucial, mostly led by the private sector. Social justice will require stepped-up public spending on energy access and other elements of the environmental management. In the face of all such challenges, India will not assume the role of a powerless victim and will do everything possible to keep earth the green paradise for generations to come.

India is currently well positioned in the transition to a green economy, given its low-carbon profile, rich natural capital, and cultural assets. There also exists a large potential for renewable energies. Consequently, India can leapfrog the green economy transition by maintaining and expanding the sustainable practices that already exist. For example, practices such as low emissions, labor-intensive agriculture, community-based forestry, ecotourism, and waste management will be central to green economy transitions with enhancement of environmental assets as overall development priority. Addressing rural energy poverty will

be the most important contribution of green transitions to an Indian economy, as it will lead to both growth and poverty reduction through job creation and income-multiplying effects. It will help to light rural homes and schools, reduce indoor air pollution, run information and communication systems, refrigerate food and medicines, power rural businesses and industry (green industrialization), enhance linkages between rural farming and non-farming activities, and improve overall environment as well as human health conditions. Making renewable energy as the primary source of technology in national energy strategies would be the most effective approach to rural energy access. Furthermore, sustainable forms of agriculture including organic farming will increase yields and revenues, open up new market opportunities, and reduce climate change and environmental vulnerability. Carbon sequestration is a striking area where India can offer green services for global markets, and rich natural resources amenable to ecotourism provide another green growth option for India. Refocusing policies and investments with required technical support will lead to economic empowerment of low-income populations and decrease the unsustainable trend of rural–urban migration. Thus, realizing green economy would deliver self-sustaining growth through provision of many avenues, viz., poverty reduction, rural empowerment through improved health and education, environment conservation and protection, and finally the much desired human development and inclusive growth, thereby facilitating achievement of MDG one through MDG eight. However, this requires rejecting the development approach concentrated on “growth enclaves” and adopting environmentally benign pattern of development based on revised federal configuration.

Greening of Federal Configuration

The mainstream policy debate in recent years focuses on both climate change and economic growth which lay at the heart of the discourse of sustainable development. In the period

immediately following the 1992 Earth Summit the sustainable development goal was widely adopted by governments and others, and in many countries had a tangible impact on the priority given to environmental objectives. The 1990s saw a clear upsurge in environmental legislation and policy and, in the business sector, environmental management. Yet by the early years of the new century momentum had significantly slowed, as it failed to attract political support in a world where GDP growth remain the core interest of voters and businesses and the overriding policy objective of governments. The evidence of dangerous human-made climate change, in particular, demonstrated that something much more profound had to be done, wherein environmental protection need not come at the expense of prosperity. In this regard, an offspring of sustainable development emerged in the form of ‘Green Growth’, which is not just a normative ideal, but carries within it a strong economic claim, both theoretical and empirical (Jacobs 2012). Consequently, the federal government seeks effective ways to prevent environmental degradation and ensure sustainable human prosperity by greening its federal configuration. To this effect, we propose a “Pooled Federalism” model, wherein the contours of environment regulatory programs would be outlined by the center through statutory mandates elaborated upon by regulatory measures. States will then be encouraged to implement those programs, in accordance with federal guidelines. During the course of implementation, federal standards will form the base, upon which the states will be free to amend the details of their individual programs to accommodate local conditions and concerns. The eligibility of states for federal financial assistance will depend upon meeting the set standards. In case of failure to adopt adequate programs, states will not only be denied funding, they will also subject to various sanctions and federal preemption of their programs. The proposed model adopts a system of dual sovereignty, where states may not be parallel cohorts, but they remain essential partners. In the event of an overly prescriptive federal orientation or proliferation of additional

requirements by the center without corresponding increases in financial assistance, states and local governments will have power to raise concerns against unfunded federal mandates. The “Pooled Federalism” model is based on the fact that the geographical and economic diversity of the nation requires local knowledge and expertise, which is often unavailable at the federal level². Moreover, the diversity of environmental problems, and their solutions, from place to place, limits the ability to adopt broad nationwide solutions to environmental concerns. The model promotes balancing of power by preventing accumulation of excessive power with any single partner. Maintaining this balance is the essence of green federalism. It advocates development pattern, which will measure and monitor economic health as against economic growth at global, national, and subnational levels through composite indexes involving triple bottom-line approach. To this effect, we propose People-Planet Fitness Index (PPFI) to measure performance across three fundamental dimensions of sustainable human development.

People-Planet Fitness Index (PPFI): Idea and Rationale

Our approach to economics is going to be the biggest threat for the humankind in the twenty-first century. It is only if we change our approach towards economics and our expectations as to what constitutes a good life; we might still avoid an ecological crash later this century, because steps to fostering resilience are also steps along the green growth path. To harness economics for people and the planet, it is necessary to restructure the economy so that it truly works for human needs. Since GDP growth is at the core of the political ambition of countries, GDP has continued to grow, while nature has been progressively depleted. However, this decline in free eco-services will increasingly limit future

²See Dwyer, *supra* note 36, at 1218. See also Henry N. Butler & Jonathan R. Macey, *Using Federalism to Improve Environmental Policy* 27 (1996).

GDP growth. Therefore, the global agenda must change its focus towards living that is in accordance with the laws of nature, and policy makers must start reflecting the economics of nature in our national accounts. Adoption of these fundamentals will enable a switch from an economy of unsustainable growth to an economy of permanence and a society in harmony with nature. There is huge scope to manage global consumption, where well-being can be delinked from consumption, economic growth delinked from rising resource use, and local development delinked from international trade. Shorter-term solutions may rely on improving efficiencies within existing modes of production and consumption (reformist changes); in the longer term, however, the need is to rethink our consumption patterns and practices (transformist changes). It is time now to identify the new vision of progress and demand new tools that reconcile development and livelihood opportunities, with the need to conserve the environment. To this effect, we propose an impeccable tool in the form of PPFi that may be used to advance good practice in multilevel governance and to enhance the capacity of local governments to be more effective on climate change issues.

Construction of PPFi

Construction of PPFi is intended to even out economic and social inequities and unlock the wealth potential of ecosystems in ways that are actually sustainable and equitable. It creates resilience that can cushion the impacts of climate change, can keep communities rooted, and can help provide needed social stability. The three pillars (people, planet, prosperity) of PPFi support the kind of development whose benefits persist in the face of a wide variety of challenges, environmental and otherwise, that we are sure to face in the future. The prime concern while constructing the index was to prepare people for the forthcoming war on enlightenment. However, the war on enlightenment has to be fought with thoughts and ideas and not with guns. To this effect, a robust instrument in the form of a PPFi is constructed for successfully progressing on

the path towards SSS (strong, stable, sustainable) economy. Pursuing this path requires new policy formulations along with existing policy changes. The challenge is difficult to overcome; however, with the execution of PPFi, it will be faced and addressed in a far more confident, resilient, and capable way.

Dimensions

Gross domestic product (GDP) was designed to measure economic activity; however, it is being used as a measure of national well-being. It accounts for neither social nor environmental costs and benefits. It is also difficult to achieve sustainable decision making aiming at sustainable progress and well-being if welfare is being considered from purely financial point of view. Therefore, to effectively measure progress, wealth, and well-being, going beyond GDP is must. This requires multidimensional index showing links among society (people), environment (planet), and economy (prosperity). To this effect, PPFi is developed based on HDI (social dimension), EPI (environmental dimension), and GDP (PPP) (economic dimension). It provides a single number for country's performance across three dimensions by assigning equal weights to the individual scores. The HDI has been incorporated without income component, as this component is being represented by the GDP. The equal weights of the individual indexes can be interpreted as their equal importance for the overall performance of the country.

Normalization of the Dataset

Higher GDP is achieved at the cost of depleting natural resource reserves. However, turning resources into waste faster than waste can be turned back into resources puts us in global ecological overshoot. If we continue to overshoot at current rates, we will very soon witness a complete collapse of ecosystems and in turn the dependent economies. From the one planet perspective, it is essential that we identify our

Table 10.1 Data sorted on GDP(PPP)

Country	GDP(PPP)	EF
Qatar	102,943	10.51
Singapore	59,711	5.34
Norway	53,471	5.56
USA	48,387	8.00
UAE	48,158	10.68
Switzerland	43,370	5.02
Kuwait	41,691	6.32
Canada	40,541	7.01
Australia	40,234	6.84
UK	36,090	4.89
Japan	34,740	4.73
Italy	30,464	4.99
New Zealand	27,668	4.89
Brazil	11,769	2.91
SA	10,973	2.32
China	8,382	2.21
Iraq	3,886	1.35
India	3,694	0.91
Pakistan	2,787	0.77
Bangladesh	1,693	0.62

Table 10.2 Data sorted on GDP(Adj.)

Country	GDP(PPP)	GDP(adj.)
Singapore	59,711	11,181.84
Qatar	102,943	9,794.77
Norway	53,471	9,617.09
Switzerland	43,370	8,639.44
UK	36,090	7,380.37
Japan	34,740	7,344.61
Kuwait	41,691	6,596.68
Italy	30,464	6,105.01
USA	48,387	6,048.38
Australia	40,234	5,882.16
Canada	40,541	5,783.31
New Zealand	27,668	5,658.08
SA	10,973	4,729.74
UAE	48,158	4,509.18
India	3,694	4,059.34
Brazil	11,769	4,044.33
China	8,382	3,792.76
Pakistan	2,787	3,619.48
Iraq	3,886	2,878.52
Bangladesh	1,693	2,730.65

ecological boundaries and operate (produce and consume) within those limits. Hence, we need to adjust GDP scores by dividing it with their respective ecological footprint (EF) scores. Table 10.1 shows country-wise GDP (PPP) and EF scores, and Table 10.2 shows country-wise GDP (PPP) and resultant GDP (adjusted) scores. On comparing Tables 10.1 and 10.2, we find that there are three countries which maintain their ranking even after adjusting GDP for EF.

However, there are eight out of twenty countries which have gone down after adjusting GDP. The significant fall has been observed in the USA (fourth to ninth), the UAE (fifth to fourteenth), and Canada (eighth to eleventh) owing to their extremely high EF. Against this, nine countries have gone up in their ranking with significant rise observed in the UK, Japan, Italy, and India from tenth, eleventh, twelfth, and eighteenth to fifth, sixth, eighth, and fifteenth ranks, respectively. This shows their vigilant performance on ecological fronts which is of utmost importance for progressing towards sustainable human development.

Final Formulation of PPFi

To bring three scores to uniformity, HDI is multiplied by 100 and GDP (adjusted) is divided by 1,000. For arriving at the final formulation of PPFi, the three normalized scores are given equal weights, and PPFi is derived by dividing the sum of the three individual scores by three. The final score of the PPFi is computed by putting values of the three scores given in table in the following formula:

$$\text{PPFi} = ((\text{HDI} * 100) + \text{EPI} + (\text{GDP(adjusted)/1000}))/3$$

Results

This proposed PPFi provides a single number for a country's performance across three fundamental dimensions of the sustainable human development. This enables the quantification and benchmarking of a county's cumulative performance along all the three dimensions in a simple and systematic way. Table 10.3 better explains

Table 10.3 Country Ranking as per GDP(PPP) Vs. PPF

Country	EPI	HDI (Non- income)	GDP(adj.)	PPFI
Norway	69.92	0.975	9,617.09	87.86
Switzerland	76.69	0.926	8,639.44	85.23
Singapore	56.36	0.851	11,181.84	84.43
Japan	63.36	0.940	7,344.61	76.94
UK	68.82	0.879	7,380.37	76.84
Italy	68.90	0.914	6,105.01	73.78
New Zealand	66.02	0.978	5,658.08	73.47
Qatar	46.59	0.757	9,794.77	73.41
Australia	56.61	0.979	5,882.16	71.11
Canada	58.41	0.944	5,783.31	70.21
USA	56.59	0.931	6,048.38	70.06
UAE	50.91	0.813	4,509.18	59.10
Brazil	60.09	0.748	4,044.33	58.44
Kuwait	35.54	0.705	6,596.68	57.34
China	42.24	0.725	3,792.76	50.89
SA	34.55	0.604	4,729.74	47.42
India	36.23	0.568	4,059.34	44.54
Pakistan	39.56	0.526	3,619.48	42.78
Bangladesh	42.55	0.566	2,730.65	42.15
Iraq	25.32	0.616	2,878.52	38.57

the importance of the PPF. As evident from the table, Qatar, USA, UAE and Kuwait which rank at first, fourth, fifth and seventh positions based on GDP (PPP) (Table 10.1) fall fiercely to eighth, eleventh, twelfth and fourteenth positions respectively on considering PPF (Table 10.3). This is due to their extremely high EF score, and mediocre performance on social and environmental fronts. Similarly Singapore, Canada, South Africa and Iraq which occupy second, eighth, fifteenth and seventeenth positions in GDP terms (Table 10.1), slip down to third, tenth, sixteenth and twentieth ranks respectively in PPF terms (Table 10.3). Although, their HDI performance is good or above average, fall in their ranking is mainly due to high EF and not-so-good or poor performance particularly on environment fronts. Against this Switzerland, Japan, UK, Italy and New Zealand which belong to sixth, eleventh, tenth, twelfth and thirteenth ranks based on GDP ranking (Table 10.1), shoot up to second, fourth, sixth and seventh positions when evaluated on PPF (Table 10.3). This progress is due to their

mediocre EF score, and strong performance on social and environment indicators.

In case of Norway, which moves up by two ranks, the high EF score is being offset by its excellent performance on economic and social parameters, as well as good environmental performance. Regarding rest of the countries, which includes Brazil, China, India, Pakistan and Bangladesh, we find that, there is an upward shift of one rank. This is mainly due to their low EF score. All of them occupy lower strata in country ranking, because of their poor GDP scores, poor EPI scores (except Brazil) and their performance on social front is also mediocre.

Discussion

The PPF as presented here is an attempt at developing and prototyping a composite index constructed from a matrix of already established indexes focusing on a particular dimension among the three fundamental dimensions – people, planet, prosperity – of the sustainable human development. During the conceptualization and prototyping exercise, we have tried to ensure that all relevant parameters and factors are included and care has been taken to avoid duplication of parameters. The simple formulation of the index allows different PPF scores to be computed by adjusting the individual weights. For instance, to compute an index based on only the economic and environmental performance, we can assign a weight of zero to the human development index and weigh the other two scores proportionately. Using the index in the proposed form will facilitate as well as compel nations to move closer to sustainability. Moreover, the criticism received by “alternative measures of progress” developed so far, regarding their accuracy, availability of data, detail, and scope, is being addressed by PPF. Although it is developed with an aim to make it functional globally, we recognize that arguments can always be put forward towards its modification. Thus, the PPF is and will continue to be a complex, evolving exercise. This is mainly because the

multitude of factors influences the relevance, robustness, and acceptance of such an index.

Conclusion

Devising a solution that works for everyone has never been easier. It requires changing the entire structure of our exploitative, wasteful, resource-intensive economy and strengthening the true development prospects, of which human being is the principal raw material. Human development that includes healthcare, education, and social well-being is now critical to economic development. As human development report of 1991 by UNDP put it, “Men, women and children must be the centre of attention with development around people, not people around development, but development must be participatory and involves local people in decision making.” For that, coordination between national and local is a must, which we could bring through green federalism. Its multilevel governance approach involves retreat from direct intervention and enables a switch from “government” to “governance” emphasizing the role of subnational governments. Instead of following traditional persuasion methods, it creates an appeal for pro-environmental behavior through greening of brains based on social and ethical norms along with economic norms. The approach necessitates central bodies to undertake institutional, technical, and financial reforms on a mission mode, enabled by state governments. By bridging the time gap fast before it is too late to reverse the damage caused every moment, green federalism promises to maintain the economic “miracles” while ascending from human development towards sustainable human prosperity without involving environmental and social costs. It aims policy prescriptions at correcting resource-intensive production and consumption patterns through mechanisms such as PPFi. Its direct benefits will enable closing price gap by internalizing the costs of environmental externalities. In addition, the indirect benefits will reach far into the broader Indian and global community,

positively affecting the lives of hundreds of thousands of people, enhancing biodiversity, and securing crucial ecosystem services. The present work guides policy reforms by responding to both ‘where to regulate’ and ‘how to regulate’ concerns.

With robust policy prescriptions accompanying proposed index, wealth can be found in natural resources and environmental and behavioral knowledge that people use to manage them, so that the loss in coping capacity of the ecological system is prevented. Moreover, judicial implementation of such policies will begin the path to healthy, sustainable, and equitable human societies, provided approach involves water in the fields and food on the table for all. It is an appropriate formula for sustainable human prosperity. The overall structure of intergovernmental fiscal arrangements needs to change in accordance with this vision. However, change can happen only when social pressure is strong and is accompanied by political support. We believe that implementation of PPFi will contribute to the social demand and acceptance for change and provide concrete ideas on how to effect the change. Furthermore, it will prove to be the most powerful change agent and the vital answer to the climate-development nexus.

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Economic Sustainability in Light of Consumer Behaviour: Gandhian Perspectives

11

Nimisha Shukla and Sudarshan Iyengar

Abstract

Human species is at crossroads. Since the era of industrialisation, rate of growth of economy has recorded rapid rise, especially since the later half of the twentieth century. In recent past, it is increasingly being realised that path that human kind has taken may not be sustainable.

In Western thought, sustainability debate is around economic sustainability. Sustainability argument has two sides: production and consumption. The latter is hardly addressed in Western thought. Neoclassical economics emphasises mainly on technological solutions to sustainability. The present lifestyle relies on exploitation of natural resources.

‘How much should we consume?’ ‘What strategies for changing consumer behaviour actually work?’ These are some questions that human society has now started asking. It is necessary to visit alternative paradigms. Gandhian economic thought is one such paradigm. The paper is divided into three sections. First section briefly explains contemporary scenario, and it is argued that perpetual growth of economy and hence consumption is a myth. The second section contains review of Gandhian vision with special reference to materialism as portrayed in Hind Swaraj. In the third section, we propose to review concept of sustainable consumption in light of Gandhian thought.

Keywords

Industrialisation • Sustainable consumption • Inter- and intragenerational equity • Economic growth • Lifestyle issues • Gandhian thought

‘Are we consuming too much?’ ‘How much should we consume?’ These are some of the questions that human society has started asking

seriously (Arrow et al. 2004; Guha 2006). Although, there is no consensus among scholars, the issue of consumption level and pattern and its temporal effects on global material resources has assumed some importance. Cumulative and accumulated effects of micro and macro level economic activities on environment and ecosystems’ services are becoming increasingly

N. Shukla (✉) • S. Iyengar
Rural Economics, Gujarat Vidyapeeth, Ahmedabad,
Gujarat, India
e-mail: nimisha63@gmail.com;
nimisha@gujaratvidyapith.org

adverse and threatening the scope of luxurious survival of human beings on the globe. The physical size of the economic system – the rate at which it takes resources from the ecosystem and spews them back as waste – should never exceed the capacity of the ecosystem to sustain it. Thus, the size is under threat.

It is not enough that ecological economists work on the size problem and post warning signals. Societies will have to reset their objectives and the mode and method of development. Even the ecological economists with the dominance of the ‘economists’ mindset tend to push the humanity towards the march of industrialisation with mass production with the help of fresh insights and methods in attempting valuation of ecosystem services and resetting production equations. The issue of sustainable consumption is addressed from the point of view of sustainable use of natural resources and ecosystems services ensuring almost infinite availability and intergenerational equity. Both the classical and neoclassical economists have retained an unbroken identity by virtue of its steadfast support for industrial development based on market system. All those who believe in the efficacy of the market system’s ‘invisible hand’ have assigned the State a valuable complementary role, but the goal is clear. Humanity has to head towards industrialisation. Constantly rising GDP is the only robust indicator that reports about the health of the society. Marx and his associates have criticised capitalism but favoured industrialisation. Thus, all in all, almost every school of economic thought has approved industrialisation. In the context of the issue of sustainable consumption, time has come for the humanity to think about alternative modes of production redefining scale, technology and efficiency. Gandhian economic thought and some experiments in the past have shown the way in this direction. There also has been substantial academic argument in ‘Small is Beautiful’.

We also need to raise and tackle important conceptual issues, such as ‘What exactly is consumption?’ ‘Which consumer activities are most ecologically significant?’ and ‘What strategies for changing consumer behaviour actually work?’ All along from the day we

have defined the mainstream economics, we have assumed that for economic analyses, preferences are given and wants are unlimited. Further and more importantly, we believe that consumption is an end in itself. We forget that it is not an end in itself. The end depends upon ethics, culture and philosophy that govern a society. Gandhian thought has discussed this issue to some extent. Gandhi has to his credit the famous quote which says that there is enough for everybody’s need, but there is not enough for even one person’s greed. Wants have to be limited, and limiting wants and choices has good potential to solve problems that have arisen in the present-day functioning of the economies. It is the determination of wants and types of preference that will support the local economies that function in the overall constraints of the local ecosystem services.

As is known, current trends in ecological economics are overly focussed on valuation. The neoclassical economists who believe in the supremacy of the market and the ability of technology and market to solve all economic problems of human race assume increasing economic growth infinitely. It is further assumed, on the basis of trickledown theory, that the growth results in higher standards of living for all. It is not that the neoclassical thinking is new but it has found new strength after the fall of the economies based on Marxian models. It has also been gradually realised that there is market failure as well. The market has failed to increase the well-being of the critical mass of the poor and marginalised section of the population even in countries such as India that has made a sincere and partially successful attempt to liberalise, privatise and globalise its economy. Market has also failed because valuation of environmental and ecosystem services has severe limitation. In reality natural capital cannot be substituted completely. In this chapter an attempt is made to understand the concept of sustainable consumption from the view point of both production and consumption. The production side review is attempted with focus on energy use and requirement for sustaining productions in the economies, and some limitations in

Table 11.1 Growth of consumption (average annual per cent growth)

Group of countries	Household final consumption expenditure				Government final consumption expenditure	
	Total		Per capita		1990–2000	2000–2007
India	4.8	6.0	2.9	4.5	6.6	3.4
Low income	3.5	4.9	1.0	2.6	0.1	6.6
Middle income	4.1	5.6	2.7	4.5	3.5	4.9
High income	2.8	2.4	2.0	1.7	1.5	2.2
World	3.0	2.9	1.5	1.7	1.7	2.6

Source: World development indicators, the World Bank, 2009

it have been examined. On the consumption side, lifestyle issues have been raised in the context of Gandhian economic thought and philosophy. The first section tries to understand the contemporary scenario and its implications. It also tries to argue that perpetual growth of the economy and hence consumption is likely to be a myth and that human societies will have to be careful in using these sources. Ehrlich (Giddens 1999) may have lost the bet once, but in the long run Julian Simon is likely to be proved wrong. If all the poor and low-income countries try to achieve the consumption levels of high-income countries with the use of energy-efficient technologies, the end result is likely to be disastrous. The second section reviews Gandhian vision with special reference to materialism as portrayed in *Hind Swaraj*, Gandhian commentary on western civilisation and modernity. Since environmental problems had not come up sharply and significantly during Gandhi's times, *Hind Swaraj* had little to say about it directly. But the lifestyle issue is discussed with eminence. In the third section of the chapter, we have tried to review the concept of sustainable consumption in the light of Gandhian thought.

The movement from soil to oil economy has resulted in increase in consumption of luxuries for human species. The production function has been further modified. Now production becomes a function of only capital where land and labour are ignored. Labour is treated as accumulated capital and land is assumed to respond positively to capital. As labour can be perfectly substituted to capital, there is no limit to growth. Economic growth becomes an ever-expanding

phenomenon as there will be no dearth of capital in the economy. Economists are optimistic about the efficiency and effectiveness of omnipresent technology and its ability to solve any problem. Table 11.1 provides a bird's-eye view to the consumption scenario of the last two decades.

The total household final consumption rate is higher during 2000–2007 for low- and middle-income countries including India. Compared to the world and high-income countries, India's per capita annual rate of consumption is high for both periods, especially during 2000–2007. Government consumption growth rate is high for India compared to the world and high-income countries. However, the data is not available for the last 2 years, but economic slowdown has affected high-income countries significantly. Annual growth rate for low- and middle-income countries is comparatively higher. More than 80 % of the world population lives in these countries, and high growth rate of consumption would imply more pressure on natural resources and other factors of production.

The use of energy should reflect the level of technology and industrial nature of the economy. With industrialisation, the energy consumption goes on increasing. Tables 11.2, 11.3 and 11.4 show the Total Primary Energy Supply (TPES) at two points of time: 1973 and 2008.

The Total Primary Energy Supply has almost doubled during the last 35 years. The same is the case for energy used for consumption purpose. The share of Oil products still dominates the scenario, but the importance of Others (geothermal, solar, electricity and heat, wind etc.) has gone up. It indicates a shift towards nonconventional energy sources world over.

Table 11.2 Share of consumption in total primary energy supply 1973 (in million tonnes of oil equivalent (mtoe))

1973	Coal	Crude oil	Oil products	Gas	Nuclear	Hydro	Combustible renewable and waste	Others	Total
TPES	1500.90 (24.5)	2866.21 (46.9)	-46.21 (-0.8)	978.94 (16.0)	53.05 (0.9)	110.23 (1.8)	646.09 (10.6)	6.00 (0.1)	6115.21 (100.00)
Consumption	621.16 (13.3)	22.11 (0.5)	2227.86 (47.6)	671.37 (14.4)	-	-	617.51 (13.2)	515.63 (11.0)	4675.64 (100.00)

Table 11.3 Share of consumption in total primary energy supply 2008 (in million tonnes of oil equivalent (mtoe))

2008	Coal	Crude oil	Oil products	Gas	Nuclear	Hydro	Combustible renewable and waste	Others	Total
TPES	3314.18 (27.0)	4144.84 (33.8)	-85.65 (-0.7)	2591.07 (21.1)	712.18 (5.8)	275.88 (2.3)	1224.81 (10.0)	90.08 (0.7)	12267.38 (100.00)
Consumption	823.09 (9.8)	20.10 (0.2)	3482.06 (41.3)	1313.42 (15.6)	-	-	1070.27 (12.7)	1719.47 (20.4)	8428.41 (100.00)

Source: Compiled from world energy statistics, 2010; international energy agency

Table 11.4 Per capita income and energy consumption in different economies

Countries	Per capita income in US dollars				Per capita energy consumption in kg oil equivalent			
	1978	1988	1999	2007	1978 Kg coal equivalent	1988	1997	2006 ^a British thermal unit (BTU)
India	180	340	450	950 (59.81)	176	100	479	15.9
% to high-income countries	2.23	1.99	1.75	1.86	2.49	1.96	8.92	5.75
Low-income countries	200	320	410	578 (36.35)	161	126	563	15.9
% to high-income countries	2.48	1.87	1.59	1.58	2.28	2.47	10.49	5.75
Middle-income countries	1,250	1930	2000	2,872 (94.34) ^b	903	585	1,368	127.2
% to high-income countries	15.46	11.30	7.77	6.73	12.79	11.47	25.47	46.05
High-income countries	8,070	17,080	25,730	37,566 (136.10)	7,060	5,098	5,369	276.2

Source: World development reports 1980, 1990, 2000/2001 and 2005. The World Bank, Washington, DC

^aData for 2006 are for different set of countries. The low-income country data is average for Africa, middle income is for Middle East and high income is for North America

^bThe income figure for higher middle-income groups has been taken for this analysis because Middle East incomes are in that range

Per capita income in India has grown over time. In 30 years it has grown five times. In case of lower-income countries, the club to which India belongs to has experienced relatively smaller increase. The average per capita income has increased by 2.9 times, although in 1978, India's average per capita income was lower to that of the average for the low-income countries. Middle-income countries have not been slow in

experiencing growth in per capita income over time; they have experienced a rise by 2.29 times. High-income countries that largely comprise of the OECD countries have experienced a steady rise in the per capita income. Between 1978 and 2007, the average per capita income increased by 4.1 times. While India and other low-income countries, which have about 40 % of the world population in 2000, are trying to run faster in the

economic growth race, the high-income countries are ahead and fast. The gap between low-income countries and the high-income countries has widened between 1978 and 2007. In case of India, the gap has declined marginally.

The energy scene is interesting and instructive. Oil equivalent use data are for two points 1988 and 1997, and when one relates it with the per capita income, there is some surprise in the store. India and low-income countries appear to be achieving increase in income by using more energy per dollar earned. In 1988 India used 0.3 kg of oil equivalent for every per capita dollar earned, and in 1999 it used 1.06 kg of oil equivalent of energy for earning 1 dollar per capita. In case of low-income countries, the story is same. In case of high-income countries, increase in income is accompanied by decrease in energy consumption. Clearly, the high-income countries are on clean technology path, and India and low-income countries are with old and perhaps dirty technologies using more energy per unit of production. Although India has experienced increase in per capita income over the last 25 years, poor people continue to exist. In the year 1999–2000, 28 % of the population was below poverty line using the national poverty line, which is slightly less than a US dollar a day. Using the international poverty line, one finds that India had about 35 % of population that earned less than 1 US dollar a day and 80 % of the total population earned less than 2 US dollars a day. In absolute numbers they are staggering figures of 350 and 800 million persons. Energy consumption data for 2006 is for British thermal units (BTU). The per cent share to high-income countries offers comparative picture.

One has to accept the fact that the life standard that was affordable to only a small proportion of population a century ago has become a reality to a larger segment of the society. The ever-increasing middle class, influenced by demonstration effect, has expanded its aspiration level with demanding more and more goods and services that result in more consumption. The system has become more prominent with the advent of globalisation. Individual independence, which is measured by more and more physical comforts she/he can

enjoy, in western thought, is rising by leaps and bounds with diversity in goods and service.

Dasgupta and Maler (2004) have argued that the economic growth issue is vexed and in a way call for a lot of care and caution. Commenting on growth experiences and growth models, Dasgupta and Maler argue that it is a little heavy burden that economists are putting on the experience of the last 250 years or so. If one takes a longer perspective in history, the effect is immensely sobering. The growth rates, including the last 200 years, even for high-income economies are not much above zero. In the sustainable development debate, arguing for non-declining consumption or non-declining utility even in a 100- or 200-year framework does not help. Non-declining natural capital stock approach, even if it is feasible to measure, is not a very meaningful exercise at an aggregate level because the impacts of environmental degradation are felt at local levels and on the local communities who eke out living out of it.

There is an issue of intra-generational equitable consumption as well. The difference between the low-income and high-income countries is sharp and has grown over time. So is true in the case of an economy. The gap between the rich and the poor in all likelihood would increase with economic growth. The rich will find substitutes and the poor would almost perish. It has already started happening. It is not uncommon to hear these days about the eco-conscious society promoting wood substitutes for living and furnishing in urban areas because we have almost exhausted the timber forests by cutting it at almost uneconomic prices. The rich have found 'substitutes', thanks to science and technology. Only poor are left high and dry. Forests are gone and hence fuel wood, food and fodder. Topsoil has eroded. Downstream land enrichment is gone and so is gone the cultivation prospects. So what do the poor do? Migrate. They go to the urban areas, crowd it further, make it filthier, create immense pressure on the minimum basic services and create all kinds of economic, social and cultural negative externalities. Even in 2003 after 14 years of freeing the economy from the clutches of the government, 80 % in India earned less than

2 US dollars per day per capita. In Schumacher's (Schumacher 1977) words, people do not become mobile; they become footloose and get eventually lost.

Globalisation means almost unrestricted movement of foreign capital and technology, which might lead to destroying the domestic systems of production and consumption. It is often feared that the ongoing process will ultimately undermine the autonomy and authority of nation states especially by the multinational and transnational national companies. In today's world, the state is supposed to safeguard the interests of the poor and marginalised section of the society. But the State and Civil society offer individual unfettered freedom, only restricting those actions that would harm others or hinder their exercise of freedom (Iyengar 2006). Liberalisation, privatisation and globalisation in economic sphere have raised new and vital threats of ecological and environmental sustainability. Society is also changing fast from family and kinship-based survival to unitary existence with increasing support of machines. Such development may threaten the sustainability of human species in the ultimate analysis. The triumph of capitalism, after the disintegration of USSR and demise of socialism, has resulted in serious implications for humanity. The individual in the society has accepted maximisation of utility from consumption of goods and services as the basic value. Enters greed. Prof. Stanislav Menshikov says, 'All economies that are based on these principles (maximisation of utility and profits) tend to create and promote unequal conditions for the people' (Menshikov 2006).

The lifestyle of the rich exerts immense pressure on natural resources that are scarce relatively and ultimately in absolute terms as well (unless of course humanity is able to tap the resources from Moon and Mars!). The earth does not have adequate natural resources, if human wants continue to be unlimited and the humanity as a whole aspires to imitate the lifestyle of the rich. In such circumstances, the existence of the earth would be in jeopardy. Increased production of luxurious goods and their conspicuous consumption has resulted into

deterioration and depletion of natural resources. The problem of various types of pollution has intensified world over. Between the developing and developed economies, only the intensity and nature of pollution differ.

It is important to draw attention towards two things. First is the form in which things are used and consumed, and second is the per capita quantities consumed and used, in other words level and composition of consumption. Thinking in terms of basic needs of human survival, i.e. food, clothing and housing, and understanding the qualitative difference that has taken place over the years, one can conclude the dominance of market economy and its precise focus. It tries to capture the middle-income group who can afford to indulge into luxuries of life, better known as consumerism. Economists have successfully convinced the world that the benefit of such consumerism would trickle down and the poor will get benefit from it in the long run.

World over, food habits have been evolved from local to global over time. Every region used to have a staple food grain and the exchange was barter. With increase in accessibility of means of transport, diversification started taking place. Initially the process was slow, but for the last decade, it has picked up phenomenal speed. The aggressive entry of MNCs in food market has changed the form of food entirely. Food market has become demand induced. The rich and poor alike are spending a substantial amount of money after eating at fancy and not so fancy eateries where demand is based on tastes and packaging rather than its nutritional value. The vicious circle is completed when pharmaceutical companies assure the consumer about the effectiveness of their products to treat her digestive system. The same is the story about clothing.

As far as housing needs are concerned, the problem of providing housing amenity to the increasing world population is doubled by the demand for better and spacious houses. With increase in spending ability, the general tendency is to move to a better house. Change in the building material, interior designing and more comforts are demanded as people earn more. The demand for housing is not like demand for food.

Table 11.5 Key energy indicators, 2008

Region	TPES (mtoe)	Electric consumption(TWh)	CO2 emissions (Mt of CO2)	Per capita TPES (toe)	Per capita electric con (KWh)	Per capita CO2 emissions (t)
World	12,267	18,603	29,381	1.83	2,782	4.39
USA	2,284	4,156	5,596	7.50	13,647	18.38
China	2,131	3,293	6,550	1.60	719	4.92
India	0,621	0,645	1,428	0.54	566	1.25

Source: International energy agency, 2010

It is more elastic. It has been observed world over that people are demanding better furnished and more spaced houses. For example, from electric fan to air coolers and from air cooler to air conditions, the demand keeps on expanding with economic prosperity. The institutes producing architects and interior designers are increasing in numbers reflect the changing lifestyle of the society.

The present form of economic regime, where private sector and state have formed nexus, has increased inequality and inequity in consumption among the countries and within the countries. Another important implication of present growth regime is environmental deterioration and degradation. In December 2009, the world leaders gathered in Copenhagen to discuss the ways and means to control climate change. In fact, climate change is a symptom; the reasons for disease lie in the present lifestyle. It has now been accepted that the manner in which the rich countries and the rich in poor countries live is not sustainable. As given in the International Energy Agency, 2010, comparison of Per Capita Carbon Dioxide Emissions (Metric Tonnes) in 2008 would give an idea of disparity between developed and developing nations. As against 18.38 MT of the USA, India's per capita emission was 01.2 s MT. The world average was 04.39 MT. Some of the other key indicators are shown in the Table 11.5.

A study by leading economists (Arrow Kenneth et al. 2002) has tried to answer the question 'Are We Consuming Too Much?' Citing other studies, they see the failure of poorer countries of the Indian subcontinent and sub-Saharan Africa to satisfy the sustainability criterion. They also concluded that as compared to changes in gross national product or human development index, 'the prospects for the future

appear much dimmer' in terms of sustainability criterion. For the developed countries, they did not subscribe to the World Bank view. The World Bank indicated that consumption in richer nations is not excessive and these countries had appeared to undertake sufficient investment to increase per capita wealth. They found this claim to be biased upward. They have also cited a few reasons in support to the conclusion. While advocating policy action, they have also suggested research to identify those areas where consumption becomes a threat to sustainability. In the next section, we would discuss the Gandhian views on consumption of the western society as expressed in his revolutionary book *Hind Swaraj*.

Perhaps Gandhi was the first influential person in the last 250 years or so to raise the issue of consumption in the analysis of economic systems. Economic development took place taking into consideration the production side. Demand side analysis also received attention, but an implicit assumption of unsuitable/infinite wants was never brought to fore nor its implications on society and environment. Gandhi could see modern civilisation leading to limitless scope to eat, clothe and leisure for the body as sole purposes of existence. It had failed to achieve improvement, elevation and exaltation of self that could achieve moral progress. The focus on the physical existence of the body per se again was not Gandhi's sole concern because he had grasped that the humanity had been in this challenge since its realisation that human existence had a significant difference than that of other species. Therefore, in *Hind Swaraj*, he had tried to show the limitations of limitless consumption. Gandhi had emphasised on equity criterion rather than widely accepted efficiency criterion. His economics, thus, was based on ethical premises. For him, economic progress was

never the ultimate aim of the humanity. Economic system was a subsystem like social, political and moral behaviour. He never accepted the dominance of economics over other subsystems. Like institutional economists, he also believed that all the subsystems are interdependent and influence each other that in turn determine development process.

In *Hind Swaraj*, Gandhi had depicted an individual in the centre of the human society who was more concerned with behaviour with self. Gandhi explained the implications of the moral standards in society with increase material prosperity and consumption. As a central critique of western civilisation, *Hind Swaraj* has focussed on material progress and physical comfort. The relationship is negative. With more material prosperity, fall in moral progress would be more. As far as Gandhi was concerned, body and bodily comforts were to be ignored. In traditional Indian civilisation, the ultimate objective of an individual is to achieve salvation for the soul. The central thesis of the religion is liberalisation of the soul rather than achieving bodily comforts. The real quest is spiritual and hence material quest is looked down upon. In the pursuit of achieving salvation, the body was to be treated as a necessary evil and hence needed to be ignored. Gandhi could see that individual liberty in western thought had been restricted to bodily comfort, hence consumption, that made merely physical existence of an individual a central issue of concern replacing liberation or emancipation in real sense of the term. For him it was important to understand the place that the body and body comforts had received in the evolution of the human society. It could be best understood in the realm of economics that as a system it had dominated the development process of mankind.

The neoclassical economists have faith in technology for limitless material growth. Initially Gandhi, too, was attracted by this grandeur that technology had brought. During his study for law in London, he, too, like the youth of that time spent a lot of money on his clothing, and he tried to look, dress and behave like an Englishman. In this process, he went for lessons in dancing and

public speaking. The promises to his mother kept him away from liquor and female company. This was the way he travelled through conspicuous consumption.

Gandhi was a successful lawyer in South Africa, earning good income. The lifestyle he adopted in South Africa was of an affording family. Everything changed when he read Ruskin's 'Unto This Last'. While writing *Hind Swaraj* at the age of 40, he emphatically stressed on the vices of modernity that was one of the characteristics of modern civilisation. He presented an alternative that he considered as a solution for the development of not only India but also of the entire world. In *Hind Swaraj*, he had said, 'We want English rule without the Englishman. You want the tiger's nature, but not the tiger; that is to say, you would make India English. And when it becomes English, it will be called not Hindustan but Englishtan. This is not the *Swaraj* I want'.

Gandhi drew a picture of Civilisation that he took objection to. He wrote, "Let us first consider what state of things is described by the word "civilization". Its true test lies in the fact that people living in it make bodily welfare the object of life. We will take sonic examples. The people of Europe today live in better-build houses than they did a hundred years ago. This is considered an emblem of civilization, and this is also a matter to promote bodily happiness. Formerly, they wore skins, and used spears as their weapons. Now, they wear long trousers, and, for embellishing their bodies, they wear a variety of clothing, and, instead of spears, they carry with them revolvers containing five or more chambers Formerly, in Europe, people ploughed their lands mainly by manual labour. Now, one man can plough a vast tract by means of steam engines and can thus amass great wealth. This is called a sign of civilization. . . . It has been stated that, as men progress, they shall be able to travel in airship and reach any part, of the world in a few hours. Men will not need the use of their hands and feet. They will press a button, and they will have their clothing by their side. They will press another button, and they will have their newspaper. A third, and

a motor-car will be in waiting for them. They will have a variety of delicately dished up food. Everything will be done by machinery. Formerly, men were made slaves under physical compulsion. Now they are enslaved by temptation of money and of the luxuries that money can buy. There are now diseases of which people never dreamt before, and an army of doctors is engaged in finding out their cures, and so hospitals have increased. This is a test of civilization. Formerly, people had two or three meals consisting of home-made bread and vegetables; now, they require something to eat every two hours so that they have hardly leisure for anything else. This civilization takes note neither of morality nor of religion. Its votaries calmly state that their business is not to teach religion. Civilization seeks to increase bodily comforts, and it fails miserably even in doing so". Also he believed that 'This civilization takes note neither of morality nor of religion'. Another quote from *Hind Swaraj* about body reads as: 'Formerly, men were made slaves under physical compulsion. Now they are enslaved by temptation of money and of the luxuries that money can buy. There are now diseases of which people never dreamt before, and an army of doctors is engaged in finding out their cures, and so hospitals have increased. This is a test of civilization'.

In *Hind Swaraj*, Gandhi had also criticised some features of modern civilisation like railways, lawyers and doctors. Let us analyse the role of doctors in the context of consumption behaviour. To quote Gandhi, 'Let us consider: the business of a doctor is to take care of the body, or, properly speaking, not even that. Their business is really to rid the body of diseases that may afflict it. How do these diseases arise? Surely by our negligence or indulgence. I overeat, I have indigestion. I go to a doctor, he gives me medicine, and I am cured. I overeat again, I take his pills again. Had I not taken the pills in the first instance, I would have suffered the punishments deserved by me and I would not have overeaten again. The doctor intervened and helped me to indulge myself. My body thereby certainly felt more at ease; but my mind became

weakened. A continuance of a course of medicine must, therefore, result in loss of control over the mind. I have indulged in vice, I contract a disease, a doctor cures me, the odds are that I shall repeat the vice. Had the doctor not intervened, nature would have done its work, and I would have acquired mastery over myself, would have been freed from vice and would have become happy'.

While defining true civilisation, Gandhi argues, 'We notice that the mind is a restless bird; the more it gets the more it wants, and still remains unsatisfied. The more we indulge our passions the more unbridled they become. Our ancestors, therefore, set a limit to our indulgences. They saw that happiness was largely a mental condition. A man is not necessarily happy because he is rich or unhappy because he is poor. The rich are often seen to be unhappy, the poor to be happy. Millions will always remain poor. Observing all this, our ancestors dissuaded us from luxuries and pleasures'.

Thus, Gandhi prescribed Indian traditional form of civilised mechanism required for liberation of an individual not only in the sense of physical existence but also for the liberation of soul – *moksha*. Physical comforts would become secondary if *moksha* becomes the sole objective of human existence. Greed, possessiveness and violence would gradually disappear from human nature. Society comprised of such individuals would improve the structure from competition to cooperation and from self-centeredness to selflessness that would in turn strengthen human being in body and in mind. It can be argued that Gandhi had never favoured reversing the clock of human growth. His emphasis for retaining the core values of ancient Indian civilisation was based on his conviction of this civilisation for building equitable and healthy sustainable society.

In this context, an Indian folklore is relevant. An old man was planting a sapling of mango in the presence of his grandson. The King happened to pass by in disguise and asked the old man about the wisdom of his action because the mango would yield fruits only after 15 years or so and the old man might be dead by then. The old

man replied that the passerby was being foolish if he thought that he was planting mango tree with the hope to eat the fruit himself. It was for his grandson. The old man's grandfather had planted a mango tree when he was a boy, and he ate the mangoes all his life, and thus he felt obliged to plant a tree for his grandson. This is our institutionalised understanding of intergenerational equity in practice.

We should perhaps remind ourselves that the 'old man and the disguised king's story' has its basis in the Vedic hymns. There should not be any doubt about the development of philosophy about life and living in India thousands of years before the western society embarked on this course. It is important for us to understand that the Vedic gurus and rishis had gained some understanding about the human existence in the vast nature and had realised that given the prakruti (nature) of manushya (human species), *saha-astitva* (coexistence with nature) was the key to sustained (eternal) and happy life of human species on this earth. The Vedic period scholars not only understood the full import of ecological services provided by nature but also realised the need for spiritual base for regulating human behaviour in respecting while using nature for survival. The reverence for nature was not created only for spiritual purpose, but it was also institutionalised for sustainable survival. Ishavasya Upanishad in its first verse makes this so clear in a rather spiritual way. It says: *Ishavasyam idam sarvam Yatkinchit Jagatyam Jagat; Ten tyaktena bhunjitha maa grudha kasya swid dhanam*. It means consume by renunciation.

In December 1916 Gandhi addressed a gathering of economic lecturers at Allahabad where he perhaps for the first time introduced the concept of voluntary poverty. He was convinced that material prosperity did not ensure high moral standards. Instead, the dash towards material prosperity has brought the moral standards down and led to decay of human society. This is reflected in *Hind Swaraj* and other articles thereafter. He believed that the societies that prospered materially experienced a moral fall. In this context later he has formulated *aparigraha* (non-accumulation) as one of the eleven vows he has advocated.

It is important to understand sustainable consumption and thereby development in the context of Gandhian thought. In this section, we have tried to put forward an alternative paradigm based on *Hind Swaraj* and other Gandhian writings. Gandhi had foreseen the situation and warned us in *Hind Swaraj*. Many scholars also subscribe this view of Gandhi. Sethi (1985) also explains this point of view by saying 'the crisis is not merely philosophic or intellectual, it is also empirical . . . The science of Economics ceased to be dismal, it rather became an art of rat race . . . In the industrialised countries, the situation of misery that was reflected in the unfulfilment of basic needs, was transformed into a situation of unfulfilled wants of infinite variety At any level of rich society economic society is perpetually poor materially of course because means would always remain scarce relative to wants Relative deprivation never goes away'. Finally, he says, 'The production philosophy of the modern industrial society is dominated by the corporate greed, technological determinism, and ecological carelessness'.

Diwan and Lutz (1985) have expressed the following views on American society that has undoubtedly attained immense economic prosperity as compared to other nations in the world. In the context of benevolence and malevolence in welfare economics, they note, 'In the rich countries the quality of life is deteriorating even if the standard of living has phenomenally improved. The value of family life and other social values are breaking down. A substantial number of children have never lived with both their parents. The single parent household is in the process of becoming the majority of the households in United States. Kidnapping and various forms of child abuse are now a national phenomenon. The adult life is marred by anxiety and job stress. Work for a large majority of workers is both stressful and meaningless. There is growing scarcity of joy or pride in the work done. Old age is full of loneliness. Life has, no doubt, been prolonged, but the lifestyle in many places has become more like a nightmare'.

Unending material prosperity has been the value that has been consistently cherished. It has

resulted in unqualified economic growth. The excessive reliance and promotion of technology as a policy prescription for continued economic growth has led to ecological disaster in practice. The present context of Gandhi's thoughts with reference to materialism lies in the consumption pattern that Gandhi had suggested. Raval (1971) has termed it as 'Gandhi effect', which has its basis in 'asceticism' and 'paternalism'. In the area of the Economics, consumption pattern among different income groups in society has been discussed at frequent intervals, and it has been argued that different income groups have different consumption pattern. Veblen had pointed out in this context that there is a tendency of emulation in consumption. He brought out that there is and would be a 'vulgar display of wealth' by the richer few of the society. This tendency was an important constraint on free choice. Dussenbury carried these analysis further and studied cross-sectional variations in consumption expenditure of different income groups and termed this phenomenon as a 'demonstration effect'. On the other hand, 'Gandhi effect' suggests control on wants because Gandhi understood that human wants given the freedom of choice were insatiable. The societal approach to accept the insatiability of human demands and then use science and technology for want satisfaction was not a sustainable approach according to him. The individual preference function has to be impacted by this. In positive economics, there is absolutely no scope for introducing this constraint and then maximising utility. Income is accepted as the main constraint. Gandhi had categorical suggestions for preferences. In a particular context (in his case the freedom struggle), the individual preference for 'Swadeshi' – the home made – was extremely important. 'It is the normative concept of preference, which I shall call 'ethical preference' that lies at the heart of the Gandhian approach to economic theory' (Dasgupta 1996).

For Gandhi, the individual was in the centre. He believed in the ability of individuals to construct society and its institutions. His main concern remained as reconstruction of non-violent society. Thus, in *Hind Swaraj* the

focus is on the individual in the context of the society which was non-violent and well governed. Gandhi saw the powerful impact of individual freedom prevailing in modern civilisation on the creativity to solve all adversities and problems of the material world and the perversions it led in the immoral behaviour damaging the ethos of the society. He believed that unless the individuals disciplined themselves, market-led socio-economic order would eventually lead to moral and ecological disasters. Neither did he support the idea of the State completely controlling the economy and therefore the lives of people. The wants control theory of Gandhi simultaneously solves the problem of consumerism and unsustainable resource use. The disciplines of ecological and environmental economics try to grapple with the equilibrium analysis by internalising the ecological and environmental externalities, but Gandhian Economics, by regulating individual wants and demand functions, has the potential to regulate and control some of the externalities.

The issue is whether the Gandhian concepts of asceticism and paternalism in consumer behaviour can be incorporated in the modelling. Professor Kenneth Boulding (Raval 1971) has opined that it was possible. Boulding says, 'Man requires both heroic and economic elements in his institutions, in his learning process and in his decision making... The familiar tools (in economic theory) like the Indifference Map and the Edgeworth Box can be easily explained to include benevolence or malevolence. The assumption in demand theory that "tastes are given" is a great illusion and would literally be true for the "birds" whose tastes are largely determined by their genetic structure and can therefore be treated as constant. In human society the genetic component is very small and the largest part of human preferences are learned, by means of mutation-selection process'. In the Pareto scheme too, welfare proposition does not admit any malevolence. Societal welfare refers to a pure state of benevolence.

If tastes are not given and can be influenced by generating the Veblenian demonstration effect

on the consumer, then the Gandhian Effect, too, should find place, and the individual demand curve need not be downward sloping for all consumers. By influencing groups with more income, (more than what is necessary to meet the basics of living), we may construct a demand curve for them that become income inelastic after a certain point (Brahmanad 1971). This would imply that after certain levels of consumption have been reached, additional income does not give rise to any new demand including leisure. Control on demand would free certain resources that can be used to produce the requirements of those who will continue to have downward sloping demand curve. It will also help in controlling the use of resources, some of which may be overexploited. If it is so, then Gandhi is relevant. Welfare economics discusses negative and positive externalities in consumption. The Veblen effect may be treated as a case of negative externality, and in a similar vein, the 'Gandhi effect' may be treated as positive externality. The point is to internalise it.

Looking at the situation in India in recent times, one would find that Gandhi's prophecies have come true. The blind imitation of Western ideology that India has accepted is leading India (and the world) almost to a point of no return. Civilisation based only on maximising physical comfort would encourage cut throat competition among human beings putting aside human values, and it would naturally lead to a disastrous situation for *Homo sapiens*. The present form of economic regime, where the private sector and the state have formed nexus, has increased inequality and inequity among the countries and within the countries. The other nexus between poverty and sustainable development gets sharply focussed in ecologically fragile zones where ethnic populations have been living and surviving for ages. However, increase in their population and exploitation of natural capital stock by the urban societies in developing economies spell doom for the poor who depend on the natural resource for their survival. As a result the poor too tend to extract the natural resources at a pace faster than its regeneration, and this

leads to serious ecosystem crisis. One of the important implications of present growth regime is environmental deterioration and degradation. Opposition against government policy to allocate private and common land for private industries has been growing all over the world. The world has become a global village for those who can afford to trot the globe, be it for individual or commercial purpose. The debate has begun for inter-generational and intra-generational equity among scholars who are concerned with the issue of sustainable development.

Two issues need to be governed in this context: the concept of 'needs', in particular the essential needs of the world's poor, to which overriding priority should be given and the idea of limitations imposed by the state of technology and social organisation on the environment's ability to meet present and future needs. The rich tend to exploit the nature in unbridled fashion; they have to be stopped. The weapon to do so obviously cannot be market or state controlled. There is an ethical issue involved. The taste and preferences and limits to human wants will have to be introduced in the society in order to contain the perpetually increasing consumption of material goods. The science and especially the technology have tremendous capacity to keep giving to the society endless number of goods having real or spurious need. Individually, man does not have control over the consequences that his action might generate today or later. But an individual has control over his/her action today as well as later. Therefore, Gandhi was in favour of determining a set of feasible actions rather than analysing and trying to predict about the consequences that were so uncertain and perhaps in a way unpredictable. This is the answer *Hind Swaraj* provides, although not very systematically. But it should be remembered that *Hind Swaraj* is not a treaty written at leisure. As Gandhi himself has admitted, it is a book written with force and passion.

What should be the structure and mechanism to restrict individual demand that would lead to sustainability in consumption? Gandhi emphasised on education for the solution. To build the

structure he desired, he advocated the right kind of education. For him education was the best instrument to create a favourable environment by inculcating basic human values. Gandhi had provided the definition of education as given by Huxley in *Hind Swaraj*. Huxley had defined education as 'That man I think has had a liberal education who has been so trained in youth that his body is the ready servant of his will and does with ease and pleasure all work that as mechanism it is capable of; whose intellect is clear, cold, logic engine with all its parts of equal strength and in smooth working order . . . whose mind is stored with all fundamental truths of nature . . . whose passions are trained to come to hell by a vigorous will . . . , the servant of a tender conscience . . . who has learnt to hate all vileness and to respect others as himself. Such a one and no other, I conceive has had a liberal education, for he is in harmony with nature. He will make the best of her and she of him'. The seed that was sown in *Hind Swaraj* took the form of *Nai Taleem* (education of head, hand and heart) in later years.

Such educated individual would be able to withstand technological determinism through self-discipline and self-control as it only enslaved human being and reject value premises. In *Hind Swaraj* he has suggested a moral man in place of an economic man that would enable moral growth and dignity in general, the fallacy of seeking happiness in individual acquisitive behaviour and the need for encouraging people to seek a life in terms of acquiring a sustainable society.

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Global Warming and Agriculture: Institutional Arrangement for Sustainable Development

12

A.K. Asthana

Abstract

India is a signatory country of Kyoto Protocol. Impact of global warming has been manifested on several fronts such as rise in temperature, extreme weather, erratic rain, rising of sea level and displacement of human settlement near the sea shore. Apart from humans, agriculture has been great casualty of global warming. At international level, several studies have examined the effects of climate change on global agricultural trade, highlighting the impacts on yields, commodity prices and imports and exports for individual countries. Negotiations amongst nations are centred on emission cut and transfer of technology. Emission of greenhouse gases is related with economic development so it cannot be easily checked without jeopardising the national growth. Transfer of technology requires huge investment which most of the developing nations cannot afford. In this critical situation, agriculture offers an alternate method of mitigation which requires less investment and technology but dedicated involvement of developing nations in utilising agriculture and agroforest for reducing global warming under clean development mechanism. Contribution of primary sector to national GDP is low in comparison to industry and service sector; despite the fact its impact on national economy cannot be underemphasised. Approximately 60 % of Indian agriculture is rainfed, so extreme temperature and erratic rain have major impact on agriculture in terms of low productivity, food shortage, high price of agricultural commodity, blockage of flow of agricultural credit, huge non-performance asset in financial system, burden on fiscal budget and trade imbalance.

A.K. Asthana (✉)
Udaybhansinhji Regional Institute of Co-operative
Management (Ministry of Agriculture, Govt. of India),
Sector 30, Gandhinagar, Gujarat 382030, India
e-mail: rduricm@gmail.com

Indian agriculture sector is characterised by cooperative institutions in credit, production, processing and marketing. Cooperative institutions have a well-developed structure from national level up to village level making presence in 98 % in villages of India. Farming community can be sensitised on global warming through training and education.

Keywords

Global warming • Multilateral impact • Institutional arrangement • Sustainable development

Global warming is one of the most debatable issues of the twenty-first century engaging policy makers, academicians, researchers and enlightened citizens all over the world. Global warming refers to an increase in average global temperature. Evidence suggests that the globe is getting hotter. Temperature recorded around the world as well as scientific study of tree ring, coral reefs and ice cores indicates that average global temperature has been risen substantially since the last 150 years (IPCC 2007). The impact of global warming is spatial and across the regions, sectors and social groups. Numerous country-centric studies have been conducted to identify how climate change might impact a particular region or sector (Smith et al. 1998 and O'Brien 2000). The objective of these assessments was to measure the positive and negative consequences of climate change. The goal was to identify climate sensitivities and vulnerabilities with emphasis on regions, sectors, ecosystems and social groups within each country (Parry and Carter 1998). Extent of vulnerability is variable as each region, sector, ecosystem and social group has its own characteristic resilience system. Biophysical vulnerability and social vulnerability are two major concerns. Amongst the regions, developing nations are more vulnerable than the developed nations. It is due to the fact that most of the developing nation's economy is predominantly agrarian, and these nations are near to equator and fall in warmer part of the globe. Agriculture is on the forefront of vulnerable sectors. The threat of climate change is real for agricultural sector. Global warming has its ugly manifestation in uncertainty of rain, unpredictable weather pattern,

extreme temperature and increased incidence of cyclonic event. Many integrated assessments of climate change seek to determine whether the net impact of climate change is positive or negative for a given sector such as agriculture (Alcama et al. 1998).

Several studies have examined the impact of climate change on global agriculture trade, highlighting impact on yield, commodity price and import and export for individual countries (Fischer et al. 1994; Reilly et al. 1994). Changes in atmospheric condition have occurred through build-up of GHGs.

Carbon dioxide (CO₂) emissions from fossil fuels contribute most of the increase in global temperature, but land use and agriculture also play significant roles in the build-up of concentration of GHGs. Overall, land use change (predominantly in the tropics) and agricultural activities globally account for about one-third of the warming effect from increased GHG concentrations (Cole et al. 1997).

Ricardian models concluded that agricultural productivity first improves as temperatures go from cold to warm, then deteriorates going from warm to hot (Mendelsohn and Schlesinger 1999). Ricardian model predicted that India will experience 38 % loss in agriculture productivity when global warming will increase and loss of 29 % when global warming will not increase further (Cline 2008).

A major breakthrough of UNFCCC came on 11 Dec 1997 when 187 signatory countries except the United States of America signed the Kyoto Protocol and agreed to reduce their GHG emission by 5.2 % of the 1990 level by 2012.

India is one of the signatory countries in the Kyoto Protocol in 1997. The negotiations amongst the nations revolved around four key issues: green technology transfer, mitigation, adaptation and finance. Developing nations had agreed to take appropriate action at national level to cut emission of GHGs including the strengthening of the “adaptation fund” at the Bali conference in 2007. This fund was meant to provide adequate funding to developing nations to implement their own mitigation and adaptation programmes to tackle climate change. But during the 15th conference at Copenhagen, these two contentious issues became a bone of contention between developed nations and developing nations.

A survey conducted by Nielsen Company and Oxford University Institute of Climate Change revealed that concern for climate change in India has increased by 1 % in the last 2 years. Majority of Indians believed that the main responsibility for solving climate change lies with the government (ToI 2009).

Agricultural lands have significant impact on earth’s carbon and nitrogen cycle. Carbon dioxide, nitrous oxide and methane are part of earth’s natural cycle of carbon and nitrogen. During agriculture activities, these three GHGs are released in the atmosphere increasing their concentration.

It is widely accepted that carbon dioxide released by burning of fossil fuel is the most important GHG. But conventional tillage practice in agriculture also produces significant carbon dioxide emission by lowering the organic carbon content of the soil. As per FAO estimate, cultivation of about 1.8 million sq km of arable land to produce corn, soybean and wheat releases 18 million tonnes of carbon dioxide annually (Steinfeld et al. 2006b). Another estimate of FAO indicates that agriculture-related deforestation may emit 2.4 billion tonnes of carbon dioxide into the atmosphere annually (Steinfeld et al. 2006a).

Agriculture has a unique capacity to reduce the concentration of GHGs released by own. It can be carried out by photosynthesis and sequestration. Both activities are together referred to as “carbon sink”. Carbon sink plays a significant role in global carbon dioxide cycle in the way that only about 50 % carbon dioxide released from fossil

fuel is accumulated in the atmosphere (IPCC 2001). Carbon sequestration tends to increase soil carbon for 20–30 years, after which soil carbon tends to stabilise and then there is no storage of carbon dioxide in soil (CAST 2004). Agriculture has unique distinction of offsetting the emission of GHGs by other sectors. It can reduce GHG emission by providing biofuel. Characteristic of modern agriculture is the huge increase in nitrogen supplied by mineral fertiliser, animal manure and nitrogen-fixing crop like soybeans to boost crop productivity (Mosier et al. 2001). Excess nitrogen in agricultural soil influences emission of nitrous oxide to the atmosphere. As agriculture tends to be more productive in crop yield, emission of nitrous oxide becomes inevitable. But nitrous oxide is another potent GHG with global warming potential of 296. Methane in soil is produced by bacteria, termed methanogens, which function under strictly anaerobic (oxygen-free condition) condition (Mosier et al. 2004). In agriculture, flooded soil such as those used for rice cultivation and other cultivated wetland crops gives emission of methane.

India needs environmental space to continue economic development. Development of economy is highly correlated with carbon dioxide emission. During the Copenhagen conference, India has set a high target of emission cut. To achieve twin objectives, the nation needs to strike a balance between development process and environmental commitment. Fast-growing service sector and industrial sector will contribute to concentration of GHGs in process of development. But this evil can be offset by agriculture sector by adopting the right kind of practice which support carbon stock and reduce emission of methane and nitrous oxide.

In the Bali conference, it was agreed upon by the nations that mitigation action would be supported by capacity buildings in a measurable, reportable and verifiable manner, besides technology and finance (Bhusan et al. 2008). Global warming is a national concern and needs attention and help of masses. People’s perception and their involvement in reducing the global warming are key for sustainable development of nations. Mere policy formation and rhetoric action will not

help in fighting menace of global warming. An institutional arrangement is needed to tackle this problem in the long run. Cooperative organisation can be a suitable mode of institutional arrangement for tackling global warming. In India, the developmental activities in agriculture are being done by the cooperative organisations. The cooperative organisations in agriculture farming can develop crops and plants that are having potential for carbon sequestration to mitigate the impact of Global warming. Cooperative society has a democratic character which is owned by its members. Responsibility towards society is one of its principles that gives cooperative society distinct character which can be aligned towards reducing global warming. Members of cooperative society take active part in the management of the society, setting its objectives and deciding its business. Majority of the members of the cooperative societies are engaged in agriculture and allied agriculture activities for their livelihood. Change in the global warming has direct bearing on the earning on these members of cooperative societies. So members of cooperative societies should be enlightened on how their agriculture practices are contributing towards global warming. They should be also made aware that they are one of the change agents in the global warming if they do responsible agriculture. Afforestation, judicious use of chemical fertiliser, organic farming and alternate crop pattern are some of the area which needs attention of the members of cooperative societies. Farmers are the most vulnerable group of vagaries of global warming, so they will be more responsive to capacity-building programme to tackle this universal problem. Global warming can be tackled at the very grass root level with the help of cooperative societies. The mitigation strategy adopted by responsible agriculture will be cost-efficient which any developing country including India can easily absorb.

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R.R. Singh and Suhail Sharma

Abstract

Infrastructure industry is experiencing a rapid growth in India. India is a country where infrastructure is the main hurdle for the growth of Indian businesses. In 2010 budget, the total allocation for infrastructure is 173,552 crores, which is 46 % of total allocation. In today's scenario, buildings which are present already are contributing 45 % of worldwide energy use. The greenhouse gas emissions from these buildings are contributing mainly for global warming, acid rain, etc. Our demand on natural and finite resources such as energy, water and building materials can be reduced, and our contribution to environmental quality can also be enhanced by incorporating green building principle into the design, construction and renovation.

Green buildings are designed and constructed to maximise the whole life cycle performance, conserve resources and enhance the comfort of occupants. This is achieved by the use of technology such as fuel cells and solar-heated water tanks and by attention to natural elements such as maximising natural lights and building orientation. This research paper is going to analyse the market opportunities available for green buildings and barriers in accepting green buildings.

Keywords

Green buildings • Sustainable path • Energy consumption • Economic perspective

Introduction

As per the Indian Green Building Council (IGBC), a “green building is one which uses less water, optimizes energy efficiency, conserves natural resources, generates less waste and provides healthier spaces for occupants, as compared to a conventional building.” It is also known as “green construction” or “sustainable building.”

R.R. Singh (✉)
Professor Civil Engineering, PEC(DU),
Chandigarh, India
e-mail: rrs837angwlm@gmail.com

S. Sharma
B.E. Civil Engineering, Final Year., PEC(DU),
Chandigarh, India
e-mail: suhailsharma90@gmail.com

Green building is a practice of creating structures and using processes that are environmentally responsible and resource efficient throughout a building's life cycle: from siting to design, construction, operation, maintenance, renovation, and deconstruction. This practice expands and complements the classical building design concerns of economy, utility, durability, and comfort (May 2007).

The main objective of designing a green building is to reduce the overall impact of the built environment on human health and the natural environment by the following measures:

- Using energy, water, and other resources efficiently
- Protecting occupant health and improving employee productivity
- Reducing waste, pollution, and environmental degradation

A similar concept is natural building, which is usually on a smaller scale and tends to focus on the use of natural materials that are available locally. This green building concept is mainly contributing to the development of the infrastructure industry, which is growing rapidly in the Indian context.

Growth of the Infrastructure Industry

India is the fastest growing economy in terms of business, import, export, and also in having good financial strength when compared to all other developing nations such as China and Brazil. However, India is a country that is mainly lacking in infrastructure development, which is becoming a major barrier for the development of many businesses. Thus, this industry gained a main focus from the entire prospect.

The foregoing facts attracted major investment toward this industry from the Union Ministry of Finance. In the 2010–2011 budget, the government allocated 40 % of the total budget amount to the infrastructure industry. Also, it allocated about \$425.2 billion in the eleventh 5-year plan (2007–2012) as compared to \$193.1 billion in the tenth 5-year plan. This industry showed a growth

rate of 5.1 % per year in April 2010, compared with 3.7 % in April 2009. The private investment contribution increased to \$157.3 billion in the eleventh 5-year plan, as compared to \$47.87 billion in the tenth five-year plan (Ratho 2008).

Issues in the Infrastructure Industry

- *Financing*: Raising funds for the infrastructure industry is the major difficulty it faces. The government is planning to invest in rupee-dominated long-term bonds to yield more return on investment in this industry.
- *Innovation*: Lack of innovation in this industry is contributing to a high-cost structure for each project.
- *Technology*: Lack of advanced technology and the latest equipment is making long-term projects even more difficult, causing delivery delays and also involving more human skills instead of using machinery: this difficulty increases required time and also costs.
- *Standardization*: There is no standardized certification process in this industry, which lack leads to poor-quality construction and fraudulent practices.
- *Environment*: The construction industry causes impacts on the environment in a number of ways, both directly and indirectly. The major impact is CO₂ emission; that is, about 50 % of carbon is emitted from this industry worldwide, contributing to climate change. These changes in turn result in global warming.
- *Politics*: The influence of political leaders in terms of bribes and the mishandling of funds leads to poor-quality construction and project delays.

A major issue faced by this industry is its contribution to global warming. According to the International Energy Agency (IEA), the buildings sector accounted for the largest share of India's final energy use between 1995 and 2005. In 2005, this sector consumed 47 % of the total final energy use. Residential buildings accounted for 93 % of the total building energy used in the same year.

Energy use is a major issue that is threatening the entire world, and all countries have initiated various measures toward the reduction of carbon emission and saving of natural energy to avoid a scarcity of renewable energy. Green building, a sustainable path, is one of the solutions accepted by many developed countries in the early 2000s to reduce the consumption of air, water, and other renewable energy, utilizing natural resources to reduce their carbon footprints (USGBC 2007).

Steps Toward a Sustainable Path

Recognizing that energy use and air pollution are important issues in India's buildings, the Indian government enacted the Energy Conservation Act (ECA 2001), which promotes energy efficiency and conservation domestically. ECA 2001 mandated the creation of the Bureau of Energy Efficiency (BEE), authorizing BEE to establish an Energy Conservation Building Code (ECBC). Under the BEE, the National Building Code of India (NBC) was first issued in 2005, but the issues of energy efficiency were marginally addressed.

However, the Ministry of Power and BEE issued ECBC in 2007, which is the first stand-alone national building energy code in India. Although it is currently voluntary, ECBC establishes minimum energy efficiency requirements for the building envelope; lighting; heating, ventilation, and air conditioning (HVAC); electrical systems; and water heating and pumping systems. To develop ECBC, BEE collaborated with a diverse group of domestic and international technical experts (Chang et al. 2007).

Nonprofit organizations such as the Indian Green Building Council (IGBC) and The Energy and Resources Institute (TERI) are actively promoting green buildings in India. The whole-building approach to sustainability was promoted by addressing performance in the following five areas:

- Sustainable site development
- Water savings
- Energy efficiency
- Materials selection
- Indoor environmental quality

In addition, LEED India has adopted several benchmarks for building performance. The rating levels "platinum," "gold," "silver," and "certified" indicate the extent to which a building exceeds the requirements of the national codes.

During the past few years, IT and ITES have been the primary contributors in the acceptance and development of "go green" philosophy. A case in point is Turbo Energy Limited's (TEL) R&D Administration Block in Paiyanoor, Chennai, which has been certified by LEED as the greenest building in India and the second greenest in the world. Other prominent green projects would include the ITC Green Centre (Gurgaon), IGP Office Complex (Bengaluru), Kalpataru Square (Mumbai), and CII-Godrej Green Business Centre (Hyderabad), although the concept is yet to catch on a wider basis. Also, a key supportive role is shown by India's biggest bank, SBI: it is offering concessions on constructing green developments (lower upfront margin up to 5–10 % and reduction in interest rate by 0.25 %) that could start a similar trend across the industry.

Advantages of Green Buildings

In today's scenario, green building has recently been accepted worldwide, but there is still a vast community that either is unaware of the sustainable design concept, indifferent to its cause, or unconvinced of its advantages. To convince owners, builders, and designers (or other stakeholders) about the benefits of sustainable design, it is necessary to make them understand the numerous advantages of the green building concept. To do that it is very important to understand the opinions of each group based on their selling points.

To an owner, the bottom line may be financial; to an architect it might be environmental, and to the engineer, it might be performance. There are many reasons to build green buildings that will provide sustainable design; architects should be equipped to provide a suitable argument relevant to the particular audience. The following are the advantages of sustainable design under environmental and economic areas (Kang et al. 2006).

Global Environmental Advantage

Because our buildings use such vast amounts of resources in their operation, and as they are made of materials that need to be extricated, processed, and manufactured, it is no wonder that approaching their design in a sustainable way could have global impacts on the environment. Sustainable design offers significant advantages in the areas of energy and water use reduction, air quality improvement, and increased material efficiency (Williams 2007).

Reduced Energy Consumption

One goal of sustainable design is to reduce the amount of energy required to cool, heat, and light our buildings. By utilizing passive strategies such as daylighting, thermal mass, and shading or by utilizing high-performance systems, we can significantly reduce the energy demand of our mechanical systems. This reduction can translate into a reduced need for extricating dwindling fossil fuels and power plant operation.

Reduced Water Consumption

With water-efficient design, green buildings can reduce the amount of water required for non-consumption uses. Efficient landscape and roof designs can also mitigate stormwater runoff, thereby lessening the burden on our storm and sewer systems. This design will positively affect local, regional, and global waterways by reducing pollution and supporting natural watersheds.

Reduced Air Pollution

There are a number of indirect (relative to buildings) sources of pollution, such as vehicle pollution from the transport of building products and the manufacturing of building products. There are also direct pollutant sources such as HVAC refrigerants and the toxic emissions from our

finished products. All these sources have impacts on global warming, ozone depletion, and air pollution.

Increased Material Efficiency

As mining, transportation, and manufacturing processes are necessary for building, using local and natural materials in our buildings has a direct benefit on all three of these strategies. In addition, utilizing recycled, reclaimed, or salvaged materials can lessen the burden on our landfills by reducing the need for dumping (Paul et al. 2008).

Economic Advantages

There are some clear economic advantages to sustainable building. Because clients generally pay for energy and water use, it would follow that reducing that consumption would lessen the financial burden of building operations.

In the case of passive heating and cooling systems, this also means a reduction in maintenance costs. Also, by improving the comfort of our buildings' occupants, we can reduce costly employee turnover. The economic benefits of sustainable design can be realized in short-term, long-term, and added-value projects (Allen 2008).

Short-Term Advantages

Sustainable buildings can offer immediate savings in the area of utility costs. By reducing electrical energy and water usage or reducing the cost of stormwater mitigation infrastructure, green buildings can lessen the cost of utility bills. In addition, buildings with efficient layouts can reduce the cost of building materials and construction waste. Also, if a building utilizes smaller HVAC equipment and relies more on passive strategies for heating and cooling, then the initial cost of the equipment could be less. There could also be financial incentives from

local utility companies for buildings utilizing sustainable design strategies (Paul and Taylor 2008).

Long-Term Advantages

Utility cost savings over the long term could pay for possible increased costs up front. Although the payback duration on items such as photovoltaic panels is debatable, some other measures may realize quick payoffs. Passive systems may need little to no ongoing maintenance; therefore, a building owner could save on the building operations budget. This concept translates into our landscape designs as well. Natural landscapes generally require less maintenance than conventional types. Another benefit is the churn rate. Buildings designed for flexible layouts can reduce the costs of reconfiguration (Joseph and Tamboli 2008).

Added Project Value

Many owners are now using “green design” as a selling point. For leasing or reselling property, sustainable buildings can attract new audiences and a new market, which could translate into quicker sales and higher rents. In addition, recruiting new employees (and keeping them) can be made easier by offering attractive and healthy facilities in which to work. Studies are showing that employees working in healthy environments work more productively, take fewer sick-leave days, and tend to remain loyal to the firm.

Disadvantage of Green Buildings

One of the most common disadvantages of green building is criticism of the additional costs required. This is an important consideration, because although the additional costs are usually balanced out by the energy savings, it is still extra money that is going out of a client’s pocket. Thus, this is a valid criticism.

The good news for this criticism is that recent growth in the green market is becoming a much

more competitive market, and therefore the additional building costs could possibly be reduced to a significant level in the near future. In fact, this is already evolving, and the competition is driving prices down. It will not be too long before the local home building superstore will have a green building section where these products are readily available at a competitive price.

However, one of the greatest disadvantages of green building happens to be its main focus, the environment, which may seem an odd statement because of the numerous benefits provided by green buildings for the environment.

For example, in recent years, American homes have become more and more energy efficient, which has added to the problem of indoor air quality. Clients’ homes have become so sealed that they are affected by indoor pollution. Even though green buildings address the issue of indoor air quality, the focus is mainly on the overall impact of the building and building process on the environment and the health of the occupants is not the priority. So, at times, this focus can be at the expense of indoor air quality, which ultimately leads to health problems (Abbaszadash et al. 2006).

Also, a green builder may choose to replace all the light bulbs with energy-efficient fluorescent lights, which are known to emit more radiation. Research studies are showing that this radiation can cause potential health problems.

Challenges in Implementing Green Building

With the recent drives initiated by private and government stakeholders, green building development is expected to pick up momentum in India. The implementation of this concept, however, has many hurdles in its path, as discussed next.

Implementation

The first and foremost requirement is the implementation of the ECBC. Upto the present ECBC

has been voluntary, but in the future, either the central or state governments should decide to adopt it as a mandatory standard. No state has adopted it yet. BEE is working closely with national- and state-level government agencies to promote ECBC. Once ECBC becomes mandatory at either the central or state level, one can assume that the implementation and enforcement approach will be similar to that employed for other mandatory building codes.

Lack of Seriousness and Leadership

All these initiatives toward conservation measures taken by the government remain as an appendix to the long-term energy policy. All the measures taken were reactive to certain events, not proactive by nature. The establishment of the BEE in March 2002 coincided with the Rio + 10 Summits at Johannesburg. Moreover, even after 3 years of its formation, BEE remained almost nonoperational. Until September 2005, it did not even have a full-time head (USGBC 2007).

Greater mobility is needed from the administration side so that the long-term goal of India as an energy-efficient, developed economic giant can be traced on realistic grounds, even if we have to pay for it in the short term.

Awareness for Global Marketing Needs

Signs of improvement in the energy intensity figures were only observed with the opening up of the economy during the past decade and a half. Increased competition, both at home and abroad, has compelled business leaders to look into alternative options to save energy costs. In this new century, as most of the industries were gearing up to boost exports, they realized that the cost of energy was robbing them of their competitive edge in the international market.

In India, the cost of power has escalated three-fold in the past 10 years, which probably explains better why the green buildings that are estimated

to reduce energy costs by 40 % are likely to be the fighting front in the global market.

Addressing the Economics Perspective

Arnulf Grubler recently mentioned that “To minimize environmental impacts by significant orders of magnitude requires the blending of good engineering with good economics as well as changing consumer preferences.” Recent experiences provide a valuable lesson on how to avoid the common pitfall of “green buildings myopia.” While noble, the benefits of the concept appealed to only the deepest green niche of consumers. The vast majority of consumers, however, will ask, “If I use the “green” building concept, what’s in it for me?” In practice, green appeals are not likely to attract mainstream consumers unless they also offer a desirable benefit, such as cost savings or improved product performance (Khataniar 2010).

Risk and Uncertainty

Although investments and interest in green building are growing rapidly, for a number of complex and varied reasons, the financial case for green building has not yet firmly taken hold in the real estate and development community. Many risks exist in the real estate community regarding green building:

- Uncertainty over reliability of green building technologies
- Uncertainty over costs of developing green real estate
- Uncertainty about the economic benefits of green real estate
- Uncertainty about green building performance over time

Lack of Experienced Workforce

Another main problem that is faced by India in implementing and making customers accept

the concept of green building is the lack of an experienced workforce. India lacks having many experienced consultants in the area of green building who are well informed in the literature and research in the rapidly growing industry. Expansion in this industry is threatened by lack of an experienced workforce, which increases the risk of inexperienced and untrained service providers entering the green building market in search of a premium on their services.

Conclusion

Green building is an emerging concept in the rapidly growing infrastructure industry. It is one solution to climate changes and global warming, which are mainly caused by worldwide carbon emission. All the developed and developing countries are very serious about their carbon emissions. Major carbon is released from transport and also from the construction industry. Green building is a sustainable building method that reduces energy use by 40 % compared to conventional building and also provides a healthy space for the occupants. Thus, this concept has attracted many countries and had already been implemented in many developed countries in the early 2000s. In India, however, this concept is still in the early acceptance stage because of the various implementation issues described in this chapter. The Indian government needs to take major steps to ensure this concept should be accepted nationwide by all state governments. Formation of a council and committee is needed to implement this concept to reduce the carbon footprint of India and thus reduce the impact of climate change and global warming.

With strong leadership, clear vision, and the right mix of policies and practices, India can

make green building the standard practice for all new and existing buildings. Today, there is a strong momentum supporting green building. We must capitalize on that momentum.

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R.N. Singh

Abstract

Mathematical modeling plays useful roles towards sustainable development in arriving at the understanding, prediction and control of developmental processes. For long term prediction ordinary differential equation models are used. We have described exponential and logistic equation models as used in studies of growth of population, water quality, fishery and economy. Equilibrium solutions and their stability have been illustrated. For controlling developmental process, the relevant utility function is maximized with the equation of growth as constraint. This methodology is illustrated from an example of economic growth model. It is concluded that for sustainable development, it is necessary to build comprehensive mathematical models of human-environmental systems.

Keywords

Sustainable development • Mathematical models • Exponential model • Logistic model • Fishery management • Optimal economic growth

Introduction

Sustainable development is defined by the Brundtland Report as "... development that meets the needs of the present without compromising the ability of future generations to meet their own needs," by Nobel Laureate Solow as "whatever it takes to achieve a standard of living at least as good as our own and to look after their next generation similarly," and

by Nobel Laureate Sen as "to combine the basic notion of sustainability rightly championed by Brundtland, Solow and others, with a broader view of human beings – one that sees them as agents whose freedoms matter, not just as patients who are no more than their living standards." Basically, sustainable development refers to creating adaptive capabilities with expanding opportunities. Sustainable development requires quantitative understanding of the coupled economic–environment system. The economic system takes natural resources from the environment and releases the wastes of production to the environment. As natural resources are finite, there is a need to consider

R.N. Singh (✉)
INSA Senior Scientist, CSIR-National Geophysical
Research Institute, Hyderabad 500 007, India
e-mail: rsingh@ngri.res.in

decreasing availability of resources in the future. Also, the environmental media have only a finite assimilative capacity to dilute and degrade waste products, so future issues for waste management, generally considered as external, need to be fully internalized in the economic system. The joint study of economic and environmental systems for sustainable development thus poses a great challenge for mathematical modeling.

Modeling requires us basically to choose the purpose of modeling, select all variables and relationships among variables, express them in mathematical symbols and equations, obtain a solution of the equations, and confront the solution with the observations. In mathematical modeling in sustainable development, environmental and social realities are described as a set of mathematical equations, in most general forms as a set of coupled partial differential equations. The terms of the equations represent advection, dispersion, reactions, storage, sources, and sinks. This relationship is set up by applying balance laws of mass, momentum, energy, and constitutive relationships relating fluxes with gradients of the dependent variables and appropriate constitutive relationships. Physical, chemical, and biological parameters enter through these constitutive relationships. These equations represent processes within the geometric domain of the environment under investigations from local domains to global domains. Models also require us to prescribe the initial and boundary conditions. For simple cases, analytical solutions in terms of elementary and special functions can be written. In most general cases, this would present a formidable computational problem. However, there is a trade-off between the complexity of the model and required resolutions. For sustainable development problems, one is looking for long-term solutions of the equations. In such case it would be advisable to look for lumped models where there is more focus on evolution in time than on resolution in space. In the ecology model, equations such as logistic equation and predator-prey equations are applied to address issues of growth, stability, and persistence. We thus are describing such social and environmental models that focus on long-term evolution of

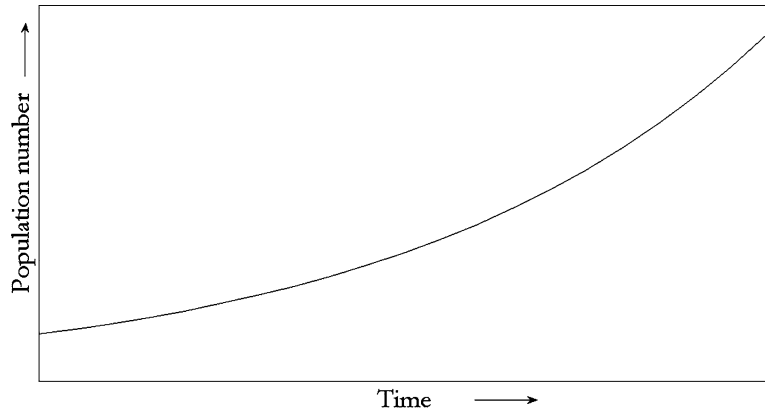
environmental quality in the presence of human modifications of the environment.

In addition to the model equation of the system under investigation, sustainable development would require some optimization criteria to be fulfilled, which may be in terms of cost or benefits or some other value or utility function. The solution then is sought that maximizes or minimizes such an objective function, given the system equations as constraints. Several methods presented in the sequel and other aspects of mathematical modeling are discussed in Kapur (1985), Beltrami (1987), Gershenfield (1999), and Meerschaert (2007). We present here exponential and logistic equation models and describe well-known applications in environmental, biological, and social problems. We give examples of growth of populations of any entity, gross domestic product (GDP) in the economy, pollutants in the lakes, and managing fisheries and economy, all related to sustainable development. These models have parameters that can be tuned to achieve economic and social objectives using optimization methods. These approaches can be applied to several problems encountered while developing sustainable development models. We have been concerned only with the time evolution of systems; however, in reality we need to have many coupled systems and also distributed (space-time) systems. To understand the sustainability of these systems, we need mathematics involving the partial differential equation constrained optimization. We do not address these complex models in this presentation.

Population Growth Models: Exponential Model

Several problems in environmental and social systems concern populations of various kinds, such as the human population and the number of species. The rate of change in these entities depends on the balance between birth and death rates, which can grow or decay with time accordingly. A growth or decay in any system variable, say population number, denoted by $P(t)$, can be described by an equation of the form

Fig. 14.1 Schematic exponential curve: population increases with accelerating rates



$$\frac{dP}{dt} = rP \quad (14.1)$$

Here the term on the left-hand side of the equation denotes rate of change of P and the term on the right-hand side assumes that this rate of change is proportional to P : this is the combined effects of birth and death rates of entities comprising the population, both assumed to depend linearly on the existing population. The constant of proportionality, r , can be zero or a positive or negative number. If it is negative, the population will decay with time, and when it is positive, the population will grow with time. If it is zero, the population will remain constant. For a given value of r , the equation can yield how the population will change with time from the given value of the initial population $P(0)$. The solution of Eq. 14.1 is given by

$$P(t) = P_0 \exp(rt) \quad (14.2)$$

The nature of this exponential model is schematically shown in Fig. 14.1, which shows that in the exponential model, the population will continue increasing with increasing rates.

We obtain the value of r from the observed values of a population at various times. The expression for r in terms of present population size and initial population size is given by

$$r = \frac{1}{t} \log\left(\frac{P(t)}{P_0}\right) \quad (14.3)$$

In general, there are random errors in population size data. In that case, from the given values of $P(t)$ for various values of time, we can use

the least squares method to know the value of r . Knowing the value of r , we can find, for instance, at what time the population will double as

$$t_2 = \log(2)/r \quad (14.4)$$

If r is negative, the population will decline and we can find the time when the population will be reduced to half as

$$t_{1/2} = \log(2)/|r| \quad (14.5)$$

These are exponential models of growth or decay. Equation 14.1 is called the Malthus equation. Malthus, in 1798, employed this model to forecast that the population will go on increasing and the necessary food will not be sufficient to support the population, so the population will collapse. r has been named the Malthusian parameter. Malthus was opposed by his contemporaries because in his model there is no role played by human scientific and technological ingenuities in creating necessary resources for survival. The exponential model is also generalized by taking the Malthusian parameter as time dependent, $r(t)$.

Frequently there are external sources to the population number that can be taken, in general, as time dependent as $f(t)$: this can be the result of migration. We then have

$$\frac{dP}{dt} = rP + f(t) \quad (14.6)$$

The solution of this equation is

$$P(t) = P_0 \exp(rt) + \int_0^t e^{r(t-\tau)} f(\tau) d\tau \quad (14.7)$$

For different source functions, we can find the evolution of a population by evaluating the integral. The foregoing models show the population to either increase to infinity or to decline to zero as time goes to infinity, depending on the sign of r . Both solutions given in Eqs. 14.2 and 14.7 have been used in various areas of natural and social sciences.

Lake Water Quality: Exponential Model

We show the application of the foregoing solutions to the problem of understanding lake water quality. The concentration of pollutants (C) in the lake depends upon loading rate and outflow from the lake. The mass balance principle governs the time variation of pollution as follows (Chapra 1975):

$$V \frac{dC}{dt} = QC_{in} - QC \quad (14.8)$$

Volume of lake, loading rate, and flow rate are denoted, respectively, by V , $f (= QC_{in})$ and Q . If the loading rate is zero, that is, only freshwater ($C_{in} = 0$) is entering the lake, then the concentration of pollutants varies from its initial value of C_0 as

$$C(t) = C_0 \exp\left(-\frac{Qt}{V}\right) \quad (14.9)$$

It can be seen that the concentration will decrease to half of its initial value at time

$$t_{1/2} = \log(2)/(Q/V) \quad (14.10)$$

In the presence of constant load, the solution is given by

$$C(t) = C(0) \exp(-Qt/V) + \left(\frac{f}{Q}\right) \left(1 - \exp\left(-\frac{Vt}{Q}\right)\right) \quad (14.11)$$

The equilibrium value that is attained as time tends to infinity is given by

$$C(\infty) = \frac{f}{Q} \quad (14.12)$$

For the more general case, Eq. 14.8 is generalized as

$$V \frac{dC}{dt} = f - QC - SvC \quad (14.13)$$

In the foregoing equation, the last terms on the right-hand side of the equations describe the pollutants also settling at the bottom (area as S) of the lake with velocity v .

The solution of this equation is given by

$$C(t) = C(0) \exp(-(Q + Sv)t/V) + \left(\frac{f}{Q + Sv}\right) \left(1 - \exp\left(-\frac{Vt}{Q + Sv}\right)\right) \quad (14.14)$$

For constant loading rate, the concentration equilibrates as time goes to infinity as

$$C(\infty) = \frac{f}{Q + Sv} \quad (14.15)$$

In the foregoing formulation, the pollutant is taken as nondegradable. In the case in which it is degradable, we have

$$V \frac{dC}{dt} = QC_{in} - QC - kVC \quad (14.16)$$

Here k is the rate of the first-order reaction. The solution of this equation is given by

$$C(t) = C(0) \exp(-(Q + kV)t/V) + \left(\frac{f}{Q + kV}\right) \left(1 - \exp\left(-\frac{Vt}{Q + kV}\right)\right) \quad (14.17)$$

The equilibrium solution as time tends to infinity is given by

$$C(\infty) = \frac{f}{Q + kV} \quad (14.18)$$

Such models have been highly effective in managing lake water quality. For instance, to predict changes in lake water quality given seasonal fluctuations in the loading rates, we can take f as time dependent and obtain a solution similar to Eq. 14.7.

Population Growth Models: Logistic Equation Model

It is frequently seen that, as time increases, the exponential model of population growth or decay is not valid. When the population P shows growth up to a limit or decays to a limit, we need to take the rate of growth, r , as a function of y . In a simplest case, we can modify this equation as

$$\frac{dP}{dt} = r(K - P)P/K \quad (14.19)$$

This is a nonlinear ordinary equation, called a logistic equation. This equation was originally proposed by Verhulst in 1847 and is also called the Verhulst equation. In this equation the first terms can be considered as production with constant rate and the second terms as destruction with rate dependent on the existing population. r denotes maximum population growth and is taken here as positive. In this model the population, P , will grow until a value K , called the carrying capacity of the population. The carrying capacity is the maximum sustainable population. It is also seen that as population becomes half of the carrying capacity, the growth rate decelerates. This point is called the inflection point.

The exact solution of this logistic, Eq. 14.19, has been given as

$$P(t) = \frac{K}{1 + \left(\frac{K}{P_0} - 1\right) \exp(-rt)} \quad (14.20)$$

This solution, shown schematically in Fig. 14.2, shows that initially the population is $y(0)$, and it becomes equal to K when time tends to infinity. The curve initially shows exponential growth in which growth rate is accelerating; it then becomes linear growth rate, and finally the growth rate decelerates to a zero value. This solution is a special case of the more general logistic function given by

$$y(t) = \frac{K}{1 + A \exp(-rt)} \quad (14.21)$$

For positive values of r , the exponential terms become zero as time goes to infinity; thus, K gives the maximum number in a population. For a positive value of r , the population continues to increase until the carrying capacity is reached. The initial population number in terms of constants appearing in logistic function is given by

$$y_0 = K/(1 + A) \quad (14.22)$$

From the initial value, the coefficient A can also be determined as

$$A = \frac{K}{y_0} - 1 \quad (14.23)$$

Also, knowing the values of the population at the initial, final, and intermediate times (t_1), the constant, r , can be determined as

$$r = \frac{1}{t_1} \log \left(\frac{A y_1}{K - y_1} \right) \quad (14.24)$$

As measured values of population numbers generally have errors, statistical methods are used to obtain values of parameters from observed data. Logistic function has an inflection point where its second derivative with respect to time is zero: this occurs at $A = \exp(rt)$. If this time is denoted by t_0 , we can write $A = \exp(rt_0)$. With this substitution the logistic function takes the following form:

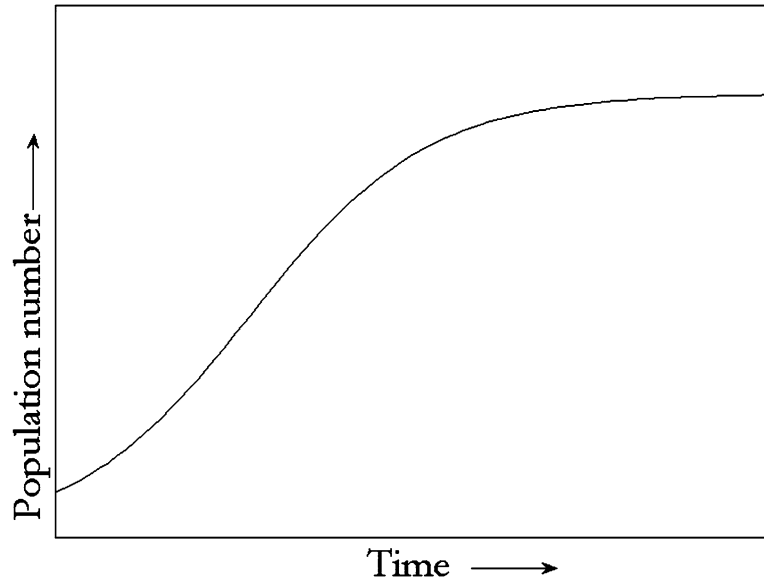
$$y(t) = \frac{K}{1 + \exp(-r(t - t_0))} \quad (14.25)$$

The logistic equation Eq. 14.8 has two equilibrium points where the time rate of change of the population is zero: these are given by equating its right-hand side as zero.

$$\frac{r(K - P)P}{K} = 0 \quad (14.26)$$

This equation has two roots: 0, K . If the initial population is at these points, there will not be any change in the population. At the former point, as there is zero population, there will be no increase by production. At the later point, there is a balance between production and destruction. However, the behavior of the population near

Fig. 14.2 Schematic logistic curve. Initially growth following the exponential model becomes almost linear and then approaches the carrying capacity value asymptotically with a decelerating rate



these points is different. Near the former point, any perturbation will cause more production than destruction. Thus, any perturbation will grow. This point is called an unstable point. However, at the later point ($P = K$), there is more destruction than production and any perturbation will decay: this is called a stable point. As systems are always subjected to perturbations, a modeler looks for stable points because the system is most likely to be found there. Logistic models have been used extensively in studying the population of various biological and ecological systems. It is interesting to recall that studies of solutions of the discrete version of the logistic equation have led to important developments in understanding the chaotic behavior of nonlinear complex systems (May 1976) so pervasive in biology and also in sociology.

Management of a Fishery: Maximum Sustainable Yield

We now describe an application of the logistic equation model for the management of natural resources such as a fishery. The fish population in a body of water such as a lake follows a logistic equation, as there is a limit to the size of the fish

population that the lake can support, called its carrying capacity, denoted by K . The population also depends upon the catch rate of fishes. We thus have the equation for the fish population, denoted by y , in the presence of fish harvesting (Schaefer 1954), as

$$\frac{dy}{dt} = ry(1 - y/K) - ly \quad (14.27)$$

Here r denotes average birth and death rates for the fish population and l is the catching coefficient. We take r as positive. This equation is called the Schaefer model.

The equilibrium solutions of this fishery model is given as $0, K\left(1 - \frac{l}{r}\right)$. The first solution represents extinction of the fishery. The second solution represent yield that does not lead to extinction. For the positive value of a fish population, we must have $l > r$: this is also a stable equilibrium population. If yield is more than this critical value, the population decreases to it, and when it is less than this critical value, it returns to this value. Thus, sustainable yield (SY) is given by

$$y_{SY} = lK\left(1 - \frac{l}{r}\right) \quad (14.28)$$

The maximum value of SY can be obtained by looking at the maximum value of SY (MSY), which is obtained by equating the derivative of SY with respect to l as zero:

$$1 - \frac{2l}{r} = 0 \quad (14.29)$$

Thus, we obtain the maximum value of l as

$$l_{max} = r/2 \quad (14.30)$$

Substituting this value of l in the expression for SY, we have the expression for MSY as

$$y_{MSY} = \frac{rK}{4} \quad (14.31)$$

This is the function of maximum growth rate and the carrying capacity. In the foregoing formulation the yield has been taken as the linear function of a population. It can be taken as a more complicated function of population as per the case under consideration. In actual practice, the optimization methods are used to schedule the yield based on maximizing economic utility functions.

Growth of GDP: Logistic Model

The logistic function can also be used to describe the rise of gross domestic product (GDP), an indicator of functioning of the economic system. Modis (2012) has fitted the following logistic function to the GDP data for the United States (USA) and India:

$$N(t) = \frac{K}{1 + \exp(-a(t - t_0))} \quad (14.32)$$

Here K and t_0 are the ceiling value of the logistic curve (earlier referred to as carrying capacity) and the midpoint time of the growth process, respectively. The logistic curve for the USA for nominal GDP in current dollars is given by using data for the period 1952–2011 as

$$N(t) = \frac{22,881.58}{1 + \exp(-0.0871(t - 2,003.02))} \quad (14.33)$$

For India, this function is given by using the data for the period 1970–2011:

$$N(t) = \frac{3,108.09}{1 + \exp(-0.1271(t - 2,039.56))} \quad (14.34)$$

This model can be used to forecast the growth of the economy. Questions such as whether growth is accelerating or decelerating can be answered by plotting the growth rate curves. It has been pointed out that developed economies such as the USA are not showing accelerated growth, whereas developing economies such as India continue to have accelerated growth.

Economic Growth Model: Exponential Model Optimized

We now look at a problem in economic development. There are three kinds of developmental paradigms. In one, the individual is independent and aims to realize its biological potentials. The individual's development takes place in the market economy with all attendant legal and governmental structures. In other models of development, the individual is not independent and depends on social structures for his development. In the third paradigm, the individuals are interdependent. We limit our discussion here to the first paradigm and look for the economic growth model.

Economics is concerned with capital, labor, and environment. For development, resources are extracted from the environment, and products and services are consumed for human well-being. The aim is to accumulate capital by increasing labor productivity and now, under the sustainability paradigm, to increase resource efficiency by such practices as reducing, reusing, and recycling. Mathematical models are used in designing optimal growth models. We take a simple case here (Dasgupta 2008). The growth of the capital, $K(t)$, in simple case is written as

$$\frac{dK}{dt} = rK - C(t) \quad (14.35)$$

Here capital grows by investing in the market at the rate of return as r and declines by consumption, denoted by $C(t)$. The initial capital $K(0)$ is known. A consumption scenario is chosen so that the following optimizing criteria, the well-being criteria, as well as utility function, is optimized:

$$\int_0^{\infty} W(C(t))e^{-\delta t} dt \quad (14.36)$$

δ , the discount rate, takes care of the intergenerational condition. Its positive value indicates that future well-being is being discounted. The function $W(C)$ is taken as

$$W(C) = A - BC^{-(\alpha-1)} \quad (14.37)$$

Constants appearing in the utility function can be derived from empirical studies. With this utility function, the equation for consumption, $C(t)$, is obtained by solving the following Euler-Lagrange equation:

$$\alpha \frac{dC}{dt} = (r - \delta) C \quad (14.38)$$

The solution for consumption $C(t)$ is

$$C(t) = C(0)e^{(r-\delta)t/\alpha} \quad (14.39)$$

For an optimal solution, the following Koopmans asymptotic condition is to be met as $t \rightarrow \infty$:

$$W'(C(t)) K(t)e^{-\delta t} \rightarrow 0 \quad (14.40)$$

This fixes the value of initial consumption, $C^*(0)$. The solution for consumption is

$$C(t) = C^*(0)e^{(r-\delta)t/\alpha} \quad (14.41)$$

From this solution the roles of parameters such as r , δ and α can be understood. Increase in α can lead to decrease in future consumption given other parameters as constants. Also, for $r > (<) \delta$, consumption will increase (decline). Substituting this consumption function in the capital accumulation equation, we obtain the solution for wealth accumulations. This model will

describe the growth of wealth with optimal consumption growth. Such growth models have been extensively used in economic theory to address various socioeconomic problems.

Concluding Remarks

Sustainable development requires designing mathematical models so that impacts in environmental and social conditions generated by developmental policies are controlled. These models should include all relevant processes and be useful for long-term predictions. Such models are given mostly by ordinary differential equations (ODE). These equations model spatial complexities in a lumped way. We have summarized a few ODE models for understanding and predicting social and environmental changes. As sustainable development aims at fulfilling an objective, solutions of the models are needed that meet the objective given as constraints on the model equation describing the human-environmental system: this requires development of the ODE-constrained optimization models. Only a few salient features of this approach have been presented here. Necessary lumping of complex spatiotemporal behavior in algebraic and ODE models leads to uncertain outcomes, which can be handled with adding noise terms in model equations and obtaining stochastic solutions. We have presented a simple model with a single variable to represent environmental and social systems. However, the human-environmental system is highly complex, and there is a need to consider a large number of variables connected nonlinearly with uncertain boundary conditions, parameters, and forces. Thus, the design of sustainable developmental programs provides challenging opportunities in building comprehensive mathematical models of the human-environmental system.

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Index

A

Adaptation, 36, 99, 146–149, 152–153, 177
Aerobic composting, 6, 9–10
Agricultural weeds, 42
Agro-ecosystem, 32, 35, 39, 40, 42
Air
 monitoring, 96
 pollution, 77–85, 96, 102, 103, 154, 181, 182
Antibacterial activities, 60
Anticancer, 65, 66
Antidiabetic potential, 68
Antifungal potential, 60–65
Antiprotozoal, 69
Atom-by-atom, 92

B

Bacteria, 49, 50, 52–55, 60–62, 97–99, 101, 103–105, 136, 138, 141, 142, 177
Bacterial biofilms, 141
Bi₂O₃, 95, 126–128
Bioactive molecules, 60
Biodegradable, 6, 7, 55, 135
Biodiversity, 1, 14, 20, 27, 39, 42, 47, 49–52, 111, 147, 159
Biofilms, 54, 55, 60, 64, 100, 141, 142
Biofuels, 11, 13, 15, 16, 92, 177
Biological oxidation, 127
Biological surfactants, 135
Biopolymers, 104, 135–142
Bioremediation, 52, 139–140
Biosurfactant-producing microorganisms, 136
Biosurfactants, 136–142
Biosynthesize, 102

C

Canopy, 33
Carbon capture, 13, 16
Carbon dioxide (CO₂) emissions, 176
Carbon sequestration, 154, 177, 178
Carrying capacity, 1, 13–14, 20, 27, 191–193
Catalysts, 5, 93, 98, 102, 106–110, 117, 118, 126, 128
Central Pollution Control Board (CPCB), 78, 79, 83
Civilisation, 163, 168, 169, 171, 172
Clean energy, 150, 152

Clean nanotechnologies, 111
Clean technology, 2, 25, 92–93, 150, 165
Climate change, 8, 16, 100, 110–111, 146–152, 154, 155, 167, 176, 177, 185
 mitigation, 152
Colonization, 52, 53, 141, 142
Conservation, 4, 14, 20, 24, 25, 31, 33, 39–42, 92, 94, 96, 146, 149, 154, 181, 184
 ecology, 39
CPCB. *See* Central Pollution Control Board (CPCB)

D

Decolorization, 108, 125
Desalination, 91, 98, 99
Diversity, 2, 14, 32–34, 37, 39, 41, 42, 47–55, 69, 141, 155, 165
Doping, 105, 110, 120, 123, 126
Dyes, 104, 106, 108, 117, 125, 126, 128
Dye-sensitized degradation, 126

E

Ecocodevelopment, 25
Ecological footprint, 27
Ecological implications, 41
Ecologically sustainable, 26
Ecological principles, 13
Ecological (environmental) sustainability, 27
Ecology
 environment, 151
 model, 188
Economics
 development, 24, 25, 28, 149, 159, 167, 177
 equity, 25
 growth, 24, 28, 95, 112, 146, 147, 149, 150, 156, 162, 163, 165, 171, 193–194
 sustainability, 27, 161–173
 system, 162, 167, 187, 188, 193
Ecosystems, 13, 14, 20, 25, 31–42, 52, 54, 111, 117, 149, 152, 156, 159, 161, 162, 172, 176
 services, 161
Electrochemical synthesis, 121, 123
Emulsification index value, 136

- Energy
 efficiency, 3, 4, 8, 146, 152, 181
 from waste, 9
 sustainability, 90
 technologies, 90
- Entrepreneurial paradigm, 25
- Environmental
 balance, 25
 cleanup, 104, 105, 118
 decline, 149
 degradation, 25, 27, 149
 federalism, 151
 flow, 13–15
 issues, 147, 148
 management, 150–151, 154
 monitoring, 96–97
 nanotechnology, 89, 102
 pollutants, 17–19, 107
 remediation, 105, 125, 128
 sensors, 102
 services, 149
 sustainability, 87–112, 149–150, 166
 technology, 2
- Environment and development, 26
- Equations, 162, 188, 189, 191, 192, 194
- Equilibrium solutions, 190, 192
- Equitable, 14, 146, 149, 154, 156, 159, 169
- Equity paradigm, 25
- Essential oils, 59–70
- Ethical, 27, 28, 112, 150, 159, 167, 171, 172
- F**
- Federalism, 145, 159
- Footprints, 8
- Forest, 27, 32–34, 38–42, 146, 151–154, 165
- Fossil fuels, 15, 92, 147, 152, 182
- Free radicals, 68, 118
- Fuel cell technology, 92
- G**
- Gandhian vision, 163
- Germination, 31–39, 42, 55
- GHG emissions, 12, 93, 152
- Global economic growth, 149
- Global environmentalism, 2
- Global industrialization, 135
- Globalisation, 165, 166
- Global packaging industry, 7
- Global warming, 95, 111, 176–178, 180, 182, 185
- Glycolipids, 136
- Gold nanoparticles, 98
- Grasslands, 32, 33, 39, 41
- Green buildings, 150, 179–185
- Green chemistry, 2, 3, 5, 6, 20, 96, 124
- Green construction, 179
- Green design, 4, 183
- Green economy, 146, 150, 154
- Green federalism, 145–160
- Greenhouse gas (GHG), 12, 16, 93, 152, 176, 177
- Greenhouse remediation, 93
- Green infrastructure, 150
- Green technology, 2–8, 13, 177
- Gross domestic product (GDP), 24, 112, 149, 152, 155–158, 162, 175, 188, 193
- Gross national product (GNP), 24
- H**
- Habitat planning, 25
- Halophiles, 50
- Halotolerant microorganisms, 50
- Hazardous materials, 94
- Hazardous waste, 5–7, 12, 20
- Health security, 13, 17, 20
- Heavy metal
 ions, 101, 125
 toxicity, 17, 20
- Heterogeneous photocatalysis., 118
- Hot spot, 95, 96
- I**
- Incineration, 5, 6, 9, 11–13
- Issues, 4, 8, 17, 19, 20, 26, 51, 52, 55, 95, 101, 104, 147–149, 156, 163, 172, 176, 177, 180–181, 185, 188
- L**
- Light-emitting diodes (LEDs), 93, 153
- Liposan, 138, 139
- Logistic equation model, 188
- Low-carbon
 economy, 150
 future, 150
- M**
- Magnetic nanoparticles, 93, 94, 101, 103
- Marine, 16, 47–55, 111, 152
 biosphere, 48
 diversity, 47
 environment, 48–52, 54
 microbial biodiversity, 49
- Material recovery, 10
- Mathematical equations, 188
- Mathematical modeling, 188
- Mathematical models, 193–195
- Medicinal plants, 65
- Mercury, 12, 19, 20, 93, 98, 101
- Metal nanoparticles, 121
- Microbial
 diversity, 47–55
 monitoring, 97
 sources, 55
- Microorganisms, 49, 51–55, 102, 103, 136, 137, 139, 141, 142

- Mitigation, 12, 16, 88, 111, 147, 150, 152–153, 177, 178, 182
- Modeling, 14, 18, 88, 188
- Molecules, 5, 51, 52, 60, 65, 68, 70, 90–92, 97, 99, 103, 104, 106, 118, 121, 125, 136, 138, 140
- Municipal solid waste, 6, 7, 9, 11, 12
- N**
- Nanocatalysts, 93, 101, 102
- Nanodevices, 92, 93, 101
- Nanoengineering, 95
- Nanofabrication, 91, 92, 102
- Nanofiltration, 99–100, 128
- Nanomaterials, 88, 89, 93, 94, 96, 98, 99, 101, 102, 106, 107, 109, 119, 121–124, 127
- Nanoparticles/nanostructures, 88
- Nanoparticulate titanium dioxide (TiO₂), 105, 106, 109, 110, 118–126, 128
- Nanoprocesses, 87, 95–96, 112
- Nanoproducts, 94–95, 112
- Nanoremediation, 104–106, 108
- Nanoscale building blocks, 88
- Nanoscience, 88, 90, 111, 112
- Nanospheres, 94, 109
- Nanostructured semiconductors, 92, 119
- Nanostructures, 87, 88, 91–93, 95, 101–104, 106, 109, 119
- Nanotechnology, 87–112
- Nanothermites, 95
- Natural building, 180
- Natural product, 52, 54, 55, 60, 96
- Natural product antifouling agents (NPAs), 54
- Natural resources, 1, 3, 13, 20, 25, 26, 112, 147, 149–152, 154, 156, 162, 163, 166, 172, 179, 181, 187
- New Economics Foundation (NEF), 149
- Noble metals, 107, 110, 120, 121
- Nonlinear ordinary equation, 191
- Nonrenewable resources, 4, 25
- NPAs. *See* Natural product antifouling agents (NPAs)
- O**
- Ordinary differential equations, 194
- Ozone, 78, 79, 82–84, 95, 99, 111, 128, 147, 182
- P**
- Participation, 25–28
- Particle-size, 124
- Particulate biosurfactants, 139
- People-Planet Fitness Index (PPFI), 148, 155–159
- Pharmaceutical wastes, 125
- Phenolic compounds, 126
- Photocatalysis, 98, 105, 109, 110, 117–120, 126
- Photocatalyst, 104–106, 108–110, 117–128
- Photocatalytic degradation, 110, 125–128
- Photocatalytic material, 128
- Photocatalytic oxidation, 128
- Photocatalyzed degradation, 125–128
- Photodecomposition, 127
- Photooxidation, 79, 105
- Phytochemical, 64, 69
- Pollution, 3, 5, 10, 12, 17, 50, 77–85, 88, 89, 94–96, 102–104, 111, 117, 121, 128, 147, 151, 154, 166, 180–183, 190
- Polymeric biosurfactants, 138–139
- Polymer nanospheres, 94
- Pooled federalism, 155
- Population
- dynamics, 31, 34, 41
 - ecology, 39
 - paradigm, 25
- Poverty reduction, 26, 28, 154
- Preservation, 25, 42, 59, 111, 135
- R**
- Rapid urbanization, 154
- Recyclable materials, 4, 7
- Recycling, 5–10, 12, 16, 93, 104, 105, 150
- Reduced emission, 150
- Regeneration, 31, 34, 39, 41, 172
- Remediation, 1, 20, 52, 88, 89, 93, 94, 98, 102, 104–108, 117–128, 139–140
- Renewable energy, 4, 11, 15, 90–92, 150, 152–154, 181
- Rhamnolipids, 136, 137
- Rhodamine B, 110, 127
- ROS species, 68
- S**
- Science and technology, 117, 165, 171
- Seeds, 31–42
- bank dynamics, 31–42
 - banks, 31–42
 - density, 31, 39, 42
 - dispersal, 35, 42
 - rain, 34–36, 39, 41, 42
- Semiconductor, 92, 94, 96, 105–106, 108–110, 118–121, 126
- photocatalysts, 110, 120
- Sensors, 89, 90, 93, 98, 101–103, 105, 106, 111
- Sequestration, 13, 16, 140, 154, 177, 178
- Social harmony, 25
- Social paradigm, 25
- Social realities, 188
- Sociocultural sustainability, 27
- Soil
- seed bank, 31–42
 - texture, 37–39
 - to oil economy, 163
- Solar photovoltaics, 91
- Sophorolipids, 136, 137, 141
- Species richness, 31, 39
- Substitutes, 12, 165

- Surfactants, 94, 117, 121–123, 135–142
- Suspended particulate matter (SPM), 78
- Sustainability, 2, 3, 6, 8, 13, 26–28, 31–42, 87–112, 146, 149–152, 158, 161–173, 181, 187
- criterion, 167
- Sustainable
- agriculture, 150, 152
 - biomass, 150
 - buildings, 182, 183, 185
 - cities, 150
 - consumption, 1, 26, 162, 163, 170
 - design, 8–9, 181, 182
 - development models, 26, 188
 - growth, 1–20, 156
 - human development, 145–159
 - human prosperity, 159
 - path, 181
 - society, 25, 26, 173
- T**
- TiO₂. *See* Nanoparticulate titanium dioxide (TiO₂)
- TiO₂ photocatalyst, 105, 110, 126, 128
- Titanium dioxide, 98, 101, 102, 107, 120, 121
- Toxic metals, 19, 20
- Traditional systems, 59
- Trehalolipids, 136, 137
- U**
- Ultrafiltration (UF), 100, 142
- United Nations Development Program (UNDP), 24, 28, 159
- W**
- Waste to wealth, 4, 20
- Water monitoring, 97
- WCED's. *See* World Commission on Environment and Development (WCED's)
- Weed
- seed bank, 35–37, 40–42
 - species, 35–37, 41
- World Commission on Environment and Development (WCED's), 26
- Z**
- Zerovalent iron, 106
- Zerovalent nanoparticles, 94