Atul Kumar Upadhyay · Ranjan Singh D. P. Singh *Editors*

Restoration of Wetland Ecosystem: A Trajectory Towards a Sustainable Environment



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Foreword

Wetlands are house of rich biodiversity of plants and animals, and provide the important ecosystem functions such as food stock, high carbon storage, availability of nutrients, flood mitigation, water purification, aquifer recharge and climate resilience. Wetlands need to be preserved, restored or constructed for managing the biodiversity, wildlife, pollution and non-point source of wastewaters. However, existing wetlands undergo ageing, degradation, rapid infilling, shrinking area and other multiple anthropogenic pressures, which might have been caused by overexploitation, mismanagement and injudicious use of naturally occurring wetland resources. Natural resources are dwindling at faster rate, leading to alterations in the water level, pollution load and other ecosystem functions. The management practices for wetland degradation caused by global warming, greenhouse gas emission and anthropogenic interference. A paradigm shift in eco-restoration towards a more sustainable wetland ecosystem is required, which enables the wetlands to provide food, shelter, energy, species richness and sustainable growth.

The present book encompasses the area of expertise of the editors. The chapters incorporated in this book cover a wide spectrum of wetland conservation, restoration, sustainable development policies and regulation, carbon sequestration, bioremediation and crucial role of different group of microbes (Algae, Fungi and Bacteria) in maintaining sustainable wetland functions such as biodiversity, waste remediation, nutrient cycling, biofuel generation, phytoremediation and carbon sequestration. The wetlands are considered good natural resources for environment sustainability and for obtaining several cost-effective, value-added products required for human welfare. The book also includes the applied role of constructed wetlands designed to serve the specific purpose with the help of latest state of the art of engineering and technology. The constructed wetlands have also started using various bio-nanotechnologies for recovery and removal of recalcitrant materials and difficult pollutants from the wastewater. Overall, all the chapters are designed in a manner which places major emphasis on the components, which provide a new insight and elaborated information to the readers towards conservation of wetland resource. I am confident that this book will benefit the readers with adequate information related to wetland ecosystem and its sustainable management. After going through the contents of this book entitled *Restoration of Wetland Ecosystem: A Trajectory Towards a Sustainable Environment*, edited by Dr. Atul Kumar Upadhyay, Mr. Ranjan Singh and Dr. D. P. Singh, I am sure that the environmental scientists, researchers, students and state-controlled agencies involved in the restoration and management of wetland ecosystems would be highly benefitted. The editors have performed commendable task in bringing out an exhaustive and informative volume of information concerning the wetland function, restoration and management. I extend my heartfelt compliments to the authors and editors.

(Prof. D P Singh) Chairman University Grants Commission New Delhi-110 002.

4th December, 2018

Preface

The rising risk and consequence of environmental changes might lead to massive loss to natural ecosystems and human population. This is a matter of serious concern for global thinkers, environmentalists, scientists and policy makers. The dangerous level of anthropogenic interference with extreme climate condition has accentuated the loss of natural resources—a key ingredient of sustainable development. There is an urgent need for restoration of the existing natural resources in their present form and formulate strategies to ensure sustainable development of both environment and society.

The present book entitled Restoration of Wetland Ecosystem: A Trajectory Towards a Sustainable Environment incorporates a broad spectrum of information and strategies required to achieve sustainable development. This book provides a fresh outlook on application of green technologies related to management of wastewater, pollutants, biodiversity, wetland restoration and ecosystem functions. The present book encompasses holistic review on recent advances in the field of bioenergy, green technology of bioremediation, biomass generation and nutrient cycling. Wetlands are one of the most important ecosystems on the earth and are known to be the largest store house of reserve carbon. They offer various ecosystem services to human societies such as shock absorber of flash flood, water and carbon reserve, water purifier, preservation of biodiversity and recreational resource for the people. Wetlands may be categorized as both natural wetlands and constructed wetlands, specifically designed for a particular purpose. The effectiveness of wetland services is largely dependent on the hydrology of wetland, diversity of macrophytes and microorganisms, other geoclimatic and environmental parameters such as pH, temperature, dissolved oxygen and level of nutrients and carbon.

The major thematic areas in this book articulate the dynamic relation of three global apprehensions: environmental pollution, resource exploitation and sustainability. This book emphasizes on the utilization of resources, mitigation measures for reduction of pollution load in the wastewater (municipal, industrial, agriculture, mine drainage, tannery, etc.), harvesting of plant and algal biomass, and their application as biofuel, biofertilizers and other value-added products. This book provides elaborate information on the current trend and futuristic management of wetlands. This book tends to bring all the scattered information about the wetlands as natural resource and throws new light on the future role of wetlands in sustainable development of both environment and society, keeping in view the latest researches in the field of wetland science, waste management, carbon sequestration and bioremediation.

We thank all the contributors of this book for their valuable input in the form of chapters, covering different components of wetland science.

Lucknow, Uttar Pradesh, India

Atul Kumar Upadhyay Ranjan Singh D. P. Singh

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About the Editors

Atul Kumar Upadhyay is a scholar in the field of environmental science. He completed his Ph.D. in the field of phytoremediation and constructed wetland technology from CSIR-National Botanical Research Institute, Lucknow, jointly with Kumaun University, Nainital, India in 2017. He received his post-graduation degree from Dr. RML Avadh University, Faizabad, India, in Botany. He did his research in construction and designing of wetland and plant-based management of different water and soil pollution in different states of India and was involved in different activities related to river water rejuvenation, wastewater treatment, wetland designing and soil management. During his research, Dr. Upadhyay has published a number of research papers, articles, and chapters in the peer-reviewed journal of national and international repute.

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Prof. D. P. Singh the Ex-Head and Dean, School for Environmental Sciences, Babasaheb Bhimrao Ambedkar University, Lucknow, India, is an eminent scholar in the field of Environmental Science. He received his Ph.D. from the Department of Botany, Banaras Hindu University, Varanasi, India. He has worked extensively in the area of wastewater treatment, microbiology, stress physiology, bioremediation and alternative energy options. He has received several honours and awards to his credit, including more than 135 research publications in high-impact factor journals of national and international repute. He has supervised more than 24 Ph.D. students and several M.Sc. and M.Tech students in their research work. He has delivered invited lectures in different seminars and symposia and served as a principal investigator for several governments funded projects. Dr. Singh has published five books in the field of environmental microbiology and biotechnology, stress physiology and sustainable management of soil and water.

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Chapter 1 Restoration, Construction, and Conservation of Degrading Wetlands: A Step Toward Sustainable Management Practices

Ibha Suhani, Monika, Barkha Vaish, Pooja Singh, and Rajeev Pratap Singh

Abstract In the current scenario, the world is facing various water-related issues, for instance, water shortage, degradation of water resources, pollution of aquatic systems, and proliferation of waterborne diseases. Moreover, the condition is getting worse in the developing economies because of the integrated effect of anthropogenic activities, escalating demand of resources, and the population explosion. In various developed countries, traditional centralized sewage treatment systems were used for combating water pollution. With the advancement of technologies, wastewater treatment (WWT) systems like activated sludge process, membrane separation, membrane bioreactors, etc. are being employed for treatment of water pollution. However, these expensive systems are not feasible enough for the widespread application along with they are not capable to treat water according to WWT standards. Thus, it is imperative to shift toward the natural way of water purification. In order to meet this demand, protection, restoration, and sustainable use of natural wetlands are essential because of being big reservoir of water on the earth. The present chapter comprehensively describes the importance of natural and artificial wetland (constructed wetland) for human beings toward achieving sustainable environment in a simple, manageable, and cost-effective way.

 $\label{eq:constructed} \begin{array}{l} \textbf{Keywords} & \textbf{Wetland} \cdot \textbf{Wastewater} \cdot \textbf{Constructed} \ wetland \cdot \textbf{Sustainability} \cdot \textbf{Restoration} \end{array}$

P. Singh

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1 Introduction

Wetlands are described as "the lands of transition zone between aquatic and terrestrial ecosystems where the land is covered by shallow water" (Mitsch and Gosselink 1986). The worldwide intergovernmental treaty on wetlands signed at Ramsar, Iran, in 1971 includes marsh, fen, bog, peatland or flowing water, static water, and fresh, salty, or brackish water whether artificial or natural areas of marine water (the depth should be maximum 6 m at low tide) into the wetland (Bowman 2002). However, in the Ramsar Convention, paddy fields, river channels, and anthropogenic water bodies are not comprised in wetland. As wetlands have zoological, ecological, botanical, hydrological, and limnological importance, they are categorized as "wetlands of international importance" underneath the Ramsar Convention (Frazier 1999). The Ramsar Convention published an international report in 2013 in the Economics of Ecosystem and Biodiversity for Water and Wetlands, which emphasizes on the need of shifting our attitude toward wetland. The Ministry of Environment, Forest and Climate Change (MoEFCC) in the notification on 26th September, 2017, has described wetlands as vital bodies of the ecosystems which support abundant biodiversity and help in hydrological cycle. Wetlands provide a broad spectrum of services and resources to the community, such as flood mitigation, water storage and purification, aesthetic enrichment of landscapes, microclimate regulation, and cultural and social activities, for recreational prospects and supporting cultural heritage (Clarkson et al. 2013).

Currently, wetlands are shrinking due to urbanization, population growth, climate change, and land use alteration (Davis and Froend 1999; Ferrati and Canziani 2005; Sebastiá-Frasquet et al. 2014). This might stimulate the qualitative and quantitative characteristics of wetland ecosystems' functions and services (Erwin 2009). Generally, wetlands are mainly influenced by the social (anthropogenic) pressures such as wastewater discharge, runoff from agriculture, and groundwater depletion by abstraction of groundwater for the utilization of urban water supply and other agricultural practices (Konikow and Kendy 2005). The majority of research has agreed that there is urgency for coordination in an attempt to restore, protect, and manage the wetland ecosystems (Hansson et al. 2005). To find the way for maintaining the sustenance of wetland and the nature, numerous authorities from governmental and nongovernmental levels should coordinate by forming policies and frameworks. In both, the developed and developing nations, various frameworks, policies, and regulations should be implemented to check the degradation of wetland.

1.1 Wetland Type (Ramsar Convention)

Under the umbrella of the Ramsar Convention, wetland types have been defined to aid sharp recognition of the wetland habitats that correspond to every Ramsar site (Table 1.1). Different codes have used to define wetland types. Ramsar sites are dependent upon the Ramsar Classification System for Wetland Type as approved by

1 Restoration, Construction, and Conservation of Degrading Wetlands: A Step Toward... 3





Recommendation 4.7 and amended by Resolutions VI.5 and VII.11 of the Conference of the Contracting Parties (Table 1.2) (Plans et al. 2009).

2 Wetlands of India

The wetland of India has been categorized into following types (Prasad et al. 2002).

2.1 Himalayan Wetlands

This type of wetlands includes the parts of Central Himalayas, Eastern Himalayas, Ladakh, and Zanskar (Pangong Tso, Chantau, Tso Moriri, Noorichan, Hanley, and Chushul marshes) and few portions of Kashmir Valley (Dal, Anchar, Haigam, Kranchu, Malgam, Wular, and Haukersar lakes).

Table 1.2 Classification of wetlands

Marine/Coastal Wetlands				
А	В	с	D	Е
 Permanent shallow marine waters in most cases less than six metres deep at low tide; includes sea bays and straits. 	 Marine sub-tidal aquatic beds; includes kelp beds, sea-grass beds, and tropical marine meadows. 	Coral Reefs	 Rocky marine shores; includes rocky offshore islands, sea cliffs. 	 Sand, shingle or pebble shores; includes sand bars, spits and sandy islets; includes dune systems and humid dune slacks.
F • Estuarine waters of estuarine and estuarine systems of delax. Inland Wetlands	G H Imad, sand or Imad, sand or Interliad marshee, mediow, salingar in- salit marshee, ist marshee, freshwater marshee.	Intertial forested wetlands; includes wrangrove avange, sipah swange and tabl freshwater awange forests.	J K Constal Tercickish taline lagoons: brackish to sallnak lagoons with at marrow connection to the sea.	ZA(a) • Karst and other ses subtranaen hydrological systems, marine/coastal
L	М	N	0	Р
Permanent inland deltas	Permanent rivers/streams/creeks; includes waterfalls.	Seasonal/ intermittent / irregular rivers/streams/creeks.	Permanent freshwater lakes (over 8 ha); includes large oxbow lakes.	Seasonal/intermittent freshwater lakes (over 8 ha); includes floodplain lakes.
Q	R	Sp	Ss	Тр
Permanent saline/brackish/alkaline lakes.	Seasonal/intermittent saline/brackish/alkaline lakes and flats.	Permanent saline/brackish/alkaline marshes/pools.	Seasonal/intermittent saline/brackish/alkaline marshes/pools.	 Permanent freshwater marshes/pools; ponds (below 8 ha), marshes and swamps on inorganic soils; with emergent vegetation water-logged for at least most of the growing season.
To	T	N/a	M	W
 Seasonal/intermittent freshwater marshes/pools on inorganic soils; includes sloughs, potholes, seasonally flooded meadows, sedge marshes. 	Non-forested peatlands; includes shrub or open bogs, swamps, fens.	 Alpine wetlands; includes alpine meadows, temporary waters from snowmelt. 	• Tundra wetlands; includes tundra pools, temporary waters from snowmelt.	 Shrub-dominated wetlands; shrub swamps, shrub- dominated freshwater marshes, shrub carr, alder thicket on inorganic soils.
Xf	Xp	Y	Zs	Zk(b)
 Freshwater, tree-dominated wetlands; includes freshwater swamp forests, seasonally flooded forests, wooded swamps on inerganic soils. 	Forested peatlands; peat swamp forests.	Freshwater springs; oases.	Geothermal wetlands	Karst and other subterranean hydrological systems, inland
Human-made wetlands				
1	2	3	4	5
Aquaculture (e.g., fish/shrimp) ponds	Ponds; includes farm ponds, stock ponds, small tanks; (generally below 8 ha).	 Irrigated land; includes irrigation channels and rice fields. 	 Seasonally flooded agricultural land (including intensively managed or grazed wet meadow or pasture). 	Salt exploitation sites; salt pans, saline, etc.
				71(-)
Water storage areas; reservoirs/barrages/dams/impoun dments (generally over 8 ha).	Excavations; gravel/brick/clay pits; borrow pits, mining pools.	Wastewater treatment areas; sewage farms, settling ponds, oxidation basins, etc.	Canals and drainage channels, ditches.	Karst and other subterranean hydrological systems, human- made

Adapted from Plans et al. (2009)

"Floodplain" here is used to denote one or more wetland types that might comprise instances from the R, Ss, Ts, W, Xf, and Xp or from other wetland categories. Few examples of floodplain wetlands are shrublands, woodlands, forests, and seasonally inundated grassland (including natural wet meadows). Floodplain wetlands are not listed as a specific wetland type herein

2.2 Indo-Gangetic Wetlands

Through the whole stretch from the river Indus at one end of west to Brahmaputra at the other end of east, there lies the largest wetland system in India called the Indo-Gangetic floodplain. The wetlands of the Indo-Gangetic plains and the Himalayan Terai are included in this type of wetlands.

2.3 Coastal Wetlands

The lagoons, mangroves, and massive intertidal expanses are included in the coastal type of wetlands. These are stretched along the 7500 km coastline in West Bengal, Orissa, Tamil Nadu, Andhra Pradesh, Karnataka, Goa, Kerala, Gujarat, and Maharashtra. This category of wetland includes Andaman and Nicobar Islands, Gulf of Mannar, Lakshadweep, Gulf of Kutch, and Sundarbans of West Bengal.

2.4 Deccan

Several tanks for storing water and numerous trivial and huge reservoirs along with few natural wetlands in nearly each town in the associated region are included in this category of wetland ecosystem (Fig. 1.1).



Fig. 1.1 Different types of wetlands of India (a) Indo-Gangetic wetland, (b) coastal wetland, (c) Himalayan wetland

3 Importance of Wetlands

Wetlands have significant socioeconomic importance like wildlife resource, tourism, energy resource, and water supply. The services and products supported by wetlands are noteworthy. There is a very broad spectrum of services and resources provided by wetlands to humans (Engelhardt and Ritchie 2001). They provide shelter, food, shellfish, livestock fodder, fish and fuel wood, medicinal plants, building materials, honey, beeswax, etc. Straightforwardly or circumstantially wetlands support people by their different functions and values. The biological, environmental, and fiscal values of wetlands are of great importance, which are directly affected by humans. Several valuable operations/services carried out by wetlands are as follows.

3.1 Water Quality

Wetlands have a very dynamic role in storing water and improving the quality of water (Clarkson et al. 2013). They purify water, revive groundwater, and also control the frequency of runoff in urban areas. Many plants growing in wetlands act as filters by doing the cleansing role for the downstream environment (Engelhardt and Ritchie 2002). So, wetlands are regarded as the kidneys of the ecosystem (Mitsch and Gosselink 1986).

3.2 Flood Control

Wetlands help in attenuating flood and decreasing the effect of flood. They maintain the groundwater levels all through the low rainfall periods (Roulet 1990). Riverbanks and shorelines are well stabilized by wetlands of that area. They play a vigorous role in checking coastal erosion by buffering the shorelines against erosion, besides also helping in alleviating the effect of natural disasters by absorbing the tidal forces (Wondie 2010).

3.3 Wildlife Habitat

As every wetland is unique in their climatic and topographic conditions, they have specific environmental conditions which provide vulnerable and endangered communities (Brinson and Malvárez 2002). They are the areas of great importance from the perspective of wildlife habitat as they have no less wildlife species than a forest habitat.

3.4 Recreation, Education, and Resources

As wetlands are the landscapes which add beauty in nature, they provide bird watching, recreational activities of fishing, boating, etc. They play a foremost part in tourism for the recreation of society, for habitat, and for supporting cultural heritage (Clarkson et al. 2013). From the perspective of education, wetlands are interesting environmental resource of carbon sequestration, disaster management, nutrient removal, biodiversity maintenance, and toxic retention (Zedler and Kercher 2005).

4 Growing Threat to Wetland Ecosystem

As wetlands are often depicted as kidneys of the landscape, this directly means it helps in biodiversity maintenance (Mitsch and Gosselink 1986). The change in the physicochemical properties of wetland mainly relies on the climate condition, nutrient availability, and topographic and hydrological conditions. The biotic response depends on the physicochemical modifications in the wetland (Gosselink and Turner 1978). From the past few decades, humans have ignored the importance of wetland ecosystems. The rapid population, land use patterns, and demands of resources have led in the degradation of wetlands. Pollution of wetlands by agricultural runoffs and domestic and industrial wastes have headed towards the major destruction to the wetland ecosystems.

Due to urbanization, demand of resources, and land use changes, wetlands are facing major troubles (Boyer and Polasky 2004). The developmental pressure is increasing day by day leading to the degradation of the wetland ecosystems. The urban water supply demand has led to over withdrawal of underground water which causes salinization and reduction in the water table of the region (Prasad et al. 2002). There are considerable ecological, biological, and economical losses due to unplanned developments. Different anthropogenic activities like agriculture, road construction, industries, residential developments, resource extraction, and disposal of wastes are a main cause of long-term losses and ecological disturbances in the wetland ecosystems (Prasad et al. 2002). The agricultural activities like irrigation by construction of dams, canals, and reservoirs have altered the hydrological activities like diversion of streams and rivers, transport of water to arid regions, changes in the drainage patterns, and construction of canals have led to the significant degradation of wetlands in the associated regions.

Wetlands are also largely affected by deforestation, as it leads in the removal of the topmost layer of the earth leading to soil erosion and siltation problems (Smith et al. 2016; Zhao et al. 2006). Besides, the unrestricted dumping of toxic wastes from industries and sewage has led in the deterioration of physiochemical properties of wetlands, giving rise to eutrophication and destruction of aquatic ecosystem of the related wetland (Russi et al. 2013). Climate change like the change in precipita-

tion patterns, global warming, increased CO_2 , increase in the occurrence of storm floods and droughts, and sea level rise could also badly affect the wetland ecosystems (Chen et al. 2003). The plant species like water hyacinth and *Salvinia* has threatened the Indian wetlands, as these species absorb the underground water and also clog the waterways (Prasad et al. 2002).

5 Strategies of Restoration and Conservation

Wetlands are considered as one of the most fertile but endangered ecosystems of the world (Cherry 2012; Maltby 1991). Extensive uses, as well as exponential population growth, have made this ecosystem more deteriorating and vulnerable to environmental changes (Zedler 2003). Anthropogenic pressure (i.e., land use change, inappropriate use of water resources, burgeoning development projects) is the well-known reason of the decline in wetland resources (Ducks Unlimited Canada 2010). In contemporary time, wetlands are modifying continuously for the human needs, and the current wetland's declining rate in India can move toward severe environmental consequences. Around 74% of the rural populations (Anon 1994) are reliant on resources coming from the wetland. Land use conversion from wetland to agricultural, industrial, and various urban development results in substantial losses in the form of hydrological perturbations, pollution, and their effects (Turner et al. 1994). In the context of Indian biodiversity, numerous flora and fauna are reliant on wetlands or their products (Prasad et al. 2002).

To control these problems, restoration practices are not the only options but the ultimate necessity. Along with various biological restoration practices, the practices of natural hydrological conditions of wetlands are able to reconstruct the physico-chemical properties like the degree of the substrate, pH, nutrient availability, anoxia, sediment properties, and soil salinity (Prasad et al. 2002). These modifications lead to a change in physicochemical environment, which also promotes to change in biotic feedback in the wetland (Gosselink and Turner 1978). Hydrological conditions in wetlands modify even slightly which can lead toward huge change in response to biota richness, species composition, and ecosystem productivity. There are some restoration methodologies for wetland as described by various authors (Pfadenhauer and Klötzli 1996; Klimkowska et al. 2007):

- i. *Fen depth*: Fen depth has been necessary since we assumed that most of the organic material will soon be lost anyway at peat depths of less than 1 m.
- ii. *Rewetting potential*: The rewetting potential is chosen as a criterion because one has to be sure that sufficient water is available in the area to allow permanent flooding and the purpose of a wetland as a sink can be restored. Assessment of rewetting potential is specifically important and must include the entire catchment area of the wetland to be restored.
- iii. *Presence of suitable target species*: The third major criterion, the occurrence of target species, is more relevant when areas cannot be rewetted sufficiently. In

that case, the existence of characteristic fen or fen meadow species is important for carrying out a more flexible plan, in which several development goals must be pursued simultaneously. It may take some time before the site conditions of the restoration area meet the requirements of the target species.

5.1 Use of GIS and Remote Sensing in Wetland Management

Remote sensing data accomplished with geographic information system (GIS) is a significant tool for wetland restoration and management. The application encloses water resource assessment, flood management, hydrologic modeling, reservoir capacity surveys, water quality mapping and monitoring, and assessment and monitoring of the environmental effects of water resources project (Adam et al. 2010; Jonna 1999).

i. Water Resource Management

Abundant of thematic maps on the hydro-geomorphological features, slope, elevation, surface water bodies, and land use are performed by remote sensing and GIS. It has been initiated for the action plan for water source development (Adam et al. 2010; Ozesmi and Bauer 2002). The result may also reveal that the underground potential basin is moderate to good (Rao 1997). Utilization of satellite remote sensing data and aerial photointerpretation impressively support in planning groundwater reconnaissance and help in discovering the sources by recognition of geomorphological units.

ii. Flood Zonation Mapping

Satellite data source is utilized for the demarcation of flood-risk zone and floodinundated regions. Temporal data promote to get correct ground facts about the status of restoration and conservation projects of wetland. IRS 1 C/D WIFS data having 180 km spatial resolution and high temporal consecutiveness has helped in demarcating the zonation of flooding areas of large river bodies. This helps in designing for basin- and state-wise flood inventories.

iii. Water Quality Analysis and Modeling

Water quality analysis has been proceeded through using the relationship between chlorophyll-a, reflectance, and suspended solid concentration. Remote sensing data is utilized for the analysis of water quality factors and modeling. In the near-infrared wavelength range, the quantity of suspended solids content is directly proportional to the reflectance. Due to the temporal and spatial resolution of satellite data information of the point of discharge and source of pollution, the inflow of sewage can be regularly examined. By means of IRS LISS-II data, the suspended load in estuarine waters was inspected (Adam et al. 2010; Sasmal and Raju 1996).

There was some program initiated by WWFs for the conservation and restoration of wetland which helps to improve water access, efficiency, and allocation for people and the environment. This program promotes water stewardship, climate change adaptation, and water safety and mainly emphasizes habitat protection. Working with the Ramsar Convention, international river basin, national governments, nongovernmental organization, and institutions play a dynamic role for wetlands includes (WWF):

- Assisting execution of international agreements and treaties on biodiversity and wetlands
- Encouraging payments for environmental services (PES) for funding freshwater ecosystem facilities
- Evaluating and growing the representativeness of freshwater habitats in protected area systems
- Forming freshwater conservation setups
- · Restoring serious freshwater habitats

5.2 Specific Techniques for Conservation

Wetland restoration technique involves modification in hydric soil condition, hydrophytic plant communities, and hydrologic conditions. Wetland functions that happened on fragmented wetland site before to moderation to the extent operable. Wetland conservation strategies involve restoring endemic, native plant and animal communities (Faulkner et al. 2011). Minimization of soil erosion is the primary reason of the most commonly applied practice, residue management, conservation crop management, no-tillage/strip tillage, conservation cover, afforestation, reduction of land use change, reduction of overgrazing, and increase in vegetative cover and irrigation (Faulkner et al. 2011).

Degradation and depletion of sea grass in a coastal wetland, which is often caused by erosion which leads to eutrophication or dredge-and-fill activities, is commonly restored by transplantation (Burkholder et al. 2007; Fonseca et al. 1994). The suitable place and donor population for replacement should receive more focus on the significant expense (Bastyan and Cambridge 2008). Along with that, seeding techniques and mechanical planting have also been used as a possible solution to restore sea grass loss (Paling et al. 2009; Van Katwijk et al. 2009).

To resolve the complication of degraded wetlands caused by *Spartina alterniflora* invasions in the Yangtze River Delta, some are the examples especially in Chongming Dongtan wetland; methods that involve breaking of rhizomes, cutting, digging and tillage, and waterlogging as well as biological substitution with *Phragmites australis* proved effective (Liu et al. 2013; Yuan et al. 2008).

6 Preparation Needed Before Starting a Restoration Project

Before beginning a restoration project, pre-preparation step should be needed enlisting of this first one: locate the degraded wetland and identify the key indicators to decide the potential of replacement, restoration, and regulation. Along with ecological restoration, elemental method should be acknowledged to estimate the feasibility of conserving the damaged ecological, hydrological, and chemical processes. The social feasibility and ecological rationality should be used to predict and identify the crucial regions and pattern of ecological conservation and restoration (Zhao et al. 2016).

Ecological restoration endeavors are frequent part of an international framework that purposes to achieve local and global restoration targets (such as the Aichi Biodiversity Targets and EU biodiversity targets), for which inhabitants afford the expense (Adams et al. 2010; Kari and Korhonen-Kurki 2013). In literature related to conservation, the idea has been referred to as the "parks versus people" debate, where safeguarding global biodiversity through so-called fortress restoration. This fortress restoration is on one end of the spectrum, and a focus on refining local people is at the other end (Miller et al. 2011; Southworth et al. 2006). To safeguard nature restoration and conservation areas from resource exhaustion of resource are necessary. Because of such limitations, people have been moved or denied access to the resources, frightening their rights and livings (Brockington and Wilkie 2015).

To stimulate support for wetland restoration and foster sustainable use of wetland restore areas, an intended approach is obligatory. Increasing realization of the problem and enhancing awareness can be a needful strategy to promote public sensitization for wetland conservation. Reflecting upon the concept of Festinger (1957), Kollmuss and Agyeman (2002) suggest the proposal that the public may show a conflict against nonconforming information, meaning that "information that boosts our current values and conceptual frameworks is readily acknowledged, whereas information that controverts or excavate our thoughts and beliefs are avoided or not able to recognize at all." This means that the pros and cons of wetland restoration should be "framed" in ways that reverberate with the people (Groffman et al. 2010).

The public may be empathetic toward the restoration and conservation of wetland and its ecosystem. In reality, when it comes to daily practice and actual environmental behavior, activities that conflict with biodiversity conservation still gain priority (Samantha et al. 2016). This emphasizes the importance of wetland restoration projects to identify trade-offs and collaboration, making them better capable of dealing with both competing and complementary targets (Mitsch and Gooselink 2000). As expressed by McShane et al. (2011), by actively involving with scientists, regional users and environmentalists can raise sensitization for wetland restoration projects, which is expected to enhance the accomplishment of wetland restoration and conservation (Cooke et al. 2013).

7 Constructed Wetland (CW): An Attempt to Optimize Wildlife Conservation and Restoration

Generally, for treating wastewater, constructed and engineered wetlands are designed in such a way to look like natural wetland to remove various contaminants or improve the water quality along with conservation of resources (Vymazal 2013; Saeed and Sun 2012). These systems chiefly encompass substrates, vegetation, water, soil, and microorganisms (Badhe et al. 2014). They employ complex processes involving physicochemical and biological mechanisms (Upadhyay et al. 2016). It has been noticed since long that the CW treat a variety of wastewater with the help of plants and microbes. On the basis of macrophytes present in the wetland, it can be categorized as under (Brix 1993):

- 1. Free-floating macrophyte-based systems: In this type of CW, free-floating plants remove the pollutants which are present in dissolved form (Upadhyay et al. 2016).
- 2. Emergent macrophyte-based systems: This system plays a critical role as the rhizomes of the plant produce suitable required environment for nutrient removal process (Hofmann 1991). The rhizome helps in bacterial growth by providing surface for filtration of solids. The aerenchymatous rhizomes supply oxygen and create oxidized microenvironment in anoxic soil that subsequently increases decomposition of organic matter and nitrification.
- 3. Submerged macrophyte-based systems: These systems are less suited for the treatment of raw sewage and therefore utilized as tertiary treatment step for improving the effluent quality or treating eutrophic natural water. The species that have been employed for the above purposes are *Ulva lactuca*, *Ceratophyllum* spp., *Elodea canadensis*, *Cladophora* spp., *Myriophyllum* spp., *E. nuttalli*, *Enteromorpha* spp., *Egeria densa*, *Potamogeton* spp., etc.

The designing of CW is based on the flow of water, i.e., vertical flow (VF), horizontal flow (HF), surface flow, and subsurface flow (Ali et al. 2013). The water hydrology and the substrates used in CW (clay, sand, rock, peat, zeolite, gravel, etc.) provide a wider range of habitat for the growth of different types of microorganism like bacteria, fungi, and algae (Cui et al. 2010; Wu et al. 2014). The microorganism growing in the designed CW ultimately degrades the pollutants present in wastewater, thereby releasing large amounts of nitrogen, phosphorus, and other organic and inorganic contaminants. These contaminants were further utilized by plants for their growth and development (Rai et al. 2013). The growth of plants acts as a house of different wildlife animals. The conservation and restoration of wetland through CW can be dealt with the following points:

- CW facilitates the growth of different groups of microorganisms in a single habitable niche.
- CW purifies a variety of wastewater coming from different resources which directly affects the nature of natural wetland.

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- The growth of plants may act as nesting sites for birds and other insects.
- CW may recharge groundwater and inhibits soil erosion.
- CW may assist in flood control and vegetation loss and provide shelter to different wildlife animals.

8 Conclusions

In the past few decades, scientists and managers have identified the multiple values and functions of wetlands. Wetlands have generally been called as "kidneys of the landscape" because of their capability to transmute and store organic content. For this reason, various types of constructed wetland are employed to deal with wide range of wastewater all over the world. Many efforts are put into investigation in the advancement and refinement of CW technology. Further researches are needed to optimize design criteria for all sorts of CWs. Also, scientific studies are much needed for the improvement of long-term performance capabilities and operational problems related with the systems.

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Chapter 2 Phytoremediation and Sustainable Developmental Policies and Practices



Atul Kumar Upadhyay, Ranjan Singh, and D. P. Singh

Abstract Phytoremediation is a green strategy of environmental decontamination and offers a cost-effective approach for the remediation of variety of pollutants. This is an emerging technology toward sustaining the future of the world and mankind. The phytoremediation technology has been successfully applied in developed and developing nations to achieve the sustainable development goal. The present chapter encompasses the basic strategies, rules, regulation policies, and protective measures for the successful implementation of plant-based waste treatment technology in a cost-effective and sustainable manner.

Keywords Phytoremediation · Sustainable development goal · Environmental pollution · Environmental policies

1 Introduction

Environmental degradation and population burst are two main components which impede the world's sustainability (Carley and Christie 2017). The current world is facing challenges like waste mitigation, water pollution, and access to safe, affordable drinking water. These challenges are produced due to inadequacy of treatment system, awareness, and unlawful policies of the government (Upadhyay et al. 2016). Besides, ignorance is the key factor responsible for pollution, drought, and starvation.

The idea of environmental cleanup through plant-based phytoremediation technology is certainly very old and has been proved as an alternative cost-effective approach in the treatment of different contaminants including organic, inorganic, pathogen, radionuclide, and hydrocarbon (Alkorta and Garbisu 2001; Paz-Alberto and Sigua 2013; Rezania et al. 2015; Salt et al. 1995; Tangahu et al. 2011). The term phytoremediation was coined in the year 1991. Phytoremediation relies on the

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combined interactions of physical, chemical, and biological processes occurred naturally in the ecosystem. Phytoremediation works on the principle of microbialinduced pollutants, degradation, sedimentation, flocculation, transformation, and uptake by the plant's root (Haarstad et al. 2012). After a certain period of time, plants used in remediation were removed and dumped to other places. This process of remediation is popularly known as phytoextraction (Salt et al. 1995; Ali et al. 2013). In addition other phytoremediation processes like rhizofilteration, phytostabilization, and phytovolatilization are also operated simultaneously for the effective removal of waste (Rai et al. 2015; Upadhyay et al. 2019). To treat the waste, the global sustainable development plan "Agenda 21" has been approved in Rio Summit for reduction of basic environmental issues including clean air and water, waste treatment, and health care through different strategies set forth by the government and local bodies of developed and developing nations to curb down and maintain the environmental health (Bartelmus 2002).

2 Phytoremediation and Sustainable Development

Phytoremediation and sustainable development are two integral parts of the sustainable world. Phytoremediation is a sustainable cost-effective remediation technology based on the plants and microbial ability to detoxify contaminants, thereby enhancing numerous ecosystem services (Thijs et al. 2016). Sustainable development is the policy of safeguarding the future of the world through interrelationship between human development and environment to maintain the livelihood and well-being (Griggs et al. 2013; Sunderlin et al. 2005). The policy of sustainable development is framed to achieve the target of poverty reduction, food security, sustainable agriculture, healthy life, sustainable management of water, sanitation and wastewater treatment, energy recovery, combatting climate change, ecosystem restoration, and economic upliftment (Griggs et al. 2014).

The Rio+20 Summit in Brazil in 2012 devoted governments to create a set of sustainable development goals (SDGs) with two priorities, i.e., protection of the Earth and reduction of poverty for human well-being (Griggs et al. 2013). The Earth is continuously deteriorating due to population increase and unmanaged exploitation of natural resource to satisfy the basic need which has created a danger of lapse for mankind. This upheaval in meeting the demand of food, energy, health, etc. could only be alleviated by transition toward renewable and infinite source. Plantbased management of water, food, and energy is the only best alternative to achieve sustainable development goal (Godfray et al. 2010; Sims et al. 2010). Phytoremediation would not be a metaphor, if crediting "pillar of a house" and "two sides of a coin" in the direction of sustainable development goal. Water, the lifeline of human beings, continuously becomes polluted which can only be purified/treated by phytoremediation technology in a cost-effective and sustainable manner (Sharma et al. 2014). Besides water, soil pollution, air pollution, radionuclides, and e-pollution could also be reclaimed by plants (Cunningham et al. 1997; Tabak et al. 2005). The interrelationship between phytoremediation and sustainable development has been presented in Fig. 2.1.



Fig. 2.1 A pictorial representation showing the interrelationship between phytoremediation and sustainable development

2.1 Sustainable Development Goal: Practices/Policies

In sustainable development, the major practices to be emphasized are waste management, species richness/biodiversity improvement, nutrient cycling, energy recovery, and poverty reduction (Lélé 1991). The sustainable developmental practices to achieve sustainable development goal (SDG) include (Griggs et al. 2013):

- Establishment of target of SDG
- Development of social movements
- Establishment of science and technology with the aim of crafting eco-sustainable environment
- Creation of sustainable economic development
- · Development of health and education
- · Poverty reduction and improvement of human conditions
- · Establishment of food security in sustainable manner
- · Establishment of potable water security
- · Improvement of affordable access to clean energy
- Development of healthy and productive ecosystem

3 Basic Practices of Sustainable Development

3.1 Waste Management and Policies

Waste management is the process of reducing contaminants present in wastewater to an acceptable level safe for disposal (Giusti 2009). The increasing population continuously produces more waste load in the environment due to insufficient treatment facility and high cost (Guerrero et al. 2013; Dincer 2000; Rai et al. 2013). Wastes are emerges from different sources, viz., household, urban effluents, industrial effluents, agricultural runoff, etc., and is directly discharged into the river without any proper treatment, affecting the ecosystem of river, lake, and reservoirs. Release of toxic gases and odour from the river, being the major source of drinking water and reservoir (sink) of wastewater, cause deadly diseases in human beings (Gracey and King 2009). So, tackling the pollution of river, lake, and reservoir, a comprehensive and lawful action must be taken for sustainable development.

Basically two strategies were employed for waste management, viz., single-site treatment and individual treatment. Single-site treatment is a large-scale treatment in which wastewater was collected from different sites and treated, while in individual treatment, wastewater is treated in the individual, small-scale, and community level (Water UN 2015).

The following strategies/policies are recommended for successful management of wastes adopted from GWP (2008):

- 1. Establishment, implementation, and enforcement of laws, standards (effluents, influents, STPs, quality management plan), and norms.
- 2. Involvement and coordination of local authorities, national as well as international authorities, for the accountability of treated waste, their disposal, and reuse.
- 3. Monitoring of progress, publication, and collection of data.
- 4. Mass awareness program to change public behavior and actions.
- 5. Creating tariffs, fees, and tax system for water use and willingly increasing pollution and water tax, etc.
- 6. Development of waste management system by industry and the organizations (local or private) which are major generator of wastes.
- 7. Involving experts of universities, institutions, or other sources for regular monitoring, reviewing, and reforming of the actions.
- 8. Upgradation or installation of wastewater treatment facilities to enhance health and environment.
- 9. The treatment plant should be away from residential area and be constructed according to the inflow of water and waste load.
- 10. Designing of new treatment plants for individual and small-scale waste treatment and their treatment potential must be standardized prior to application in the field.
- 11. Multidisciplinary research attitude should be developed and promoted on wastewater management.

For the effective treatment of wastewater, different cost-effective, green, and sustainable alternatives like STPs, CETEP, and constructed wetland are operational in different parts of the world.

3.2 Biodiversity, Species Richness, and Policies

Biodiversity is the life insurance of humans, and its losses could be one of the greatest catastrophes and challenges for society and sustainable development. Biodiversity covers all the sectors of SD like food, shelter, medicine, waste management, climate change, health, and economy, encouraged in the form of agriculture, farming, fisheries, and tourism (Pretty and Smith 2004; Kiss 2004; McNeely 1994). Climate change, habitat destruction, and pollution are the biggest threats of biodiversity. Without biodiversity sustainability is a remote talk for any nation of the world. Phytoremediation and sustainable development are interrelated to each other (Thijs et al. 2016). Phytoremediation protects the biodiversity by providing habitat for the growth and development of different flora and fauna in the nature or a system designed (constructed wetland, open pond system, multistage wetland system, etc.) for the treatment of waste (Dobson et al. 1997; Rai et al. 2013). The designed system may act as a protected area in which assemblages of plants and microbes degrade waste and assimilate the nutrients for their survival (Upadhyay et al. 2017). The constructed wetland, man-made designed system based on phytoremediation, offers many ecosystem services to humans such as sustainable food, water purification, recreation, and nutrient cycling (Engelhardt and Ritchie 2001). Wetland acts as a sink for increasing the level of CO₂, thereby reducing carbon load and global warming (Brix et al. 2001; Whiting and Chanton 2001).

Biodiversity is an indispensible component of phytoremediation. The restoration and sustainable use of biological diversity make it easy to cope with the anthropogenic and natural challenges like population growth, pollution, drought, flood, etc. (Maxwell et al. 2016; Omann et al. 2009). The concept of phytoremediation basically relies on the species richness. A greater number of species represent high remediation efficiency of the pollutants present in the environment. The agenda of conservation of biodiversity is included in chapter 15 of Agenda 21 (United Nations Conference on Environment and Development) adopted in Rio Summit in 1992. Plants ranges from cryptogams to phanerogams has the potential to be used in phytoremediation as a bioindicator, tolerant/resistant agent, hyperaccumulator, and resource recovery phytoagent (Diekmann 2003). Of these, bryophytes and pteridophytes are found only on restricted locations and more prone to be extinct in the near future. They have the capability to grow in high metal-rich condition (Chen et al. 2002), wastewater (Vermaat and Hanif 1998), and polluted air (Szczepaniak and Biziuk 2003) and work as sustainable entities demarking the nature of the area or type of particular pollution and enrichment of a specific type of contaminants. By identifying these plants, they can be preserved, protected, and recultured, and thus using these plants in phytoremediation will automatically enhance biodiversity.
In addition, one of the richest ecosystems of inhabiting microbiota in the root system of plants also plays a very crucial role in the success of phytoremediation in a sustainable manner (Bulgarelli et al. 2012). The microbes present in soil-plant interface reduces metal toxicity and assist in transformation of organic and inorganic compounds, mineral cycling, translocation of ion, improve soil fertility and thus, contribute to plant growth and phytoremediation (Deng and Cao 2017).

The continuous loss of biodiversity through natural and anthropogenic activities is a matter of great concern to sustain the world (Miller 2005). Biodiversity loss has negative effect on food, water supply, shelter, and livelihood. The World Bank, UNESCO, UN Biodiversity Conservation Board, and other agencies are actively engaged in conservation of biodiversity through safeguarding policies, protection of natural area and forests, conservation of coastal area, etc. Here are some policies associated with biodiversity conservation and are adopted from OECD-FAO (2011), OECD (2013):

- · Prohibition on access of protected area and conserved area and deforestation
- Regular environmental impact assessment (EIA)
- Controlling and minimizing the use of pesticides, fertilizers, and herbicides in agri sector to safe microbial niche and land productivity
- Promoting afforestation along with community awareness and education
- · Management of natural wetland, fisheries, lake, and other reservoirs
- Biobanking
- Establishment of tradable permits like water right, carbon emission, and development right
- · Subsidies for reforestation and public investment
- Development of eco-labeling and certification scheme such as timber certification, organic farming certification, green manure certification, etc.

3.3 Sustainable Energy Recovery

An adequate supply of energy has been a prerequisite for economic and social development in societies (Tainter 1990) which are continuously increasing due to population growth. The overexploitation of resources to fulfill the demand causes a significant loss of the fossil reserves which create a panic situation in front of the scientist, global thinkers, policymaker, and experts owing to save the reserves (Ayres and Ayres 2009; Matthewman 2016). In addition, urbanization and industrialization worsen the environment, affecting millions of the peoples for safe water, food, shelter, and energy.

To lessen the impact, a number of policies/strategies and plans have been implemented by the governmental and nongovernmental authorities; however, no measurable cure is still optimized. Seeking the disaster, an integrated transition toward a more sustainable, cost-effective, and green alternative of fossil reserves which fulfill the energy demand in sustainable manner is of utmost priority. Energy production

Feedstocks	Examples	Biodiesel productivity	References	
First generation	Zea mays L.	152 kg/ha/year	Mata et al. (2010)	
	Glycine max L.	562 kg/ha/year	Mata et al. (2010)	
	Helianthus			
	annuus			
Second generation	Jatropha curcas	656 kg/ha/year	Mata et al. (2010)	
	Tobacco seed		Usta (2005)	
	Jojoba oil		Canoira et al. (2006)	
Third generation	Microalgae	20,000-80,000 L/hac/	Demirbas and Demirbas	
		year	(2011)	

Table 2.1 Comparative account of biodiesel production efficiency by different feedstocks

through agriculture crop (maize, sunflower, *Glycine max, Jatropha*, rapeseed, etc.) and algae could be a viable resource for sustainable energy recovery without impairing biodiversity (Pandey et al. 2016; Sharma et al. 2012; Tilman et al. 2011). Besides, these plants phytoremediate a significant amount of heavy metal and other toxic elements by sequestering into its body, thus involving in the phytoremediation (Pandey et al. 2016). The agricultural crops used in the production of biodiesel are considered as first-generation feedstock of biofuel as they use for the first time to generate fuel (Brennan and Owende 2010). However, due to its utilization in the global feed source, it disturbs the global food market which leads to food and fuel crisis. Cultivation of maize for biogas generation could yield 33,000-46,000 kWH/ hectare/year renewable energy which reduces up to 21,000 kg/ha/year CO₂ if used as fossil fuel substitute (Meers et al. 2010). To minimize the dependency on edible food, nonedible feedstocks were used in the production of biodiesel as a secondgeneration feedstock which also failed due to long harvesting time, large land area, and low biomass (Canakci 2007; Canoira et al. 2006; Ghadge and Raheman 2006; Ma and Hanna 1999; Usta 2005). The algae are considered as third-generation feedstock of biofuel because of its fast growth rate, high biomass and lipid yield, easy to culture, and ability to grow in a variety of habitat (Ahmad et al. 2011). Algae utilization in treatment and biofuel generation has been reported by various authors (Singh et al. 2018; Upadhyay et al. 2016), playing dual role of sustainable phytoremediation and energy recovery. A comparison of all three-generation feedstock to their biodiesel productivity has been mentioned below (Table 2.1).

3.4 Climate Change and Phytoremediation

The current world is facing the major hazards of elevated level of CO_2 due to fast industrial insurgency and technology development (Leakey et al. 2009; Seto et al. 2012). High CO_2 concentration in the atmosphere causes floods, drought, changes in precipitation pattern, greenhouse effect, and global warming which deteriorates the lives and may lead to extinction of human civilization (IPCC 2014). The reality and seriousness of climate change have emerged since 1980. The environmental community and scientist accredited global high CO_2 as being the major pollutant for climate change and global warming, the interchangeable misnomer. However, the National Research Council in 2001 explained the technical differences of climate change and global warming. Thinking the seriousness of elevated CO_2 level, the Kyoto Protocol was developed in 1997 with the aim of reducing the emission of CO_2 , the major contributor of global warming (McCright and Dunlap 2000). The IPCC (Intergovernmental Panel on Climate Change) and other scientific bodies such as the American Meteorological Society (2003) and American Geophysical Union (2003) stated that the Earth's climate change is affected by anthropogenic activities.

The impact of climate change is one of the problems which has negative effects on productivity of grains and other crops (Lobell and Field 2007; Thomason et al. 2010). The impact of climate change can be overcome by increasing sequestration of elevated level of CO₂, afforestation, and agroforestry (Brown et al. 1996). Agroforestry climate change mitigation offers food safety, food security, and pollution minimization. Besides, wood carving facilitates long-term locking up of carbon in carved wood and tree plantation to sequester carbon (Pandey 2002; Zazai et al. 2018). Tree planting along with agricultural crops improves soil fertility and controls soil erosion and water logging, thereby limiting eutrophication (Zazai et al. 2018). Reducing greenhouse gas emission is an utmost priority for the sustainability in the urban world. This can be achieved by management of population increase, energy consumption, and waste production; development of local and sustainable agenda for the pollution control, involvement of local authorities, communities, and policymakers; and finally education and awareness related to environmental degradation (Wilbanks and Kates 1999). The adaptive measures/policies that need to be implemented are as follows:

- Switching to heat-tolerant crop.
- Construction of seawall to avoid flood due to sea level rise.
- Building bridges in the coastal area.
- Designing of flexible policy as high uncertainty of climate change could happen slowly or quickly and unexpectedly.
- Strengthening construction standard (building houses and dams of large size) to reduce uncertainty.
- Tree plantation and agroforestry.
- Development of buffer zone, migration corridor, and protected zone for unmanaged resources like wetland, forest, coast, etc., as they are more susceptible to uncertainty.
- Development of hydropower system.
- Designing of constructed wetland, pond, reservoirs, and STP for waste management which can mitigate climate change.
- Development of corridors for the migration of the species during instant unfavorable circumstances. The corridor developed should be either from a long time or during disaster. However, already established corridor could provide instant habitable location for the migratory species for sustainability and survivality.

3.5 Phytoremediation and Society

Phytoremediation offers many societal benefits to human and nature. The environmental benefits include biodiversity enrichment, soil protection and preservation, carbon sequestration, water management, energy and aesthetics, stability, and sustainability (Adams et al. 2013; Dickinson et al. 2009; Robinson et al. 2003). The phytoremediation strategies of gold phytoextraction can be used in gold mining as a simple and financial pleasing move (Anderson et al. 2005; Wilson et al. 2012). In addition, mercury is also phytoextracted. In the mercury mining, area contaminated with mercury was grown with high biomass-producing plant species (Rodriguez et al. 2007). After a certain period of time, solubilization of Hg was done by certain amendments which facilitate accumulation of Hg in the plant parts. Finally, the plants were harvested and processed to recover metals. In a field experiment, Anderson (2013) reported that under optimal condition, a single crop of plant recovered ~15–20% of gold from the soil. A number of ancillary benefits are mentioned below:

- Pulp of phytoremediator plant *Phragmites communis* is better and cheaper than derived from straw and bush and suitable for the manufacture of artificial fibers.
- The reeds' plant material can be used in the manufacture of paper which definitely cuts down the loss of a huge amount of timber and forest.
- The aquatic plant Vossia cuspidata provides short-fibered pulp of poor strength.
- Fresh leaf stalks of *Eichhornia crassipes*, *Cyperus papyrus*, and *C. antiquorum* are also used for manufacture of paper.
- *Eichhornia crassipes* could be used for manufacturing of cellulosic materials such as artificial silk.
- *Azolla* sp. could be useful for mosquito control when encouraged to form a dense mat over ponds. This gave the plant the name "mosquito fern."
- *Nymphaea alba* and *Nuphar* sp. have been used for mordanting properties and employed in dyeing and tanning in European countries.
- The leaves of *Typha* sp., *Cyperus* sp., and *Schoenoplectus* sp. are used for weaving and basketry.
- The hairs of *Typha* sp. flowers are used to stuff pillows.
- Cyperus papyrus is used for making ropes, canvas, and sails.
- *Lemna* sp. dried sample provided an excellent substitute of conventional feed like soybean and fish meal.

4 Conclusions and Future Prospects

The natural ecosystem on the Earth has been deteriorating due to anthropogenicinduced worsening which might lead to uncontrolled collapse during the course of time. The alteration in biological diversity and hydrological pattern together causes climate change, energy crisis, and environmental health. Therefore, conservation of water resource and biological diversity is of utmost priority for the sustainable world. An integrative approach and research are appreciated to encourage the researcher and policymakers to find ways to mitigate the Earth's pollution load effectively. In addition, conservation of biodiversity and a wise use of bioresource are also mandates for which policies should be developed by policymakers and scientists. In order to be sustainable, developments have to unite in three chief elements: fairness, protection of the environment, and increase in economic efficiency. Besides, some future research such as assessment of biofuel production quality, remediation potential, efficiency of production, and genotoxicity in relation to petro plants might be helpful for the sustainable world.

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Chapter 3 Wetland as a Sustainable Reservoir of Ecosystem Services: Prospects of Threat and Conservation



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Abstract A wetland is a type of ecosystem saturated with water throughout the year possessing various ecosystem services in the environment. Wetland is composed of abiotic and biotic components and acts naturally as a reservoir of food, shelter, and habitat for biological communities. Increasing human population leads to more industrialization and urbanization which continuously alter the landscape and interfering nutrient cycling. Further, changes in precipitation pattern and global climate leading to hydrological and environmental imbalances cause frequent flood and drought. As a result of rapid development and human interference, wetland ecosystem is degrading day by day which needs to be conserved for environmental sustainability. Microbial communities play an important role in nutrient cycling and conservation of wetland.

Keywords Wetland · Biological communities · Ecosystem services · Nutrient cycling

1 Introduction

Wetlands are water-saturated ecosystems and provide different ecosystem services to humans (Groot et al. 2012). According to the Ramsar Convention, wetland includes natural as well as man-made system like peatlands, rivers, lake aquifers, estuaries, marshes, wet grasslands, deltas, mangroves, ponds, coastal lands, coral reefs, rice paddies, etc. (Aber et al. 2012). Wetlands act as a sustainable reservoir of

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food, feed, shelter, and habitat because of their complex hydrology, nutrient cycling, and presence in both urban and unmanaged areas (Costanza et al. 1997; Mitsch et al. 1995).

Wetland degradation is continuous. The direct cause of wetland loss includes salinization, nutrient enrichment, pollution of pesticides and heavy metals, and the invasion of exotic flora and flora (Davis and Froend 1999). Besides, the environmental alterations and anthropogenic-induced worsening cause disaster of flood, drought, earthquake, global warming, and high temperature and lead to degradation of wetlands ecosystem severely (Kercher and Zedler 2004; Mentzer et al. 2006). Freeman et al. (2001) studied that hydric soils under permafrost are the sources of active gases at high-latitude system, which alters wetland chemistry. The functioning of the wetland is directly related with microbial diversity present in the wetland and decides the community composition in different wetlands (Mentzer et al. 2006; Sundh et al. 1997). The community composition in different wetlands was studied by various authors by using PLFA analysis as well as across gradients of nutrient stress in peatlands (Borga et al. 1994; Boon et al. 1996; Sundh et al. 1997). Wetlands provide many important ecosystem functions to society; this explains why in recent years, much attention has been directed toward the formulation and operation of sustainable management strategies for wetland conservation (Davis and Froend 1999). Zedler and Kercher (2005) have reported that wetland covers about 40% of the earth's renewable ecosystem services. The monetized value services provided by the wetlands are very high. A study conducted by Constanza et al. (1997) explains and calculated the value of different shallow water habitat wetlands such as mangrove, swamps, marshes, floodplain, estuaries, etc. A summary of the cost of different services is mentioned below in Table 3.1:

Ecosystem services	Categories	USD/ha/year	USD/ha/year (in billions)
Hydrological services	Water regulation	15-30	
	Water supply	3800-7600	
	Gas regulation	38–265	
Water purification	Nutrient cycling	3677-21,100	
	Waste remediation	58-6696	
Biodiversity	Biological control	5-78	
	Habitat	8–439	
	Food production	47–521	
	Raw material	2–162	
	Recreation	82-3008	
	Cultural	1–1761	
	Disturbance regulation	567-7240	
Global total	Coastal wetland		8286
	Inland wetland		4879
	Total for global wetland		13,165

Table 3.1 The cost of shallow water wetland services

Modified and adopted from Constanza et al. (1997)

Various central and state policies have been implemented for the restoration of wetland against natural and man-made constraints yet fail to preserve the ecological processes (Whigham 1999) due to lack of knowledge of wetland hydrology and ecology, miscoordination between governments, and public awareness (Davis and Froend 1999). The present chapter covers the wide area of wetland ecology, conservation, and role of microbes and plants in wetland management.

2 Wetland: Ecology and Types of Wetland

The current world is facing a mega challenge of climate change and ecological imbalance. This might lead to deteriorate the lives of the flora and fauna of the various ecosystems. The ecology of wetlands deals with the relationship of plants and microbial community to their environment which directly or indirectly depends on the geographic distribution, climatic condition, hydrology, human interference, soil condition, altitude and latitude, etc. which alters its functioning and behavior. Three main environmental factors are essential to study the wetland ecology, i.e., structure, community composition and function (Keddy 2010). These three factors are increased nutrients (eutrophication), increased water (flooding, drainage), and increased disturbances (construction, burning, etc.).

Wetlands are highly productive ecosystems occurring almost everywhere on the earth. Wetlands may be natural and man-made. Natural wetland includes marshes, swamps, estuaries, lakes, ponds, fens, deltas, coral reefs, lagoons, bogs, and flood-plains, whereas ponds, constructed wetland, reservoir, sewage farm, canal, etc. are artificial (Aselmann and Crutzen 1989). Some important wetlands are described here (adopted from Federal Geographic Data Committee 2013):

Marshes include wetlands in which soil is continuously saturated with water and characterized by the presence of soft-stem vegetation. Marshes reduced the damages by recharging groundwater, slowing down the flow of flood, and storing excess water. The slow movement of water in marshes enhances the chance of settlement of nutrient to the base formation of high biodiversity rice microorganism and utilization of nutrients for the growth and development of the plants present in marshes. Microorganism present in marshes degrades the organic and inorganic constituent of water and wastewater and reaches to the marshes.

Swamps are defined as flooded woodland or shrublands. Swamps occur in low lying are supersaturated soil wetland. Swamps are characterized by wet soil during growing season. Swamps are categorized into forest, shrub, and mangrove swamps. Forest swamps receive water from lake and rivers and occur at the coast side of water reservoirs. The trees that grow in swamps are dry and deciduous in nature and often include maple, oak, bald cypress, water tupelo, etc. Mangrove swamps are characterized by salt-tolerant plants and coastal wetland extended from tropic to subtropical zone of the vegetation.

Bogs are characterized by peat-deposited freshwater wetland and evergreen trees prevalent in southeastern part of the United States. The water source in the bogs is rainwater and usually occurs in glaciated areas of the Northern United States. Bogs are formed by the natural decaying of leaf, litter, and other organic substances during the course of time through active microbial processes. The soil of bogs is acidic in nature due to secretion of weak acid during the process of leaf decomposition by the microbes.

Estuaries are developed where river water is mixed with seawater, creating a biodiversity rich zone for the growth of microorganism and plants. Estuaries included deltas, tidal mudflats, salt marshes, etc. Estuaries, having variable physical, chemical, and biological conditions, make them a house of different wildlife which make them a habitat of high conservation value (Davidsson et al. 1997). Estuaries are fragile ecosystems affected by inappropriate catchment development, degree of tides, increased algal bloom, nutrient input, and climate change. Estuaries can be protected by native vegetation, reducing sedimentation process, improving catchment area, and reducing pollution, restricted fishing, and other anthropogenic activities.

Fen wetland system is a natural wetland and characterized by abundance of grasses, sedges, and low shrubs. These are alkaline wetlands. In fen, water mostly surface water and groundwater are used for soil saturation. Fens, like all wetlands, have experienced a dramatic decline in acreage since the 1970s as they are drained for cropland, mining, and human expansion – threatening the survival of many of the plants and animals that depend on these unique environments. The nutrient-rich conditions in a fen provide a diversity of plant life, which then supports a number of animal species that thrive in such highly productive habitats.

Coral reefs are among the most productive ecosystems, which cover 0.1-0.5% of the ocean floor (Moberg and Folke 1999; Spalding and Grenfell 1997). McAllister (1991) reported that approx. one third of marine fishes are found on the coral reefs and provide goods and services to the people inhabiting near the sea. However, coral reefs are declined due to urbanization and population growth which needs immediate effects for its protection and management.

Constructed wetlands are an engineered system, designed with ecological principles that encompass physical biological and chemical processes for waste remediation in soil and water (Rai et al. 2013; Upadhyay et al. 2017). The CW successfully mitigates the variety of wastewaters including pharmaceutical waste, leachates, mine drainage, industrial effluents, and sewage (Vymazal 2011).

Sewage farm is waste disposal and treatment farm where various types of wastewater are stored, distributed, and treated for their further utilization in irrigation and other purposes (Saber et al. 2016).

3 Wetland Degradation

Wetlands are one of the most vulnerable ecosystems around the globe, increasingly facing several anthropogenic pressures and refer to physical loss in spatial extent or loss of wetland functions. Thus, the rapidly expanding human population, land use

change, burgeoning development projects, and improper use of watersheds have all caused a substantial decline of wetland resources of the nations (Zedler and Kercher 2005). The current wetland loss rates in India can lead to serious consequences. Anon (1991) reported the 74% of the human population is rural, and many of these people mainly depend on natural resource for their livelihood. Most problems affecting India's wetlands are related to population growth. Although India contributes to 16% of the world's population (Foote et al. 1996), yet it contains fewer natural wetlands with respect to wetland percentage of the world. Therefore, restoration of these converted wetlands is quite difficult once these sites are occupied for other purposes.

The degradation of wetland directly or indirectly is the result of alteration in soil chemistry, soil nutrient status, and microbial assemblage (Hartman et al. 2008). Microbial assemblages of known and unknown entities play a major role in wetland functioning. Fundamentally wetlands are influenced by two factors, i.e., anthropogenic and environmental (Fig. 3.1). Nutrient enrichment condition supports microbial biodiversity in the wetlands which affects the wetland behavior. Anthropogenic factor includes land use change, eutrophication, and incorporation of toxic organic and inorganic contaminants, while environmental factors such as flood, heavy rain, natural shift, etc. also influence wetland system (Hartman et al. 2008; Zhang et al. 2007). Acute and chronic losses are two broad groups of wetland losses in India



Fig. 3.1 A generalized view of causes of wetland loss

(Prasad et al. 2002). Acute loss of the filling up of wet areas with soil constitutes the chronic losses in the gradual reduction of forest cover following sedimentation and erosion of the wetlands since decades.

3.1 Acute Wetland Losses

3.1.1 Agricultural Conversion

In the Indian scenario, due to rice cultivation, there has been a significant loss of wetlands (Prasad et al. 2002). Rice farming is a wetland-dependent activity developed in the area saturated with water in most of the time such as river deltas, estuaries, etc. In a report of Anon (1993), out of 58.2 million hectares of wetlands, 40.9 million hectares are under rice cultivation in India. This huge agriculture conversion significantly affects the functioning of the wetland ecosystem.

3.1.2 Direct Deforestation in Wetlands

Mangroves are flood- and salt-tolerant vegetation which grows along the coastal area and significantly provides fish, livestock fodder, fuel wood, building materials, food products, wax and chemicals, etc. (Ahmad 1980). With the increased population load and advent of alternative farming methods and fisheries production for sustaining lives, people exploits many mangrove areas which leads to degradation of wetland ecosystem (Naylor et al. 2000). In addition, most of the coastal mangroves are degenerating due to the increasing economic demand on shrimps, excessive withdrawal of freshwater, and increased pollution load on water like lime, organic wastes, pesticides, chemicals, and disease-causing organisms (Funge-Smith and Briggs 1998).

3.1.3 Hydrologic Alteration

Wetlands are considered as the heart of nature and water hydrology as lungs to various ecosystem services (Cowardin et al. 1979). Modification in the hydrology pattern can influence the character and functions of wetlands. The changes in hydrology include either the removal of water by evaporation, precipitation, transpiration, flood, and mechanical loss as in constructed wetland or raising the land surface elevation (Talukdar and Pal 2017).

3.1.4 Inundation by Reservoirs

There are more than 1550 large reservoirs covering 1.45 million ha; 1.0 lacs small and medium reservoirs covering 1.1 million ha in India (Gopal 1994). Dam and reservoirs are the main drivers for flow change which might be resulted into water scarcity in floodplain wetland (Talukdar and Pal 2017). Floodplain wetland depends on the timing and magnitude of the water flow and because of construction of reservoirs accounts for >70% loss of floodplain wetland (Constanza et al. 1997).

3.2 Chronic Wetland Losses

3.2.1 Change in Upper Watersheds

Watershed conditions influence the wetlands (NRC 1999). The land where precipitation falls, collects, and runs off into the soil will influence the characteristics and hydrology of the downstream wetlands. Agriculture, deforestation, and overgrazing reduce the water holding capacity of the soil which influences the soil erosion. Large areas of India's watershed area are being physically stripped of their vegetation for human use.

3.2.2 Degradation of Water Quality

Water quality degradation is directly linked to human population and its mismanaged practices and activities. Chopra (1985) reported that ~50,000 small and large lakes are being polluted to the point of considered as "dead." The major factors are untreated sewage, industrial pollution, and agricultural runoff, which may contain fertilizers, pesticides, herbicides, etc. (Chaudhry and Malik 2017).

3.2.3 Groundwater Depletion

Groundwater deteriorates continuously at very fast rate. Water-flooded wetlands were the ultimate source of groundwater recharge which now become extinct due to various well-known causes and direct ignorance of the government bodies. Draining of wetlands has depleted the groundwater recharge. In an estimate, Prasad et al. (2002) reported that in rural India, about 6000 villages are without a source for drinking water due to the rapid depletion of groundwater.



Fig. 3.2 Graphical representation of factors and their interconnection causing wetland devastation

3.2.4 Introduced Species and Extinction of Native Biota

More than 2400 species of birds found in the wetlands of India are under threat due to its degradation and loss (Mitchell and Gopal 1990). The introduction of invasive species like *Eichornia crassipes* and *Salvinia molesta* causes wetlands to degradation and waterway clogging. Samant (1999) reported that more than 700 potential wetlands are threatened.

A graphical representation showing the major factors which are responsible for wetland degradation has been mentioned below (Fig. 3.2).

4 Conservation of Wetlands

The Ramsar Convention signed in Iran in 1991 is the most important initiative for wetland conservation. Wetland conservation in India is indirectly influenced by a range of policies and legislative measures. Some of the key legislations are given below (NAEI wetlands of India 2006):

- The Indian Fisheries Act 1857
- The Indian Forest Act 1927
- Wildlife (Protection) Act 1972
- Water (Prevention and Control of Pollution) Act 1974

- Territorial Water, Continental Shelf, Exclusive Economic Zone and other Marine Zones Act 1976
- Water (Prevention and Control of Pollution) Act 1977
- Maritime Zone of India. (Regulation and fishing by foreign vessels) Act 1980
- Forest (Conservation Act) 1980
- Environmental (Protection) Act 1986
- Coastal Zone Regulation Notification 1991
- Wildlife (Protection) Amendment Act 1991
- National Conservation Strategy and Policy Statement on Environment and I Development – 1992
- National Policy And Macro level Action Strategy on Biodiversity 1999

Interest in conservation of wetlands can be traced back in the recent history to the late nineteenth century. Around 1897, protection of the coastal belt system was initiated. The Fauna and Flora Protection Ordinance of 1937 can be considered as a major step in wetland conservation. Under this legislation, Department of Wildlife Conservation declared importance to wetlands in bird protection and conservation. Wetland is the habitat of different flora and fauna. It was year 1971 when the intergovernmental treaty was adopted aiming to minimize the loss of wetland degradation and its wise use through local, national, and international cooperation toward attaining sustainable development goal (Quental et al. 2011). As reported by Ramsar Convention on wetlands on September, 2018, states that wetland diversity is disappearing three times faster than forest ecosystem with havoc consequences for the future unless urgent feat is taken to guarantee their survival. Major strategies for wetland conservation include exploration of major threatening factors, improving the conservation policies of wetlands, strengthening the wetland legislation, and increasing government and public participation, research attribute, and education for wetland conservation (Keddy 2010; Max Finlayson 2012; Moore et al. 1989). The conservation of wetland is challenging because of availability of inaccurate and old data related to wetland distribution, localization, type, and degradation status (Junk et al. 2013; Zedler and Kercher 2005). For the global wetland conservation, an ideal inventory such as US Fish and Wildlife Service National Wetlands Inventory, the Australian Wetlands Database and the Directory of Important Wetlands in Australia, Manual of European Union Habitats - EU-27, and the Canadian Wetland Inventory system containing all the fundamental information related to wetland conservation should be present (Junk et al. 2013). Thus, knowing wetland distribution is the first step for defining a specific conservation plan (Nel et al. 2009; Vörösmarty et al. 2010).

5 Contribution of Microbial Community in the Wetlands Conservation

Wetland is the house of diverse microbial community which regulates wetland functioning. Microbial communities of wetland play an important role in pollution removal, assimilation, mineralization, and metal uptake (Singh et al. 2018). A number of microbial-driven conversions occur inside wetland which ultimately controls the vegetation of the wetland (Lamers et al. 2012). Nitrifying and denitrifying bacteria constitute an important group in wetland microbial community and play an important role in nitrogen removal (Enwall et al. 2005; Zumft 1992). Yamamoto et al. (2008) reported anammox (anaerobic ammonium oxidation) bacteria constitute another bacterial group, the *Planctomycetes*, which contributes in the removal of nitrogen by oxidizing ammonia to nitrogen gas using nitrite as an electron acceptor under anoxic conditions. Determining the structure of wetland microbial communities is important for understanding the biological processes that occur in soil-water-plant wetland system. Besides, nitrogen-related bacteria, the distribution of methanotrophic bacteria, iron-oxidizing/iron-reducing bacteria, sulfur bacteria, etc. play a detrimental role in methane cycling, iron redox, and sulfur dynamics in the wetland (Dedysh et al. 1998; Dedysh 2002). The bacteria responsible for iron redox have potential to support the large microbial population in wetland. The methanogenic bacteria (Methanococcus, Methanobacter, Methanosarcina, etc.) present in the wetland decompose organic compound present in the wetland, thereby producing the methane (Segarra et al. 2015). Besides, bacteria, fungi and invertebrates also play a significant role in solubilization and degradation of phosphorus in wetland. The fungal association inside the wetland restricts the entry of toxic metal and decomposes litter present in the wetland (Gingerich et al. 2015).

6 Contribution of Plant Community in the Wetlands Conservation

The plants present in wetland significantly determine the fitness of the wetland. Plants maintain the floral diversity, shelter of birds, and other organisms and remove water pollution, assisting nutrient cycling and toxic metal uptake (Rai et al. 2013; Upadhyay et al. 2017). Plants present in wetland enhance the species richness, biodiversity, and services of wetland to society such as contributing to atmospheric CO_2 fixation, recreational opportunity, and water purification. The harvested biomass of plants grown in wetland may be utilized as energy resource like biofuel, biogas, or biocompost generation in sustainable means (Rai et al. 2015). Loss of plant communities in the wetland leads to reduction in primary production, loss of faunal diversity and habitat, decreased sediments, increased nutrient content, etc. Thus, maintaining the plant biodiversity is crucial for restoration of wetland.

7 Conclusions

Wetland ecosystem is under continuous deterioration due to human interference and changes in global climate. The eminent role of wetlands for human welfare and microbial contribution in the functioning of wetland necessitates the intensive assessment of behavior and ecology of wetland microbes in the coming future research. Significant alteration in wetland hydrology, diversity, and services due to climate change also brings a mega challenge toward conservation of wetland for the sustainable world. As microbes being one of the most important components, its ecological boundaries, resistant behavior, tolerant nature, and functioning study must be imperative for sustainable functioning and conservation of wetland.

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Chapter 4 Carbon Sequestration and Storage by Wetlands: Implications in the Climate Change Scenario



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Abstract The impacts of climate change are discernible and can only be reduced through proper adaptation and mitigation techniques. Wetlands represent an excellent example of natural ecosystems providing a wide range of ecosystem services valuing billions of dollars. The service of carbon sequestration by wetlands is directly linked to greenhouse gas regulation and climate change. They are known to have higher rates of carbon sequestration than any other terrestrial ecosystem on this planet. This is because of their higher above- and belowground productivity, anoxic soil conditions, and higher sedimentation rates. The most important factor affecting carbon sequestration in wetlands is substrate availability which depends on the type and composition of vegetation. Wetland vegetation is mainly responsible for determining the detritus quality and the carbon sequestration capacity of wetlands. Unfortunately, wetlands are under various anthropogenic pressures which affect their functional capacity of acting as sinks of carbon. Climate change also has a positive feedback on their functioning. Therefore, their maintenance and conservation are imperative, for they act as an important pool to balance the deleterious impacts of climate change. If climate change is not taken care of, then wetlands may act as a source of carbon, stored by them over years, and can augment the problem. Moreover, the concept of constructed wetlands needs to be encouraged to increase the number of potential carbon sinks. Their methane emissions can also be controlled by regulating C:N and N:P ratios in their soils.

Keywords Climate change \cdot Carbon sequestration \cdot Ecosystem services \cdot Constructed wetlands

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1 Introduction

Global climate change is considered as one of the most serious environmental challenges of the twenty-first century as it is posing threat to the survival of species and the health of natural ecosystems. The main driver of global climate change is escalating concentration of the greenhouse gases in the atmosphere particularly carbon dioxide (CO_2) . The anthropogenic emission of CO_2 in the atmosphere contributes 72% of the anthropogenic greenhouse effect due to its stronger infrared heat absorption band coinciding with the strongest black-body radiation band of the Earth's surface (Ussiri and Lal 2017). Wetlands represent an excellent example of ecosystems with the highest carbon sequestration rates than any other ecosystem on this planet (Mitsch and Gosselink 2015). Undoubtedly, they are the largest emitters of another greenhouse gas, i.e., methane, but its global warming capacity fades away within a time frame of 100 years, and within that time span, most of the wetlands act as natural sinks of carbon. Wetlands, like other ecosystems, cannot run away from the deleterious impacts of climate change, affecting particularly their own functioning capacity of acting as a carbon sink (Erwin 2009). Therefore, their maintenance and conservation are urgent as the increasing temperature can result in their higher rates of decomposition. Hence, these sinks may turn into sources of carbon dioxide and thus aggravate the problem. It is pertinent to mention here that conservation of the already existing wetlands is more fruitful rather than the restoration of the degraded wetlands as the later will require a longer time period for regaining their carbon sink capacity.

2 Increasing Carbon Dioxide Concentrations, Its Impacts, and Mitigation Techniques

Carbon dioxide emissions resulting from energy generation are the main drivers of past and future CO₂ increase in the atmosphere. It is released from anthropogenic sources such as cement production, fossil fuel combustion, and changes in land use patterns mainly deforestation. The Intergovernmental Panel on Climate Change (2013) estimates that cement production and fossil fuel combustion together have emitted 375 Pg of CO₂ in the atmosphere, whereas the change in land use pattern and deforestation released 180 Pg to the atmosphere. From 2006 to 2015, the average annual CO₂ emissions are estimated to be 10.3 ± 0.5 PgCyear⁻¹ from various anthropogenic sources (Le Quéré et al. 2016). The atmospheric concentration of CO₂ was 390.5 ppm in 2011, and by 2015, it has increased to 400 ppm (CDIAC 2015; WMO 2016). The longest record of continuous monitoring of CO₂ in the atmosphere at Mauna Loa, Hawaii, started in 1958 by C.D. Keeling and reported that the level has reached to 407 ppm by May 2018 (NOAA 2018). This rapid increase of CO₂ in the atmosphere and changes in climate have created a concern

about the potential damaging consequences and regulation of that rate of CO_2 emission.

2.1 Mitigation Techniques

According to IPCC WGII AR5 (2014), the risks related to climate change can be reduced and managed only through appropriate adaptation and mitigation techniques. Therefore, compatible strategies are required to neutralize the excess of CO₂. Furthermore, in order to meet the goal of Paris Agreement (2015) of keeping average global temperature increase below 2 °C, it is essential to have negative emissions of GHGs. Broadly speaking, there are three options of reducing the atmospheric greenhouse gas emissions which include reducing the global energy use, developing low or no-carbon fuel, and sequestering carbon emissions through natural and engineering techniques from their point sources (Lal 2008). Of these three options, sequestration of CO₂ emissions by various aquatic and terrestrial sinks is more cost-effective and eco-friendly option to neutralize the excess of CO₂. Since the effects of climate change are becoming evident, there has been an increasing emphasis on comprehending and assessing carbon sequestration that comes partially from the need to find ways to enhance carbon pools in soil and biomass to attenuate the effects of greenhouse gases (GHGs) in the atmosphere.

Carbon sequestration is one of the prime regulatory ecosystem services provided by wetlands, and it occurs in wetlands at a substantial rate than in any other ecosystem on the planet (Mitsch et al. 2012; Mitsch and Gosselink 2015). Table 4.1 shows the carbon sequestration rates (CSR) of different wetland ecosystems in various continents except Antarctica which is devoid of wetlands. A great variation in the CSR among the different wetland types can be seen with the highest values recorded in freshwater marshes (15-2200 g-C m⁻² year⁻¹). Carbon sequestration occurs through two main processes in fresh water wetlands, viz., sediment deposition from uplands and on-site organic matter production, compared to the peatlands wherein carbon is sequestered only through on-site plant production (Bridgham et al. 2006). Wetlands, no doubt, cover only 6-8% of the freshwater surface; they are estimated to account for one-third of the world's organic carbon pool (Mitsch and Gosselink 2007). In India, wetlands cover about 4.7% of the total geographical area. These include about 18,154 natural and 9249 man-made wetlands representing about 5.31 m ha and 2.27 m ha of the total area, respectively (SAC 1998). Of this huge figure, only 26 wetlands have been designated as Ramsar sites with the world's total figure of about 2266 Ramsar sites (Finlayson et al. 2018). Wetland carbon represents an essential component of the global carbon cycle and plays a vital role in atmospheric and terrestrial ecosystem interactions. Currently, carbon stored in wetlands is close to that stored in the atmosphere (Lenhart 2009). Wetland ecosystems are characterized by the presence of stagnant water during least part of the year. This allows the development of specialized hydric roots and hydrophytic vegetation adapted to the presence of water and to the saturation of the soil (Reddy and De

Continents	Country	Sites	$ \begin{array}{c} R_{carbon} \\ (gCm^{-2}year^{-1}) \end{array} $	Source
North America	Canada	Prairie wetland	270	Badiou et al. (2011)
	USA	Freshwater peatlands	107.5	Craft et al. (2008)
	Ohio	Cattail marsh	210	Bernal and Mitsch (2012)
	Costa Rica	Tropical flow-through wetland	306	Mitsch et al. (2012)
	Virginia	Dismal swamp	105	Craft et al. (2008)
	Florida	Upper St. Johns floodplain	117–244	Brenner et al. (2001)
	Oregon	Reed-bulrush marsh	116	Graham et al. (2005)
	California	Anderson tule marsh	106–155	Kim (2003)
Europe	Estonia	Freshwater marsh	15-2200	Mander et al. (2008)
	Finland	Temperate peatlands	10-46	Turunen et al. (2002)
	Netherlands	Peat meadow	280	Hendriks et al. (2007)
	Austria	Danube floodplain	180	Zehetner et al. (2009)
	Denmark	Reed marsh	504	Brix et al. (2001)
Asia	China	Dexingan Mountain	203	Bao et al. (2010)
	China	Changbai Mountain	200	Bao et al. (2010)
	S.E. Asia	Mangrove swamps	90–230	Suratman (2008)
	Georgia	Grass-sedge marsh	56	Craft and Casey (2000)
South America	Brazil	Brasileira	260	Bonotto and Vergotti (2015)
	Brazil	Cristalino	28	Devol et al. (1988)
	Brazil	Demarcacao	365	Bonotto and Vergotti (2015)
	Brazil	Calado	70	Smith et al. 2002
Australia	S.E. Australia	Undisturbed sites	105–137	Howe et al. (2009)
	S.E. Australia	Disturbed sites	64–89	Howe et al. (2009)
Africa	Botswana	Tropical seasonally flooded wetland	42	Mitsch et al. (2012)
	Uganda	Cyperus wetland in Uganda	480	Saunders et al. (2007)

Table 4.1 Carbon sequestration rates (CSR) of various wetland ecosystems across the globe

Laune 2008). They are known to provide an optimal natural environment for the sequestration and long-term storage of carbon dioxide from the atmosphere. Their high sequestration efficiency is because of the high water table, high productivity, and low decomposition rate, leading to the carbon storage in their detritus, sediment,

and soil (Whitting and Chanton 2001). Thus, wetlands act as a great carbon sink of various interlinked carbon pools.

3 Carbon Sequestration in Wetlands

Carbon sequestration refers to the removal of CO_2 from the atmosphere and its transfer and accumulation into the soil pool of wetlands as soil organic matter (SOM). In other words, sequestration in wetlands involve photosynthetic removal of CO_2 by wetland producers and its conversion into cellulose and other carbon compounds and later on its transformation from detritus into soil organic matter. The three main processes responsible for carbon sequestration in wetlands include photosynthesis or primary productivity, sedimentation, and nutrient enrichment through external factors (Miria and Khan 2014) (Fig. 4.1). Photosynthesis by producers is the main process which is responsible for the addition of all the organic matter to the wetland floor. Since, wetlands are highly productive ecosystems; their plants sequester carbon readily from the atmosphere and store it in their standing biomass. All of the organic carbons which find its way to the wetlands, either exogenously or endogenously, are manufactured by the plants (Kayranli et al. 2010). Exogenous sources include eroded soil material and terrestrial plant debris, whereas endogenous sources comprise of plankton and aquatic macrophytes. Thus, they get the



Fig. 4.1 Carbon input, retention, and output in wetlands. (Modified and adopted from Kayranli et al. 2010)

additional nutrient enrichment from uplands in the form of eroded material which remains suspended in the water inflowing into the wetlands (Bridgham et al. 2006). In addition, sedimentation process involved in the wetland also enhances the carbon storage in wetlands. Sedimentation is the process of settling down of the suspended particle present in the water. This process in the wetland is performed by the plants through slowing down the water velocity, providing a substrate for adhesion of particles, and preventing resuspension (Miria and Khan 2014). The process of carbon sequestration in the wetlands is dependent on the balance between carbon inputs and outputs. Carbon inputs mainly constitute carbon dissolved and suspended in inflowing waters and runoff (allochthonous) (Roner et al. 2016), as well as carbon contained in organic matter from senesced vegetation in and around the wetland (autochthonous) (Alongi 2014). Carbon outputs include suspended and dissolved organic carbon in outflowing waters, as well as the inorganic forms of carbon released as CO₂ and CH₄ in the process of mineralization during organic matter decomposition. However, scientists working on wetlands have revealed that higher C inputs leading to higher C accumulation result in the yield of higher gas emissions. The reason being the more C inputs to the soils, the more C to be potentially sequestered as SOM, which means more abundant substrate is available for decomposition and hence exported to downstream waters and to the atmosphere.

3.1 Forms of Carbon in Wetlands

Wetland carbon occurs in five main forms: particulate organic carbon, dissolved organic carbon, plant biomass carbon, microbial biomass carbon, and gaseous end products such as methane and carbon dioxide. Except plant biomass carbon, all others are present in detritus, water, and soil (Kadlec and Knight 1996). However, plant biomass carbon represents the active standing biomass, and it occurs in various life forms including emergent, submerged, or floating types. Carbon cycle is comprised of many forms of soil carbon in case of wetlands such as plant biomass, standing dead plants, dissolved organic carbon, particulate organic carbon, and refractory carbon (i.e., resistant carbon, which retains its strength even at high temperatures) (Wynn and Liehr (2001). Plant biomass is the active biomass, and it also includes periphyton (detritus and microorganisms attached to submerged surfaces). The particulate organic carbon comprises of particulate influent and organic substances, decaying plant material, and microbial cells (Mostofa et al. 2009). The dissolved organic carbon comprises of dissolved biochemical oxygen demand and other carbon components in solution. Microbial biomass carbon occurs in heterotrophic microfloral catabolic activities, converting organic carbon back to its inorganic form and mineralizing dissolved organic carbon and particulate organic carbon. Gaseous forms of carbon are the result of either aerobic or anaerobic decomposition processes in the wetland soils.

3.2 Factors Affecting Carbon Sequestration in Wetland

Carbon sequestration in wetlands is dependent on a number of factors which are described as under:

3.2.1 Substrate Availability

The mechanisms that drive organic matter (OM) decomposition include a variety of physical, chemical, and biological processes. These interact with each other favoring the decomposition of easily degrading organic materials by soil microbes leading to the accumulation of recalcitrant components in the soil, which microbes cannot degrade efficiently. Depending on the type and source of soil organic matter, the organic carbon undergoes complex cycling, part of which can be chemically oxidized to either CO₂ or CH₄ during decomposition, and part can be buried, either in situ or exported and buried elsewhere, or lost as dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) in drainage water. The factors which are known to slow down OM decomposition and serve its accumulation in the soil include nutrient scarcity that limits the growth of microbes, high content of organic compounds with low degradability, and physical protection of organic particles through the formation of aggregates (Hernes et al. 2007; Kuzyakov 2010; Six et al. 2002). Thus, substrate availability will largely depend on the type and composition of the vegetation as they are the main source of the detritus being added to the wetland floor.

3.2.2 Temperature and Oxygen

Temperature controls the metabolic activities of microbes and can directly shift the microbial populations, affecting the SOM degradation process and the production of SOM-degrading enzymes in the wetland soils. Warming is predicted to globally increase plant biomass but at the same time also decreases the global soil C pools. Temperature does not drive the decomposition of SOM as much as substrate availability does, as biological reactions are expected to double with every 10 °C rise in temperature (Hartel 2005). Northern wetlands are known to store over 50% of the global organic carbon due to slower rates of organic carbon decomposition because of cold temperatures and wet surface conditions (Hugelius et al. 2013). Temperate freshwater wetlands have shown highest rates of carbon sequestration among the selected wetlands investigated by Mitsch et al. (2012) in their study on different wetland types.

Wetlands are characterized by anaerobic conditions due to the waterlogged conditions prevailing in them. In anaerobic conditions, the microbial metabolic pathways are less efficient than in aerobic conditions. Anaerobic conditions limit the enzymatic activity involved in SOM degradation, for two important reasons; firstly, they need O_2 availability particularly in the case of phenol oxidases (enzymes capable of degrading recalcitrant materials such as humin and lignin). Secondly, the activity of SOM-degrading enzyme activity is inhibited by the compounds that get accumulated under anaerobic conditions. For example, the activity of hydrolases is confined by the presence of phenolic compounds that tend to accumulate in the absence of phenol oxidase in the wetlands.

3.2.3 Global Change Scenarios

A slight change in the wetland equilibrium could result in the overall change in their functioning. If hydrological regimes of wetlands are altered, it would increase soil aeration, thereby increasing the enzymatic activity resulting in the decomposition of recalcitrant SOM. Similarly, SOM mineralization may also increase through highly loaded dissolved organic matter in flowing waters or through increased belowground biomass in the soil. This increase in SOM mineralization into the wetland is known as "priming effect." This effect is common in the rhizosphere, as plants through their root exudates provide electron donors to the soil microbial communities thereby increasing the microbial activity and ultimately the SOM decomposition. If such ecosystem change occurs, it would lead to a rapid increase in belowground organic inputs to the soil or to the deepening of root profile. Similarly, nutrient-rich water inputs in the wetland may stimulate the wetland plant growth, but studies have revealed a decrease in the root production of most wetland grasses and sedges as a result of nitrogen fertilization and thus can decrease the belowground C inputs to SOM. Therefore, in both the cases, if there is decreased root production or increased SOM mineralization because of high nutrient inputs into the wetland, it can result in collapsing of wetlands (Deegan et al. 2012).

3.2.4 Carbon Export

DOM is mostly ignored while estimating C sequestration since it is transient and mobile compared to the SOM sequestered C which represents the long-term C pool. However, it can be a significant pool as large quantities of DOM can enter deep soil layers, getting retained in the wetland mineral soil and is, thus, sequestered efficiently. It mostly comes from root exudates or from the surface standing water and gets released into the soil pore water. The contribution of DOC depends upon its nature whether recalcitrant or degradable, and it is considered as the source of C for deep pools where plant roots mostly remain unreachable.

4 Methane Emissions from Wetlands

Undoubtedly, wetlands are huge emitters of methane gas. They are estimated to emit about 20–25% of global methane emissions which is about 115–170 Tg of methane per year. Methanogenesis in wetlands is controlled by various factors. Among the various factors controlling methanogenesis, detritus quality plays a significant role (Fonseca et al. 2015). Interspecific variations in macrophytes result in the variance in detritus quality. The detritus known to have low C content or low C:N, C:P, and N:P ratios are considered to have high detritus quality as it results in lower accumulation in sediment. In addition to detritus quality, root exudates (organic compounds) released from living plants favor methanogenesis in wetlands. Similarly, the oxygen released through the roots into the sediment is responsible for methane oxidation in the rhizosphere (King 1994). Other controlling factors involved in methane emissions from wetlands include soil temperature, water table position, trophic status, salinity, pH, and availability of electron acceptors (Bianchini and Cunha-Santino 2016; Moore and Roulet 1995). The consumption of atmospheric methane is, thus, the result of two distinct groups of microbes: (a) the methanotrophs and (b) an autotrophic nitrifier community. Methanotrophs are known to consume about 30 Tg-CH₄ year⁻¹.

Different wetland ecosystems vary in their annual rate of methane emissions. Tropical wetlands are more important as 50% (132Tg-CH₄ year⁻¹) of the total methane emissions from wetlands and rice paddies comes from tropics (Bloom et al. 2010). It is believed that methane emissions in the tropics are greater from mineral soils than wetlands with organic soil. Methane production is much higher in the freshwater wetlands than in salt water wetlands. This is because of the higher concentration of sulfates in the saltwater relative to freshwater that competes with carbon for oxidizable substrate. Global contributions of northern peatlands to the methane emissions are 28 g-C m⁻² year⁻¹, while the range is 15–20 g-C m⁻² year⁻¹ in case of the boreal wetlands. In temperate wetlands, methane emissions range from 40 to 75 g-C m⁻² year⁻¹ although numbers are often variable. The trend of methane emissions from different wetlands lies in the decreasing order of emissions as bogs [<] fens [<] swamps [<] marshes [<] rice paddies (Aselmann and Crutzen 1989).

In order to minimize the methane emissions from freshwater wetlands, there are various management approaches. One of the approaches is to allow the wetlands to have their natural fluctuating hydroperiods and, in some cases, a pulsing hydrology. Another approach is to maintain the C:N ratio of wetlands at lower levels by enriching them with nitrogen, as lower CH_4 emissions were observed in rice fields which were un-composted than the composted ones. Enhanced sulfate reduction is often suggested as a management alternative to reduce CH_4 emissions.

5 Climate Change Feedbacks

Climate change scenario anticipates an additional stress on wetlands in addition to other anthropogenic pressures, mainly because of changes in temperature, hydrology, and a rise in sea level. Wetlands although act as buffers in hydrological cycle and as sinks for organic carbon, counteracting the effect of the increased CO₂ concentrations in the atmosphere. One of the interesting things about wetlands is their positive feedback related to climate change that could occur in near future if they are not managed properly. Climate change will affect wetlands in two fundamental ways: it will affect their functional capacity and will shift the geographical location of wetlands (Erwin 2009). There is more carbon stored in the world's soils than in the atmosphere. If the climate is to warm and the decomposition will accelerate, then wetlands, particularly peat lands, would become an additional major source of carbon, through aerobic respiration and possibly fires to the atmosphere. The Intergovernmental Panel on Climate Change (IPCC, AR5 2014) predicts that increasing temperature will have a greater effect on high latitudes than on tropical and subtropical regions indicating the higher vulnerability of northern wetlands to the changes in temperature. Wetland ecosystems are susceptible to changes in quantity and quality of their water supply, and climate change will have a noticeable effect on wetlands through alterations in their hydrological schemes. These include changes in precipitation and temperature regimes with great global variability. IPCC predicts that there will be an increase in global temperature from 1 to 5 °C during the twenty-first century. In general, it is predicted that the higher latitudes will experience an increase in rainfall whereas the lower latitudes will experience a decrease in precipitation (Day et al. 2005; Dore 2005). Wetland habitat responses to climate change will be different on the basis of regional and mega-watershed level. Wetland in the tundra region may be lost if any melting of the permafrost will take place. There will be a northward shift in the belt of permafrost soils, hence releasing large quantities of CH₄ and CO₂ to the atmosphere. In case of the most of tropical and subtropical wetlands, the occurrence of an explicit dry and wet cycle will hinder the accumulation of organic carbon in them. Moreover, coastal wetlands will be squeezed between advancing sea and civil constructions as a result of rising sea levels. This reveals a multitude of impacts on different wetland ecosystems as a result of climate change because of their regional variability which ultimately can turn them into grave sources of C (Junk et al. 2013). In short, maintaining hydrology, controlling exotic vegetation, reducing pollution, and protecting biological diversity are important in order to maintain and boost the resiliency of wetland ecosystems so that they may continue to provide important ecosystem services under changed climatic conditions (Ferrati et al. 2005).

6 Comparing Net Balance of Carbon Sequestration and Methane Production in Wetlands

There is a great confusion on the part of wetland conservationists and climatologists as to where wetlands fit into climate change. This is because they act as a doubleedged sword where on one hand they store huge amounts of carbon and on the other hand they are emitters of other important greenhouse gas methane (CH₄). Mitsch et al. (2012) developed a dynamic model to investigate whether they act as sinks or sources of carbon by comparing their CO₂ and CH₄ emissions. Model parameters included half-life of 7 years and global warming potential (GWP) for CH₄, and the results revealed that most of the wetlands become net sinks of radiative forcing within 100 years of time period. This is because the impact of CH₄ emissions in the atmosphere is temporary as it ultimately decays to CO₂ which is then followed by its permanent burial in the wetland soil. The model suggested that if the wetland is sequestering some CO_2 from the atmosphere and its natural hydrology is intact, it will, with a little question, be a net sink of radiative forcing and thus good for the climate. Furthermore, 20-30% or more of soil organic carbon is stored in wetlands, and it may be liberated if climate becomes dryer and warmer or if they are lost because of their inadequate management.

7 Knowledge Gaps and Future Directions

India is gifted with an enormous number of wetlands having tremendous carbon sequestration potential. This figure comprises more of natural than man-made wetlands, and the former usually act as carbon sinks, whereas the later become carbon sinks only when the switchover point is reached (Moomaw et al. 2018). Specifically, Kashmir Himalayan wetlands need to be highlighted because of the prevalent moderate weather conditions responsible for lower decomposition rates and hence higher carbon accumulation rates. Macrophytes are the main sources of adding organic carbon to the wetland floor, and hence the substrate quality entirely depends on their composition. However, only little work has been done on the carbon sequestration potential of wetland macrophytes except a few attempts in recent past by Maqbool and Khan (2013) and Pal et al. (2017). Realizing the potential of wetlands and its different carbon pools, their ecology is to be maintained and conserved. The concept of constructed wetlands also needs to be implemented; it can help in increasing the number of carbon pools in soils and biomass to mitigate the effect of GHGs in the atmosphere. The number of Indian wetlands designated as Ramsar sites is limited as the policy-makers are unaware of the important C storage and various other roles of wetlands, and hence their net contribution in greenhouse gas regulation should be highlighted so that the number of sites designated as Ramsar is increased. Recently, many studies have focused on the huge carbon sink capacity and emphasized on their maintenance and conservation, but it has to come into

action from lower (local, sub-national) up to the higher (national, international) levels by incorporating climate resiliency and GHG management strategies into specific projects as well as providing education on ecological resiliency, carbon management, and even their vulnerability to the climate change to a larger audience.

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Chapter 5 Wetlands: A Major Natural Source Responsible for Methane Emission



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Abstract Methane (CH₄), an important greenhouse gas (GHG), contributes $\sim 33.0\%$ to the total global GHGs emissions and accounts for 15–20% to the global warming. As the second most important human-generated GHG after CO₂ CH₄ is strongly linked with various climate phenomena. Most of the wetlands from tropics to temperate have been reported to have significantly enhanced emissions of CH₄ during recent years. In wetland, microbial communities are a major determining factor in controlling the carbon cycle. The terrestrial wetlands are also among the key CH_4 emitters and play a major role to climate change. The role of wetland expansion in CH_4 emissions and its consequences on climate change and global warming might be a major concern for the future world. The methanogens and methanotrophs, two physiologically different microbial communities, seem to be crucial for future research investigations while comparing the CH₄ production and consumption in wetland ecosystems. Anthropogenic disturbances related to wetlands are likely to influence the altering of microbial community composition of methanogens and methanotrophs and consequently net CH_4 flux. The terrestrial wetlands have been reported to act as a source and sink for atmospheric CH₄. Therefore, recent concerns about CH₄ emission from terrestrial wetlands could be addressed properly because it is one of the major causes in contributing the status of CH₄ in the environment.

Keywords Methane \cdot Wetlands \cdot Climate change \cdot Land use \cdot Methanogens \cdot Methanotrophs

1 Introduction

Methane (CH₄), a potent GHG, contributes about one third to the worldwide greenhouse gas emissions (Singh and Gupta 2016). It has 25 times more warming potential than CO_2 over a 100-year time scale (Bridgham et al. 2013; Fazli et al.

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2013; Forster et al. 2007), and little changes in its concentration could have a large consequences in the environment, climate and human being. Bridgham et al. (2013) reported that human alone contributes ~18% of total CH₄ which makes it second most important greenhouse gas after CO₂ (Singh and Strong 2016). The global warming contribution of CH₄ is 15–20% (Tiwari et al. 2015). CH₄ molecules that absorb the infrared radiation emitted from the earth become energized and start to emit heat in all directions (Fazli et al. 2013; Nema et al. 2012). The present concentration of CH₄ is 2.5 times higher than observed in ice cores dated to the period of AD 1000–1750 (Amstel 2012). Agriculture and fossil fuel together account for 230 Tg CH₄/year and are dominant natural source of methane emission, i.e. wetland is 174 (~100–231) Tg/year. Wetland emissions thus react to global warming and wetting. The anthropogenic CH₄ is produced by different sources and includes energy production, landfills, waste, cattle and milk production, agriculture and biomass burning, etc. (Amstel 2012; Bridgham et al. 2013; Denman et al. 2007; Wang et al. 2004).

The CH₄ emissions from the wetlands are the largest biogenic source of CH₄ budget, contributing to one third of total growing atmospheric emissions from various sources (Bhullar et al. 2014; Bridgham et al. 2013). CH₄, being the second most anthropogenic GHG after CO₂, is strongly associated with climate feedbacks. The degree to which wetlands expansion and CH₄ emissions will evolve and consequently driven climate feedbacks is thus a question of major concern. Besides, potential feedbacks between global change perturbations and CH₄ emissions from wetlands, climate change, CO₂ level and deposition of sulphate and nitrogen are also the major apprehensions of methane emission (Bridgham et al. 2006; Zhuang et al. 2006). In an estimation, the developing nations currently contribute approx. three-quarters of direct GHG emissions and seems to represent the fast-growing GHG emission sources in the coming decades (Boateng et al. 2017).

1.1 Wetlands and Methane Emissions

Wetlands occupy 3.8% of the Earth's land surface, amounting to 20–40% of global CH₄ emissions (Aselmann and Crutzen 1989; Ciais et al. 2013; Solomon et al. 2007). Despite of being a major source, wetlands are among the most prominent sources of unexplained spatial and temporal variability in global methane emission estimates (Bousquet et al. 2006). The main CH₄ emitting sites in wetlands are the littoral zones where helophytes form a channel for methane production via sediment–root–stem–atmosphere continuum (Bergstrom et al. 2007). Bergstrom et al. (2007) reported that the dense vegetation of emergent macrophytes in natural wetlands may account 90% of the methane emission. However, it was supposed that anthropogenic sources are to be the only driver responsible for the increasing atmospheric CH₄ burden from the late seventeenth century (Taylor et al. 2011). Paddy fields are one of the important sources of CH₄ (Fazli et al. 2013; Tyagi et al. 2010) and responsible for 15–20% of total anthropogenic CH₄ emission (Li et al. 2011; Xu et al. 2007) with an estimated 25–100 Tg CH₄/year (Xu et al. 2007).

A very significant variation in CH₄ emission across different types of wetland could be due to the variations in time, space and the factors operating within the wetland ecosystem (Kirschke et al. 2009; Melton et al. 2013). The main processes controlling the seasonal and inter-annual variations in wetland CH₄ emission includes carbon availability, rate of decomposition, wetland inundation and temperature (Yvon-Durocher et al. 2014). Other controls are the presence of macrophytes (Laanbroek 2010), organic C decomposition rates (Miyajima et al. 1997), and pH (Singh et al. 2000), etc. Methane emitted from natural wetlands is a significant component of atmospheric methane budget. Biogeochemistry and atmospheric inversion models estimate the total wetland emissions to be 100–230 Tg CH_4 /year, under the present climate condition (Denman et al. 2007; Tang et al. 2010). Although wetlands occupy only 2–6% of Earth's land surface (Whiting and Chanton 2001), they significantly contribute a larger proportion of the total carbon stored in terrestrial reservoir (Schlesinger 1991). Zhang et al. (2017) reported that the climate change-induced enhancement in boreal wetland and tropical CH_4 emissions would be the dominate anthropogenic CH₄ emissions source by 38–56% at the end of the twenty-first century. The various reports suggested that climate mitigation policies must be in legislation to balance the wetland CH₄ feedbacks to maintain average global warming below 2 °C (Zhang et al. 2017). The wetland may play a crucial role in atmospheric methane concentration in coming decades because of the huge stocks of organic carbon and mineral stored under anaerobic conditions in both boreal and tropical regions. In an estimate, carbon storage in histosols (wetland soil type composed of mainly organic materials) ranges from 3% to 68% of the total soil organic carbon reservoir (Post et al. 1982). The combination of elevated water tables, high productivity and lower decomposition rate has led to significant carbon storage in histosols (Gorham 1991) and contributes global methane balance.

2 Overview of the Methane Emissions and Methane-Producing Bacteria

The bacterial clusters involved in the emission and reduction are crucial in the methane flux of soil. The study explores that solutions are required to be developed to decrease the emission rate or encourage consumption of CH_4 by methanotrophic bacteria to minimize its concentration from flooded soils, particularly to the rice fields.

The methanogens and methanotrophs are actively involved in the biogeochemical cycling of CH_4 in soil (Fazli et al. 2013). The methanogenic bacteria are accountable for releasing CH_4 . They are obligate anaerobes and active in flooded, swampy areas (Pazinato et al. 2010). However, the methanotrophs are aerobic microorganisms, ubiquitous in nature and mostly active in oxic soil. Methanogens and methanotrophs have been reported from several environmental conditions likely sludge digesters (Hwang et al. 2008), lakes (Antony et al. 2012), peatland (Godin et al. 2012), freshwater and marine sediments (Newby et al. 2004) and rice soil (Fazli et al. 2013; Wang et al. 2010).

2.1 Methanogens

The methanogens are obligate anaerobes (Garcia 1990) that belong to kingdom Eurvarchaeota of Archaea domain (Ferry 2010). Borrel et al. (2011) reported that methanogenic group consists 31 genera under the phylum Euryarchaeota based on 16S rRNA sequence analysis (Rosenzweig and Ragsdale 2011). Methanogens produce CH₄ through diverse metabolic pathways termed as methanogenesis (Singh 2009). The methanogenesis includes acetoclastic methanogenesis and hydrogenotrophic methanogenesis pathway to release CH₄, i.e. the conversion of acetate to CH_4 and CO_2 and H_2 and CO_2 to CH_4 , respectively (Conrad et al. 2006; Dubey 2005). In fact, methanogens are engaged in the biodegradation of organic compounds anaerobically in wetlands and rice fields (Rosenzweig and Ragsdale 2011). The 16S rRNA analyses showed that methanogenic archaea can be classified under three important groups, i.e. group I contains of Methanobacterium and Methanobrevibacter, group II comprises Methanococcus and group III includes Methanospirillum and Methanosarcina. They multiply in anaerobic environments, for example, swampy areas, sediments, flooded water, the digestive tract, etc. (Dubey 2005). Most of the methanogens thrive in mesophilic conditions and actively function from 20 to 400 °C temperature range (Dubey 2005). The methanogens have also been reported from extreme environmental conditions such as deep hydrothermal vents sustaining at temperatures >100 °C. Methanogenic Archaea generally takes acetate (contributing up to 80% of total CH₄ production) as carbon source. In addition, H_2/CO_2 and formats also contribute 10–30% in CH₄ release (Dubey 2005).

2.1.1 Methanogens in Paddy Soil

The paddy rhizosphere is a vital habitat for methanogens (Ma and Lu 2011) due to the decay of paddy roots and the liberation of H₂ and CO₂, which provides nutritional support to microbes (Watanabe et al. 2010). Das et al. (2011) and Datta et al. (2013) reported that higher populations of acetoclastic methanogens are found in Indian rice soil than hydrogenotrophic methanogens. The pathway of methanogenesis in rice fields has been investigated globally. But the detailed information about methanogenic population in paddy soil is limited. First of all, Rajagopal et al. (1988) isolated and characterized the methanogenic Archaea from Louisiana paddy soils and elucidated about the presence of strains similar to Methanobacterium and Methanosarcina. Joulian et al. (1997) showed the existence of methanogenic bacterial population in the paddy soils of the Philippines, France and the United States. In addition, Reichardt et al. (1997) reported that the root extracts of adult paddy plants were rich in methanogenic bacteria. Four genera Methanobacterium, Methanosarcina, Methanobrevibacter and Methanoculleus were isolated from Italian paddy fields (Fetzer et al. 1993). Asakawa et al. (1995) reported that only couple of strains (Methanobrevibacter arboriphilus and Methanosarcina mazei) have been identified in rice fields. Similarly, Adachi (1999) reported *Methanobrevibacter* and *Methanobacterium* spp. from Japanese paddy soil.

2.1.2 Methanogenesis

The CH₄ is released in the anoxic layers of rice soil by methanogenic breakdown of organic substances (Dubey 2005). The anoxic conversion of organic matter takes mainly four steps: (1) action of hydrolytic organisms on polymers, (2) action of fermentative bacteria on organic compound for acid formation, (3) action of syntrophic bacteria or homoacetogenic on fermentations metabolites for acetate formation and (4) liberation of CH₄ from H₂/CO₂, acetate, etc. Emancipation of CH₄ from the organic matter also involves various important coenzymes, some of which are solely found in methanogenic archaea. At least nine methanogen-specific enzymes are used in the mechanism of CH₄ removal from H₂ and CO₂ (Dubey 2005).

2.1.3 Factors Affecting Methane Production

Methanogens are influenced by variety of natural as well as anthropogenic factors. It has been reported that acetoclastic methanogenesis is accountable above two third of the CH₄ liberation and remaining portion of CH₄ is emitted by hydrogenotrophic methanogens (Das and Adhya 2012). Moreover, at elevated temperatures (40–50 °C), the phenomenon methanogenesis is shown by hydrogenotrophic methanogenic archaea. In addition, the expanding CO₂ level favours hydrogenotrophic methanogenesis in the environment (Das and Adhya 2012). For instance, Wang et al. (2010) reported the following methanogenic archaea in a Chinese rice field: Methanomicrobiales, Methanosaetaceae, Zoige cluster I (*ZC-I*), Methanosarcinaceae and Methanocellales.

Wang et al. (2010) also stated that the types of methanogenic structure found in rice field are different due to soil type, sampling location, moisture content and temperature (Das and Adhya 2012). Sugano et al. (2005) demonstrated that before the mid-season drainage, the methanogenic communities included rice cluster I, Methanomicrobiales and Methanosarcinales, but after this period. the Methanomicrobiales were perceived. Methanomicrobiales and rice cluster I are the archaea accountable for breakdown of paddy straw under flooded environment. The water management can also influence the methanogens community composition by changing the moisture content of soil; subsequently it is an important aspect for CH₄ emissions (Yao et al. 2006; Zhao et al. 2011). The alternate wetting and drying of the soil could modify the population, community structure and transcriptional functions of methanogens (Watanabe et al. 2010). Since, methanogens are more active under flooding environments as compared to dry soil (Watanabe et al. 2009). Thus, draining the soil reduces CH₄ production from rice field (Khosa et al. 2011; Zhang et al. 2011). In addition, drainage might also augment the nitrous oxide (N_2O) liberation (Johnson-Beebout et al. 2009; Zhao et al. 2011) due to denitrification of nitrate in anoxic and flooded situation (Fangueiro et al. 2010; Malla et al. 2005). Therefore, the issue needs more specific research to reduce the production of CH_4 along with of N_2O release. Ghosh et al. (2003) suggested that the use of nitrification inhibitors likely dicyandiamide might have a reducing impact on CH₄ and N₂O emission. Malla et al. (2005) also reported that dicyandiamide plays a significant role as a sink for CH₄. Similarly, Smith et al. (1997) showed that addition of dicyandiamide after urea application could decrease N_2O production up to 82%. The polymer-coated fertilizers are also potent to reduce N₂O release (Akiyama et al. 2010). It has been showed that at low C:N ratio in soil improves N₂O emission. As a result, C:N balance could shrink the emission, though the threshold ratio needs to be explored. The addition of fertilizers can modify the methanogens found in soil. The N fertilizer stimulates the denitrifying bacteria, which are more competent than methanogenic archaea for growth nutrients. Consequently, N fertilizers suppress CH_4 production, for example, $(NH_4)_2SO_4$ reduces CH_4 emission than urea application (Ghosh et al. 2003).

Elevation in GHGs, especially CO₂, is a serious concern. The increased concentration of CO₂ in atmosphere can simultaneously decrease the methanogenic activity, reducing the CH₄ oxidation in paddy fields (Das and Adhya 2012). To overcome the situation, water management could be a suppressing tool for CH₄ production (Epule et al. 2011; Tyagi et al. 2010; Zhao et al. 2011). Temperature of the soil also plays an important role in CH₄ production (Khalil et al. 1998; Yang and Chang 1998). Yang and Chang (1998) reported the enhanced emission of CH₄ emission at temperature 4 to -37 °C. Nozhevnikova et al. (2007) also reported CH₄ formation at temperature 15–20 °C in anaerobic soil.

2.2 Methanotrophs

Methanotrophs include aerobic and anaerobic CH_4 -oxidizing important bacterial groups. The methanotrophs have been categorized into couple of groups: type I (*Gammaproteobacteria* which takes CH_4 adapting the RuMP pathway) and type II (*Alphaproteobacteria* which oxidize CH_4 via the serine pathway) (Rosenzweig and Ragsdale 2011). However, Hanson and Hanson (1996) added 'type X' group of methanotrophic cluster, likely *Methylococcus* and *Methylocaldum* (Bowman 2006). Moreover, the type X can be considered as a subdivision of type I. Irrespective of few resemblances, the type X (having low levels of enzymes of the serine pathway) showed differences with other members of type I methanotrophs. But, information regarding the group is still lacking (Semrau et al. 2010). Methanotrophs oxidize the CH₄ produced by methanogens in soil and the rhizospheric region of plants (e.g. rice) (Bodelier et al. 2005; Conrad et al. 2006) and use CH_4 as sole carbon and energy source. Moreover, the CH_4 consumers have a major role in regulation of CH_4

production from submerged soils, such as rice fields and natural wetlands (Hoffmann et al. 2002).

2.2.1 Methanotrophy in Paddy Soil

Type I and II of methanotrophs are natural inhabitants of paddy fields and thrive in different niches based on oxygen and CH_4 availability (Mayumi et al. 2010). Type I CH₄ oxidizers grow in environments with high oxygen and low CH₄ intensity as compared to type II methanotrophs which sustain well in poorer oxic soils (Mayumi et al. 2010). In flooded condition, the interchange of oxygen from outer environment to the root might develop an oxygen-rich environment in the root and rhizosphere which support the high growth and activity of methanotrophs are prevalent in place of type II (Mayumi et al. 2010). Additionally, a positive correlation has been shown between methanotrophs and the age of paddy plants due to elevation in plant biomass, decrease in soil moisture content and NH_4^+ -N concentration in tropical rice fields (Yue et al. 2007).

2.2.2 Factors Affecting Methanotrophs Activity

Methanotrophic activity is affected by various factors such as type of plants species, variety of the plants, pattern of crop rotation and other environmental constrains (Min et al. 2002; Xuan et al. 2011). The specific cultivar of rice has influenced the CH_4 consuming activity and methanotrophs level in paddy roots and rhizosphere as reported by Win et al. (2011). However, another study reported that paddies have no significant impact on methanotrophs population (Wu et al. 2009). The community composition of soil methanotrophs can be affected by type and crop rotation pattern including Verrucomicrobia (Xuan et al. 2011) which might be due to the production of different root exudates affecting the soil microbial community (Doornbos et al. 2012). Wu et al. (2009) reported that type I methanotrophs are sensitive to environmental factors. However, type II methanotrophs showed more stability (Vishwakarma and Dubey 2010). The pH of the medium significantly alters the community of methanotrophs and CH₄ production in soil. The optimum condition of CH₄ oxidation may be between pH level 6 and 8 in paddy soil (Min et al. 2002), which ultimately assists in the alleviation of methane. Paddy soil having pH <6 needs to be adjusted for better crop productivity. Results suggested that addition of crop residues, lime, pyrite and other organic amendments may improve the population of methanotrophs in rice fields and crop productivity (Li et al. 2011; Singh et al. 2010). Amendment of N fertilizer (urea) may inhibit the methanotroph population; however, the addition of N and K together (e.g. potassium chloride) or the combination of N, P, K and crop residues stimulates the growth of methanotroph abundance (Zheng et al. 2008).

3 Mechanistic Pathways of Methane Emission

For a better understanding of the processes which involved in the process of CH_4 emission from paddies, a brief introduction of plant and soil chemistry is essential. Carbon is the basic prerequisite for methanogenic growth generated from three basic sources: the death of crop root tissue, decay of both fresh organic matter and humus and carbohydrate exudates (Wassmann et al. 2000). The methanogens can produce CH_4 either from the H_2 or CO_2 (Wassmann et al. 2000) as follows:

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

Or

$$CH_3COO^- + H^+ = CO_2 + CH_4$$

Summary line

 $2(CH_2O) = CO_2 + CH_4$

Schütz et al. (1989) explained CH_4 emission from paddies via three pathways including diffusion (<1%), ebullition (10%) and plant-mediated transport (90%) from rice plant itself. The rice plants have an efficient gas exchange system between the anaerobic soil and the troposphere which can change the exchange pathway according to soil condition and CH₄ concentration (Holzapfel-Pschorn et al. 1986; Wassmann et al. 2000). In rice growing in the temperate region, the main route of CH_4 (>90%) emission is plant transport (Dubey 2005), while in the tropics, CH_4 evolution takes place by the process of ebullition (transportation of gas in the form of bubbles) particularly in the early months of the season and high organic input (Dubey 2005). The process of ebullition of CH₄ flux is also commonly observed in natural wetlands (Dubey 2005) and found to be significant in the case of high fertilization (Sass et al. 2000). Dubey (2005) also reported that in the case of unvegetated plant and plant with undeveloped aerenchyma, ebullition plays a key role in CH₄ emission (Dubey 2005). However, CH₄ emission restricted to the surface layer and the rate of emission is regulated by the concentration of CH₄, porosity of the soil, temperature of the soil and plant aerenchyma (Li 2000). Methane diffusion through the soil is a very slow process as the rate of diffusion of CH₄ is extremely low in liquid phase (~104 times slower than diffusion through the gas phase) and thus hardly contributes to the total CH₄ flux (Aulakh et al. 2000). The CH₄ diffusion phenomenon across the flooded soil and overlying water of the paddy field to the atmosphere is a function of wind speed, surface water concentration of CH₄ and CH₄ supply to the surface water (Dubey 2005).

4 Adaptive Measures Controlling CH₄ Emission

From the centuries, European wetlands have been continuously drained for agricultural and other industrial needs. In estimation, more than 50% of all the peatlands in Europe were lost due to anthropogenic interference (Nivet and Frazier 2004; Jerman et al. 2009). However, with the increasing importance of the wetland functions, utilization and approaches towards wetland conservation have now been changed from Europe to all over the world. The major restoration strategies along these include cessation of agricultural practices, protection, conservation and re-establishment of wetland and its hydrology (Rosenthal 2003). The malpractices of wetland exploitation in agriculture in Europe have reversed to land subsidence and sequestered atmospheric CO_2 as peat accretes (He et al. 2015).

Wetlands are the biggest non-anthropogenic resource of atmospheric CH_4 and key global carbon reservoir. Therefore, characterizing the belowground wetland microbial communities which participate in carbon dynamics might be a broad area of research to understand the microbial importance and their responses to changing land and climate. Wetlands cover 5–8% of the total land area of the Earth (Jerman et al. 2009) and support various ecosystem services, viz. wildlife habitat, flood control, water purification, etc. Wetland, as a major terrestrial carbon reservoir, covers 20–30% of the global soil carbon pool (Jerman et al. 2009) and plays an important role in global carbon cycling. However, wetlands are continuously shrinking due to agricultural, urbanization, population growth and industrial insurgency (Jerman et al. 2009), releasing stored carbon into the atmosphere and enhancing global climate change. In addition to reversing land subsidence, the high primary production and low rate of decomposition in restored wetlands may result in a net atmospheric CO_2 sequestration, allowing them to act as 'carbon farms'.

Climate and land use changes directly affect ecosystem processes by influencing the plant community composition (Sutton-Grier and Megonigal 2011), nutrient availability, organic carbon concentration and nutrient cycling in wetlands (Mitsch et al. 2013; Petruzzella et al. 2013; Singh et al. 2018). In addition, transport of oxygen in the root tissue may alter the accessibility of oxygen in the sediment, resulting into methanogenesis suppression or CH_4 oxidation (Sutton-Grier and Megonigal 2011).

Recent concern of global warming has developed interest in the role of terrestrial ecosystems in minimizing CH_4 levels (Chan and Parkin 2000). Terrestrial systems function as net sources or sinks for atmospheric CH_4 . Methane flux measured at the soil/atmosphere interface is the result of CH_4 oxidation and methanogenesis (Knowles 1993). A negative CH_4 flux (consumption of CH_4 by soil) occurs when the magnitude of the CH_4 uptake is larger than the process of methanogenesis and generally found in arable land, when conditions are predominately aerobic (Hansen et al. 1993). A positive CH_4 flux indicates net CH_4 production and occurs when the magnitude of the methanogenic process is larger than CH_4 uptake and predominates in anaerobic condition such as paddies and wetlands (flooded or water saturated)



Fig. 5.1 Natural and anthropogenic sources of CH₄. (Modified from Amstel 2012)

(Lauren and Duxbury 1993). The process of CH_4 flux is supported by soil, wetland systems and mixture of anaerobic and aerobic sites. The natural sources of CH_4 include wetlands, oceans, hydrates, geological sources, termites, animals, wildfires, etc. (Fig. 5.1).

5 Conclusions and Future Prospects

This manuscript emphasizes the aspects of methanogenesis and CH_4 oxidation in different wetlands and the environment. The CH₄ has been recognized as one of the most important GHG in the atmosphere. Because of the strict anaerobic environment for CH₄ generation, natural wetlands are considered as the main sources of biogenic CH₄. Off all the wetland, tropical wetlands are the largest natural contributor of global CH_4 budget. Continuous increase in atmospheric CH_4 and other GHG level are predicted to raise global temperature with several implications. The assessment of climatic changes by CH₄ and other GHG can be assessed only by measuring the quantity of the production, oxidation and emission of CH4 from all the natural and anthropogenic sources and characterizing their responses on the plants and animals. The available database on CH_4 flux to the atmosphere is insufficient in relation to the large variety of climatological and edaphological factors that would allow to extrapolate data at a global scale and to design more precise models on the impact of the global climatic change leading to a better forecast of future state of affairs. The increasing demands of rice due to population load could lead to further expansion of the areas used for rice cultivation and, therefore, would add to higher CH_4 level. As a result, rice cultivation would put a massive load on future global warming. Therefore, the research should not be focused only on rice cultivation but also

in the development of technologies for better analysis of CH_4 production and its oxidation. Besides, it is imperative to develop possible mitigation approaches to diminish and/or suppress emissions of this hydrocarbon in a sustainable manner.

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Chapter 6 Wetlands Conservation and Restoration for Ecosystem Services and Halt Biodiversity Loss: An Indian Perspective



Rima Kumari, S. K. Shukla, K. Parmar, Nirmali Bordoloi, Amit Kumar, and P. Saikia

Abstract Wetlands are one of the most productive ecosystems that support diverse habitats and biodiversity and are known for its various ecosystem goods and services. About half of global wetlands have found to be lost, and the conditions of remaining wetlands are deteriorating due to natural as well as anthropogenic cause. The negative economic, social, and environmental significances of diminishing water quality in wetlands are one of the major issues of concern for degraded wetlands in India. Thus, it is imperative to emphasize on the restoration of the degraded wetlands along with the conservation and management of the existing wetlands since they are one of the most valuable and fragile components of the watershed. The present research strongly suggests the management practices for wetland conservation should be based on the traditional knowledge and resource uses that will eventually aid in fostering biodiversity and preserving key ecosystem services in cost-effective and sustainable way.

Keywords Wetland · Biodiversity · Ecosystem services · Restoration

1 Introduction

Wetlands are one of the maximum productive ecosystems that support diverse and unique habitats and biodiversity and known for its diverse ecosystem goods and services. They do not only ameliorate environmental impacts of agriculture and other ecological disturbances in watersheds but also offer various ecosystem services to human society (Zedler 2003). The sustainable use of wetlands is critical to improve

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social cohesion and economic stability and also to adapt to changing climatic conditions. According to Cowardin et al. (1979), wetlands are "transitional lands between terrestrial and aquatic systems where the water table is usually at or near the surface or the land is sheltered by shallow water" and "must have categorized into the following three attributes: (1) The land supports predominantly hydrophytes (2) Predominantly un-drained hydric soil (3) The substrate is non-soil and is saturated with water by shallow water at the growing season of each year." Based on the ecological, hydrological, and geological characteristics, wetlands are categorized into marine (coastal wetlands), estuarine (including deltas, tidal marshes, and mangrove swamps), lacustrine (lakes), riverine (along rivers and streams), and palustrine ("marshy" marshes, bogs, and swamps) (Cowardin et al. 1979). The diversity and abundance of macrophytes richness in a wetland are governed by its water regime.

The depth, frequency, duration, amplitude of change, and the time of the year are the five important components of water regime which regulate several life processes throughout the life cycle of various macrophytes as well as aquatic fauna (Gopal 2014). Most of the freshwater wetlands are threatened, and few are already degraded and vanished due to urbanization, increased in population, and economic activities (Central Pollution Control Board 2008). The undesirable economic, environmental, and social consequences decline the water quality in wetlands, and these are one of the major issues for degraded wetlands in India (Bassi et al. 2014). Thus, it is authoritative to emphasize the restoration of the degraded wetlands along with the conservation of the existing wetlands since they are one of the most valuable as well as friable components of the watershed.

2 Present Status of Wetlands in India

In India, a numerous acts and legal provisions have been applied in order to conserve the fragile wetland ecosystem, and as a result of which the Ministry of Environment, Forest and Climate Change, Government of India has declared 17 sites as notified wetlands, while 26 have already been declared as Wetlands of International Importance under Ramsar Convention (Tables 6.1 and 6.2). Apart

S.		Status (total		
no.	Particulars	no.)		
1	1 Total no. of wetlands in the country as per the latest National Wetland			
	Atlas			
2	No. of natural wetlands under conservation:			
a. Wetlands designated as Ramsar sites and under NWCP 119				
b. Wetlands under NLCP 61				
c. Wetlands under NRCP 39				
d. C	219			

Table 6.1 Present status (numeric) of wetlands in India

Sources: Data compiled from MoEF (2007, 2012) and Ramsar Convention on Wetlands (2012)

S. no.	Wetland's name	State	Ramsar criteria
1	Ashtamudi Wetland	Kerala	1,2,3,8
2	Bhitarkanika Mangroves	Orissa	2,4,6,8,9
3	Bhoj Wetland	Madhya Pradesh	2,4,5,6
4	Chandertal Wetland	Himachal Pradesh	2,3
5	Chilika Lake	Orissa	2,4,5,6,8,9
6	Deepor Beel	Assam	2,5
7	East Calcutta Wetlands	West Bengal	1
8	Harike Lake	Punjab	2,5,6
9	Hokera Wetland	Jammu and Kashmir	2,5,6
10	Kanjli	Punjab	3
11	Keoladeo National Park	Rajasthan	2,5,6
12	Kolleru Lake	Andhra Pradesh	2,4,5,6
13	Loktak Lake	Manipur	2,5,6
14	Nal Sarovar Bird Sanctuary	Gujarat	2,5,6
15	Point Calimere Wildlife and Bird Sanctuary	Tamil Nadu	2,4,5
16	Pong Dam Lake	Himachal Pradesh	2,5,6
17	Renuka Wetland	Himachal Pradesh	3,4
18	Ropar	Punjab	5,6
19	Rudrasagar Lake	Tripura	2,3,8
20	Sambhar Lake	Rajasthan	2,5,6
21	Sasthamkotta Lake	Kerala	1,2,7,8
22	Surinsar-Mansar Lakes	Jammu and Kashmir	2,3,4
23	Tso Moriri	Jammu and Kashmir	2,6
24	Upper Ganga River (Brijghat to Narora Stretch)	Uttar Pradesh	2,5
25	Vembanad-Kol Wetland	Kerala	4,5,6
26	Wular Lake	Jammu and Kashmir	2,5,6

 Table 6.2
 List of wetlands designated as Ramsar sites in India and their criteria

Source: Ministry of Environment and Forest, Govt. of India

from this, the several wetlands covered by the National Wetland Conservation Programme (NWCP) and National Lake Conservation Plan (NLCP) have also increased to 115 and 61, respectively (MoEF 2012). In the valuation of wetlands in India, a total of 4.63% of the geographic area has been verified under wetlands (Fig. 6.1) (MoEF 2011). India has 63% natural wetland (66, 23,067 ha), and the remaining 37% have human-made inland wetlands (39, 41,832 ha). Besides, India has 4,140,116 ha of coastal wetlands (of which the intertidal mudflats of Kutch alone contribute about 51%), and 555,557 ha of wetlands are smaller than 2.25 ha each. The paddy fields were also included as wetlands in this inventory (Gopal 2014). Rapid urbanization and industrialization have excessive impact on wetland, and the urban wetlands are the most threatened for their existence as it is being used as regular landfill sites or dumping sites of solid wastes. The discharge of untreated industrial wastewater and domestic wastewaters in the wetland is the significant factor causing degradation of wetlands ecosystem (Upadhyay et al. 2019). Cattle browsing have the major impact on the wetlands because it removes the native plant



Fig. 6.1 Percentage of category-wise distribution of wetlands in the country. (Source: MoEF, Government of India 2011)

species. Furthermore, by compacting the fragile wetland soil, cattle alters water flows and nutrient dynamics across the wetland, reducing the capacity of the wetlands to function as ecological filters of agricultural runoff, with the consequent increase of contaminants in water (Cisneros 2010). Freshwater bodies are often subject to changes in land use in their catchments leading to the reduction in inflows and deteriorating quality of the "runoff" traversing through agricultural fields and urban areas. On the other hand, many of them act as the "sink" for untreated effluents from industries (Gopal 2014).

3 Strategies for Wetlands Conservation

Ramsar Convention is a major step at the global level for the conservation of the wetlands, which forms an agenda of intergovernmental collaboration on wetland. It is an international treaty taken up with a moral duty of "conservation and sensible use of all wetlands by local, national and international cooperation towards achieving sustainable development." Ramsar Convention was adopted in 1971 in the city of Ramsar, Iran, and came into existence in 1975. After implementation of the agenda, ~2331 wetlands have been designated as Ramsar sites through analyzing 9 criteria set forth in the Ramsar Convention for designation of the wetland. Besides Ramsar Convention, various steps are now being implanted at the national or regional level to save the wetlands. Dyana (2015) reported that the situation for the conservation of wetland in India is poor due to lack of any administrative jurisdiction, care, and responsibility rather than the management of wetland ecosystems is controlled by Ministry of Environment, Forest and Climate Change. However, the conservation of wetlands in India is indirectly influenced by a range of policies and legislations (Parikh and Parikh 1999). Some of the important regulations that contribute to wetland conservation are:

- The Indian Fisheries Act, 1857: This act highlights the conservation of fishes and banned the use of all the activities which influence the quality of water and cause the destruction of fishes.
- The Indian Forest Act, 1927: The wetlands were occasionally included under protected areas.
- Wildlife Protection Act, 1972: This act provides protection of aquatic faunal diversity by including them under various lists of the law.
- Water (Prevention and Control of Pollution) Act, 1974: The act was endorsed with the aim to prevent and control water pollution and maintenance of water integrity.
- Forest Conservation Act, 1980: The act was mainly passed to conserve the forests. This act also indirectly contributes to conservation of wetland by preventing the soil erosion and siltation due to the deforestation and land use change.
- Environment Protection Act, 1986: Environment Protection Act is more effective and strong measure to tackle the problem of pollution of air, water, and soil thus involved in conservation of wetland.
- Coastal Zone Regulation Notification, 1991: The act has certain provisions that assist in preservation of the fresh water and marine life. The act also classifies some coastal zones as ecologically sensitive zone and prohibition of the human activities around there.

Apart from these legislations, there are other rules like The Wetlands (Conservation and Management) Rules, 2010, that are involved in the conservation of wetlands. These rules prohibit certain activities that are directly or indirectly liable for wetland degradation. The Government of India along with National Committee on Wetlands, National Committee on Mangrove and Coral Reefs, etc. continuously puts efforts to frame a guideline for identification of wetland type through ground level mechanism to conserve the wetlands (Ministry of Environment and Forest 2011).

4 Wetland: Conservation of Biodiversity and Services

Since many decades, wetlands have been used for ecological, societal welfare (services), and biodiversity conservation and play important role in sustainment of the future generation (CBD 2015; Wetlands Rules 2010). All wetlands regulate water quality by nutrient cycling. Besides, wetlands are equipped with perennial macrophytes, and trees/plants check soil erosion (Upadhyay et al. 2019). The wetland in India is richly distributed from the Trans-Himalayan to Terai regions of Himalayan foothills, floodplains of Brahmaputra, Gangetic plains, and swamps of northeastern India, Gujarat, and Rajasthan (Memon et al. 2018). The wetlands of India alone support approx. 2400 species and subspecies of birds and assist in protecting the declining population of species by making them resilient by acting as habitat and refuge for various biodiversity (Paul and Chanda 2011). They are considered as the

favored feeding and resting stations along migratory flyways for shorebirds, ducks, and waders, which in turn allure a large number of raptors and thus form the reservoir of biodiversity (Cannicci and Contini 2009). Thus, the importance of wetlands should be highly acknowledged to halt and reverse biodiversity decline.

Wetland services are also involved in food security as they enable the availability of various food products such as fish, rice, and other crops grown along the edges of wetlands, etc. (Kakuru et al. 2013). Rice and fish being the highest contributor of food for more than half of the world's human population, wetland provides the most important benefits for humans. All these services necessitate the need to prioritize the conservation of wetland; however, restoration and protection of ecosystem services and biodiversity are difficult as the accepted paradigm of conservation excludes the productive use of resources (Cisneros 2010). Temporarily wetland stores floodwater and thus protects downstream areas from the flood. The various ecosystem services provided by wetlands are given in Table 6.3. The increase in the recognition of laws, regulations, and plans to restore and protect the wetlands

Ecosystem service	Le d'acida al EQ	Description	
(ES) type	Individual ES	Description	
Supporting	Biogeochemical cycling	Maintenance of natural flux of material and energy between living and nonliving components	
	Biotic interactions	Pollination of wild species, seed dispersal, preservation and maintenance of trophic chains	
	Habitat	Habitat for transient and resident population	
	Plant food/raw material	The proportion of gross primary production that can be extracted as food/raw material	
Provisioning	Animal food/raw material	The proportion of secondary production that can be extracted as food/raw material	
	Water supply	Filtering, retention, and storage of fresh water for human use	
	Climate regulation	Regulation of the chemical composition of the atmosphere, global temperature	
	Hydrological dynamics	Regulation of natural hydrological flows, role of land cover in regulating runoff, infiltration	
Regulating	Water quality	Retention and removal of xenic compounds, water purification	
	Regulation of extreme events	Capacity and integrity of ecosystem response to environmental fluctuations such as floods, storms	
	Regulation of soil fertility	Soil maintenance and formation, prevention of erosion, accumulation of organic matter	
	Regulation of invasive species, pests	Regulation of invasive species population, pest population	
Cultural	Recreation	Provision of opportunities for recreational activities	

Table 6.3 Principal ecosystem services (ES) supplied by wetlands

Source: MEA (2005)

around the world (Cherry 2011). All the efforts as mentioned earlier in the strategies of wetland conservation are designed to protect or conserve wetlands and ecosystem services they provide.

5 Wetland: Role in Carbon Sequestration

The floral constituents of the wetland found to have a significant contribution toward sequestering carbon because of their high growth rate (Adhikari et al. 2009). Furthermore, their soils have also been proved as great carbon storage because of their anaerobic nature where the carbon gets incorporated into the soil and takes time to decompose (Singh 2016). Wetlands help in the reduction of atmospheric carbon dioxide which is either sequestered in the plant biomass and animal biomass or as organic material in the soil. The reduced decomposition rates result in buildup and accumulation of large organic carbon in wetland sediments (Department of Sustainability, Environment, Water, Population and Communities 2012), which causes a reduction in the atmospheric CO_2 (Adhikari et al. 2009). Pant et al. (2003) reported that the wetlands are the highest carbon density reservoir in terrestrial ecosystems with capacity to sequester additional CO₂. In a study of UNFCCC (2014), mangroves, tidal marshes, and seagrass meadows in wetland were found to be over 1000 mg CO₂ ha⁻¹. Wetland covers 6–9% of the earth's surface and contains \sim 35% of global terrestrial carbon (Ramsar/ STRP/ CBD 2007). In addition, wetlands are responsible for the horizontal transport of carbon and may consume carbon-rich sediments from catchment area (Department of Sustainability, Environment, Water, Population and Communities 2012). Thus, wetlands have a contribution to climate change regulation. Degradation of wetlands has also been found to be a reason behind the release of a significant amount of stored carbon back into the atmosphere (Adhikari et al. 2009; Singh 2016). However, under anaerobic condition, wetland discharges various gases such as methane and nitrous oxide which are potent environmental pollutants and contribute in global warming (Barlett and Harriss 1993). With the increased globalization and simultaneous fast loss and degradation of wetlands, it is estimated that around 0.45 billion tons of CO₂ per year would be released into the atmosphere (UNFCCC 2014).

6 Restoration of Wetlands and the Future World

To enhance the enhance wetland's ecosystem services, restoration of degraded wetland has become an important priority. About half of the global wetlands have already been lost, and the condition of the remaining is deteriorating (Clarkson et al. 2014). Wetlands, despite disproportionation in their aerial extent, support the huge biodiversity and the several benefits to humans; it failed to draw the attention of the people toward their conservation and management (Gopal 2015). The restored wetlands have been found to provide higher levels of provisioning, regulating, and conditioning ecosystem services than the degraded ones (Meli et al. 2014). In order to ensure the health of watersheds, one of the most valuable and fragile components, it is essential to restore wetlands to their natural state not only considering as an indispensable unit but also as a rich resource of human for the sustainable world and the environment (Halls 1997). The effectiveness of approaches toward achieving anticipated conservation goals varies and depends on the site conditions, practices employed, and specific ecoservices. Apart from these, the restoration technique application is also dependent on the type of disturbances. Through the restoration practice, much of the biodiversity and the ecosystem services can be recovered (Zedler 2005). The techniques that can be applied in order to restore the degraded wetlands generally fall within three broad categories (National Research Council 1992):

- · Re-establishment or management of wetland hydrology
- · Elimination or control of chemicals and other contaminants affecting wetlands
- · Re-establishment and management of native biota

The basic design for restoration of wetland ecosystem has been described in Fig. 6.2 (WRP 1992).

7 Recommendation and Future Research

The conclusion which emerges through this research implies that the services provided by the wetlands are key regulators for the current world and sustainability. The present research suggests the management practices for conservation of the natural resources based on traditional knowledge and resource uses which will definitely speedup the biodiversity and the different ecosystem services. Additionally, research including appropriate measurement and ecosystem modeling is needed to collect the quantitative data on species diversity found in different wetland and their contribution in socioeconomic development. The following points are suggested to justify the services received from the wetlands:

- Establishment of management strategies which might conserve both wetlands and cultural practices.
- A detailed seasonal inventory of aquatic flora and fauna with special emphasis to macrophytes, microphytes, phytoplanktons, algae, fish, birds, amphibians, crustaceans, and mollusk must be required for its betterment.
- Conservation of habitat for different animals, birds, insects, other wild animals, etc.
- A comprehensive assessment of the socioeconomic as well as ecological benefits provided by the wetland should also be measured.



Fig. 6.2 The basic design for restoration of wetland ecosystem. (Source: WRP 1992)

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Chapter 7 Microbes Biology: Microbes in Wetland and Bioprospection of Microbes



Avinash Singh, Prashant Kumar Singh, Wenjing Wang, and Alok Kumar Shrivastava

Abstract Over-increasing population, climate change, and the environmental pollutants are exerting negative pressure on biodiversity as well as our natural resources. Wetlands are a crucial gear of our natural environment. They support not only biological diversity but also the microbial communities of such systems that play an important role in biogeochemical cycles, global greenhouse gas emission, and nutrient (re)cycling. Therefore, wetlands are ecologically as well as economically indispensable systems owing to their high yield. The highly productive and diverse microbial community inhabitant of wetland ecosystems continuously transforms nutrients from dead vegetation into sources of nitrogen, phosphorous, and other nutrients that can be used by the plants, and in turn the plant-root exudates serve as a food source for the microbes. Unfortunately, the composition and diversity of microorganisms in such type of ecosystems are poorly explored. Hence, the analysis of microbial biodiversity and their correct prospecting from these ecosystems will help in isolating and identifying new and potential microorganisms having high specificity for various applications. This chapter consists of literature on the diversity of predominant microbes such as bacteria, fungi, and actinomycetes from

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© Springer Nature Singapore Pte Ltd. 2020 A. K. Upadhyay et al. (eds.), *Restoration of Wetland Ecosystem: A Trajectory Towards a Sustainable Environment*, https://doi.org/10.1007/978-981-13-7665-8_7 wetland ecosystems and on the underlying mechanisms that structure microbial communities in wetland ecosystems.

Keywords Biodiversity · Bioprospecting · Biogeochemical cycles · Microorganisms · Nutrient recycling · Wetland ecosystem

1 Introduction

The European Commission (CE) and US Environmental Protection Agency (USEPA) jointly define wetlands as "Areas which are inundated or saturated with surface or ground water at a frequency and duration sufficient to support, and that under normal situations do support, a prevalence of vegetation typically reformed for life in saturated soil conditions" (Federal Register 1980, 1982). Wetland ecosystem includes marshes, swamps, bogs, and similar areas, as well as the transition zone between terrestrial and aquatic ecosystems. Wetlands cover ~5-8% of the Earth's land surface and one of the most important ecosystems due to their high productivity, ability to cycle (recycle) the nutrients, and contribution to global greenhouse gas emissions (Bodelier and Dedysh 2013a, b). The wetlands also prevent eutrophication of inland as well as coastal waters by acting as a buffer between terrestrial and aquatic ecosystems (Alam and Jia 2012). The simultaneous activities of both aerobes and anaerobes blossom in wetlands due to its proximity of oxicanoxic conditions often generated due to wetland plant roots (Bodelier and Dedysh 2013a, b). The wetland system is highly productive due to nutrient input and its fast recycling by microbes (Upadhyay et al. 2019). With the recent surge in anthropogenic activities and climate change globally, wetlands are under high pressure (Chen et al. 2018). Any changes in the land use or altered hydrology due to climate change will have a devastating effect on the wetlands. The biomass of wetland can be utilized as a nutrient removal material and source of biofuel (Bodelier and Dedysh 2013a, b). Unfortunately, the functionality and diversity of the microbial communities in the wetlands are highly unexplored.

1.1 Types of Wetlands

1.1.1 Coastal Wetlands

A coastal wetland ecosystem includes estuary and marshy systems that are heavily used and vulnerable natural system (Barbier et al. 2011; Halpern et al. 2008). The coastal ecosystem globally decreases due to anthropogenic activities and a reported reduction of 50% salt marshes, 55% mangroves, and 29% seagrasses (MEA 2005; Waycott et al. 2009). In coastal wetlands, water levels and salt concentrations are continuously fluctuating and develop such habitats which are unfit for the growth of plants (MEA 2005). Therefore, only those plants having potential to tolerate the

extreme environment may flourish and adapt to these flexible conditions to form unique communities. Examples are mangroves, grasses, and other halophytes.

1.1.2 Inland Wetlands

Inland wetlands are the most common type found on the flooded plains along the rivers and streams, lakes, ponds, and land depressions, where the soil environment is under constant saturation (Carter 1996). Unlike coastal ecosystem, the salinity of inland wetlands is not a key contributing factor. However, salinity is essential for various plants and microbial communities, and little fluctuations in the salt concentration are observed.

1.2 Characteristics of Wetland

1.2.1 Physical Environment

Wetlands are identified as a transition zone between terrestrial and aquatic environment (Casey and Klaine 2001). Water hydrology is a very important component of wetland ecosystem, which generally determines the water budget. The water budget directly or indirectly influences the structure of the soil environment, and diversity of flora as well as fauna residing in the wetland (Carter 1996). Wetland soil has been classified as hydric and possesses characteristics that are associated with reducing soil conditions.

1.2.2 Hydrology

Water availability plays a crucial role in exploring wetland processes. The inundated area is either permanently or periodically at mean water depths ~6.6 ft or the saturated soil at the surface in growing season (Upadhyay et al. 2017). In general, the wet environments, such as aquatic wetlands and flooded wetlands, experience higher rates of anaerobic respiration (e.g., denitrification, methanogenesis, iron reduction, and sulfate reduction) than aerobic (nitrification). Continuous water saturation in wetland causes severe oxygen depletion, which leads to switch the microbial population toward other substrates for energy (Balser et al. 2006). In wetlands, both wet and dry conditions prevail, and during wet periods, anaerobic pathways may be used for energy (denitrification, etc.), while in dry periods, oxygen is present allowing for aerobic pathways for energy.

1.2.3 Soil Structure

The wetland soil texture plays a crucial role in the processes performed by the microbial community and mainly hydric soil to support strictly anaerobic conditions under increased redox potential.

1.3 Biological Interactions

1.3.1 Plants

Plants are the critical components of wetland (Upadhyay et al. 2016). The predominant vegetation comprises macrophytes which are typically adapted to areas of water saturation and provide substrate for the growth of diverse microbes (Dhir 2013; Vyamazal 2013). Hydrophytic species can grow and effectively compete, reproduce, and persist in anaerobic as well as aerobic conditions. Examples are *Phragmites* sp., *Typha* sp., bulrushes, sedges, water lilies, pondweed, waterweed, etc. (Rai et al. 2015). These plants are the main components in the ecosystem functioning and making wetland the most productive ecosystem on Earth. Wetlands offer an enormous amount of dissolved organic matter via photosynthesis and subsequent death and decomposition (Dhir 2013). Moreover, the macrophytes are not the only organisms capable of photosynthesis in wetlands; there is a large population of cyanobacteria and algae, capable to fix carbon dioxide (Richey et al. 2002).

1.3.2 Animals

A variety of animal species are an inhabitant of wetland environments (Zedler and Kerchar 2005). The standing water and overabundance of algae, as well as photosynthetic bacteria availability, make the habitat an ideal for insect growth including mosquitoes and gnats. Wetlands also supported the reptiles and amphibians due to the close proximity of open water to vegetated areas and a wide range of insects inhabiting the ecosystem (Roe and Georges 2007). Birds and mammals are also abundant in marshy environments (Benoit and Askins 1999). Overall, the wetland food web is complex due to the presence of different groups of organism from different environment.

1.3.3 Microorganisms

Microbes play crucial roles in the food web, by functioning as primary producers as well as decomposers (Upadhyay et al. 2017). Producer microorganism includes photoautotrophic organism and is essential in ensuring the strong food web. After the death of higher trophic organisms, microbes degrade them and, thus, assist the

recycling of valuable power and reintroduce it into the system as dissolved organic carbon (Rai et al. 2015). This overall process is known as the microbial loop.

2 Key Developments in Wetland Microbiology

Various authors (Kolb and Horn 2012; Lamers et al. 2012a, b; Lovell and Davis 2012; Pester et al. 2012) have described the development of wetland microbiology in the first decade of the twenty-first century. Kolb and Horn (2012) represented the microbial methane (CH₄) and nitrous oxide (N₂O) consumption in acidic wetlands. Acidic wetlands are the global sources of methane and nitrous oxide, the greenhouse gases. Though the use of these atmospheric gases has been observed in various wetlands, the microbial mechanisms are rarely known. At subsoil horizon, methane is substantially consumed by aerobic methanotrophs at anoxic-oxic interfaces (e.g., rhizosphere of vascular plant roots, tissues of Sphagnum mosses) (Kolb and Horn 2012). The likely candidates for the consumption of atmospheric methane in acidic wetlands are methylocystis-related species (Methylocystaceae members) whose activities are regulated by the availability of oxygen (Don et al. 2005). Acidic wetlands act as a temporary source or sink of nitrous oxide since nitrous oxide is produced and consumed by microbial denitrification. Based on the analysis of N2O reductase gene in acidic wetlands, the acid-tolerant Proteobacteria can mediate N₂O consumption acidic wetlands. Lamers et al. 2012a, b analyzed the microbial activities' effect on the growth of plants. The wetland microbes participate in the nitrogen, sulfur, and iron cycling, thus, having a profound impact on the performance and growth of plants. Lovell and Davis (2012) highlighted the role of diazotrophs in the maintenance of nutrient-limited salt marshes. Their studies suggested that the highly varied diazotrophic community shows clear biogeography within the salt marsh and even differs between plant species, pointing a niche differentiation of nitrogen fixer diazotrophs within the wetlands. Pester et al. (2012) studied the sulfate-reducing microorganisms in freshwater wetlands and reported that though sulfate reducers form a small population in freshwater wetlands, they are very much capable of catalyzing significant sulfate reduction rates and interacting with microbes which are involved in other cycles. Freshwater wetlands consist of a highly diverse sulfate-reducing community in contrast to marine habitats, and this community is mostly comprised of microbes which are not related to cultured representatives (Reyes-Sosa et al. 2018).

3 Microbial Abundance, Diversity, and Spatial Distribution

Microbial communities in the wetland systems play an important role in biogeochemical cycles, crucial for wetland functions (Truu et al. 2009). Recently, by the advancement in the science and technology especially in the field of molecular

biology, approaches toward next-generation sequencing, identification and analysis, and research on microbial diversity in various natural wetlands have rapidly developed (Reyes-Sosa et al. 2018). For example, the 16S rRNA tag-encoded pyrosequencing approach has been adopted to study microbial diversity in different natural wetlands (Deng et al. 2014). Deng et al. (2014) also reported that the diverse microbial community in different wetlands using same experiments revealed that the sizeable bacterial diversity in these wetlands includes the following organisms:

(A) Bacteria

The bacterial population which is abundant in the wetland ecosystem includes:

- i. *Proteobacteria* is relatively high in abundance in wetlands (37.5%) and is capable of some essential functions ranging from nitrogen fixation to denitrification and reduction of iron and sulfate. *Proteobacteria* are chemotrophs and obtained their energy from the chemical breakdown of inorganic and organic compounds instead of light (or photosynthetic) energy. These *Proteobacteria* in wetland ecosystem are mainly composed of *Nitrospira* (nitrate reductions-denitrification), *Nitrosomonas* (ammonia oxidations), *Pseudomonas* (capable of degrading contaminants naphthalene, toluene, etc.), *Desulfovibrio* (sulfate reducers), and *Geobacter* (Deng et al. 2014).
- ii. *Actinobacteria* **or** *actinomycetes* are also chemotrophic bacteria and found in lower abundance (17.3%) in the wetland communities due to slow decomposition rates. Some examples include *Streptomyces* (most common, degrade resistant substrates) and *Arthrobacter* (degrade toxic compounds).
- iii. Bacteroidetes also belong to a lesser amount (11%) and include Firmicutes such as Bacillus (facultative aerobes) and Clostridium (17.3%). Besides this, there are also photosynthetic bacteria mainly cyanobacteria that are present in wetlands. The high abundance of Proteobacteria and Actinobacteria was not surprising as they are prevalent in the soil of various ecosystems.

(B) Archaea

The archaea in wetland ecosystem are responsible for the anaerobic reductions of sulfate as well as ammonia as lithotrophic organisms are classified as nitrifiers, methanogens, and anaerobic methane oxidizers (Head et al. 1998). Examples are Euryarchaeota, Methanobacteria (methanogenesis), Methanosarcina, Crenarchaeota, etc.

(C) Eukaryotes

Algae and other higher organisms, such as daphnia and ciliates, are also integral parts of wetland communities that perform photosynthesis and are a primary source of energy for higher trophic levels (Singh et al. 2018). Fungi are important in nutrient cycling by acting as a decomposer and are present in the relatively minor population in wetland communities due to the anoxic environment; decomposition rates of fungi are low which limits the importance of fungi in the wetland (Lodge and Cantrell 1995). In several wetlands such as in northern Russia, Florida Everglades,

and North Carolina coastal plain, the *Bacteroidetes* composition was found to be less than 1%; however, they were found relatively abundant in high-altitude wetlands of Chile (Bridgham et al. 2000; Deng et al. 2014; Dorador et al. 2013; Serkebaeva et al. 2013). Apart from this, wetlands constitute one of the dominant species in the sediments and freshwaters of Tibetan Plateau lakes (Yun et al. 2014). Thus, the relatively high abundance of *Bacteroidetes* in the three wetlands of the Qinghai-Tibetan Plateau might be partially associated with factors shared between these high-altitude environments; however, investigations are required to understand their ecological role in these systems. In natural wetlands, methane is released as a final product of anaerobic degradation of organic matter which is performed by methanogens and methanotrophs (Conrad 1999; Reeburgh 2003). Thus, both methanogens and methanotrophs are the key components in methane cycling of natural wetlands. The composition of the methanogen community depends upon various factors, and more studies are required to understand which factors play critical roles in structuring methanogen populations.

Recent studies reveal that bacterial communities in lake ecosystems are strongly correlated with a multitude of environmental factors over horizontal gradients ranging from hundreds of kilometers to centimeters (Ding et al. 2015). Various approaches were applied by Preston et al. (2012) for the characterization of depth-dependent microbial community structure and function. They found that irrespective of the nutrient contents in different systems, a similar dominant microbial taxon is found to be abundant. These microbes are identified through their microbial activity, the quality of the available substrate, and the presence or absence of potential microbial inhibitors.

4 Microbes Processing and Output in Wetlands

Wetland microbes mediate various vital biogeochemical processes such as nitrogen, carbon, sulfur, phosphorus, and iron cycles (Lamers et al. 2012a, b). The microbes present in the anoxic wet soils are primarily responsible for the various redox reactions in wetland ecosystems. A long disputed question in the methane emission in rice paddies is to what extent the rice straw affects the methane production (He et al. 2015). Conrad et al. (2012) utilized a combination of stable isotope fractionation and molecular detection techniques to demonstrate that methane formation pathways in degradation straw (rice vs. maize) were rather simple despite the involvement of methanogenic communities of the soils. Hence, the path of methane production is mainly regulated by the soil type rather than the straw type. Sun et al. (2012) studied the rate of methane production in three peat lands with different characteristics: two acidic peat bogs and a minerotrophic fen. In this study, they tried to analyze the inducible shifts in methanogen population on the addition of substrates (acetate and hydrogen) to peat during short-term incubation. They concluded that different metabolic substrate supply is a driving force for methanogen species sorting in wetlands. Thus, methanogenic substrates predominantly control

the methane formation and emission from wetland soils. A study conducted by Irvine et al. (2012) reveals that salt marshes' methanogens may be nitrogen-limited, which could be an alternative explanation for increased emission of methane from wetlands by addition of nitrogen. This was never considered before due to general acceptance that increases in methane emissions upon addition of nitrogen are due to both plant biomass increases and methane consumption inhibition. However, this finding urges to rethink the nitrogen control of methane emission from wetlands and thus opens up many possibilities for new research.

Nitrogen and nitrogenous fertilizers have been shown to affect the consumption of methane in wetlands and upland soils, though solid mechanistic explanations supported by experimental data are still lacking. Alam and Jia (2012) experimented using rice soil and demonstrated that up to certain levels, the addition of nitrogenous fertilizers stimulates specific methane oxidizers (i.e., type I). The obtained result was consistent with the earlier studies performed on different rice soils. However, when higher doses of ammonium-based fertilizers were used, methane oxidation was inhibited. This might be acted through the activity of nitrifiers given the robust correlation between nitrate production and methane oxidation. In opposed to the above, in situ addition of nitrogen to a natural littoral wetland in a boreal lake does not yield any effect either on methane oxidation potential or on methane flux. Siljanen et al. (2012), in their study, observed that nitrogen load activates pmoA gene transcription of type I methanotrophs but at the same time decreases the relative abundance of pmoA gene transcripts of type II methanotrophs. Thus, the net methanotroph activity remained unaffected by the nitrogen augment. Hence, while evaluating nitrogen load on methane oxidation, in situ observation needs to be considered.

Apart from nitrogen, methanotrophic bacterial dispersal and distribution play a regulatory role in methane cycling in wetland. Putkinen et al. (2012) studied the role of water dispersal in the colonization of *Sphagnum* mosses by methanotrophic bacteria. *Sphagnum* plantlets, particularly hyaline cells of these mosses, are known to be colonized by methanotrophs and are responsible for methane oxidation on its way from anoxic peat layers to the atmosphere (Bodelier and Dedysh 2013a, b). Putkinen et al. (2012) showed that inactive methanotroph-free *Sphagnum* plantlets acquired methane-oxidizing activity and respective methanotroph population after a few days of transplantation next to methanotroph-containing mosses. They concluded this colonization as a resilience mechanism for peatland methane dynamics by allowing the re-emergence of methane oxidation activity in *Sphagnum*.

5 Bioprospecting of Wetland Microbe's Present and Future Scenarios

The Earth's three-fourth surface is covered with water and of which 96% is in the form of marine ecosystems. Aquatic ecosystems, i.e., marine and freshwater, are biodiversity rich and are responsible for the environment's healthy functioning; unfortunately, most of these life forms are still uncharacterized. Furthermore, this biodiversity is currently under threat due to various anthropogenic activities including rising environmental pollution, particularly in wetland ecosystems. Many of these life forms are very important for the proper functioning of our healthy life, and their role must need to understand. This leads to an urgent need for bioprospecting of biological diversity as well as bioactive compounds from the wetland ecosystem. Bioprospecting can be defined as the discovery and commercialization of new products based on natural resources (Strobel and Daisy 2003). In the last few decades, scientists have taken attention toward wetland biodiversity. Dedysh (2011) successfully cultivated the peat-inhabiting microbes and identified the bacterial diversity from northern wetlands. Figure 7.1 is showing the taxonomic composition of bacterial communities in northern Sphagnum-dominated wetlands of various geographic locations. An overview of the 16S rRNA-based diversity assessment of acidic northern peatlands in different geographic locations identified six cultivation-independent wetland microbes (Fig. 7.1). Interestingly, the bogs in the north, as well as tropical acidic showing a similar bacterial diversity pattern and, are mainly dominated by Acidobacteria and Proteobacteria.



Fig. 7.1 Northern *Sphagnum*-dominated wetlands' microbial communities of various geographic locations. The taxonomic composition of identified bacterial communities, determined in different cultivation-independent studies. (Adopted and modified from Dedysh 2011)

Stovea et al. (2014) have characterized microbial diversity in the sediment cores of different wetlands based on 16S rRNA and two functional gene transcripts (*mcrA*, involved in archaeal methane cycling, and *glnA*, implicated in nitrogen metabolism). They advocated that the bacterial communities are highly diverse and Archaea are mostly methanogens. Raina et al. (2018) have discussed the sediment microbial biodiversity using traditional and modern techniques for understanding the nutrient cycling and spatiotemporal variations in brackish water ecosystem of Chilika Lake. Padhi et al. (2011) have identified red alga *Gelidium* and *Gracilaria* from Chilika Lake which is a useful source of agarose. Gayathri et al. (2010) have bioprospected the endophytic bacterial population of mangroves and salt-marsh plant from India. Out of 104 identified bacterial isolates, 36 were defined as a fast-growing isolate and were screened for biological activities. Of 36 isolates, 28 (77%) have demonstrated to possess antimicrobial activity and 94.4%, 58.3%, and 52.7% of isolates with pectinase, protease, and inulinase as well as invertase activities. Table 7.1 shows the plant growth promoting the activity of strains.

Furthermore, the pollutant-degrading activity that was tested for these endophytes was also recorded. The malachite green and phenol-degrading activities were observed in 12 (33.3%) and 20 (55.5%) endophytic bacterial isolates, respectively. Again, 34 (94.4%) and 31 (86.6%) endophytic isolates are tolerant to 7.5% and 10% NaCl concentrations, respectively. These results have proved that the wetlands like mangroves are the sources of endophytic bacteria with bioprospecting potential, which deserves further studies.

6 Conclusions

In response to climate change, aquatic ecosystems are changing rapidly due to alteration of the landscape, which in turn affects not only the hydrology but also the cycling of nutrients. Microbes play a dominant role in the geochemical nutrients cycling in anaerobic freshwater sediments. Unfortunately, most of these tiny creators remain under enigma and not identified although the efforts are going on to decode the role of microbes in wetland ecosystems and their identification. However, identification by metagenomic data provide useful information, but these need to be mined and analyzed, and proper statistics need to be maintained so that relevant information can be used for the betterment of the environment and humanity.

S. No.	Number of isolates	% of population	Nutrient production
1	22	61.1%	Ammonia
2	25	69.4%	Acetoin
3	26	72.2%	Nitrogen fixation
4	6	16.6%	Phosphate solubilizing
5	7	19.4%	Indole acetic acid (IAA)

 Table 7.1
 Plant growth is promoting the activity of isolates of marsh wetland
Notably, there are certain drawbacks and bottlenecks in metagenomics, which need to be understood. Furthermore, to understand the interactions, dynamics, response to environmental changes, and biochemical and physiological processes of microbial communities, we need to focus more on in-depth studies of their metagenomes and monitor changes in populations over time. These studies will eventually help us to design a model toward structuring the biochemical processes and dynamics of entire ecosystems, henceforth allowing us to predict the effects of complexities of environmental conditions, including pollution, drug treatment, the release of transgenic organisms, or climate change.

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Chapter 8 Contribution of Microbes in the Renovation of Wetlands



Prem Chandra, Enespa, and Mukesh Kumar

Abstract A wetland ecosystem is an important reservoir of microbial diversity and contributes significantly in mitigation of the Greenhouse gas emissions. Increased nitrogen (N) inputs from agriculture and fossil fuel combustion have been recognized as a severe threat to biodiversity loss and ecosystem functioning of wetlands, such as control of greenhouse gas emissions. The intensive biogeochemical activities in the wetlands are performed by microbs, which have an important role in improving water quality and nutrient recycling. It is well known that the structure and function of the microbial community enhance the restoration of nutrient cycling in wetlands. Investigating the interactions of structure and functions of microbes with wetland plants is important because the microbial taxa can be interconnected to specific transformations, biodegradation, biogeochemical cycles, survival, and restoration of the wetlands. The processes of nitrification, denitrification, mineralization, humification, and absorption are performed by physical, chemical, and microbial processes for the sustainability of the wetland. This chapter suggests that microbially mediated processes are directly and indirectly crucial in the restoration of wetland function and ecological aspects. The phenomenon and the working principle of microbes in wetlands are discussed in detail with emphasis on nutrient cycling. This chapter also describes how microbes are an indispensible part of wetland functioning and restoration.

Keywords Bioremediation · Restoration · Microbes · Sustainability · Wetlands

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1 Introduction

Wetlands are the most productive ecosystems on the Earth. According to their genesis, they exhibit enormous diversity in geographic location, water regime and chemistry, dominant species, soil and sediment characteristics (Bassi et al. 2014). The transitional areas flanked by land and water are known as marshlands or wetlands, categorized by superficial overlying waterlogged soils sheltering a rich diversity of flora and fauna (Stickney 2005). The freshwater ecosystem includes a rich diversity of macrophytes and microphytes such as diatoms, algae, and other phytoplankton (Browder et al. 1994; Upadhyay et al. 2019). Macrophytes and microphytes that grow in freshwater require nutrients for their proper growth, which are facilitated by the activity of different microbes present in the freshwater system (Momot 1995). Moreover, the existence of plants in the environment depends on the consortia of microbes and their different communities, such as the detrital microbial floor covering, microbial biofilm, and planktonic phycological, bacteriological, and mycological assemblages. These microbial communities contribute significantly to biogeochemical nutrient cycling, that is, nitrification, denitrification, sulfate reduction, methanogenesis, and metal ion reduction, which maintains the sustainability of natural ecosystems (Wu et al. 2012). The assemblage of microbes as a biofilm normally occurs on the foliage regions of waterlogged plants, on the rhizoplane of the rhizosphere, and on the hard surfaces of sediments. The ecosystem is continuously exposed to degradation from eutrophication, worsened by anthropogenic input (Jackson et al. 2001). Increased human interference erodes water, air, and soil ecosystems, in which the aquatic ecosystem is highly prone to loss (Cole et al. 2007). Interaction of the microbes and macrophytes influences water quality.

Wetlands cover about 5–8% of the Earth's land surface (Baron et al. 2002). Generally, the wetlands consist of freshwater, soil, vegetation (macrophytes and microphytes), and microbes (Bardgett et al. 2001; Bambaradeniya et al. 2004). Wetland studies are mainly focused on the ecological systems, their conservation, biodiversity, water quality improvement, and flow of nutrients (biogeochemical cycle), and the restoration of ecological systems (De Groot et al. 2002). Wetlands are categorized into two types: naturally occurring and manmade (i.e., constructed wetlands) (Ghermandi et al. 2010). The most widely used wetland classifications systems are characterized as marine (coastal wetlands), estuarine (mangrove swamps, deltas, tidal marshes), lacustrine (lakes), riverine (along rivers and streams), and palustrine (bogs and swamps), based on their hydrological, ecological, biological, and environmental characteristics (Junk et al. 2014). The ecosystems of constructed wetlands have similarities to naturally developed wetlands. Water covers the soil in regions known as natural wetlands such as marshland, fenlands, sloughs, and bogs (Keddy 2010). Presently, however, these ecosphere wetlands are shrinking because of the development of farmlands, expansion of industrial areas, and urbanization, liberating stockpiled carbon into the atmosphere and hastening environmental transformation (Misra 2012). The grass Spartina alterniflora that grows in coastal wetlands protects coastal lands from erosion and land loss. The microorganisms of coastal plants improve restoration efforts by improving the stabilization of the soil (Deegan et al. 2012). Restoration is achieved by microbially induced formation of biofertilizers in the wetland (Khan 2005) and its utilization for plant germination, improving the health of plants, which restore soil health and stabilize the area by providing habitat for beneficial communities of microorganisms (Chandra and Singh 2016). Biogeochemical and nutrient cycling of wetlands are very important functions to restore biodiversity and thus human lives sustainably (Verhoeven et al. 2006). This chapter is focused on the broad aspects of sustainable wetland renovation and the function of microbes for macronutrients and micronutrients such as nitrogen (N), sulfur (S), iron (Fe), zinc (Zn), carbon (C), etc., with respect to their cycling in the functioning and progression of plant communities in the wetlands.

2 Increasing Risks to the Wetland Biome

Freshwater wetlands ecosystems are commonly used and exploited for sustainable development and human safety (Kivaisi 2001). During the twentieth century more than 50% of specific types of wetlands were converted in parts of North America, Europe, Australia, and New Zealand (Davidson 2014). Approximately 5000 km² of wetlands vanish yearly because of the increase in agriculture acreage, construction of dams, and other uses in Asian countries alone (Tockner and Stanford 2002). Most of the global population depends upon water and other natural resources in this environment, which has impacted global ecology and the entire environment directly (Vörösmarty et al. 2010). Consequently, these wetland-dependent species are either extinct or globally threatened: bird species (21%), mammal species (37%), and freshwater fish species (27%) (Gotelli and Colwell 2001). The loss of wetlands causes adverse impacts on the functioning of ecosystems (Erwin 2009). Suburbanization, changes in land use, drainage systems from agricultural use, development of infrastructure, pollution from industrial effluents and agricultural runoff, climate changes, and changeability are the main causes of wetland loss (Brinkmann 2016). In Indian scenarios, significant changes have been caused by these factors on wetland ecosystems, as discussed in the subsequent subsections.

2.1 Urbanization and Land Use Changes

To satisfy its basic needs, an increasing population always puts pressure on natural ecosystems and biodiversity (Cordell et al. 2009). In India, being a country of fast population growth, land use change has dramatically increased: cultivated land increased about 129–156 m hectares (ha) between 1950–1951 and 2008–2009 (Bhalla and Singh 2009), and commercial or residential use increased from 9 to 26 m ha (Data Source: India state) (Sato et al. 2013), which caused alterations in

primary forests, floodplain areas, associated freshwater ecosystems, and grasslands (Motha and Baier 2005; Bassi et al. 2014). For example, the waterspread area of the Kolleru Lake (Andhra Pradesh) was about 34,000 ha, but has been cultivated for agriculture in current years.

Further, the large reservoir projects involved in water supply, flood control, irrigation, and power production are critical in devastation of natural habitats, leading to loss of the wetlands and other ecosystems (Postel and Richter 2012). The rapid increase of artificial water possessing systems without proper planning also put a load on natural resources (Nilsson and Renöfält 2008). This improper planning has caused extensive loss and disintegration of freshwater habitats (Bond et al. 2008), This substantial utilization of the wetlands environment and aquatic systems by the suburbanized population has influenced the structure and function of wetlands, mostly by transforming the hydrological and sedimentation patterns and the changing factors of nutrients and biochemical pollutants (Meyer and Turner 1992). The urbanization impact has equally disturbed natural water bodies in the metropolitan cities (McKinney 2008). In the National Capital Territory (NCT) of Delhi, a study declared that of 629 water bodies, 232 cannot be rejuvenated because of the large-scale encroachments. Similarly, the Greater Bengaluru region, 66 wetlands with a waterspread area of about 1100 ha have vanished as the result of urban extension between 1973 and 2007 (Bassi 2016). Additionally, poor administration, the shortage of effective conservation plans, increasing pollution, and fast increase in localized demands by suburban areas for water are pushing these valuable eco-balancers to death (Economy 2010).

2.2 Agricultural, Municipal, and Industrial Pollution

Most of the Asian rivers, waters, lakes, streams, and wetlands have been heavily damaged by pesticides, runoff of agricultural fertilizers, and discharge of wastewaters, which cause extensive eutrophication from the presence of N and P (Rabalais 2002). As a result of increased agricultural activities during the past years, use of fertilizers in India increased continuously, from about 2.8 million tons in 1973-1974 to 28.3 million tons in 2010–2011 (Zhang et al. 2012). It is also observed that 10-15% of nutrients added to the soil through such enrichments ultimately find their way to the shallow water system (Asner et al. 2004). The rich nutrient content stimulates the growth of algae, leading to eutrophication of shallow water bodies (O'Neil et al. 2012; Singh et al. 2018a, b). Non-point source pollution such as agricultural runoff is the main source for the Indian rivers flowing through the Indo-Gangetic plains (Chattopadhyay et al. 2005). Populations of fish and other animals are decreased by the lake eutrophication process because of oxygen deficiency and the loss of many other services provided by lakes (Cooke et al. 2016). Unprocessed wastewater also contributes significantly to pollution of water bodies (Shrimali and Singh 2001).

In India, less than 31% of the sewage wastewater that emerges from urban centres is treated, whereas 80% treatment of sewage wastewater takes place in developed countries (Capodaglio 2017). The situation in smaller urban centres is very poor as treatment capacity exists for only about 18% of the sewage generated in Class I cities (population of 100,000 or more but other than metropolitan cities) and 9% of the sewage generated in Class II towns (population between 50,000 and 100,000) (Agrawal et al. 2010). Because of nonfunctional treatment plants and the insufficiency of the sewage collection system, actual sewage treatment has decreased. Consequently, most of the untreated sewage waste is discharged in natural water bodies such as ponds, streams, lakes, and rivers (Dadi et al. 2017). The River Yamuna, one of the secret rivers of Indian mythology, receives about 1789 million liters per day (MLD) of unprocessed wastewater from the capital city of Delhi alone, and also passes the other six states of India. Every day approximately 78% of the total effluent load is discharged into the river. Consequently, the hydrological character and water quality in the area of the Delhi division of the River Yamuna is the most polluted in terms of dissolved oxygen (DO) and biological oxygen demand (BOD) as compared to other sections (Bhatnagar and Devi 2013).

2.3 Climate Change

In wetland ecosystems, global climate change is projected to become an important driver of loss and alteration of the ecosystem (Bunn and Arthington 2002). These findings are very important in the Indian subcontinent because the mean atmospheric temperature and frequency of occurrence of intense rainfall events have increased, whereas the duration and amount of rainfall have declined because the concentration of greenhouse gases such as CO2, CH4, and N2O is increasing in the atmosphere (Trenberth et al. 2003). Climate change affects wetlands of high altitude and the coastal region in India, such as mangroves and coral reefs. For example, climate change caused the expanding level of glacial-fed water at high-altitude lakes, such as Lake Tsomoriri in Ladakh, which is an important breeding centre of migratory birds such as the black-necked crane and bar-headed goose, which has submerged the habitats (Pangare et al. 2006). Climate change in coastal wetlands such as the Sunderbans mangroves affects fish dispersal and has caused the devastation of a substantial portion of the mangrove ecosystem, with rising sea surface temperature, and rise in sea level also, because of thermal expansion (Alongi 2002). As per estimations, by increasing the water level of the sea approximately 1 m, about 84% of coastal and 13% of saline wetlands vanished in India because of climate change (Michener et al. 1997). Consequently, the species of various flora and fauna were affected severely, especially those that cannot rearrange their appropriate habitats, as do migratory species which depend on a variety of wetland types throughout their life cycle (Bellard et al. 2012). Generally, the characteristic hydrological changes in wetlands change the climate, rather than observing the real physical and socioeconomic processes responsible for such changes (Adger et al. 2003).

3 Microbial Diversity

3.1 Microbial Processes

The transitional zones between land and water bodies are categorized by shallow overlying water-logged soils harboring a rich floral and faunal diversity known as wetlands (Caughman and Ginsberg 1987). The microbial communities of wetlands interact in several of the energetic biogeochemical proceedings in the surrounding environments. The elemental cycles such as carbon, nitrogen, phosphorus, sulfur, and iron all have some role in wetland societies from the presence of various bacterial groups (Robertson and Vitousek 2009). In all inland water habitats the microorganisms dominate, and the established functioning of an aquatic environment is sustained by the rich microbial diversity that depends upon the nutrients and normal environments (Hurst et al. 2007). Freshwater microbial diversity belongs mostly to culturable Actinobacteria, Alphaproteobacteria, the bacterial groups Betaproteobacteria, Gammaproteobacteria, Firmicutes, Bacteroidetes, and Archaea (Munshi and Chattoo 2008). The majority of bacteriological groups are often present mostly in freshwater; the graphical arrangement of the biofilm is shown in Fig. 8.1. This slimy matrix-based extracellular polymeric substance contains polysaccharides, proteins, nucleic acids, and lipids in which microbial cells remain surrounded, secreted from the bacteria as a porous meshwork known as biofilm (Wotton 2004). In the biofilm, the cells of microorganisms are alive in a modified microniche in a multifarious microbial homeostatically recognized community having a stable metabolic existence, which purifies naturally altered characters of the microorganisms. With the changing of habitats and ecological conditions, the assemblage of microbes in a biofilm is vigorous and susceptible to being considerably altered

	PHYLA OF BACTE	RIAL GROUP PRESEN	NT IN AN AQUATIC ECOS	YSTEM	
↓ Actinobacteria Gram-negative ↓	l Alphaproteobacteria Gram-negative Gram-positive	F Betaproteobacteria Gram-negative	Gammaproteobacteria Gram-negative (abundant in fresh water)	Firmicutes Gram-negative Gram-positive	I Bacteriodetes Gram-negative & nonspore
Corynebacterium spp. Frankia spp. Leifsonia spp. Mycobacteria spp.	* Methylobacterium spp. Rhizobium spp. Wolbachia spp. Rickettsia spp.	+ Nitrosomonas spp. Burkholderia spp.	↓ Enterobacter spp. Vibrio spp. Pseudomonas spp.	↓ <i>Clostridia</i> spp. <i>Bacillus</i> spp.	↓ Bacteroides spp.
Streptomyces spp.	ţ	ļ	ţ		
(N ₂ fixation and plant commensals	(Degrade organics) plant symbionts)	(Ammonia oxidising Metal accumulating Organics degrading)	(Omnipresent and well studies groups)		

Fig. 8.1 Bacterial groups commonly present in an aquatic system with the most common examples

(Johnson et al. 2015). In the various plant species, accommodating altered bacterial communities are observed. This observation shows that the bacterial communities are altered by accommodating the various plant species (Martiny et al. 2006).

3.2 Aquatic Plant–Microbe Interaction and Its Role in Freshwater Ecosystems

The macroscopic flora containing the members of four various groups are limited: developing (*Phragmites australis*), free-leaved (*Hydrilla* spp.), freely floating (*Pistia stratiotes*), and waterlogged macrophytes (*Chara* spp.) (Fig. 8.2) (Wersal and Madsen 2012). The microbial species and aquatic plant distribution mostly depend upon the presence of nutrients in freshwaters in the following order: oligotrophic > mesotrophic > eutrophic (Dodds 2007).

The rhizoplane regions of the macrophytes are the most active zone in the presence of several communities of microbes (Laanbroek 2009). The microbial community structure in the microcosm is not affected by macrophytes, and provides resilient proof in maintenance of the advanced accomplishments of natural plant-microbe communications, even in the residues (Moss et al. 2009). Each microbe sets the continuous supply of nutrients, organic carbon, and oxygen for the benthic microbial community and acts as a modified niche (Davey and O'Toole 2000). Similarly, the microbes and aquatic plants obtain mineral nutrients and defensive immunity among each other and form firm interrelationships (Dordas 2008). Several environmental factors in water such as pH, electrical conductivity, concentrations of salts, dissolved oxygen, dissolved organic matter, toxic organic pollutants, some



Fig. 8.2 Plant and microbe interaction in an aquatic wetland

redox reactions, and the availability of nutrients are responsible for plant-microbe interactions in freshwater bodies (He et al. 2005).

Very limited evidence is available about the significance of plant-microbe interactions in an aquatic ecosystem from climate change (Read and Perez-Moreno 2003). However, plant-microbe interactions and their role in the aquatic system are given in Table 8.1. The table also indicates the interaction of microbes with aquatic macrophytes, mostly in the nutrient cycle. The high microbial activity in the rhizo-plane region of aquatic plants has a different water chemistry compared to other regions of the water column (Francoeur et al. 2012). Generally, the microbes form endophytic and ectophytic symbiotic relationships with aquatic plants involved in colonization of internal tissues of plants such as fixing of N_2 diazotrophs and arbuscular mycorrhizal fungi (AMF) nutrient assimilators (Srivastava et al. 2017). Ectophytes form an important plant-microbe interaction that involves both roots

Plant species	Microbial species	Role in ecosystem	References
Typha domingensis	Acinetobacter junii TYRH47	Siderophore, indole-3-acetic acid (IAA) production	Rehman et al. (2018)
Brachiaria mutica, Phragmites australis	Bacillus subtilis LORI66, Klebsiella sp. LCRI87, Acinetobacter junii TYRH47, Acinetobacter sp. LCRH81	Siderophore, IAA production, 1-aminocyclopropane-1- carboxylic acid (ACC) deaminase	Rehman et al. (2018)
Juncus acutus	Sphingomonas sp. U33, Bacillus sp. R12, Ochrobactrum sp. R24	Improves efficiency of wetland plants	Corrêa et al. (2018)
Spartina alterniflora	Pseudomonas putida and Pseudomonas fluorescens	Nitrogen transformers, phosphorus solubilizers, siderophore producers	Bledsoe and Boopathy (2016)
Phragmites japonica, Polygonum cuspidatum	Gigaspora margarita	Increase N and P uptake	Sarkar et al. (2016)
Brachiariamutica	Bacillus licheniformis BRSI58	Siderophore production	Fatima et al. (2015)
Lemna minor	Pseudomonas sp. RWX31	Denitrification	Srivastava et al. (2017)
Phragmites australis	Nitrosomonas spp.	Ammonia oxidation	Okabe et al. (2012)
Utricularia spp.	Scenedesmus spp., Characiopsis spp.	Improving P supplements	Srivastava et al. (2017)
Nuphur spp.	Mesorhizobium loti	Nitrogen fixing	Taylor and Qiu (2017)
Chara aspera	Members of Cytophaga, Flavobacteria, Bacteroidetes	Allelopathic activity against algae and Cyanobacteria	Goecke et al. (2010)
Ulva australis	Pseudoalteromonas tunicata	Allelopathic effect on other algae	Wietz et al. (2013)

 Table 8.1
 Plant-microbe interactions in the aquatic ecosystem

and leaves, wherein several biochemical reactions are completed at the interactive surface and stimulate the elemental cycles in the aquatic ecosystem (Shelake et al. 2018).

4 Biogeochemical Renovations in Wetlands Driven by Microbes

Water quality is improved by wetlands naturally by sedimentation, recycling of micro- and macronutrients, and uptake by microbes and plants (Liang et al. 2006). In the form of sediments, nutrients and pathogens contribute to non-point sources of water pollution that degrade downstream water quality (Carpenter et al. 1998). The procedure of methane formation is constant in spite of the fluctuating composition of the communities. In order, the altering communities may be associated with the pathway of carbon degradation and the subsequent substrates for methane formation (Lu et al. 2015). The rate of methane production in relationship to the variety and dynamics of methanogens was studied in three peatlands with conflicting features: two acidic peat bogs and a minerotrophic fen (Ye et al. 2012). Inducible shifts analyzed in the populations of methanogen in response to substrates (acetate and hydrogen) added to peat in instant cultivation was investigated. The rates of CH₄ production stimulated by acetate amendment in a fen peatland soil increased the relative abundance of Methanol sarraceniaceae (Sun et al. 2012). By contrast, addition of H₂ stimulated CH₄ production in two acidic bog soils and enhanced abundance of the E2 group of Methanol regulaceae. The supply of varied metabolic substrates is a driving force of methanogen species-sorting in wetlands. Therefore, the methanogenic substrate mainly controls methane formation and emission from wetland soils (Bodelier and Dedysh 2013). The elements are required by methanogens for energy generation and strengthening biomass, which has never been observed in marshland systems. Nitrogen fertilizers influencing the consumption of methane in wetland and an upland soil have been shown (Chirinda et al. 2018). As well as nitrogen, the scattering and dissemination of methanotrophic bacteria can perform as an adaptable characteristic in methane cycling in wetland ecosystems (Filstrup et al. 2012). The plantlets and hyaline cells of *Sphagnum* moss are inhabited by methanotrophs and are accountable for the oxidation of CH₄ on its way from anoxic peat layers to the atmosphere. The elemental cycles (Fe–N, S–N cycle) in groundwater and fenland residues are focused on interactions (Fig. 8.3). The nitrate reducers of iron-oxidizing presence and potentially co-occurring iron reducers were assessed in an iron sulfide- and nitrate-rich groundwater in a freshwater wetland (Scherer et al. 2000). Nitrate-reducing iron oxidizers showed a potential role by molecular analyses. Sulfur and nitrogen cycles interact in a wide range of apparent residues, representing disparity in major monitoring factors that were measured (Fru et al. 2012).



Fig. 8.3 Role of prominent wetland species in biogeochemical cycling of trace elements

5 Significance of Microbes in Wetlands Restoration

Unique ecological features that are found in wetlands offer several products and services to humanity (Turner et al. 2000). Wetland loss caused by pollution, flood, biodiversity, drought, land use changes, and climate change can only be restored by the active participation of the microbes present in the wetland (De Groot et al. 2010; Erwin 2009).

5.1 Pollution and Its Control

In several agricultural and urban landscapes, wetlands acts as sinks for environmental contaminants (Jackson and Pringle 2010). Naturally occurring wetlands, such as riparian wetlands, remove nitrate and phosphorus from surface and subsurface runoff and thus reduce the nutrient load of flowing water (Verhoeven et al. 2006). Wetlands in temperate regions have a maximum potential rate for the removal of nitrogen and phosphorus ranging from 1000 to 3000 (kg N/ha/year) and from 60 to 100 (kg P/ha/year), respectively (Sidiropoulos et al. 2017). In India, release of agricultural runoff and untreated wastewaters of urban areas causes much pollution of wetlands (Novotny 1999). Hence, the increasing pollution load degrades the natural wetlands, affecting biodiversity and wildlife habitats.

5.1.1 Removal of Organic Contaminants

Aquatic ecosystems are the most threatened systems because of the massive field applications of various compounds such as chlorinated organic compounds, polybrominated biphenyls ethers (PBEs), polyaromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs) (Shannon et al. 2010; Srivastava et al. 2017). The resident microorganisms are renowned bio-remediators and have the capability to reduce practically all biological compounds by catabolic activity (Haritash and Kaushik 2009). The microbes follow with catabolic degradation of recalcitrant organic compounds to unite organic carbon with electron acceptors, readily obtainable in the rhizospheric regions of terrestrial and aquatic macrophytes (Chandra and Singh 2014). The quantity of microbes and the concentrations of xenobiotic compounds determine the rate of biodegradation in natural waters, following the secondorder kinetics reaction (Suflita et al. 1983). However, the communities of microbes mainly depend upon the species of macrophytes (Van Donk and van de Bund 2002). Additionally, the plants provide organic carbon to the rhizospheric microorganisms to help degrade complex recalcitrant organic compounds, for example, PAHs and pyrenes. Rhizospheric microbial degradation of PAHs provides growth hormones such as indole acetic acid (IAA) as a mutual benefit (Chandra and Singh 2016; Enespa and Chandra 2019). Sinorhizobium meliloti P 221, isolated and identified as a microbe that produced the association of the ectorhizosphere with aquatic plants, has the capability to synthesize IAA after the degradation of PAHs (Srivastava et al. 2017). The dynamic aquatic environment of algae is the best survival mode for bacterial communities because the bacteria use the algal derivative carbon resourcefully to nurture and proliferate (Margulis and Sagan 1997). After proliferation, the bacterial colonies produce odor and taste problems in fresh and potable waters from the degradation of organic and inorganic waste. The biofilms of associated aquatic plants can degrade amines, aliphatic aldehydes, and phenolic substances, and dissolved PCBs and atrazine organic matter (Dodd 2012). Methanotrophic bacteria and a group of proteobacteria utilizing methane as a carbon source for energy are found in the rhizoplane of aquatic plants (Eller and Frenzel 2001). The methanotrophs Methylosinus trichosporium OB3b and Methylococcus capsulatus produce particulate methane monooxygenase (pMMO), which degrades toxic organic compounds and chlorinated ethanes via a cascade of enzymatic reactions containing formaldehydes that later produce the terminal compound of CO₂ (Oldenhuis et al. 1989).

5.1.2 Removal of Inorganic Contaminants

Low levels of metal ions are naturally found in aquatic systems, as they move very slowly from the soil and rocks and do not affect the aquatic microflora. Excessive metal ions are generated in various countries by industrial, agricultural, and municipal waste processes (Bolan et al. 2014). The mobilization of metallic ions in the water is prejudiced by numerous biochemical factors such as pH and electrical conductivity of water, hydrated iron oxides, carbonates of metals, the biofilms of rhizospheric macrophytes, and plant–microbe interactions (Elzinga et al. 2012; Urakawa et al. 2017). The formation of cations in water is adhered by the essential role of the exopolymers (EPS) matrix of biofilm, which inhibits the entrance of metallic ions into the plants (Coetser and Cloete 2005). The roots and submerged parts of aquatic macrophytes retain iron plaque and sequestrations of metallic ions from the water

(Hansel et al. 2001). Precipitation of iron oxide layers from various sources and the production of plant parts occurs by oxidation of iron, or by molecular O₂, or by ironoxidizing bacteria such as Ferroplasma sp. and Leptospirillum ferrooxidans (Vera et al. 2013). The loss of radical oxygen depends on the root porosity of the plants, which improves the level of oxygen at the rhizoplane (Stottmeister et al. 2003). In the aquatic ecosystem, reduction of sulfates is another important metal-removing process after the oxidation of iron, whereby macrophytes with the association of sulfate-reducing bacteria as biofilm degrade sulfate compounds into sulfides, and lower the pH so that metallic ions from the water bodies can be absorbed by the cells of microbes (Mkandawire 2013). The microorganisms also interact with algae to remove pollutants from the aquatic water bodies in spite of the macrophytes (De-Bashan and Bashan 2010). Microalgae such as Chlorella sorokiniana, associated with the bacterium Ralstonia basilensis, adsorb Cu (II) exclusively because of having more binders compared to other metals (Singh et al. 2018a, b). Free-floating macrophytes such as Pistia stratiotes, Eichhornia crassipes, Ipomoea aquatica, and Spirodela polyrhiza are also important in the removal of nutrient ions such as dissolved inorganic nitrogen (Srivastava et al. 2008).

5.2 Biodiversity Hotspots

Natural aquatic habitats or wetlands support species diversity. Most invertebrates and vertebrates depend on wetlands for their entire life cycle (Dudgeon et al. 2006). Recycling of nutrients and photosynthesis take place in the wetland environment and have a significant role in the support of food chains between plant microbes and animals (Holguin et al. 2001). Freshwater ecosystems such as lakes and rivers represent almost all taxonomic groups and support a large diversity of biota in India. Aquatic plant species provide a valuable source of food for waterfowl (Prasad et al. 2002). The Western Ghats in India, a biogeographic region of freshwater ecosystems that runs along with the west coast, has about 290 species of fish, 77 species of Mollusca, 171 species of Odonata, 608 species of aquatic plants, and 137 species of amphibians, covering a total area of 136,800 km² (Arya and Syriac 2018). Also, about 53% of freshwater fish species, 36% of freshwater Mollusca, and 24% of aquatic plant species are prevalent in this region. Similarly, the largest natural aquatic ecosystem in the northeast region of India is the Loktak Lake of Manipur, which supports a rich biodiversity (Jena and Gopalakrishnan 2012). The lake is famous for phumdi, floating mats of vegetation, being a refuge for the endangered Manipur brow-antlered deer also known as Sangai (Rai and Raleng 2011). The 75 species of phytoplankton and 120 species of rotifers have also been recognized in the Loktak Lake. Migratory birds and other wildlife are protected and breed in wetland habitats frequently (Sahoo et al. 2003). Indian wetlands invite several migratory species of birds from western and European countries for seasonal feeding and breeding such as the Bharatpur wildlife sanctuary in Rajasthan, and little Rann of Kutch and coastal areas of Saurashtra in Gujarat (Rangarajan 2005). Approximately 24% of total bird species are recorded as migratory birds in Indian wetlands. More than 450 species of migratory birds are seen every year in the capital city Delhi alone after Nairobi (Keiper et al. 2002).

5.3 Flood Regulator

A wetland regulates floods by absorbing the water and decreasing water flow. Moreover, throughout the loading period, the water flood traps suspended solids and nutrient load. So, the scarcer suspended solids and nutrients will be transported to the rivers and streams flowing into rivers through wetlands (Sharpley et al. 2013). For conventional flood control, reserves such as dykes, dams, and embankments are considered to be a natural capital substitute for wetlands (Maltby 2009). In a river watershed study in Canada the wetland area increased 10%, which reduced 11.1% to 18.6% of the total volume of the flood. Mangrove forest-protected areas have lower losses (US\$ 33.31) in the villages compared to villages without the shelter of mangrove forests. In the Indo-Gangetic floodplains area (a large wetland system of India), many lives are lost and economic output is ruined every year by increased flooding (Bassi et al. 2014). Complementarily, increasing groundwater pumping for farming in the eastern part of India (in West Bengal) adversely affected the wetlands (Alauddin and Quiggin 2008). During the winter and summer seasons, when agricultural water demands increase, lowering of the water table of shallow aquifers actually increases. So, the shallow temporary wetlands are drying up (Bates 2009), which affects more those families who depend upon shallow water bodies for catching fish, irrigation purposes, and domestic water supplies (Knight 2003).

5.4 Repossession of Carbon

The carbon cycle in the atmosphere functions naturally with the sink of the swamps, mangroves, peat lands, mires, and marshes and wetlands. The sediment of wetlands has a high capacity of carbon storage (Mitsch et al. 2013), whereas the existing biomass of plants, animals, bacteria, algae, and fungi solubilizes and stores carbon for the short term in various components in the groundwater and surface waters. However, the wetlands contribute about 40% of global methane (CH₄) emissions (Horwath 2015). Terrestrial ecosystems have less carbon density than wetlands and have more capacity to sequester additional carbon dioxide (Chmura et al. 2003). The soil of wetlands contains 200 times more carbon compared to its vegetation. Organic matter input has a high rate of carbon sequestration in the wetlands and reduces the rate of decomposition (Chapin et al. 2002). A sink of atmospheric CO_2 reverses the restoration of wetlands. The potential of carbon sequestration restoration in the wetlands (over a 50-year period) is about 0.4 ton C/ha/year, as per estimates (Bruce et al. 1999). Most carbon sequestration takes place in the coastal

wetlands of India. About 43,000 km² of coastal ecosystems are located in India (Godoy and Lacerda 2015). In eastern India, the mangrove wetlands are more important than those on the western coast as a carbon sink. Also, these have higher diversity, larger size, and show more complexity from the canal network and tidal creeks (Tomlinson 2016). Generally, the mangroves have a carbon sequestration capability of about 1.5 mt per hectare per year. Methane (CH₄) is one of the primary greenhouse gases emitted by the marshland and wetlands, using approximately 19% of their carbon sequestration potential (Roulet 2000). Similarly, a lagoon along the West Coast of India, Vembaland Lake of the tropical coastal wetlands, releases as much as 193.2 mg/m²/h CH₄. The wetlands functions depend on their biogeochemical processes and hydrology as net producers of greenhouse gases such as CH₄. Mitigation of carbon is their potential role in climate change (Canadell and Raupach 2008).

5.5 Multiple Use of Water Facilities

Water is used for irrigation, domestic activities, fisheries, and recreational uses, groundwater recharge, and flood control and silt capture restoration in wetland tanks, ponds, lakes, and reservoirs (Ramachandra 2001). The largest concentration of irrigation tanks, found in the southern states of India such as Andhra Pradesh, Karnataka, and Tamil Nadu, amount to 0.12 million and account for nearly 60% of India's tank-irrigated area (Thakkar 2000). The same traditional tank systems are also available in the states of Bihar, Orissa, Uttar Pradesh, and West Bengal, and account for nearly 25% of net tank irrigated area. During the monsoon season, harvesting the surface runoff water is vital for using the water in various purposes later (Shah 2009). The water stored in the tanks is used for multiple purposes such as fisheries, domestic activities, nutrient-rich soils, fodder grass collection, and making brick. The tanks are also helpful in the conservation of soil, water, biodiversity, and groundwater recharge in the ecological perspective (Arunachalam et al. 2014). Several lakes of India, such as Carambolim (Goa), Chilka (Orissa), Dal Jheel (Jammu and Kashmir), Deepor Beel (Assam), Khabartal (Bihar), Kolleru (Andhra Pradesh), Loktak (Manipur), Nainital (Uttarakhand), Nal-sarovar (Gujarat), and Vembanad (Kerala), have long provided recreational, tourism, fisheries, irrigation, and domestic water supply services.

5.6 Constructed Wetland Approach for Wetland Restoration

Constructed wetlands (CW) are manmade engineered ecosystems employed for the treatment of waste and restoration of natural wetland integrity (Upadhyay et al. 2016). Restoration in CW is achieved by treating a variety of wastes before it enters into natural systems, thereby reducing the pollution load in the wetlands.

Macrophytes present in the wetland act as a sink for C and other toxic heavy metals by sequestering and accumulation in parts of the plants, from which further extraction removes the heavy metal load (Postel and Carpenter 1997; Rai et al. 2013; Upadhyay et al. 2016, 2017). Generally, the wetlands prevent the entry of pollutants to streams and rivers because the water is recollected from shallow and subsurface regions of runoff (Kent 2000). However, the loading of nutrients in wetlands far exceeds their capability to retain and remove pollutants through nitrification, sedimentation, adsorption, and uptake by aquatic plants because of increased suburbanization and land use changes (Carey and Migliaccio 2009).

6 Management of Wetlands by Institutional Approaches

The Ministry of Environment, Forests and Climate Change (MoEF and CC), Government of India, has the principal responsibility for the management of ecologically sensitive zones (Prasad et al. 2002). Both the Ramsar Convention on Wetlands and the Convention of Biological Diversity were signed by the Indian Government, but the regulatory framework in India for conservation of wetlands is not completely clear (Farrier and Tucker 2000). So, the subsections of wetland management schemes containing the legal context and support of policy for the conservation of wetland are discussed here (Metcalfe et al. 2013).

6.1 Legal Agenda

In India, separate legal provisions for wetland conservation are not found. Other legal provisions indirectly influence wetlands conservation (Junk et al. 2013), including the Forest (Conservation) Act 1980; Biodiversity Act 2002; Wildlife (Protection) Act 1972; Indian Forest Act 1927; Indian Fisheries Act 1857; Environmental (Protection) Act 1986; Wildlife (Protection) Amendment Act 1991; Water (Prevention and Control of Pollution) Act 1974; Territorial Water, Water Cess Act 1977; Maritime Zone of India (regulation and fishing by foreign vessels) Act 1980; Continental Shelf, Exclusive Economic Zone and other Marine Zones Act 1976; and Scheduled Tribes and Other Traditional Forest Dwellers (Recognition of Forest Rights) Act 2006 (Paul et al. 2011).

6.2 Procedure Provision

Procedural support for marshland conservation in India was essentially nonexistent until the early 2000s (McDonald et al. 2007). The international obligations made in the Ramsar Convention then indirectly finalized the selection of other procedures

for management actions for wetlands, such as The Coastal Zone Regulation Notification, 1991; National Conservation Strategy and Policy Statement on Environment and Development, 1992; National Policy and Macro Level Action Strategy on Biodiversity, 1999; and National Water Policy, 2002 (Verma and Negandhi 2011). The Ramsar Convention was signed for the protection of these wetlands. The two sites identified by the Government of India were Chilika Lake of Orissa and Keoladeo National Park in Rajasthan, as International Importance of Ramsar Wetlands in 1981 (Reddy and Char 2006). After that, the National Wetland Conservation Programme (NWCP) was launched in 1985–1986 in partnership with state governments (Arya and Syriac 2018). The Ramsar site was recognized for protection and management only designated under the Programme of MoEF and CC 2007 (Gopal 2013) because of infringement, weed infestation, siltation, catchment erosion, weed infestation, wastewater discharge, and agricultural runoff carrying pesticides and fertilizers. Several procedures were undertaken to capture further degradation and reduction of the recognized wetlands (Cullet et al. 2012). The National River Conservation Plan (NRCP) with an objective to improve the quality of the water of Indian rivers through the operation of pollution works in majority has been operational since 1995 (Ghosh and Ponniah 2001). The National Water Resources Council also distinguishes the need for the conservation of a river access strip and wetlands and water bodies in a systematic manner that is cleared by the National Water Policy, 2012 (a new draft) (Vos and Boelens 2014). The recognized procedure, that there is no official scheme of wetland directive in the country outside the international commitments, was prepared in respect of Ramsar (De Stefano 2010). There is a prerequisite of a legitimately enforceable regulatory mechanism for recognized appreciated wetlands, to inhibit their disintegration and improve their preservation (Freeman and Farber 2004). The National Forest Commission made such approvals, the directions of the National Environment Policy, 2006; and the Central Government notified the Wetlands (Conservation and Management) Rules, 2010 (Huang et al. 2010). The Central Wetlands Regulatory Authority (CWRA) was constituted under the Secretary of Environment and Forest as per the provision under Rule 5 of the wetlands rules (Daily et al. 2009). However, on the basis of implications, only selected wetlands that performed functions for the overall well-being of the people were regulated under these rules (Meli et al. 2014). The selection of wetlands is, under the Ramsar Convention: ecologically sensitive wetlands; recognition of wetlands under sites of UNESCO World Heritage; wetlands at high elevation of 2500 m with an area equal to or greater than 5 ha; wetlands below 2500 m elevation with an area equal to or greater than 500 ha; and other wetlands is recognized by the Authority (Wetlands Rules 2010) (Salzman and Ruhl 2000). Moreover, the river channels included as wetlands under the Ramsar Convention and irrigation tanks are accepted for protection status under the Wetland Rules (Dudgeon et al. 2006).

7 Conclusions

Diversified and unique environments are disseminated across various topographic and climatic organizations supporting the wetlands ecosystem in India. An essential part of the hydrological cycle and its extremely dynamic schemes in the natural forms are considered under this agenda. The microbial communities in wetlands and their processes are needed to ensure successful delivery of ecosystem services by mitigation links to ecological drivers and the protocol of assessment. Microbes are accountable for driving of nutrient cycling, and accepting their dynamic forces in reaction to wetland mitigation accomplishments can offer a view into the suitable administration and nurturing of reinstated areas. If the environmental conditions are appropriately restored, the successful restoration of denitrification will occur. The process of renovation is directed by microbes such as microalgae, bacteria, and plants and assimilated by biological processes. The various components of wetlands such as water biota, plants, algae, bacteria, litter, and soil are active throughout all these processes. The key processes of transformation are ammonification, nitrification, and denitrification, wherein nitrate (NO_3) is converted to harmless nitrogen gas (N₂), which constitutes 85% of atmosphere. Manifold services are provided by the wetlands in India such as irrigation, water supply for domestic purposes, fisheries, and recreation. Recharge of groundwater, control of flooding, sequestration of carbon, and abatement of pollution are accomplished by wetlands, although insufficient attention is present in the national water sector agenda for the management of wetlands. Anthropogenic pressures are generated on many of the wetlands in urban and rural areas: changes in land use in the catchment, industry and household pollution, tourism, encroachments, and overexploitation of their natural capital. No significant progress has been made on the conservation and wise use of wetlands, although India drafted the Wetland (Conservation and Management) Rules in 2010 after countersigning the Ramsar Convention on Wetlands.

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Chapter 9 Phytoremediation: Role of Mycorrhiza in Plant Responses to Stress



Bimal K. Chetri

Abstract Phytoremediation is not a new concept. However, it is important to understand plant's ability to remediate contaminated soil and water alone or in association with microorganisms by absorbing toxic substances, metabolizing them into useful compounds within and eventually transpiring excess of them. Native plants due to their unique characteristics are able to clean up soil and water very often in association with mycorrhizal fungi. This chapter focuses phytoremediation as eco-friendly cleaning tool, its basic strategies, role of native plants in restoring wetland habitats and limitations.

Keywords Phytoremediation · Mycorrhiza · Soil · Water · Native plants

1 Bioremediation and Phytoremediation

Phytoremediation is the method of removing pollutants in eco-friendly manner, by using plants for cleaning the nature (Suresh and Ravishankar 2004; Yadav et al. 2016). Bioremediation is the method of elimination of contaminants (especially heavy metals) from the polluted area by using bio-adsorbents such as bacteria, fungi, and algae (Bestawy et al. 2013).

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2 Phytoremediation Is a Useful Tool to Clean Up Polluted Soil and Water

Phytoremediation is a useful process of cleaning the polluted soil and water. In phytoremediation, plants like cattails are used to treat acid mine drainage and municipal sewage of wetlands (Hinchman et al. 1996). Italian researchers reported Ni accumulation in Alyssum bertolonii (Ouyang 2002). Similarly, the accumulation of lead in the shoot of Indian mustard (Brassica juncea) and high biomass of plant when grown in Pb polluted soil was reported by Blaylock et al. (1997). This shows the ability of mustard to remove the lead from the lead-contaminated area as cited by Ouyang (2002). The other plants like Thlaspi caerulescens and Viola calaminaria are the first plants found to be accumulating high levels of heavy metals (at the end of nineteenth century). Similarly, the plant of genus Astragalus is also capable of accumulating selenium (Lasat 2000; Singh et al. 2018). The movement of metal in plants are mediated by the transport proteins, and sensitive mechanisms maintaining the intracellular metal concentration (Ouyang 2002). Bioremediation is the use of living organism primarily the microorganism to remove pollutants from soil and water. Mostly bacteria and fungi or plants (naturally occurring) are used to degrade or detoxify substances hazardous to human health and environment. These microorganisms are called the bioremediators, and they can be either native to the contamination site or they can be isolated from some other places. Bioremediation is applicable mostly for sites that have been contaminated with organic pollutants (Jadia and Fulekar 2009). The most common examples of plants used in phytoremediation practices are water hyacinths (Eichornia crassipes), poplar trees (Populus spp.), forage kochia (Kochia spp.), alfalfa (Medicago sativa), Kentucky bluegrass (Poa pratensis), coontail (Ceratophyllum demersum), American pondweed (Potamogeton nodosus), and the emergent common arrowhead (Sagittaria latifolia). According to Paz-Alberto and Sigua (2013), tomato and mustard plants were able to extract different concentrations of each heavy metal (Cu, Cr, As, and Pb) from the soils, and scientists favor Brassica juncea and Brassica oleracea for phytoremediation because these plants appeared to remove large quantities of Cr, Pb, Cu, and Ni from the soil. The principle application behind phytoremediation of moderately contaminated soils and waters is the material to be treated is at a medium depth, and the area to be treated is large. The plants should also grow quickly (easy harvesting) besides accumulation and/or volatilization of contaminants (Paz-Alberto and Sigua 2013). Essentially, if the plants are left to die in situ, the contaminants will return to the soil; thus, it should be cut and disposed (Paz-Alberto and Sigua 2013). For example, vetiver grass is useful in phytoremediation as it has several unique characteristics as reported by the National Research Council (Alexander and Smith 1988). These unique characteristics include a massive and deep-rooted system, tolerance to extreme climatic variations (prolonged drought, flood, submergence, fire, frost, and heat waves), and soil acidity, alkalinity, salinity, sodicity, and elevated levels of Al, Mn, and heavy metals (Truong and Baker 1998). Its root system (main, secondary, or fibrous roots) does not expand horizontally but penetrates vertically deep into the soil (up to 5 m). In China, vetiver grass was planted in large scale for pollution control and mine tail stabilization (Chen et al. 2000). In Thailand, vetiver hedges had an important role in the process of decontamination of pesticides, preventing them from contaminating and accumulating in crops (Truong 2000).

Bioremediation is a process that uses aerobic bacteria like *Pseudomonas*, *Alcaligenes, Sphingomonas, Rhodococcus* and *Mycobacterium*, whereas, phytoremediation is an eco-friendly technology where plants are used to repair the contamination of soil, water, and sediments (Oh et al. 2014). Plants that can take up toxic substances are grown, and this specific plant accumulates different substances which cannot be consumed when harvested (bioremediation) (Yadav et al. 2017). For example, *B. juncea* (Indian mustards) is a rapidly growing plant that has an ability to accumulate Ni and Cd in its shoots (Jadia and Fulekar 2009; Chowdhary et al. 2018). Plants used in phytoremediation are:

- Rhizofiltration *Brassica juncea* (for heavy metals), *Helianthus annuus*, *Phaseolus coccineus*, *Eichhornia crassipes*, *Hydrocotyle umbellata* (pennyworth), *Lemna minor* (duckweed), *Azolla pinnata* (water velvet)
- Phytostabilization Brassica juncea
- Rhizodegradation Morus rubra (red mulberry), Malus fusca (crabapple), Maclura pomifera (osage orange), Mentha spicata (spearmint), Medicago sativa (Alfalfa), Pinus taeda (Loblolly pine), Glycine max (soybean), Sorghastrum nutans (Indian grass), Agropyron smithii (western wheatgrass), Bouteloua curtipendula (sideo-ats grama), and Bouteloua gracilis (blue grama), Oryza sativa (rice)
- Phytovolatilization *Medicago sativa*, *Brassica juncea*, *Brassica napus* (canola), *Hibiscus cannabinus* (kenaf), and *Festuca arundinacea* (tall fescue)

It is put in practice by people to speed up the cleaning process without affecting the environment and the organisms (Cheng 2003). The basic concept behind bioremediation is to convert hazardous substances in the environment into less hazardous substances by biological means (Paz-Alberto and Sigua 2013). For example, microorganisms (Fig. 9.1) are the main concern when implementing these methods since they are easy to use and exhibit diverse reactions (Paz-Alberto and Sigua 2013).

Phytoremediation is an environment-friendly technology employed to remove contaminants in the environment by the use of green plants. With the help of plants, soils, sludge, sediments, and water which were contaminated with organic and inorganic contaminants are cleaned in biological means in the phytoremediation (Indelicato 2014).

Generally, the key difference between bioremediation and phytoremediation is that bioremediation includes the overall process of decontamination of the environment using biological agents (microorganisms and plants), whereas phytoremediation is the process which uses only the green plants to decontaminate the environment. Bioremediation includes both in situ and ex situ types, whereas phytoremediation involves only one mode of bioremediation called in situ bioremediation (Indelicato 2014).



Fig. 9.1 Mechanism of salt removal from tsunami-affected soil by bioremediation. (Moqsud and Omine 2013)

3 Role of Native Plants in Bioremediation

Native plants degrade the contaminants by increasing the microbial growth in their root zone (mostly the gram-negative bacteria) (Devinny et al. 2005). Microbe growth increases with the increase in the exudation of carbohydrate, amino acids, and other compound from roots (Devinny et al. 2005). The rhizosphere (soil region subjected to plant root and their associated microorganisms) will have high density of microorganism than the surrounding soil; therefore, rhizosphere bacteria play a dominant role in degrading contaminant. Since bacteria are more abundant, they degrade xenobiotic contaminants (by acting synergistically) (Devinny et al. 2005). Native plants, Coreopsis drummondii and Pteris vittata when planted with Trifolium repens (legumes), have adverse effects on Cu-polluted soil. Since the root of T. repens is symbiotically associated with mycorrhiza, it increases the ability of root to absorb more nutrients and water from soil (Chibuike 2013). Mycorrhiza also increases the resistivity of plant against diseases and detoxifies the toxic substances (Chibuike 2013). Bioremediation can also be used successfully as some microorganisms absorb, precipitate, oxidize, and reduce heavy metals in soils. Mustard (Brassica juncea Linn) soaks up heavy metals such as Cr, Ni, Pb, U, and Zn, and it also acts as a hyperaccumulator for Cu (Indelicato 2014). Seed plants of Brassica napus Linn, water hyacinth (Eichhoria crassipes), and hydrilla (Hydrilla verticil*lata*) are accumulators for Cr, Pb, and Hg (Indelicato 2014). Vetiver grass (Vetiveria zizanioides) (Fig. 9.2) has been used in Hong Kong for land protection and to mitigate soil erosion, with a high tolerance to a range of trace elements such as As, Cu, and Cd. Other grasses worth of mention are colonial bentgrass (Agrostis castellana) and native (Indelicato 2014). Thus, native plants in association with microorganism make bioremediation successful in nature.



Fig. 9.2 Native plants involved in bioremediation (a) *Hypericum perforatum*, (b) sunflower, (c) rapeseed plant, (d) chives, (e) vetiver grass, (f) coconut plants (Indelicato 2014)

The plants used for remediating a particular contaminated can be either native or non-native, but native plants are most desired plants for bioremediation because of following advantages:

- Maintains local heritage of plants
- Restores biodiversity (variety of natural plant and animal life) to a damaged area
- · Requires less maintenance, as plants are already adapted to the environment
- Reduces the risk for introduction of exotic plants to sensitive ecosystem (Devinny et al. 2005)

Native plants are suitable for rhizosphere degradation and phytostabilization. Since native plants are well adapted to the local climate and soils, it supports the animals at that area. For example, according to Hellmers et al. (1955), native plants of South California have dense and deep root systems which help this plant to adapt the seasonal rainfall of the Mediterranean climate as stated by Devinny et al. (2005). Native plants clean up the contamination site as well as help in habitat restoration. Some native plants promote degradation of hydrocarbons through their rhizospheres and at the same time provide food and habitat for rehabilitated ecosystems (Devinny et al. 2005). Native plants species have proper mycorrhizal associates in the soil which affect the availability of root exudates to the rhizosphere and enhances microbial composition in the rhizosphere. Diverse community of native plants can

increase the assemblage of this native plant and provide different aboveground habitats which help in greater rhizosphere degradation (Devinny et al. 2005).

4 Strategies of Phytoremediation

Phytoremediation involves various process of remediation (Fig. 9.3) for the successful reduction of contaminant present in wastewater and soil (Fig. 9.2). The basic strategies are as follows:

i. Phytoextraction

Phytoextraction is a process of planting a crop or plant species that can accumulate the contaminants in the root. Mostly phytoextraction is used to extract heavy metals for the soil where the concentration has reached at toxic level (Upadhyay et al. 2019). This process involves extraction and accumulation of contaminants from the soil by plants species. These contaminants are transferred to shoot and other plant parts. Subsequently, the roots and shoots are harvested to remove the contaminants from the soil. With successive cropping and harvesting, the levels of contaminants in the soil can be reduced (Jadia and Fulekar 2009). Then the plant biomass and the contaminants are disposed or recycled. At the same time, transpiration and volatilization from the plant surface can also remove the contaminants.

It is the subarea of phytoremediation in which plants are used to accumulate the metals and other organic compounds from the soil. If the absorbing plant is an herb,



Fig. 9.3 Processes involved in phytoremediation (Oh et al. 2014)

then the biomass is harvested from the accumulated part (i.e., heavy metal from the soil in plant is harvested). The plants used in extraction of heavy metals are *Quercus petraea*, *Prunus avium*, *Taraxacum officinale*, and *Urtica dioica*, whereas *Brassica juncea* is considered as hyperaccumulator of lead (Stanković and Devetaković 2016). Similarly, hyperaccumulator of Zn is *Thlaspi caerulescens* and *Viola calaminaria*, respectively.

ii. Phytostabilization

The term phytostabilization is defined as a process in which certain heavy metals and organic contaminants in soils can be concentrated in the root zone in which this process does not degrade but reduces the mobility of the contaminant and prevents migration to the deeper soil or groundwater and enhances the precipitation and conversion of soil metals to insoluble forms (Rhizosphere processes) (Morikawa and Erkin 2003). For example, some plants immobilize (restrict movement) contaminants through absorption by roots, adsorption onto root surface and precipitation within the area of plant roots (Jadia and Fulekar 2009). Phytostabilization occurs through the adsorption, precipitation, complexional or metal valence reduction processes. These plants also involve the use of plants and plant roots to prevent contaminant migration via wind and water erosion, leaching, and soil dispersion. The root limits the contaminants mobility and bioavailability in the soil. It decreases the amount of water present in the soil matrix that can form hazardous leachate. The root also acts as a barrier to prevent direct contact with the contaminated soil and prevent soil erosion and the distribution of contaminants (Jadia and Fulekar 2009). According to the United States Protection Agency (2000), phytostabilization is useful in treating lead, zinc, arsenic, cadmium, copper, and chromium. The contaminants are preserved in the ground and surface water, and this process doesn't involve the disposal of hazardous plant biomass (Jadia and Fulekar 2009). Phytostabilization happens through root zone by altering the soil environment (pH of soil). The pH of soil is usually changed by the exudates of root or through the production of CO2. This process not only affects the solubility and mobility of metals but also impacts the dissociation of organic compounds (Adams et al. 2000). According to Stanković and Devetaković (2016), phytostabilization method is used to stabilize the soil, sediments, and sledges (that is present in the root zone and deeper) by using heavymetal-tolerant species that restores vegetation in the contaminated area (also minimizes the contamination).

iii. Phytodegradation

It is defined as a type of phytoremediation in which organic and inorganic substances including atmospheric nitrogen oxides and sulfur oxides are taken up by plants and transformed or degraded (Morikawa and Erkin 2003). Dioxins are reported to be not taken up by plants. Thus, it is simply a use of plants to uptake, store, and degrade contaminants within its tissue (Tangahu et al. 2011). Phytodegradation is the breaking down of contaminants that are absorbed by plants either by metabolic processes within the plant or the breakdown externally through the effect of compounds (enzymes) produced by the plants. It is also called as phytotransformation. Phytodegradation involves uptake of contaminants, metabolism, and transformation.

The compound must be taken up by plants for phytodegradation, but the uptake depends on hydrophobicity, solubility, polarity of the compounds, type of plant, age of contaminant, and other physical and chemical characteristics of the soil (Adams et al. 2000). Metabolism and transformation are the two processes through which plants uptake contaminant.

The breakdown of contaminants in the soil through microbial activity that is enhanced by the presence of the root zone is called rhizodegradation. The concept is that natural substances are released by the plant roots (sugars, alcohols, and acids provide food for soil microorganisms) so that it establishes a dense root mass that takes up large quantities of water and degradation occurs (Tangahu et al. 2011). It involves the metabolism of plant that leads to the breakdown of contaminants taken up by the plants. The breakdown of contaminant may happen external to plants through the release of compounds (enzyme) by the plant (Adams et al. 2000). Phytodegradation occurs when plant absorbs moderately hydrophobic organic compounds, and these absorbed compounds are translocated within the plants (hydrophobic organic compound cannot be translocated in the other part of plants, but it bounds to the root). The molecules that are polar in nature will get translocated in plant parts while nonpolar doesn't (Adams et al. 2000).

iv. Rhizofiltration

In this type of phytoremediation, plant roots take up metal contaminants or excess nutrients from growth substrates through rhizofiltration (root) process, the adsorption, precipitation onto plant roots, or absorption into the roots of contaminants that are in solution surrounding the root zone. Generally, this process is for metals, excess nutrients, and radionuclide contaminants in groundwater, surface water, and wastewater medium (Tangahu et al. 2011). It is the adsorption or precipitation of contaminants in solution surrounding by root zone. The contaminants are accumulated in the root, and then it is harvested by hydroponic techniques. Exudates from the plant roots might cause precipitation of some metals. This technology does not work well with soil, sediments, or sludges because the contaminant needs to be in solution in order to be absorbed to the plant system.

v. Phytovolatilization

It is defined as process in which uptake contaminants from the soil and release into the atmosphere in the modified form through transpiration (Jadia and Fulekar 2009). Phytovolatilization is the plants' ability to absorb and subsequently volatilize the contaminant into the atmosphere (Vara Prasad and de Oliveira Freitas 2003). Phytovolatilization of trichloroethylene (TCE) by poplar (Chappell, 1998) and methyl tertiary-butyl ether (MTBE) by eucalyptus (Newman et al. 1999), selenium by Indian mustard (de Souza et al. 2000), and methyl mercury by tobacco (de Souza et al. 2000) and yellow poplar (Jadia and Fulekar 2009) have been reported earlier. Once volatilized, these compounds may be degraded by hydroxyl radicals in the atmosphere or stay as air pollutants. It is the uptake and transpiration of a contaminant by a plant, with release of the contaminant or a modified form of the contaminant to the atmosphere from the plant through contaminant uptake, plant metabolism, and plant transpiration phytoremediation. The contaminants are transformed into volatile forms and transpiring them into the atmosphere. In laboratory, N. tabacum and Arabidopsis thaliana that had been genetically modified to include a gene that are used to reduce mercuric ions. The ionic mercury is converted to less toxic metallic mercury and then volatilized it (Jadia and Fulekar 2009). It is the method of absorption, adsorption, and precipitation of contaminants (solution surrounding the root zone) by the plant roots in surface water, wastewater, or extracted groundwater (Stanković and Devetaković 2016; Adams et al. 2000; Vishnoi and Srivastava 2007). The process involves absorption or adsorption and translocation of contaminant (depends on the types of contaminant) within the plants (Adams et al. 2000). The exudates from the root may lead to precipitation of some metals, while some contaminants get accumulated within the plants. These contaminants are removed by physically removing the plant (Adams et al. 2000).

In the following section, basic processes for phytoremediation are briefly summarized. Phytoaccumulation: The process is also called phytoextraction and defined as extraction of metals or organics substances by plant roots from contaminated soil and water to translocate them to aerial parts of plants (shoots tissue). Metal hyper accumulators are those plants which accumulate more than 1.0% (Mn) or 0.1% (Co, Cu, Pb, Ni, Zn), or 0.01% (Cd) of leaf dry matter (Fig. 9.4) (Morikawa and Erkin 2003). According to Baker et al. (2000), more than 400 species or about 0.2% of all angiosperms of 80 families are known as metal accumulator, and such plants have been used at Chernobyl Nuclear Power plant accident site in Ukraine (Dobson et al. 1997).



Fig. 9.4 Uptake of metals (Nickel) by phytoextraction (Morikawa and Erkin 2003)
5 Phytoremediation Process of Heavy Metals with Specific Plants Used and Its Limitations

Cotton wood and hybrid poplar trees were used to remove heavy metal, nutrients, and pesticide contaminants of shallow groundwater of East and Middle East (Adams et al. 2000). Poplar tree is used because rate of transpiration in this plant is high. Wright and Roe (1996) found that poplar trees on a landfill transpired 70 acreinches of water per acre of trees (as cited in Adams et al. 2000). Similarly, cotton wood trees in Southwestern Ohio pumped 50-350 gal per day per tree (Adams et al. 2000). The process involves the absorption, translocation, and transpiration of contaminant along with water. Through transpiration, removal of contaminant or modified volatile contaminant takes place. According to Cheng (2003), Eriachne pallescens has got high phytoremediation against Cu contaminant, and Lycopodiaceae and Melastomataceae species were found to be accumulating large amount of Al, in Al-contaminated soil. Similarly, Salix matsudana was found to accumulate high amount of Cd. Leguminous species are considered as most prominent scavenger of heavy metals than any other plants because the root of leguminous species is symbiotically associated with the mycorrhiza (mycorrhiza helps in more absorption of contaminants) (Cheng 2003). Plants absorb heavy metals from the soil, and these heavy metals also get accumulated in root and the aerial part of the plants (Cheng 2003). The accumulated heavy metal either transpires along with water or gets modified and transpires in air (Stanković and Devetaković 2016). Phytoremediation is one of the natural processes of removing the contaminants from the nature, and it has got some limitations.

- i. Phytoremediation is not applicable to shallow streams and groundwater (Vishnoi and Srivastava 2007).
- ii. The plant may suffer from toxicity due to high accumulation of contaminants.
- iii. Though it helps in removing the contaminants in the soil, it also pollutes the atmosphere (Vishnoi and Srivastava 2007).
- iv. Some plants are involved in altering the solubility of toxic metals; therefore, if the solubility of toxic metal is increased, it may leach into the groundwater causing environment risk (Cheng 2003).

6 Phytoremediation Process of Heavy Metals

According to Baker and Brooks (1989), the largest numbers of temperate climate hyperaccumulating species belong to the Brassicaceae, but in the tropics, the Euphorbiaceae is the best represented group. One of the most striking examples of metal hyperaccumulation is displayed by a New Caledonian tree (*Sebertia acuminata*), which has over 11% of Ni in its latex (Baker and Brooks 1989). The plant for phytoextraction would be able to tolerate and accumulate high level of heavy metals, grow rapidly, and be able to produce a high biomass yield (Ensley et al. 1997).

The first reported field trials of metal accumulators on soils demonstrated the feasibility of phytoextraction as per Baker and Brooks (1989). The site was contaminated by Ni- and Zn-containing sludges. The best metal accumulator identified in this trial was *Thlaspi caerulescens* (require 13–14 years of continuous cultivation to clean the site).

Generally, phytoremediation can be a time-consuming process, and it may take at least several growing seasons to clean up a site, and the intermediates formed from those organic and inorganic contaminants may be cytotoxic to plants (Tangahu et al. 2011). Phytoremediation is also limited by the growth rate of the plants and time as compared to traditional cleanup technologies (Tangahu et al. 2011). Phytoremediation may not be the remediation technique of choice and best suited for remote areas where human contact is limited or where soil contamination does not require an immediate response (EPA 2000). Further, the success of phytoremediation may be limited by factors such as growing time, climate, root depth, soil chemistry, and above all low remediation efficiency (Salido et al. 2003).

7 Limitation of the Plants Used in Metal Phytoremediation

- The pH of the influent solution may have to be continually adjusted to obtain optimum metals uptake.
- A well-engineered system is required to control influent concentration and flow rate of metal through the plant.
- · Periodical harvest and ultimate disposal of plant biomass is necessary.
- Metal immobilization and uptake tested in laboratory and greenhouse studies might not be achievable in the field.
- It is limited to shallow soil, streams, and groundwater.
- Absorption of high contaminant substances is toxic to plants as well.
- Climate change and other seasonal factors can increase the treatment period.
- Phytoremediation requires large area (Vishnoi and Srivastava 2007).

8 Phytoremediation Plays Important Role as an Eco-friendly Low-Cost Technology in the Field of Agriculture and Food Safety

Phytoremediation makes the soil or the cleansed site more fertile (Robinson et al. 2003). Therefore, crops and other vegetables can be grown in such areas (not much complex equipment needed to make soil fertile and the process used to make the soil fertile is eco-friendly). In this developing world, the urbanization and industrialization have led to the pollution of agricultural land by adding heavy metals and other organic pollutants in soil (Oh et al. 2014).

If an agricultural field is contaminated with heavy metals and other pesticides or insecticides, phytoremediation is the cheapest and eco-friendly method to improve the quality of the soil (and to remove the contaminant from the soil). Since heavy metal stress inhibits the germination and growth of crops, it leads to reduction of crop productivity (Sinclair and Krämer 2012). Therefore, plants that absorb the contaminant should be planted together with the other crops (make sure no allopathic effect is there in crop) in the field so that these plants absorb the unwanted contaminant and allow the crops to grow (the product will also be free of chemicals like pesticides). Phytoremediation also reduces the movement of pollutant in groundwater, sustains soil structure, and enhances the soil quality and productivity (Oh et al. 2014).

Therefore, phytoremediation is the cheapest method for agricultural field because it prevents the loss of soil resources and energy is fully supplied by the sun (no external energy is required) (Oh et al. 2014). Thus, food safety is also maintained when agricultural pollutants are removed from soil.

The key role of phytoremediation in the field of agriculture and food safety is that phytoremediation is a natural and in situ remediation system done by solar and green plants and can also conserve the soil resources (Cheng 2003). It is inexpensive, does not induce the secondary contamination, can reduce movement of pollutants toward groundwater, sustains the soil structure, and enhances the soil quality and productivity (Wang et al. 2003). In broad sense, phytoremediation does exploit natural plant physiological processes and can be used to decontaminate agricultural soils and food chain safety by phytostabilization of toxic elements; thus, it is a lowcost and environment-friendly technology targeting removal, degradation, or immobilization of contaminants (Schwitzguébel et al. 2011). Contaminants such as heavy metals cause a significant threat to agricultural crops (Neilson and Rajakaruna 2015). It can alter the plant growth and development as intake of such toxins affects important physiological processes such as photosynthesis, respiration, translocation, nutrient uptake, etc. To prevent the huge loss of agricultural products, removal of contaminants is important, but techniques such as solidification, vapor extraction, and thermal desorption are costly and also cause harm to plant productivity.

9 Mycorrhizal-assisted Phytoremediation

There are two common types of mycorrhizae that remediate the polluted soils; it includes arbuscular mycorrhiza (AM) and ectomycorrhiza (EcM) (Doidy 2012). The mostly used mycorrhiza is the AM type because it has the ability to colonize almost all types of plants, whereas EcM colonizes mostly woody species (Chibuike 2013). In the case of AM fungi, highly branched hyphae called arbuscule is surrounded by a plant membrane called the periarbuscular membrane (PAM). The nutrient exchange or movement of molecules takes place between PAM and cell wall of fungi through periarbuscular space (PAS) which is between the fungal cell wall and PAM. PAM unlike the normal cell of plant (non-arbusculated cells)

contains mycorrhiza-inducible transporters that help in transferring the nutrient from the mycorrhizal interface to plant (Doidy 2012). The processes involved in the removal of contaminant are phytoextraction and phytostabilization (Chibuike 2013). The nutrients and other compounds (heavy metals) are absorbed by the fungus and are transported to plant which get accumulated in the plant, thus removing the contaminants from the soil and water.

Generally, mycorrhizal fungi, being the most prevalent beneficial organisms associated with plants, can be applied for phytoremediation purposes (Aroca et al. 2008). Mycorrhiza can assist in phytoremediation either by making contaminants more available for uptake by the plants or by reducing metal toxicity in their host plant and rely on various extracellular (chelation and cell wall binding focus on the prevention of metal entry) and intracellular (binding to nonprotein thiols and transport into intracellular compartments reduce the metal concentration in the cytosol) defense mechanisms (Fig. 9.5) (Coninx et al. 2017). Similarly, ericoid mycorrhiza is best suited for the remediation of metal-polluted, acidic, nutrient-poor soils, as members of the Ericales (plants associated with this type of mycorrhiza) are dominant in these types of environments (Danielson and Visser 1989). Acidic soil conditions increase the availability of potentially toxic metals, which makes it even more challenging for organisms to survive and reproduce in these areas (Danielson and Visser 1989). Mycorrhizal fungi contribute to the degradation of man-made xenobiotic compounds by the process rhizodegradation so that plants absorb such compounds from roots to aerial parts by the process phytoextraction before releasing these toxic elements to the atmosphere as remedy for environment pollution (Allen and Boosalis 1983). Drought is one of the plant stresses which affects growth and development of many plants, but there are some plants species that are drought resistant. There are numerous reports which describe drought tolerance of the plants by fungal symbiosis. Drought stress in plants is due to osmotic adjustments, altered stomatal activity, production of antioxidants, and altered transcriptional and translational regulation, and Malinowski and Belesky (2000) stated that fungal symbiont involves the osmotic adjustments and altered stomatal activity. It is found that



Fig. 9.5 Schematic diagram of plants colonized by ECM (green) root tips, AMF (red) vesicles, and ERM (blue) root hairs. (Coninx et al. 2017)

there is significant increase in drought tolerance in fungal endophytes from the forage grass and tall fescue (Rodriguez et al. 2004).

9.1 Mycorrhiza and How It Is Different from AMF

Mycorrhiza is the symbiotic association between the hyphal fungi and the root of the plant whereby both benefited from each other (the fungi provide nutrients to plants while plants provide fixed carbon to fungi) (Coninx et al. 2017). AMF is a kind of mycorrhizal fungi (called arbuscular mycorrhizal fungi) that colonizes the plant roots and regulates the growth of plant by obtaining fixed carbon from plant for their own survival (Coninx et al. 2017). It was coined by Albert Bernhard Frank describing the symbiotic association of plant roots, and it literally means fungus root (Bagyaraj 2014). According to Coninx et al. (2017), mycorrhiza is broadly categorized into ectomycorrhizae, orchid mycorrhizae, ericoid mycorrhizae, and arbuscular mycorrhizae. Ectomycorrhizae are association between basidiomycetous fungi (genera *Boletus, Suillus, Russula*, etc.) or some ascomycetous fungi with forest tree species in the families Pinaceae, Salicaceae, Betulaceae, Fagaceae, Tiliaceae, Rosaceae, Leguminaceae, Myrtaceae, and Juglandaceae with key role in the uptake of nutrients from soil, protect roots against invasion by pathogens and decompose organic matter (Bagyaraj 2014).

The most common type of mycorrhizal association which is about 85% occurring in crops (agriculture and horticulture) is the arbuscular type of mycorrhizal association, and it's different from other mycorrhizae. It is an association between most tropical plant species except Pinaceae, Betulaceae, Orchidaceae, Fumariaceae, Commelinaceae, Urticaceae, and Ericaceae and fungi genera *Glomus*, *Gigaspora*, *Scutellospora*, *Acaulospora*, and *Entrophospora* (obligate fungi) (Bagyaraj 2014).

The key difference between mycorrhiza and AMF is that there is presence of vesicles and arbuscules in AM fungus (Fig. 9.5) in the roots (Bagyaraj 2014). AMF symbiosis is a unique relationship as some parts of the fungus (intraradical hyphae, arbuscules, and vesicles) are inside the root and some other parts of the fungus (extra radical hyphae and extramatricular chlamydospores) are outside the root in soil unlike mycorrhiza (Bagyaraj 2014).

It is also described as fungus root which serves as water and nutrient transfer interface where both the plant and the fungi are benefited (Mutualism). According to Smith and Read (2008), mycorrhizae can also be formed between hyphal fungi and the underground organs of many lower land plants (Coninx et al. 2017). According to Smith and Read (2008), mycorrhizae can also be formed between hyphal fungi and the underground organs of many lower land plants (Coninx et al. 2017) and AMF is the most common type of mycorrhizae. According to Brundrett (2009) AMF are found in mutualistic relationships with over 74% of flowering plants and with over 80% of vascular plants but host can also be non-vascular, some gymnosperm and angiosperm (Coninx et al. 2017). AMF are the dominant mycorrhizal type in boreal and temperate forests and are generally regarded as obligate

biotrophs. They form a special structure called the arbuscules and vesicles (Coninx et al. 2017). Arbuscules are temporary structures which will stay for around 2 weeks. When they mature, vesicles may act as reproductive structures and act as the site for nutrient exchange between the host and the fungi (Sharma et al. 2015).

9.2 Role of Mycorrhiza in Plant Responses During Drought

It is found that there is a relationship between proline accumulation and drought tolerance. The low proline accumulation in plant is due to less injury by water stress (Rodriguez et al. 2004).

- i. AMF inoculation in *Brassica juncea* has increased the proline content by 63.47% (Coninx et al. 2017). Proline accumulation helps to maintain high osmotic levels in plant cells suffering from water deficit (Cicatelli et al. 2014).
- ii. According to Auge (2002), lower accumulation of sugar in AMF has led to successful avoidance of drought stress as cited in Rodriguez et al. (2004). According to Schellenbaum et al. (1998), lower accumulation of sugar in AMF is due to utilization of sugar by the fungus, e.g., *Glycine max* (Rodriguez et al. 2004).
- iii. Tian et al. (2004) found that there is increase in the activities of antioxidant enzymes in plants inoculated with mycorrhizae during drought conditions, and this reduces the accumulation of intracellular ROS in plants during stress (Rodriguez et al. 2004).
- iv. AMF plants reduce the transpiration rate under drought stress, and they exhibit higher values of root hydraulic conductivity.
- v. AMF increases the root water absorption during drought condition.
- vi. AM symbiosis regulates ABA contents of the host plant under drought conditions (Aroca et al. 2008).

It is found that mycorrhizal plants grew better than non-mycorrhizal with accumulated Cu and Zn. Roots of mycorrhizal plants can accumulate one or both metals at higher concentration (Cicatelli et al. 2014). According to Cabral et al. (2015), mycorrhizal either makes metals more available for uptake by the plants or reduces metal toxicity in their host plant as cited in Coninx et al. (2017). But the mycorrhizal fungi should be able to first establish a mycorrhizal symbiosis for effective phytoremediation. Mycorrhizal fungi have the ability to increase the metal availability in the soil and also increase the transfer of metals from soil to roots. Even if it is harmful for the host plants, the toxic metals are translocated to higher plant parts from roots (Coninx et al. 2017). Ectomycorrhiza association in P. involutus increases phytoextraction of metals. AMF in Oryza sativa could increase phytostabilization of cadmium (Cd). Most of the phytoremediation of organic contaminants are through direct degradation. Mycorrhizal fungi produce surfactant which helps in organic degradation using enzyme and a non-specific free-radical-based mechanism (Coninx et al. 2017). It provides a stable soil for plant growth by production of a substance that binds soil aggregates (glomalin) (Chibuike 2013).

Drought stress in the plant leads to serious changes in the metabolism of nitrogen and carbon and often decreases the photosynthetic activity (reducing assimilation) (Pinior et al. 2005). Therefore AM induces drought stress tolerance in several plants. The AMF increases enhance the supply of phosphorus to plant (Pinior et al. 2005). It was observed that AMF increased the content of polyamines in alfalfa plant and also increased the free amino acid and sugar content in Rosa hybrid (showing the adaptation of mycorrhizal plants to drought) (Pinior et al. 2005). Physiological changes occurred in the AM-induced drought stress-tolerant plant. The changes include modification of parameters (enhances internal entropy) involved in foliar water relation (gas exchange, leaf potential, leaf tissue elasticity, and stomatal behavior) and alteration of root turgor and root to shoot signals (Pinior et al. 2005). According to Wu and Zou (2017), mycorrhizal plants could adapt the drought stress in morphology, especially if leaf epicuticular wax and root morphology and mycorrhizal plants have direct pathway of water uptake by extraradical hyphae. In a study done by Wu and Zou (2017), AMF had shown to enhance drought tolerance in plants (release glomalin into soil, improve soil structure, and regulate water relation of plants or soil). According to Aroca et al. (2008), AM symbiosis enhances plant tolerance to drought through the alteration of plant physiology and the expression of plant stress marker genes (Lsp5cs, Lslea, and Lsnced). Arbuscular mycorrhizal plants always reduced transpiration rate under drought stress and allow a more adequate balance between leaf transpiration and root water movement during drought (Aroca et al. 2008). As experimented by Pinior et al. (2005), Rosa hybrida (rose plants) inoculated fungus Glomus intraradices (arbuscular mycorrhizal) with four different water stress conditions revealed that mycorrhizal association prevented drought damages and maintained higher water contents as compared to a nonmycorrhizal soil. This is because of the aggregating outcome of mycorrhizal hyphae on soil structure (Augé et al. 2001). Also hyphae can enter pores that are too small for root hairs to access and hyphae proliferated well beyond the limit of root hairs giving plants access to more water (Allen and Boosalis 1983).

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Chapter 10 Integrated Approach for Bioremediation and Biofuel Production Using Algae



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Abstract Large-scale industrialization and anthropogenic activities have led inordinate disposal of waste water into fresh water bodies, causing imbalance in aquatic ecosystem and degradation of water quality. Waste water contains significantly high amount of organic, inorganic substances as well as toxic heavy metals. To neutralize the negative impact of waste water, effective remediation processes are required. At present, numbers of conventional waste water treatment technologies have been employed, but they require high operational cost, large input of energy and huge land area, which leads to its failure at the ground level. Therefore, bioremediation of waste water using microalgae has emerged as an alternative approach that provides simple and cost-effective technology of waste treatment with simultaneous production of value-added products. Microalgae are very efficient in assimilating nutrients and other pollutants from waste water for huge biomass production. Harvested algal biomass is a rich source of carbohydrates, proteins, lipids and secondary metabolites that can be used as animal feed, biofertilizer and feedstock for biofuel production. Therefore, this chapter highlights the different mechanisms involved in nutrient removal by microalgae and subsequent utilization of algal biomass for biofuel production.

Keywords Microalgae · Waste water treatment · Biofuel · Nutrient removal

1 Introduction

The last few decades witnessed rapid increase in human population as well as industrial development; consequently, our dependence on fossil fuel has increased in such a way that these finite sources of fuels are at the brink of extinction. Excessive

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utilization of these petroleum reserves has also posed serious hazard to human as well as environmental heath including much serious anomaly, for instance, global warming (Udaiyappan et al. 2017). Furthermore, continuous generation of waste water due to various anthropogenic activities and its disposal without adequate treatment results in water pollution. Phosphorus and nitrogen being the main components of waste water cause eutrophication that further contributes to excess growth of plants and algae; this process results in oxygen depletion followed by total devastation of fresh water ecosystems (Renuka et al. 2013; Gonçalves et al. 2017). Surface water pollution has become a worldwide challenge; in most of the developing countries, human health is facing serious threat as large portion of fresh water bodies are polluted with heavy metals, organic pollutants, eutrophication and acidification (Conway et al. 2015; Salama et al. 2017). A survey conducted in 1993 by the International Lake Environment Committee stated that the eutrophication level in the lakes and water reservoirs of North America, Asia and the Pacific, South America, Europe and Africa are 48%, 54%, 41%, 53% and 28%, respectively (ILEC 1994; Cai et al. 2013).

As discussed earlier, phosphorus and nitrogen are the main factors that caused eutrophication; they are mainly removed during the tertiary treatment with the help of both biological and chemical treatments. There removal comprises several cycles of anaerobic digestion, nitrification and denitrification until acceptable level is reached. Whereas during chemical treatment, excess phosphate and nitrogen are removed by the process of precipitation using common precipitating agent such as iron and aluminium salts (Singh and Thomas 2012). Although both of these processes are very effective, they require huge setup in terms of large land area, high maintenance and operational cost and large manpower that make overall processes very costly and energy consuming (Gonçalves et al. 2017; Queiroz et al. 2007; Udaiyappan et al. 2017).

Microalgae (common term used for eukaryotic green algae and prokaryotic cyanobacteria) offer an optional practice for the treatment of waste water loaded with plenty of nutrients; they have the ability to grow in fresh, brackish, sea as well as waste water (Patel et al. 2017). Microalgae are photosynthetic microorganisms that convert carbon dioxide (CO_2) and water with the aid of solar energy into various bioenergy forms (Wijffels and Barbosa 2010). They are 20% more efficient than other terrestrial plants in terms of photosynthetic efficiency (Lindeman 1942). In addition, algal biomass could be used a sustainable feedstocks for biofuels and other value-added products. At present, on a yearly basis, only 9000 tons of algal biomass is produced worldwide with the production cost of $20-200 \text{ kg}^{-1}$ (Wang et al. 2016; Singh et al. 2018). However, the high production cost of biomass is still the major bottleneck in the production of algal biofuel. Therefore, algal cultivation integrated with waste water treatment (Fig. 10.1) is an alternative and economic approach by which overall cost of algal biofuel production and waste treatment could be reduced (Wang and Lan 2011; Wang et al. 2016). This ability of microalgae makes it useful in the process of coupling waste water treatment to other useful products such as biofertilizers and animal feed (Chinnasamy et al. 2010). Several microalgal species (Chlorella sp; Chlamydomonas reinhardtii; Scenedesmus obliquus; Dunaliella tertiolecta) have the ability to utilize almost 80-100% of phosphorus and nitrogen from



Fig. 10.1 Schematic diagram showing integrated technology of algal biomass production for waste water treatment and biofuel production. (Adapted and modified from Sivakumar et al. 2012)

waste water (Sydney et al. 2011; Zhu et al. 2013); moreover, some species have been reported to uptake much harmful chemical like heavy metals (Upadhyay et al. 2016).

2 Algal Cultivation

Bioremediation of waste water using algae can be carried out by two culture systems, viz., suspension culture and immobilized algal cell system. Both of these systems have their own advantages as well as disadvantages (Mallick 2002; Gómez-Serrano et al. 2015). Suspension culture is rather widely used process in which microalgae are grown in culture flasks, photobioreactors and open ponds (Pires et al. 2013). Culture flasks and photobioreactors are basically used in controlled laboratory conditions that have an advantage of controlling several culture parameters including light intensity, pH, temperature and CO_2 supply, apart from these; they also offer an advantage of higher cellular growth, minimal contamination and evaporation of media (Posten 2009; Ugwu et al. 2008). Besides these advantages, photobioreactors have disadvantage in terms of construction and operational cost. There are a number of photobioreactors that are being currently used such as bubble column, tubular



Fig. 10.2 Schematic diagram showing (**a**) flat plate bioreactor, (**b**) bubble column bioreactor, (**c**) tubular photobioreactor, (**d**) raceway pond. (Singh and Sharma 2012)

and flat plate bioreactor (Fig. 10.2). On the other hand, open pond facility can be used to treat large quantity of waste water at a time. They may be natural ponds, lakes, lagoons and raceway ponds (Fig. 10.2d). Open pond cultivation of algae is rather less expensive as it has lower construction and maintenance cost. But, the major problems associated with open pond system are contamination, lack of mixing of nutrient, lower light availability and loss of water due to evaporation (Lee 2001). Raceway pond system, however, is more effective as they contain paddle wheels that ensure proper mixing of nutrients and availability of sunlight to microalgal cells (Gonçalves et al. 2017; Narala et al. 2016).

Immobilized algal cell system is yet another approach that is being widely used in the industries. The significance of this process lies in the fact that it minimizes the overall cost required to separate algal biomass from the rest of the medium/waste water (Mallick 2002). After waste water treatment, algal biomass need to be separated; if not, it might contribute to 60–90% of total biological oxygen demand (BOD) of effluent (He and Xue 2010). The harvesting process itself is cost intensive and time-consuming; 20–30% of total production cost for algal-based products is utilized by the harvesting process (Fasaei et al. 2018). Therefore, natural and artificial methods of algal immobilization provide an alternative means that prevents free movement of algal cell in the suspension (Tampion and Tampion 1987). The natural process of immobilization is through algal biofilm formation carried out by the natural property of algal cells to adhere to specific surface. On the other hand, algal cell is immobilized artificially by various processes such as capturing in semipermeable membrane, covalent coupling with polymers and entrapment in liquid-liquid emulsions (Hameed and Ebrahim 2007; Eroglu et al. 2015). During this process, the algal cells are entrapped inside the polymer matrix; polymer does not allow the free movement of the algal cell, whereas substrate and the product are able to move freely in and out of the matrix. The most commonly used polymeric matrix for entrapment is alginate and carrageenan. Chevalier and Noüe (1985) reported higher biomass content of microalga *Scenedesmus obliquus* under immobilized conditions; not only biomass, pigments and lipid productivities were also found to be higher under immobilized conditions (Gonçalves et al. 2017). In spite of several advantages, the cost factor associated with the immobilization process to treat large quantity of waste water is a major drawback.

3 Application of Microalgae for Industrial and Domestic Waste Water Treatment

Present-day waste water treatment strategies of industrial and agro-industrial waste have some drawbacks as they produce large amount of sludge. As a result, the disposal and operational cost of this sludge contribute to higher capital investment (Greben and Oelofse 2009). Apart from this, another problem associated with sludge is odour, especially in the countries with average higher temperature. Therefore, modern techniques of waste water treatment using algae, biofilms and membrane filtration offer an alternative opportunity to overcome these problems. After considering their potentials and drawbacks (Table 10.1), microalgae seem to be a way ahead for efficient waste water treatment in comparison to other existing processes (Udaiyappan et al. 2017).

Having rich amount of micro as well as macro nutrients, waste water is a kind of low-cost and readily available medium that can be used for microalgal cultivation (Ding et al. 2015). Phosphate (PO_4^{-3}), nitrate (NO_3^{-1}), ammonia (NH_4^+), urea and trace metals are abundantly present in waste water (Ji et al. 2013). To provide sufficient nutrients to the growth medium/waste water, the ratio of N/P should match Redfield ratio, i.e. 16:1; however, it is not a standard optimum value; the idea is to provide adequate nutrients and support luxuriant growth of algae (Klausmeier et al. 2004). Table 10.2 shows the potential of various microalgae for waste water treatment and biofuel production.

On the basis of type of carbon source, the growth of the microalgae may be autotrophic and heterotrophic. During autotrophic mode of growth, microalgae consume CO_2 , whereas organic carbon source was consumed during heterotrophic mode of nutrition. During treatment, microalgae reduce the amount of nutrients thereby reducing chemical oxygen demand (COD) and BOD of the waste water. Algae-mediated treatment reduces the higher demand of chemicals, energy and cost input to treat the waste water (Prajapati et al. 2013); the nutrient uptake ability of microalgae is exceptionally high due to its small size and large surface area (Bich et al. 1999).

Types of			
treatment	Potential	Drawbacks	References
Membrane	High productivity	Membrane fouling	Qureshi et al. (2005)
	Able to achieve high cell density inside reactor	High cost	-
	Clear permeates for further separation		
Biofilm	High reactor productivity with high cell concentration	Require centrifugation of waste water	Qureshi et al. (2005)
	Longer operation time	Bioclogging in porous media	
	Lower cost		
Anaerobic digestion	Does not use CO ₂	Temperature sensitive	Diamantis et al. (2007), Dobre et al. (2014) and
	Produce biogas	High energy consumption	Zanirun et al. (2014)
	Less sludge formation	Ammonia inhibition	_
	Reduce greenhouse gas emission and global warming	Application mainly on solid waste	

 Table 10.1 Different types of waste water treatment with their potential and drawbacks (Udaiyappan et al. 2017)

 Table 10.2
 Biomass and lipid accumulation potential of algae using different sources of waste water

		Biomass		
Microalgae	Waste water	Content	Lipid content	References
Neochloris oleoabundans	Digested dairy Waste	88.3 mg/L/d	2.57 mg/L/d	Levine et al. (2011)
Botryococcus braunii	Industrial (carpet mill, untreated)	34.0 mg/L/d	13.2 mg/L/d	Chinnasamy et al. (2010)
Dunaliella tertiolecta	Industrial (carpet mill, untreated)	28.0 mg/L/d	15.20 mg/L/d	Chinnasamy et al. (2010)
Scenedesmus sp.	Municipal	0.99 g/L	30.0%	Fortin and
UM284	Wastewater (filtration+ autoclaved)	-		Campbell (2001)
Chlamydomonas mexicana	Piggery waste water effluent (filtration w/ (0.22 µm) membrane)	0.92 g/L	33.0%	Abou-Shanab et al. (2013)
Botryococcus braunii	Domestic sewage	0.64 g/L	36.0%	Chen et al. (2016))
Auxenochlorella	Municipal	2.5 g/L	21.0%	Hu et al. (2012)
protothecoides	Wastewater (filtration+ autoclaved)			

3.1 Mechanism of Nutrient Removal by Microalgae

As discussed earlier, phosphate and nitrogen are the main component of waste water that causes eutrophication. With the help of different pathways, these nutrients are taken up by the microalgae. The understanding of these pathways can be used to improve the efficacy of algae to enhance its phytoremediation potential (Schenk et al. 2008). Mechanism involved in the removal of phosphorus, nitrogen, and carbon is outlined in Table 10.3.

3.1.1 Nitrogen Removal

Nitrogen is one of the most common pollutants of waste water; it is generally found in various inorganic forms such as nitrite, nitrate, ammonia, ammonium, nitric acid, nitrous oxide, nitric oxide, nitrogen dioxide and molecular nitrogen (Barsanti and Gualtieri 2014). Microalgae play an important role in the process of assimilation of inorganic nitrogen (nitrate, nitrite and ammonium) into its organic form such as proteins, amino acids, etc. Blue-green algae (cyanobacteria), on the other hand, fix atmospheric nitrogen into ammonia. Nitrate is thermodynamically stable and commonly found in aquatic environment; however, it cannot be directly assimilated by the algae unless and until it is reduced into ammonium (Gonçalves et al. 2017). Two important enzymes, nitrate and nitrite reductase, play an important role in the reduction of nitrate and nitrite, respectively. Nitrate reductase converts nitrate into nitrite; this reaction is facilitated by reduced form of nicotinamide adenine dinucleotide

Nutrients	Mechanism	Cell incorporation
Carbon		
CO ₂	Integration in the Calvin cycle	Diffusion (5.0< pH <7.0) or active transport (pH >7.0)
Organic	Integration in the respiration metabolism	Diffusion or active transport
carbon		(depending on molecule size)
Nitrogen		
N ₂ -N	Fixation by prokaryotic microalgae (cyanobacteria) into ammonia, followed by conversion into amino acids	
NO ₃ -N and NO ₂ -N	Reduction into ammonium, followed by conversion into amino acids	Active transport
NH ₄ -N	Direct conversion into amino acids	Active transport
	Stripping due to volatilization (high pH values and temperature)	n.a.
Phosphorus		
PO ₄ -P	Phosphorylation	Active transport
	Chemical precipitation (high pH values and	n.a.
	dissolved oxygen concentration)	

 Table 10.3
 Mechanism involved in nutrient removal by microalgae (Gonçalves et al. 2017)

(NADH), followed by further reduction of nitrite into ammonium by the enzyme nitrite reductase (Eqs. 10.1 and 10.2). Finally, the enzyme glutamine synthase catalyses the formation of amino acid glutamine from ammonium in the presence of glutamate and adenosine triphosphate (ATP) (Hellebust and Ahmad 1989; Cai et al. 2013; Gonçalves et al. 2017).

$$NO_{3}^{-} + 2H^{+} + 2e^{-} \xrightarrow{Nitrate reductase} NO_{2}^{-} + H_{2}O$$
(10.1)

$$NO_{2}^{-} + 8H^{+} + 6e^{-} \xrightarrow{Nitrite reductase} NH_{4}^{+} + 2H_{2}O$$
(10.2)

The assimilation of ammonium requires least energy as it does not involve any redox reaction. Maestrini et al. (1986) reported that the ammonium is the preferred form of nitrogen source, as algae do not assimilate nitrate until and unless ammonium is completely consumed. Therefore, ammonium-rich waste water can readily be consumed to produce higher biomass of algae. Nevertheless, there are few reports indicating that the higher concentration of ammonium has inhibitory effects on the growth of the algae; the optimum ammonium concentration ranges from 25 to 1000 μ mol per litre of the culture medium/waste water (Morris and Syrett 1963; Collos and Berges 2004).

3.1.2 Phosphorus Removal

Phosphorus is another important nutrient that is mainly responsible for the eutrophication of fresh water bodies (Correll 1998). Besides this, it plays an important role in algal cell growth and metabolism and is found as a chief component of lipids, nucleic acids and proteins. Inorganic phosphorus enters microalgal cell in the form of $H_2PO_4^-$ and HPO_4^2 - through active transport (Chalivendra 2014). Conversion of inorganic to organic form of phosphate inside microalgal cell is carried out by substrate-level phosphorylation, oxidative phosphorylation and photophosphorylation (Martinez et al. 1999). These three processes generate adenosine triphosphate (ATP) from adenosine diphosphate (ADP) with the input of energy. In case of substrate-level phosphorylation and oxidative phosphorylation, the energy comes from mitochondrial electron transport system and through oxidation of respiratory substrates, while, during photophosphorylation, energy come from light through photosynthesis (Kuenzler 1965). Besides taken up by the algal cells, phosphate removal is also carried out by precipitation at higher dissolved oxygen concentration and pH levels (>8.0) (Cai et al. 2013; Gonçalves et al. 2017).

3.1.3 Carbon Fixation

In microalgae, photosynthesis plays an important role to assimilate carbon in the form of CO₂, either from atmosphere or from industrial flue gases. Autotrophic algae assimilate inorganic form of carbon, while heterotrophic algae take up organic carbon from the sources such as glycerol, glucose, acetate and ethanol. At lower pH levels (pH 5.0–7.0), soluble carbonates serve as a source of CO₂ that enters into the algal cell through diffusion. At higher pH values (\geq 7.0), the main source of inorganic carbon is bicarbonate that transported actively inside the microalgal cell with the help of enzyme carbonic anhydrase (Neilson and Lewin 1974; Picardo et al. 2013; Sydney et al. 2014). Within the microalgal cell, bicarbonate is converted into CO₂ followed by conversion into energy-rich molecules by the action of ribulose bisphosphate carboxylase/oxygenase (rubisco) (Gonçalves et al. 2017).

3.1.4 Heavy Metals Removal

Apart from phosphate, nitrogen and carbon, waste water also contains heavy metals. Industries such as tanneries, petroleum refineries, metal plating, battery manufacturing and mining use chemicals which are loaded with huge quantity of heavy metals; waste water from these industries contain significant amount of heavy metals (Eccles 1999). As heavy metals are non-biodegradable, various methods such as chemical precipitation, filtration, ion exchange, chemical oxidation/reduction, electrochemical treatment and evaporation are being used to get rid of these heavy metals (Ahluwalia and Goyal 2007). But, the production of toxic sludge is the biggest problem associated with these processes; moreover, these processes are cost intensive, and most of the time, the removal efficiencies of metal ion is very low (Perales-Vela et al. 2006; Udaiyappan et al. 2017). Therefore, much effective and modern technique of microalgal-assisted waste water treatment is considered as one of the best solutions for heavy metal removal. Various microalgal species are having inherent ability to synthesize certain peptides that have the ability to bind with heavy metals. When compared to other biological entities such as fungi, bacteria and yeast, heavy metal adsorption capability of microalgae is significantly high due to the presence of several biomolecules (proteins, polysaccharides and lipids) on their cell wall (Tüzün et al. 2005). These bimolecular have a number of functional groups, for instance, hydroxyl, sulphate, phosphate, carboxyl and amine, that are involved in binding metal ions very tightly (Gong et al. 2005). Not only living cell but dead microalgal cells have also been reported to have biosorbent capabilities for heavy metal bioremediation (Monteiro et al. 2009); however, bioconcentration capacity for metal ions is dependent on several factors such as pH, temperature, nutrient availability, cell number and size, structure and concentration of chemical (Kosek et al. 2016).

4 Biofuel from Microalgae

Biofuel is defined as fuel which is derived from biological feedstock. On the basis of the feedstock, biofuel is grouped into three main categories, i.e. first-, secondand third-generation biofuels. The feedstocks of first-generation biofuels are basically food crops, and the major disadvantages associated with these fuels are increased prices with shortage of food supply and utilization of arable land for their cultivation (Mandotra et al. 2014). The second-generation feedstocks are mainly lignocellulosic biomass that comprises food processing and agriculture residue and nonfood crops. The disadvantages with second-generation biofuel are the requirement of cultivable land area, slow growth rate and physical and chemical treatments for its conversion to liquid fuels suitable for transportation (Chisti 2008). Thirdgeneration biofuel is derived from algal feedstock. There are a number of advantages of using microalgae for biofuel feedstock; they can be grown in a wide variety of waste water with wide range of pH and chemical composition. Few microalgal species have been reported to yield as much as 80% lipids of their dry cell weight (Chisti 2008; Mandotra et al. 2014, 2016). At present, several new technologies have been applied to improve the efficacy and reduce the overall production cost of microalgal-derived biofuel (Mandotra et al. 2018).

Biodiesel production from microalgae is carried out by extraction of lipids followed by transesterification to convert them into fatty acid methyl esters (biodiesel) (Kumar et al. 2016). Apart from biodiesel, biohydrogen and biomethane are also produced using certain microalgae; during this process, algae provide carbon source for methanogens. On the other hand, hydrogenase enzyme plays a key role in the production of hydrogen. Few species of *Chlamydomonas* and *Scenedesmus* have been reported to produce considerable amount of hydrogen under sulphur-deprived condition (Nguyen et al. 2009; Dasgupta et al. 2015). At present, much of the efforts have been made on microalgal-based bioethanol production. During ethanol production, microalgal biomass is used as carbon source for certain bacteria and yeast that catalyses the production of bioethanol (de Jesus Raposo et al. 2013; Udaiyappan et al. 2017).

4.1 Transesterification

Transesterification is a chemical reaction in which fats or oils are converted into fatty esters and glycerol (Fig. 10.3). The process of transesterification or alcoholysis is reversible in nature; therefore, excess of alcohol is used to shift the reaction equilibrium towards the product formation. Reaction rate and product yield are improved with the use of catalyst that catalyses the stepwise conversion of triglyceride to diglyceride to monoglyceride and finally to glycerol with the production of 1 mole of fatty ester at each consecutive step (Leung et al. 2010).



Fig. 10.3 General reaction of transesterification

There are three main categories of catalysts used in transesterification process, viz., enzymes, acids and alkali. At commercial scale, enzymes are not very much popular, as they are costly and require long reaction time. The soap formation is, however, negligible during enzyme-catalysed transesterification that makes purification process more simple. Alkali and acid catalyst are widely used in transesterification process (Leung et al. 2010). They are broadly divided into homogenous and heterogeneous catalysts; homogeneous catalysts are named so because they are in the same phase as that of reactants (soluble catalyst) (Leung et al. 2010). On the other hand, heterogeneous catalysts are in different phase that of reactants, immiscible liquids (catalysts) also comes under this category (Chalivendra 2014). Homogenous catalysts have higher activity, low temperature and pressure requirement and often more efficient than heterogeneous catalysts. Low-cost sodium and potassium hydroxide and concentrated sulphuric acid are commonly used as alkali and acid homogenous catalysts, respectively (Leung et al. 2010). Most of the heterogeneous catalysts are in solid phase; therefore, they are easily separated from the product and do not require the washing step. Calcium oxide and titanium dioxide are most commonly used alkali and acid heterogeneous catalysts, respectively (Singh and Singh 2010).

4.2 Hydrotreating and Hydrocracking

Hydrotreating is a traditional refinery process that can be used to convert algal lipids into a drop-in (does not require engine modification) hydrocarbon fuel (Rye et al. 2010). During this process, heteroatoms (oxygen, nitrogen and sulphur) are removed from the fuel up to the extent that fulfils the minimum requirement of the American Society for Testing and Materials (ASTM). The major purpose of this process is to remove oxygen from the triglyceride, so as to release alkanes from lipid, propane from glycerol backbone and water from oxygen molecule. Hydrocracking, on the other hand, is the process of conversion of large molecule of crude algal oil into smaller and more volatile one. But the major disadvantage associated with this process is the lower oil yields due to the evaporation of lighter fractions (Duan and Savage 2011).

5 Conclusions

The present chapter reviews the potential application of microalgae for waste water treatment and biofuel production. Increasing demand of energy sources, global warming and pollution of fresh water bodies are major global concern. As far as agricultural, industrial and municipal waste is concern, several conventional technologies are being employed for their treatment and disposal into fresh water bodies. But these technologies are not as effective as they are very costly and energy intensive. Microalgal-based bioremediation offers cost-effective means of reutilization of nutrients for biomass production. Microalgal biomass is utilized as animal feed, biofertilizer and biofuel feedstock. Being a third-generation biofuel feedstock, microalgae offer a number of advantages over other fuel cops for sustainable biofuel production. Algae-based integrated technology of nutrient removal and biofuel production is a sustainable approach; however, further research is needed to explore different waste water sterilization techniques to make the process more effective.

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Chapter 11 Dual Role of Microalgae: Phycoremediation Coupled with Biomass Generation for Biofuel Production



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Abstract Environmental pollution has become a worldwide concern for developing as well as developed nation. During the last two decades, a serious attention has been given in the management of environment pollution caused by hazardous material. Currently, water pollution is a serious threat for mankind which continuously deteriorated due to industrial revolution. Various physicochemical processes such as precipitation, evaporation, ion exchange, filtration, etc. are being used in the treatment of wastewater. However, several disadvantages are associated with these processes. Algae are the photosynthetic microorganism having potential to grow in both fresh and marine water bodies and can be safely utilized for contaminant removal from wastewater without imposing any hazard to the environment. The term "phycoremediation" is now being used for the process which involves algae for the removal or biotransformation of pollutants from wastewater. Apart from removal of contaminants, they also reduce biological and chemical oxygen demand of water bodies. Therefore, algae are now emerging as a desirable treatment option and could be a sustainable biomass feedstock for biofuel production. So, the dual use of microalgae, i.e., phycoremediation, as well as biomass production is a feasible option. Therefore, this chapter provides a detailed account regarding the wastewater, phycoremediation, nutrients and heavy metal uptake mechanism, and potential benefit and limitation of using wastewater as a source of nutrients for cost-effective biofuel production from microalgae.

Keywords Wastewater \cdot Microalgae \cdot Biofuel \cdot Phycoremediation \cdot Sustainable energy

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1 Introduction

Water pollution is an alarming problem for the whole world. Population burst coupled with industrialization caused serious threat to the environment due to release of millions of liters of untreated waste to nearby water bodies (Singh and Pandey 2018a, b). Coal, the unsustainable source of energy, was the primary catalyst for industrialization and to meet the increasing demand of fuel for fast-growing population; thus, exploiting of petroleum fuels and natural gas increased (Gupta and Demirbas 2010). The major drawback associated with the use and dependence on fossil fuels is their limited resources. In a study, it has been stated that with this current consumption rate, petroleum reserves will exhaust in less than 50 years. Moreover, use of fossil fuel causes adverse effect on our health and environment (Rawat et al. 2011) with undesirable consequences, i.e., release of CO₂ in the environment, depletion of fossil fuel reserve, and global warming (De La Torre Ugarte 2000). Burning of fossil fuel causes release of CO₂ a greenhouse gas which has direct effect on the environment. The global CO₂ emission increased from 22.7 billion tons in 1990 to 33.9 billion tons in 2011 (Judkins et al. 1993; Ma et al. 2015). A study conducted by Winkelman et al. (2015) shows that continuous burning of petroleum reserve is enough to melt Antarctic ice sheet which result in increased global sea level (Winkelmann et al. 2015). The vegetation in the Arctic region increased considerably from 1984 to 2012, owing to the increase in temperature, the changes in the annual growing season, soil physiology, and soil nutrition (Ju and Masek 2016). So, there are drawback associated with fossil fuel dependence and physicochemical treatment of wastewater. Keeping this thing in mind, scientist around the world is searching for alternative resources which not only efficiently and economically depollute the wastewater but also helps in the production of renewable source of energy to move from petro-economy to bioeconomy. In this regard, algae seem to be the appropriate choice to function as an eco-friendly tool for treatment of wastewater with biomass production coupled to biofuel generation. Phycoremediation is a promising option for treatment of wastewater as it lessens the requirement of chemicals and energy than conventional wastewater treatment methods, i.e., centrifugation, filtration, floatation, gravity settling, etc. (Wu et al. 2012).

It has been estimated that as many as 200,000–800,000 species exist, of which only about 35,000 species have been identified and described (Tabatabaei et al. 2011). It is reported that algal cellular respiration produces approximately half of the atmospheric oxygen on earth and consumption of vast amounts of the greenhouse gas carbon dioxide (Chisti 2007). Microalgae can be cultivated in nonarable land by utilizing brackish or wastewater as growth medium of food production (Chisti 2007; Dismukes et al. 2008). Alga has potential to produce bio-hydrogen (Ghirardi et al. 2000). Integrated use of microalgae in biofuel, bio-hydrogen production coupled to wastewater treatment emphasizes its potential applications. Downstream processing of biofuel production from algae is receiving increasing attention as it significantly contributes 60% of the total biodiesel production cost. Apart from this, microalgae play an important role in aquatic system, i.e., primary

producers, water quality indicators, biofuel feedstock, and pharmaceutically important bioactive compound and dyes. The fossil algae are being used to reconstitute the lake evolution, climate change, and pollution level (Singh et al. 2017).

It has been reported that when microalgae are grown under controlled condition, it produces >20 times more oil/hectare than the terrestrial oilseed crops (Chisti 2007; Benemann 2008; Sheehan et al. 1998). However, the investment and downstreaming cost of algae-based biofuel production system are still very high (Tampier 2009). The concept of microalgae- mediated wastewater treatment was introduced by Oswald and Gotass (Gotaas and Oswald 1955). High-rate algal ponds (HRAPs) are shallow, open, and raceway ponds and have been used for the treatment of wastewaters (municipal, industrial, and agricultural) and algal biomass generation. There is an increasing demand of clean water and sustainable energy. This demand can only be sustained through using pioneer technology, which may improve energy efficiency, greenhouse gas (GHG) mitigation, and production of clean and safe water with low cost and low energy consumption (Elimelech and Phillip 2011). Algal biomass contains significant amount of proteins, essential amino acid, fatty acids, carbohydrates, chlorophylls, carotenoids, vitamins, etc. that can be utilized as health supplements for humans and animal feed and in cosmetics and pharmaceutical industry (Kay and Barton 1991). Alga produces several secondary metabolites that has been investigated for their medicinal properties and reported to possess antibacterial, antioxidants, antifungal, anticancer agents, anti-inflammatory, and antidiabetic activities (Sarkar et al. 2006). This chapter describes the applicability of microalgae in phycoremediation as well as in wastewater treatment.

2 Physiochemical Treatment of Wastewater

Water pollution has been in existence since time immemorial (Singh and Pandey 2018b). Dumping of solid and liquid wastes in nearby water station seemed convenient for humans, which leads to water pollution. Wastewater treatment is an important initiative, for the betterment of society and our future (Rawat et al. 2011). Water is a rare and precious gift to humans, and approximately 0.03% of earth's water reserves constitutes the water stations, which is useful for human exercises (Singh and Pandey 2018a). Industrial revolution and population burst result in the constantly growing demand for useful water, the supply of which remains constant; therefore, there is an increasing demand over supply (Armaroli and Balzani 2007). Hence, existing situation demands water consumption minimization as well as to return it back to the earth with minimum possible pollution because of limited potential of self-purification in water bodies (Singh and Pandey 2018b). Inclusive information about the nature and composition of wastewater is essential for design and operation of wastewater treatment units (Singh and Pandey 2018b).

On the basis of chemicals and techniques used, treatment of wastewater can be classified into three types, i.e., physical, chemical, and biological treatment methods. Figure 11.1 enlists the unit operations involved within each category. Out of



Fig. 11.1 Unit operations involved in physical, chemical, and biological wastewater treatment methods (Singh and Pandey 2018b)

these three treatment methods, physical treatment strategies are the most commonly used techniques. This method involves the use of mechanical forces such as centrifugation, filtration, and gravitational settling for contaminant removal from wastewater (Upadhyay et al. 2019). The other wastewater treatment method is chemical treatment technique which utilizes the chemical reaction to depollute the wastewater (Upadhyay et al. 2019). Chemical treatment processes always been used in combination with physical and biological methods. Chemical treatment method has disadvantages, and the drawback linked to use of chemical treatment methods is that it results in a net increase in the dissolved content of wastewater (Armaroli and Balzani 2007). This is an important thing to keep in mind if water has to be reused. However, biological treatment method involves the use of microorganism to treat wastewater in primary, secondary, and tertiary process of waste treatment (Madigan et al. 1997; Maier et al. 2000).

3 Phycoremediation of Wastewater

Phycoremediation is broadly defined as the utilization of algae for the removal of contaminants from water. The term "phycoremediation" was coined by John J. in 2000 to denote remediation carried out by microalgae. However, the first report regarding the involvement of microalgae for wastewater treatment was reported by

bacteria, heavy metal, biological oxygen demand (BOD), and chemical oxygen demand (COD) (Raouf et al. 2012; Olguin et al. 2003; Rawat et al. 2011). Algaebased wastewater treatment is applicable to various types of wastewater, i.e., human sewage, industrial wastes, agro-industrial wastes, livestock wastes, piggery effluent, food processing waste, and other agricultural wastes (Raouf et al. 2012). Microalgae, both aerobically and anaerobically, are being used for treating industrial effluents. Remediation is generally subject to an array of regulatory requirements and also can be based on assessments of human health and ecological risks where no legislative standards exist. Phycoremediation of municipal sewage has been a subject of research and development for several decades (Oswald 1963, 1988). Microalgal biomass also has potential to quench or absorb xenobiotics or heavy metal from the polluted wastewater (Upadhyay et al. 2016). Additionally, the algal systems can also be utilized for treating acidic waters, CO₂ sequestration, biotransformation, and degradation of xenobiotics and toxic element (Dominic et al. 2009; Gupta et al. 2016; Leung et al. 2014; Olgun 2003). Phycoremediation is one-step efficient wastewater treatment method, whereas conventional wastewater treatment processes are multistep and require intensive chemicals and energy, therefore very expensive. Phycoremediation also results in the photosynthetic aeration and therefore reduces BOD and COD of wastewater (Munoz and Guieysse 2008). Wetlands are those areas that are saturated with surface or groundwater at a level to support the life of vegetation (Upadhyay et al. 2019). It generally includes bogs, swamps, marshes, and similar areas. Natural wetlands are those that do not require human support for formation (Verma et al. 2012). However, natural wetlands are not effective in removal of pollutants from wastewater, since water often short-circuits through natural wetlands, giving little time for treatment (Verma et al. 2012). To overcome this problem, wetlands are now being constructed to increase the effectiveness of phycoremediation process by targeting either specific pollutants or group of pollutants. Physiochemical property of wetland gives an insight about pollutant remediation. Constructed wetlands are considered as complex ecosystem because of inconstant hydrology, species diversity, soil and sediment type, and water composition (Upadhyay et al. 2019). Constructed wetlands are being predominantly intended to eliminate a wide variety of contaminants such as bacteria, enteric viruses, suspended solids, nutrients (N and P), heavy metals and metalloids, volatile organic compounds, pesticides, explosives, and petroleum hydrocarbons and additives (Hazra et al. 2011). These pollutants should be precisely removed or bio transformed for the success of phycoremediation. There are several types of constructed wetland treatment strategies. However, microalgae grown in constructed wetland have potential to remove nutrients, heavy metals, and reduction in the level of biological oxygen demand as well as chemical oxygen demand without using arable land (Upadhyay et al. 2017). In addition to wastewater treatment, algal biomass produced can be utilized to extract lipid which by the process of transesterification can be converted to biofuel (Upadhyay et al. 2019). Carbon chain length of produced triglycerides depends upon the species and growth condition (Herath and



Fig. 11.2 An integrative approach phycoremediation coupled to biofuel generation at constructed wetlands

Vithangen 2015). Algal biomass can be directly used as human food, supplements, or animal fodder, and it has been reported to produce several by-products such as dyes, polyunsaturated fatty acid, antioxidants, vitamins, anti-cancerous, and hepatoprotective agent (Fig. 11.2) (Singh et al. 2017).

3.1 Removal of Nitrogen and Phosphorus Compounds

Various anthropogenic activities are responsible for the presence of nitrogenous and phosphatic compounds in wastewater. Wastewater is treated by both aerobic and anaerobic biological degradation; however, the treated water still contains inorganic compounds (Barsanti and Gualtieri 2006). Ammonium (NH_4^+) ion is the most abundant form of nitrogen in wastewater and others are nitrate (NO_3^-), nitrite (NO_2^-), or nitrogen (N_2) (Barsanti and Gualtieri 2006). Presence of unionized ammonia or nitrate/nitrite in higher concentration is toxic to aquatic organisms and humans, as well as their presence causes eutrophication/microalgal blooms in wastewater is essential prior to discharge to nearby water bodies.

Nitrogenous compounds are necessary for the biosynthesis of peptides, proteins, ribonucleic acid (RNA), deoxyribonucleic acid (DNA), etc. (Cai et al. 2013; Conley et al. 2009). Microalgae assimilate nitrogen by converting inorganic form to organic

form required for cell synthesis. However, the most preferred form of inorganic nitrogen by microalgae is ammonium ion because it can easily be converted to amino acid glutamine without the involvement of redox reaction therefore utilizes less cellular energy (Cai et al. 2013; Flynn et al. 1997). (NO_3^-) and (NO_2^-) are also assimilated by microalgae by reducing them to ammonium ion. However, this reaction pathway is complex and requires various enzymes and intermediate product (Dortch et al. 1984). Reduction of nitrate to nitrite is mediated by an enzyme nitrate reductase, afterward nitrite to ammonium by nitrite reductase (Cai et al. 2013; Flynn et al. 1997). Apart from utilizing nitrogen inside cell indirect removal, ammonia stripping also occurs because of increased pH with algal cultivation (García et al. 2000).

Phosphorus is another important macronutrient that plays a key role in cellular metabolic processes (Tiessen 1995). It is present in nucleic acids (DNA, RNA), proteins, lipids, and the intermediate of biosynthesis and metabolism of nucleic acids, carbohydrates, and proteins. Major forms of phosphorus present in wastewater are orthophosphate, polyphosphate, or organic phosphate; however, the bioavailability of phosphorus varies with chemical speciation (Schindler 1977). Nonetheless, higher nitrogen and phosphorus concentration lead to the eutrophication in water bodies (Schindler 1977; Tiessen 1995). Agricultural and domestic wastes are the major sources of phosphorus in wastewater (Bennett et al. 2001; Soranno et al. 1996). Therefore, wastewater needs further treatment for the removal of phosphorus at acceptable level before disposal to natural system (Kadlec and Knight 1996).

Microalgae are reported to utilize phosphorus from wastewaters mainly in the form of orthophosphates (HPO4²⁻ and H₂PO⁴⁻) and utilizes the orthophosphates during biosynthesis of various compounds such as nucleic acid, phospholipid, and protein via phosphorylation (Powell et al. 2009). It is also used in various metabolic processes which utilize ATP/ADP as energy transfer processes, as it forms the primary part of ATP and ADP (Conley et al. 2009). During favorable condition, excess amount of phosphorus is taken up by microalgae and stored it in the form of polyphosphate granules for future uses (Rasoul-Amini et al. 2014). Acid-soluble polyphosphate granules are directly utilized in biosynthetic processes, whereas acid insoluble granules are stored for future use when P is limited or exhausted (Powell et al. 2009). Like nitrogen, indirect removal also occurs in case of phosphorus because algal culture results in increased pH which causes precipitation of phosphate (Nurdogan and Oswald 1995). Table 11.1 shows the nutrient (N and P) removal efficiency of some reported microalga.

3.2 Reduction in BOD and COD Level

BOD are broadly defined as amount of dissolved oxygen needed by aerobic microorganisms to break down organic compounds present in the given water sample (Fig. 11.3) (Singh and Pandey 2018b). Therefore, it is a measure of oxygen demand by bacteria to metabolize the organic compound. Chemical oxygen demand (COD) measures the organic compound that can be chemically oxidized rather than just the

gorySpeciesWaste stream typeProcess time (day)Removal L^-1Initial timitialRemoval friciency (%)Removal conc. MgRemoval friciency (%)Removal conc. MgRemoval friciencyroophyteChlorella sp.DigestedBatch21100-24076-8315-3063-75Wang eroophyteChlorella sp.DigestedBatch3168 $8-19^{n}$ 10-12 $8-20^{o}$ Lee andC. kesslerimanure3168 $8-19^{n}$ 10-12 $8-20^{o}$ Lee andC. sorokinianaMunicipalBatch10 $ -$ 22HongysC. ukgarisIndustrialBatch1013-41023-100°5-846-94°Alan aC. ukgarisIndustrialBatch1013-41023-100°5-846-94°CondiC. ukgarisIndustrialBatch2-1013-41023-100°5-846-94°CondiC. ukgarisIndustrialBatch2-1013-41023-100°5-84-4212-100(2006)C. ukgarisMunicipalBatch2-1048-155055-884-4212-100(2006)C. ukgarisMunicipalBatch2-1048-155055-884-4212-100(2006)C. ukgarisMunicipalBatch2-1048-155055-884-4212-100(2006)C. ukgarisMunicipalBatch2-1514-4430-100°20		יו דיווי אווא מווח די		n na	5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5 5	Total nitrog	en	Total phosp	horus	
ι SpeciesWaste stream typeProcessRemoval time (day) L^{-1} Removal efficiency (%) L^{-1} $(\%)$ ReferencinghyteChlorella sp.DigestedBatch21100-240 $76-83$ 15-30 $63-75$ Wang eC. horsella sp.DigestedBatch21100-240 $76-83$ 15-30 $63-75$ Wang eC. horsella sp.ArtificialBatch3168 $8-19^{9}$ 10-12 $8-20^{9}$ HenanceC. pyrenoidosaIndustrialFed-batch5 267 $87-89$ 56 $45-72$ HongyaC. pyrenoidosaMunicipalBatch10 $$ $$ 22 70HenanceC. wugarisArtificialBatch1-1013-410 $23-100^{\circ}$ $5-8$ $46-94^{\circ}$ Aslan aC. wugarisIndustrialBatch $5-9$ $3-36$ $30-95^{\circ}$ 112 $20-55$ 60034 C. wugarisIndustrialBatch $2-10$ $48-1550$ $55-88$ $4-42$ $12-100$ (2006) C. wugarisMunicipalBatch $10-30$ $12-9$ $4-28^{\circ}$ <						Initial	~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~	Initial	Removal	
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C. kessleri Artificial Batch 3 168 $8-19^{a}$ $10-12$ $8-20^{b}$ Lee and <i>c. pyrenoidosa</i> Industrial Fed-batch 5 267 $87-89$ 56 $45-72$ Hongya <i>C. pyrenoidosa</i> Municipal Batch 10 $ 22$ 70 Hernand <i>C. sorokiniana</i> Municipal Batch 10 13-410 $23-100^{\circ}$ $5-8$ $46-94^{\circ}$ Aslan a <i>C. vulgaris</i> Artificial Batch $1-10$ $13-410$ $23-100^{\circ}$ $5-8$ $46-94^{\circ}$ Aslan a <i>C. vulgaris</i> Industrial Batch $5-9$ $3-3-36$ $30-95^{\circ}$ 112° 2006 <i>C. vulgaris</i> Municipal Batch $2-10$ $48-1550$ $55-88$ $4-42^{\circ}$ $12-100$ $Khan a$ <i>C. vulgaris</i> Municipal Batch $2-10$ $48-1550$ $55-88$ $4-42^{\circ}$ $12-100^{\circ}$ $20-55^{\circ}$ $500-55^{\circ}$ $500-55^{\circ}$			manure							
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C. pyremoidosa Industrial Fed-batch 5 45-72 Hongya C. sorokiniana Municipal Batch 10 $ -$ 22 70 Hernano C. sorokiniana Municipal Batch 10 $ -$ 22 70 Hernano C. sorokiniana Municipal Batch 1-10 13-410 23-100° 5-8 46-94° Aslan a C. vulgaris Industrial Batch 5-9 3-36 30-95° 112 2005) 2008) C. vulgaris Municipal Batch 2-10 48-1550 55-88 4-42 12-100 Khan a C. vulgaris Municipal Batch 2-10 48-1550 55-88 4-42 12-100 Khan a C. vulgaris Municipal Batch 2-10 48-1550 55-88 4-42 12-100 (2008) C. vulgaris Municipal Batch 10-30 129 4-42 12-100 (2008)			medium							
C. sorokinianaMunicipalBatch10 $ 22$ 70 HernanC. vulgarisArtificialBatch1-1013-41023-100° $5-8$ $46-94^{\circ}$ Aslan aC. vulgarisIndustrialBatch $5-9$ $3-36$ $30-95^{\circ}$ 112 2005 (2006) C. vulgarisIndustrialBatch $5-9$ $3-36$ $55-88$ $4-42$ $12-100$ Khan atC. vulgarisMunicipalBatch $2-10$ $48-1550$ $55-88$ $4-42$ $12-100$ Khan atC. vulgarisMunicipalBatch $2-10$ $48-1550$ $55-88$ $4-42$ $12-100$ Khan atC. vulgarisMunicipalBatch $2-10$ $48-1550$ $55-88$ $4-42$ $12-100$ (2008) C. vulgarisMunicipalBatch $2-10$ $48-1550$ $55-88$ $4-42$ $12-100$ (2008) C. vulgarisMunicipalBatch $0-30$ 129 $42-83^{\circ}$ 120 $13-14^{\circ}$ (2008) ScenedesmusArtificialBatch $0.2-4.5$ $14-44$ $30-100^{\circ}$ $13-14^{\circ}$ (2010) ScenedesmusArtificialBatch $0.2-4.5$ $14-44$ $30-100^{\circ}$ 14° $20-55$ $60nal$ ScenedesmusAntificialBatch 9 $ 112$ $20-55$ $60nal$ S. dimorphusIndustrialBatch 9 $ 12-55$ $60nal$ <tr< td=""><td></td><td>C. pyrenoidosa</td><td>Industrial</td><td>Fed-batch</td><td>5</td><td>267</td><td>87–89</td><td>56</td><td>45-72</td><td>Hongyang et al. (2011)</td></tr<>		C. pyrenoidosa	Industrial	Fed-batch	5	267	87–89	56	45-72	Hongyang et al. (2011)
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C. vulgaris Municipal Batch $2-10$ $48-1550$ $55-88$ $4-42$ $12-100$ Khan an (2008); C. vulgaris Artificial Batch $10-30$ 129 $42-83^c$ $12-100$ (2008); C. reinhardtii Artificial Batch $10-30$ 129 $42-83^c$ 120 $13-14^b$ Kong el Scenedesmuus Artificial Batch $0.2-4.5$ $14-44$ $30-100^{c_{1.4}}$ $1.4-6.0$ $30-100^c$ Zhang el Sp. medium Batch $0.2-4.5$ $14-44$ $30-100^{c_{1.4}}$ $1.4-6.0$ $30-100^c$ Zhang el Sp. medium Batch $9.2-4.5$ $14-44$ $30-100^c$ Zhang el S. dimorphus Industrial Batch $9.2-8.5$ $7-6.5$ $70-755$ $60rzal$		C. vulgaris	Industrial	Batch	5-9	3–36	30–95°	112	20-55	Gonzalez et al. (1997)
C. reinhardtiiArtificialBatch $10-30$ 129 $42-83^{\circ}$ 120 $13-14^{\circ}$ Kong etmediummediumMedium $0.2-4.5$ $14-44$ $30-100^{\circ.a}$ $1.4-6.0$ $30-100^{\circ}$ Zhang etScenedesmmusArtificialBatch $0.2-4.5$ $14-44$ $30-100^{\circ.a}$ $1.4-6.0$ $30-100^{\circ}$ Zhang etS. dimorphusIndustrialBatch 9 $ 1112$ $20-55$ Gonzal-S. obliauusMunicipalBatch $0.2-8$ 27 $79-100^{\circ}$ 12 $49-78$ Ruiz et		C. vulgaris	Municipal	Batch	2-10	48-1550	55–88	4-42	12-100	Khan and Yoshida (2008) and Ruiz et al. (2010)
Scenedesmmus Artificial Batch 0.2-4.5 14-44 30-100 ^{c. a} 1.4-6.0 30-100 ^c Zhang e sp. medium batch 9 - - 112 20-55 Gonzale <i>S. alimorphus</i> Municipal Batch 0.2-8 27 79-100 ^c 12 49-78 Ruiz et		C. reinhardtii	Artificial medium	Batch	10–30	129	42–83°	120	13–14 ^b	Kong et al. (2010)
S. dimorphusIndustrialBatch911220-55GonzalS. obliauusMunicipalBatch0.2-82779-100°1249-78Ruiz et		Scenedesmmus sp.	Artificial medium	Batch	0.2-4.5	14-44	30–100 ^{c, a}	1.4–6.0	30–100°	Zhang et al. (2008)
S. obliauus Municipal Batch 0.2–8 27 79–100° 12 49–78 Ruiz et		S. dimorphus	Industrial	Batch	6	I	I	112	20-55	Gonzalez et al. (1997)
		S. obliquus	Municipal	Batch	0.2–8	27	79–100 ^c	12	49–78	Ruiz et al. (2010)

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Cyanobacteria	Arthrospira sp.	Animal	Semi-cont.	1	I	84–96°	1	72–87 ^b	Olguin et al. (2003)
		wastewater							
	A. platensis	Industrial	Batch	15	2–3	$96-100^{\circ}$	18-21	87–99 ^b	Phang et al. (2000)
	Oscillatoria sp.	Municipal	Continuous	14	498	100	76	100	Craggs et al. (1997)
Diatoms	P. tricornutum	Municipal	Continuous	14	498-835	80-100	76-116	50 - 100	Craggs et al. (1995)
Haptophytes	I. galbana	Artificial	Batch	8	377	66	I	I	Valenzuela et al.
		medium							(1999)
	1 / 2010 10 2/0								

Source: Cai et al. (2013, 19: 360-369)

a Nitrate (NO₃⁻ – N), Nitrite (NO₂⁻ – N) ^bTotal orthophosphates ($PO_4^{3-} - P$) ^cAmmonia nitrogen (NH₄⁺ – N)



Fig. 11.3 Mechanism of photosynthetic aeration in water bodies

level of biodegradable pollutants (Raouf et al. 2012). Excess BOD leads to the depletion of dissolved oxygen in water bodies and responsible for fish death and anaerobiosis (Raouf et al. 2012). Colak and Kaya (1988) studied the possibilities of microalgae in reduction in BOD and COD level and reported the net reduction of 68.4% and 67.2% for BOD and COD, respectively, in domestic wastewater. Photosynthetic microorganism utilizes nutrients present in wastewater for their growth and releases oxygen in the water, and then heterotrophic aerobic bacteria then utilizes this released oxygen and in turn the CO₂ released from bacterial respiration (Munoz and Guieysse 2006). And this released CO₂ will then utilized by photosynthetic microorganisms (Fig. 11.2). Hence, by using phycoremediation, both BOD and COD level decreased without external mechanical aeration.

3.3 Biosorption of Heavy Metal

Industrial and agricultural wastewater reported to have considerable amount of heavy metals, and when they intermixed with water banks, they remain in the water bodies for long durations and finally deposited to the sediment systems (Agarwal 2005). Hence, the sediment systems act as reserve for heavy metals, and metals are released into the aquatic system from the sediments because of prevailing environmental factors (Gupta et al. 2006). Wastewater containing unacceptable level of heavy metals needs to be treated thoroughly because biomagnification occurs in biological system and has deleterious effect to aquatic organism and eventually to humans through aquatic food chain (Babu and Gupta 2008; Gupta et al. 2006). Conventional physicochemical heavy metal treatment from the metal-contaminated wastewater treatment is complex. Hence, the need of the hour is the economically feasible and eco-friendly sustainable technologies for heavy metal removal from wastewater (Sandau et al. 1996). Alga-/cyanobacteria-mediated treatment plants are emerging as alternative bioremediation techniques over conventional methods for heavy metal removal from metal-contaminated wastewater, industrial effluents, and soil matrix (De Philippis et al. 2011; Sandau et al. 1996). Studies have demonstrated the applicability of cyanobacteria in in situ removal of metals without external input of chemicals and energy (De Philippis et al. 2011). Alga removes heavy metals from the water bodies either
by adsorption/diffusion or binding over the surface, which is facilitated by specific structure of cell wall. This extracellular binding of metals to the algal cell surface is passive uptake followed by slow intracellular active uptake (Gupta et al. 2006).

Several algal species have potential of sequesterating toxic heavy metal from aqueous environment, and this sequestering process involves various mechanisms (Upadhyay et al. 2019). Basically, it depends upon the algal species, metal ions, solution condition, and whether the algal cells are living or nonliving (Han et al. 2007). Living microalgal cells accumulate micro elements (Co, Mo, Ca, Mg, Cu, Zn, Cr, Pb, and Se) inside their cell through active transport (Ajjabi and Chouba 2009; Han et al. 2007; Kiran and Thanasekaran 2011; Rajfur et al. 2012; Tuzen and Sari 2010; Yee et al. 2004; Yuce et al. 2010). A field trail conducted by Gale (1986) reported that photosynthetic microalgae have high potential to detoxify metal from mine wastewater. Soeder et al. (1978) showed that algae *Coelastrum proboscideum* can absorb 100% of Pb from 1.0 ppm solution within 20 h at 23 °C and about 90% after only 1.5 h at 30 °C, while Cd was absorbed only 60% from 40 ppb solution after 24 h. Mc Hardy and George (1990) studied *Cladophora glomerata* in artificial freshwater channels and found it as an excellent accumulator of zinc.

4 Common Sources of Biofuel

Fossil fuels are the primary energy source for the energy demand of world (Singh et al. 2018). However, its limited resources and unsustainable nature alarmed the research communities around the globe to search for the alternative energy source which is sustainable and eco-friendly. Therefore, the biofuels originated from renewable resources could be more effective and feasible option (Upadhyay et al. 2019). Biofuels are classified into first-generation biofuels which require edible plant substrate such as oilseeds and grain, thus creating a food vs. fuel dilemma; second-generation biofuels which are produced from nonedible plant parts such as straw, wood, and biomass; and the third-generation biofuels which are generated from algae (Mohr and Raman 2013). Third-generation biofuels have emerged as a viable option, since they do not require arable land and food vs. fuel dilemma does not occur (Daroch et al. 2013). Recently, fourth-generation biofuels have been introduced which use genetically modified organisms (mainly algae) to achieve sustainable production of biofuels (Daroch et al. 2013). Algal lipid is well characterized for having high energy, low-cost production, and renewable resource for biodiesel production (Borowitzka and Moheimani 2013; Gupta et al. 2014).

4.1 Microalgae: Resource of Biofuel

Biofuel may be defined as fuels derived from renewable raw materials. The application of algal biomass for the biofuel production involves the same procedure as involved in biofuel production through terrestrial biomass (Daroch et al. 2013). Algal species are now being used for the production of renewable energy such as biodiesel, bioethanol, biogas, bio-hydrogen, etc. (Demirbas 2011).

Like plant-derived feedstocks, algal feedstocks can also be making use of directly or processed into liquid fuels and gas through several biochemical or thermochemical conversion processes (Amin 2009; Demirbas 2009; Rittmann 2008). Dried up biomass of alga may be utilized to produce energy by direct combustion (Kadam 2002), but this mode of algal biomass utilization for biofuel production is least utilized. Thermochemical conversion of algal biomass to yield gas or oil-based biofuels involved several procedures, i.e., gasification, pyrolysis, hydrogenation, and liquefaction of the algal biomass (Rittmann 2008). However, biochemical conversion procedures include fermentation and anaerobic digestion of the biomass to vield bioethanol or methane (McKendry 2002a, b; Miao and Wu 2004). Besides, this bio-hydrogen can be produced by the process of bio-photolysis (Melis 2002). Lastly, lipids mainly in the form of triacylglycerol can be extracted, isolated from harvested microalgae biomass, and trans-esterified to produce biodiesel of variable carbon chain length (Chisti 2007). It has been reported that biodiesel is lesser toxic, releases lesser gaseous pollutants, and contains very minute quantity of CO2 or sulfur in comparison with petro fuels after combustion (Rawat et al. 2013). Therefore, the biodiesel is now being accepted worldwide among scientific community as an alternative for traditional fuel resources. This third-generation biofuel addresses the limitation of plant-/food-derived biofuels (Sivakumar et al. 2012).

5 Utilization of Wastewater Grown Microalgae for Biofuel Production

It has been already described and proved that microalga has potential to grow well in certain wastewater conditions; therefore, these effluents can serve as an appropriate sustainable medium for biofuel feedstock (Singh and Gu 2010). Since, largescale production of microalgae has been used since two decades for production of health supplements and treatment of wastewater (Chisti 2007). Microalga is capable of removing nutrients from wastewater as described in Table 11.1. Hence, they proliferate well in wastewater due to the availability of nutrients (C, N, and P). Sometimes, they produce very high amount of lipid up to 80% of their biomass, and composition of accumulated lipid depends upon the growth condition and microalgal species (Dean et al. 2010). However, it is also found that when nutrient stress is given in growth medium, it leads to higher lipid production but lower biomass production (Dean et al. 2010). Therefore, through the studies conducted, it has been suggested that biomass productivity needs attention rather than lipid productivity, basic need of biofuel production (Singh et al. 2018).

Proliferation of alga in wastewater provides an efficient method to remove nutrient permanently, not possible with traditional mode of wastewater treatment (Rodolf et al. 2009). Chinnasamy et al. (2010) conducted a study utilizing carpet industry effluents as a medium for biomass generation and reported that the consortium of 15 native algal isolates represent >96% reduction of nutrient load. If a very large amount of carpet-industry wastewater is available, that could be a resource for generation of algal biomass and potentially biodiesel.

6 Economic and Environmental Advantage of Phycoremediation

Phycoremediation coupled to biofuel generation provides several environmental and financial incentives in comparison to traditional wastewater treatment given below.

Phycoremediation	Traditional wastewater treatment system
Economically feasible, requires investment of less amount of money	Not economically feasible, requires higher amount of money
Permanently removes nutrient from wastewater, extent of removal depends upon microalgae species and wastewater	Does not remove permanently; the extent of removal depends upon the method utilized, physical or chemical
No need of trained operator, quite easy to handle fluctuation in quality and quantity of effluent	Requires a trained operator, to regulate the flow and quantity of effluent in tank, because fluctuation affects the treatment system
No specificity toward the types of waste; it can be industrial, municipal, or agricultural	There is different method of treatment with respect to types of effluent
Photosynthetic aeration: oxygen required for oxidation of pollutants obtained through photosynthesis. Less energy expensive	Mechanical aeration: artificial method of aeration to provide oxygen for oxidation of pollutants, more energy expensive
Does not require any kind of chemical, so there is no need of further separation in treated water, lessen the operational cost	Requires various chemicals, so further separation needed in treated water to remove these chemical, increases operational cost
CO ₂ sequestration through photosynthesis, environment friendly	No such process,
Compatible with traditional method of treatment	Noncompatible, process specific
Single step process, nutrient removal, pigment removal, and reduction in BOD and COD can be achieved once algae grown in wastewater	Multistep process, removal of each parameter obtained through step by step
Lesser amount of sludge generation	Higher amount of sludge generation
Phycoremediation will result in the production of algal biomass, which has several commercial advantages, from bio-based chemical to biofuel	Mostly generated sludge used as fertilizer and landfills, but greater attention requires avoiding them from becoming further source of pollution
Does not require any kind of instrument so energy expenditure in this process is very low	Requires several instruments like centrifugation machine, mixer grinder, and more energy expensive

7 Conclusions

Presently, the key disadvantage related with algal biofuel production is that existing technologies do not economically support cultivating algae alone for biodiesel generation because it is very costly and does not result in positive energy returns. Integrated application of microalgae for wastewater treatment, with biofuel production, is therefore a smart choice to overcome operational costs, greenhouse gas emissions, nutrients, and water scarcity problems. In addition, major problem associated to algal biofuel generation is designing of cultivation system. Therefore, further research is needed to identify algal species and optimization of operational parameters for cellular lipid production that can be used to prevent eutrophication of nearby water stations as well as production of biofuel.

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Chapter 12 Microalgae and Microorganisms: Important Regulators of Carbon Dynamics in Wetland Ecosystem



Nisha Yadav and D. P. Singh

Abstract Wetlands, a dynamic and natural ecosystem characterized by waterlogged conditions, are used for the benefit of mankind since decades. One of the most important ecological functions of the wetlands is their ability to sustain rich biodiversity and storage of carbon. The carbon stock in the wetlands is mainly regulated by carbon cycling mediated by microorganisms and photoautotrophs (algae and plants) in the wetland. Carbon storage in the wetlands is often controlled by both decomposition of labile carbon and carbon fixation by the photosynthesis. This internal carbon dynamics in the wetland ecosystem influences the atmospheric carbon cycle. Under anaerobic condition, detritus chain involves microbial conversion of biodegradable material into a mixture of methane (CH_4) and carbon dioxide (CO_2) with small amounts of ammonium and hydrogen sulphide (H₂S). Methanotrophs are unique group of aerobic, gram-negative bacteria that use CH_4 as a source of carbon and energy. Wetlands act as biofilters through a combination of physical, chemical and biological factors which contribute in the reduction of pathogen and waste water. Since algae play a crucial role in carbon dynamics, the present chapter emphasizes the role of algae in regulation of carbon, water hydrology and other ecosystem services of the wetland.

Keywords Wetland \cdot Carbon reserve \cdot Ecological functions \cdot Methanotroph \cdot Bioindicators

1 Introduction

Wetlands are found in all the climatic regions, inhabiting about 4-6% of the total land area on the earth (~530 to 570 mha) (Mitra et al. 2005). Wetlands are formed in zones where soil drainage is deficient due to occurrence of impermeable rocks bed, permafrost and the area where annual precipitation exceeds the natural loss of water (Tiner 2005). These days the wetlands are being destructed, pose a potential

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threat to the environment by releasing high concentration of carbon in the atmosphere (Kim and Kirschbaum 2015; Yvon Durocher et al. 2014). Undisturbed wetlands are the active sinks of carbon, although they also emit the greenhouse gas methane in huge amounts (Moreno-Mateos et al. 2012). Wetlands in most of the parts in the world have been drained, occupied or damaged for construction of houses for agricultural activities, roadways or other developmental work (Mitra et al. 2005). This loss of wetlands has deteriorated water quality, caused habitat reduction for plants and animals and stressed the ecosystem. However, due to lack of knowledge, awareness and loose policies of government regarding to the conservation and protection of resources significantly contribute to the degradation of wetland.

After the Rio Earth Summit in 1992, the World Summit on Sustainable Development (WSSD), held at Johannesburg in 2002, was the first serious effort to draw the world attention towards providing a platform for conservation of wetland as natural resource. Various governments, researchers and policymakers accepted the crucial role of wetlands as an important natural resource on earth (Rebelo et al. 2018). The 'sustainable use' of wetlands refers to the human use of a wetland so that it may yield the continuous benefit to the present generation, without the hampering the need for future generation.

In fact, the Ramsar definition of wetlands broadens covering the areas of riparian and coastal zones adjacent to wetlands, the islands or bodies of the marine water at low tide. The US Environmental Protection Agency (EPA) defines the wetlands as areas where water is present either at or near the surface of the soil for varying periods of the year or throughout the year. In wetlands, seasonal fluctuations in water levels are a key feature which accounts for highly productive nature of the wetlands ecosystem (Abril et al. 2014). Wetlands include marsh, fen, peatland or waterlogged areas, which have static or flowing freshwater, brackish or salty water). Peatlands are important natural ecosystems with high value for biodiversity conservation, climate regulation and human welfare. Peatland are unique wetland ecosystems characterized by accumulation of organic matter (peat) derived from dead plant materials under the condition of permanent water saturation and represent at least one third of the global wetland resource (Parish et al. 2008). They cover more than 4 million km² area worldwide (3% of the world's total land area) and contain 30% of total soil carbon reserve (Immirzi et al. 1992; Joosten and Clarke 2002).

These waterbodies may be natural or artificial, temporary or permanent. These wetlands are known to emit methane (a major greenhouse gas). Out of the abovementioned wetland types, peatland is the major contributor of methane.

The climate change is a worldwide major concern of the mankind as the ecological effects of climate change will have devastating impact on human survival (Root et al. 2003). The IPCC has predicted that the global temperatures will rise from 1 to 5 °C during the twenty-first century. A fast rise in temperature will affect the coastal life and leading to changes in precipitation. Therefore, the impact of climate change on wetland habitats on a regional and global level needs to be recognized. The miscellaneous functions of wetland make it little more difficult to understand the relation between climate change and wetland ecosystem. The projected changes in the climate are likely to affect the extent and nature of wetland functions including change in a carbon sink, carbon storage and sequestration within the system (Moor et al. 2015). The temporal variations in carbon fluxes are found to be larger in water-logged wetlands than drained wetlands. Nakano et al. (2004) reported that carbon fluxes from the waterlogged sites in Siberian permafrost areas were much higher than the relatively dry sites, where carbon fluxes were almost absent or frequently negative.

Since wetlands by definition are permanently or temporarily flooded areas, altering the water level (water budget/wetland hydrology) to its original level is the foremost problem that needs to be tackled for wetland restoration. The water budget of the wetland includes precipitation, surface water flow, groundwater flow and evaporation (Owen 1995). However, with the increased population growth, pressure on wetlands increased by change in base flow of water (depth and hydrology), sedimentation and land use patterns of wetlands. This causes a significant degradation of wetland ecosystem. Thus, the water balance is an important determining factor for wetland conservation. The major restoration concept on these lines includes the re-establishment of wetland hydrology, nutrient availability, pH, soil conditions, biodiversity and conservation of wetland habitat (Rosenthal 2006; Scholz and Lee 2005).

As per global carbon emission is concern, it is not yet clear whether the conservation of wetland should also be integrated with international trading schemes of carbon emission as in Kyoto Protocol. Microalgae being one of the important living entities on the earth could regulate the carbon of wetland in a sustainable way and can mitigate the global impact of CO_2 . The present chapter describes the role of microalgae in carbon dynamics and also emphasizes the wetland specific management and restoration issues.

2 Function of Wetland Ecosystem

Wetlands have been often treated as wasteland. This is also the reason of being ignored by the people. Due to ignorance, the wetlands are sometimes drained and filled for many development activities (building construction, dumping grounds for domestic and industrial solid wastes, etc.). But, the ecologists and environmentalists have started considering the wetlands as ecologically rich and highly productive natural resource on the earth, which can be easily compared with the rainforests and coral reefs ecosystems (Cronk and Fennessy 2016). The wetlands are natural abode of diverse and rare of species of microbes, algae, plants, insects, amphibians, rep-tiles, birds, fishes and mammals (Cronk and Fennessy 2016). Particularly, the coastal wetlands act as ecotone between the marine, freshwater and terrestrial ecosystems and exhibit high species diversity.

The ecological function of wetlands is significant due to their ability to regulate water regime, act as natural filters and display amazing nutrient dynamics (Mulligan et al. 2001). Wetlands provide many ecosystem services to the mankind (Mitra et al.

2005; Mitsch and Gosselink 2007). The term ecosystem function includes all the physico-chemical and biological processes that characterize the wetland ecosystems. Major functions of the wetland ecosystem are water storage and groundwater recharge, flood control, water quality control, moderating climate and community structure, sustaining biodiversity and wildlife (Turner et al. 2000). Wetlands immensely contribute to recreational and aesthetic value, biodiversity, environmental and commercial values, etc. In addition, due to their anoxic wet conditions, wetland also provides natural environments for sequestering and storing carbon from the atmosphere (Mitsch et al. 2013). Besides, the ecosystem services provide the global economic values. The global value of ecosystem services provided by the coastal areas and wetland ecosystems is estimated to be about 15.5 trillion US dollars per year, which is about 46% of the total value of services provided by other ecosystems (Costanza et al. 1997).

3 Carbon Storage in Wetlands

There is a large amount of carbon stored in the wetlands, which is about 350-535 Gt C, accounts for 20-25% of the world's total organic carbon in the soil (Mitra et al. 2005). Nahlik and Fennessy (2016) also reported that about 20-30% of global soil carbon is stored in wetland. The net carbon storage by the wetlands depends upon the difference between decomposition of carbon and photosynthetic CO₂ fixation. Many coastal, riverine wetlands and estuaries also receive large amount of carbon-rich sediments from natural and anthropogenic sources, contributing to carbon reserve of these wetlands (Xue et al. 2009; Ni et al. 2008).

Sometimes the wetlands, owing to sparse vegetation, carbon turnover are limited as compared to other wetlands like salt marshes and tropical forests. The anaerobiosis nature of wetlands gradually increases the net carbon accumulation in the different wetland like peatlands over a period of time (Vespraskar and Craft 2016). The litter, peat and bogs are C-rich sediments. It has been estimated that bogs absorb globally about 0.1 Gt C per year, while global C-sequestration in peatlands and other wetlands range from 0.1 to 0.7 Gt C per year (Mitra et al. 2005).

Mechanisms of carbon processing in the wetland environment is complex as it varies with the decomposition of organic matter taking place in different horizons; e.g. respiration and methane oxidation occur in the aerobic zones, while methanogenesis occurring in the anaerobic strata of the wetland (Pandey et al. 2014). However, the rate of carbon decomposition is found to be higher in the upper strata of wetland, i.e. wetland surface, where input of labile organic matter is higher. Wetland plants and microphytes convert atmospheric carbon dioxide into biomass. Hence, carbon trapping in the wetlands is mediated by the photosynthesis, growth of vegetation, latitude of wetlands, temperature and nutrients (Nahlik and Fennessy 2016). Although wetlands occupy only 4-6% of the total land area (~530 to 570 mha) on the earth surface, they are major carbon sinks mediated by photosynthetic fixation of atmospheric CO₂ (Nahlik and Fennessy 2016). Depending upon

the existing environmental conditions, the wetland vegetation traps the atmospheric CO_2 just like other ecosystems; however, the rate of carbon decomposition varies within a wetland ecosystem and influenced by the factor includes temperature, water level, flow of water and nutrients, etc. (Brinson et al. 1981).

The hydrological cycle, changing land use pattern, climate change and other environmental conditions enormously influence the role of wetlands in the global carbon cycle. It has been reported that with increase in temperature, melting of the permafrost results into reduced carbon storage and carbon sequestration in the wetlands (Schuur et al. 2015). A rise in the temperature could be important factor for rise in the sea-level and changes in the precipitation pattern, which can adversely affect the wetlands as carbon stores (Junk et al. 2013). Therefore, any environmental perturbation might influence the carbon budget in the wetlands. The wetlands like boreal and tropical peatlands have highly labile carbon pool which gets oxidized to carbon dioxide, if the water level is lowered. The sequestration of carbon dioxide into wetland ecosystem occurring via photosynthesis gets altered. These changes in the carbon budget can be determining factor to assess the contribution of wetlands into global carbon cycling. According to a study conducted by Frolking et al. (2011) on peatlands, they observed that draining of peatlands leads to enhanced mineralization process and resulted into sharp rise in the emission of carbon dioxide. Therefore, protecting wetlands is a practical way of maintaining the present level of carbon reserves and, thus, preventing the emission of GHGs like carbon dioxide and methane. Since the role of wetland-borne carbon fluxes in the global carbon cycle is not fully understood, more information would be needed about wetland types and their functioning as both sources and sinks of carbon.

4 Wetlands and Bio-geocarbon Cycle

The stored organic matter within a wetland ecosystem is removed by biodegradation, photochemical oxidation, sedimentation, volatilization and sorption (Burgoon et al. 1995; Reddy and D'Angelo 1997; Stottmeister et al. 2003). However, the longterm net carbon storage in the wetlands is often controlled by both decomposition of labile carbon and carbon fixation by the photosynthesis. This internal carbon dynamics in the wetland ecosystem influences the atmospheric carbon cycle (Fig. 12.1). Various factors like level of groundwater, temperature, availability of substrate, nutrient level and microbial population also influence the carbon dynamics (Shepherd et al. 2007). Under anaerobic condition, detritus chain involves microbial conversion of biodegradable material into CH_4 and CO_2 with small amounts of ammonium and hydrogen sulphide (H_2S). The solubility of carbon biomass in wetland is higher which facilitate the formation of acid forming bacteria and methanogenic bacteria. The activity of these bacteria depends on the pH and temperature of the medium.

Organic matter accumulation in wetland is enhanced when the primary productivity is higher than the corresponding decomposition of organic matter (Mitsch and



Fig. 12.1 Carbon cycling in wetlands

Gosselink 2007). Due to slower rate of organic matter decomposition, different soil layers have different level of organic matter. The accumulated organic matter in the wetlands is considered potential energy source for microbial communities (Reddy and Delaune 2008; Turcq et al. 2002). The decomposition of dissolved organic matter is expected to occur via heterotrophic carbon consumption by aerobic and anaerobic bacteria and photodegradation. Several authors have reported the transformation of dissolved organic matter by algae (Kragh and Sondergaard 2004), wetland plant material (Pinney et al. 2000), microorganisms (Ibekwe et al. 2003; Li et al. 2008) and soil fixation of carbon into carbonates (Qualls and Haines 1992) in the wetland. It is also believed that various other conditions such as temperature, organic matter quality, residence time of organic matter, level of oxygen, wetland maturity, sedimentation rate and sediment texture impact the organic matter decomposition (Barber et al. 2001; Lafleur et al. 2005; Savage and Davidson 2001; Shepherd et al. 2007; Turcq et al. 2002; Wolf et al. 2005; Yurova and Lankreijer 2007).

Wetlands have both aerobic and anaerobic interfaces in water, soil and organic matter (Scholz et al. 2007). Under anaerobic conditions, both carbon dioxide and methane are formed, whereas under aerobic conditions, only carbon dioxide is formed. Earlier studies (Kadlec and Knight 1996; Mitsch and Gosselink 2007) have indicated that the aerobic respiration in wetland systems is far more effective in the organic matter degradation than the anaerobic fermentation and methanogenesis. Wetlands are known to emit large amounts of methane, which is essentially more potent greenhouse gas (GHG) than CO_2 . An internal carbon cycling could be an important factor in the carbon budget of the wetlands.

5 Microorganisms in Wetland and Methane Production

Wetlands are important ecosystems on the earth. The microbial population in wetlands play important role in internal global carbon cycling. Thus, these microbial communities in wetlands are ultimate regulators of both primary productivity and carbon decomposition (Pant et al. 2003). The mineralization of soluble organic matter is the primarily ecological role of heterotrophic microflora in soil sediments, which facilitate the recycling of energy and carbon within and outside the wetland ecosystem (Li et al. 2008). Under anaerobic condition, methane formation (a source of carbon) by methanogenic bacteria is important process in the freshwater wetlands (Hornibrook et al. 2000; Pandey et al. 2014). The production and consumption of methane in wetlands involve complex physiological processes of plants and microorganisms, which are regulated by climatic and edaphic factors, mainly soil temperature and water table level (Joabsson et al. 1999). The interaction of these processes with heterogeneous environments results in large variations in the methane fluxes.

Since methane is an important gas that contributes to 15% of the greenhouse effect, several studies have been conducted to analyse the methane production and its emission from the wetland ecosystem. However, most of the ecological studies assessing the production, consumption and emission of methane have been performed in boreal and temperate wetlands, yet there are few studies evaluating these activities in tropical wetlands (Bartlett and Harriss 1993; Roulet et al. 1992; Turetsky et al. 2014). It has been estimated that methane emission from the wetlands is about 115–227 Tg-CH₄ per year, which contributes 20–25% of total global methane emissions (Whalen 2005; Bergamaschi et al. 2007; Bloom et al. 2010). Bloom et al. (2010) also reported that the rice fields emits about 60–80 Tg-CH₄ per year.

The methanogenic bacteria (MB) are members of the Archaea domain, and they comprise a morphologically diverse group of short and long bacilli, cocci, and several arrangements of the basic forms in large chains or aggregated clumps (Whitman et al. 2006). They include important genera like *Methanobacterium*, *Methanothermobacter*, *Methanobrevibacter*, *Methanothermus*, *Methanococcus*, *Methanothermococcus*, *Methanobalobium*, *Methanosarcina*, *Methanosalsus*, etc. (Torres-Alvarado et al. 2017).

The reduction of methane from wetland ecosystem is mainly attributed to the existence of methanotrophic bacteria, which contribute significantly to CH₄ mitigation under both aerobic and anaerobic conditions (Conrad 2009; Borrel et al. 2011). Methanotrophs are unique group of aerobic, gram-negative bacteria that use CH₄ as a source of carbon and energy (Khmelenina et al. 2018; Pandey et al. 2011). The important methanotrophic bacterial genus includes *Methylomonas, Methylococcus, Methylobacter, Methylosinus, Methylocapsa, Methylocystis*, etc. The population size and community composition of methanotrophic bacteria in any ecosystems may be an important factor to determine the flux of methane in a wetland ecosystem. The CH₄ oxidation depends on the availability of oxygen; therefore this process occurs mainly in freshwater wetlands during the dry periods, when the level of

the water table descends and the soil of the wetland is exposed to air (Torres-Alvarado et al. 2017; King 1994). In peatlands, CH_4 oxidation is accomplished in the first 7 mm layer where oxygen can easily penetrate (Moore and Roulet 1993). The oxidation of CH_4 is carried out by the methane oxidizing bacteria (MOB) as well as nitrifying bacteria. These strict aerobic microorganisms oxidize CH_4 to CO_2 using oxygen as electron acceptor, releasing methanol as an intermediate product.

6 Role of Microorganism (Algae) in Wetland Function

6.1 Algae in Purification of Water

Wetlands are natural wetlands as well as constructed, used in the purification of pollutants present in soil and water. Constructed wetlands are artificially engineered systems that are the controlled system usually designed with specific objectives for particular process (Upadhyay et al. 2017). The constructed wetlands are designed to take advantage of the same processes occurring in a natural wetland (Vymazal 2010). Wetlands are characterized by several factors including the presence of water, nature of soil and the presence of vegetation (Cheng et al. 2002). The natural or constructed wetlands can best serve as polishing waterbody for partially treated waste water and removal of specific pollutants such as nitrogen, phosphorus, copper, lead, selenium, organic compounds and pesticides from agricultural and urban storm runoff (Banuelos and Terry 1999; Upadhyay et al. 2019). Algae also play a very important role in the remediation of organic pollutants of swamps, bogs and mangroves wetland (Chekroun et al. 2014).

6.2 Algae as Bioindicators in Wetlands

Algae have a long history of use and possess many of the features valued in ecological indicators. The growth of microalgae is indicative of water pollution as they easily respond to many chemicals (Rai et al. 2013, 2015). Algae serve as the indicators of changes in wetlands and provide precise assessments of changes in wetlands (Van Dam et al. 1998). Algae exhibit a wide variety of sensitivity/tolerance and may exploit for toxicity bioassay (Florence et al. 1994). The ecological importance and distinguishing features of algae, particularly as indicators of nutrient pollution, make them conducive as assessment endpoints for numeric nutrient criteria development for water quality management purposes under the Clean Water Act (USEPA 2000).

Kolkwitz and Marsson (1909) were the pioneers who classified algal species based on their tolerance to various kinds of pollution. They stated that the presence of certain species of algae could define various zones of degradation in a river. Palmer (1969) published and explains the algal species which can be used to indicate clean and polluted waters. Patrick (1971) proposed a numerical approach to study water quality using diatom flora attached to glass slides as artificial substrates (Omar 2010). Algae are also used in laboratory bioassays to study water quality, using media for culturing indicator species from the field or defined media (Ho 1979). Omar (2010) has also reported that blue-green algae and algae like *Anabaena*, *Microcystis*, *Oscillatoria*, *Nostoc*, *Dinobryon*, *Chroococcus*, *Staurastrum paradoxum* and *Mallomonas* are indicators of toxicity and pollution in aquatic ecosystems. A list of different algae found in different type of water is mentioned below (Table 12.1).

6.3 Waste Water Remediation Through Algae

Biological treatment of waste water is environmentally most compatible and least expensive method for waste water treatment (Comninellis et al. 2008). The water purification and groundwater recharge ability of the wetlands has been an attractive option for waste water treatment due to its low-cost and easy operation. The use of algae to treat waste water has been in vogue for over 40 years. The term phycoremediation was for the first time used by Rawat et al. (2011) to refer to the remediation of waste water by using algae only. The use of microalgae for the treatment of

Fresh water algae	Algae grow in waste water	Brackish water algae
Achnanthes minutissima	Achnanthes exigua	Cocconeis sp.
Achnanthes oblongela	Achnanthes exigua var. Heterovalva	Coscinodiscus argus
Achnanthes woltereckii	Hantzschia amphioxys	Coscinodiscus antiques
Cocconeis placentula	Nitzschia amphibian	Coscinodiscus excentricus
Cocconeis pediculus	Nitzschia fonticola	Coscinodiscus decipiens
Cocconeis thumensis	Nitzschia palea	Coscinodiscus symmetricus
Eunotia pectinalis var. Minor	Pinnularia biceps	Cyclotella comta
Fragilaria capucina	Pinnularia biceps f. petersenii	Cyclotella striata
Gomphonema acuminatum	Pinnularia microstauron	Diploneis ovalis
Psammothidium bioretii	_	Diploneis interrupta
Surirella linearis		Diploneis bombus
Surirella tenuissima	_	Nitzschia littoralis
		Nitzschia obtuse
		Nitzschia obtuse var. Scalpelliformis
		Nitzschia sigma
		Surirella ovalis

Table 12.1 List of algae as an indicator of clean, polluted and brackish water

Adopted and modified from Wan Maznah and Mansor (2000)

municipal waste water has been a subject of research and development for several decades (Clarens et al. 2010). Extensive work has been conducted to explore the feasibility of using microalgae for waste water treatment, especially for the removal of excess nitrogen and phosphorus (Harun et al. 2010). The phycoremediation of waste water offers (i) nutrient removal from the different effluents, (ii) accumulation and biodegradation of organic contaminants, (iii) CO₂ sequestration, (iv) xenobiotics transformation and degradation and (v) working as bioindicator of toxic compounds. The algal treatment is considered to be a cost effective tertiary treatment of the waste water. The capability of microalgae to degrade hazardous organic pollutants is now well known. The algal species of Chlorella, Ankistrodesmus and Scenedesmus species have been successfully employed for treatment of olive oil mill waste waters and paper industry waste waters (Mata et al. 2010) One way to investigate the capability of algae to biodegrade organic pollutants in municipal waste is to encourage the algal cells to grow in the presence of pollutants. (Lima et al. 2003) reported that p-nitrophenol can be removed by a consortium of Chlorella vulgaris and Chlorella pyrenoidosa.

The concept of constructed wetlands (CWs) was first designed to increase the efficiency of phytoremediation process, targeting a specific pollutant or group of pollutants as compared to natural wetland (Rai et al. 2013; Upadhyay et al. 2017). The CWs are particularly designed to remove a wide spectrum of pollutants including pathogens, suspended solids, nutrients (ammonia, nitrate, phosphate), metals and metalloids, volatile organic compounds (VOC), pesticides and other organohalogens, TNT and other explosives and petroleum hydrocarbons and additives (Brix 1994; Haberl et al. 2003; Wu et al. 2015).

The constructed wetlands are shown to be capable of removing a wide variety of pathogens including bacteria, viruses and protozoan cysts (McCarthy et al. 2009). Wetlands act as biofilters through a combination of physical, chemical and biological factors which contribute to reduction in the number of harmful bacteria (Ottová et al. 1997). Sedimentation is one of the mechanisms of reducing microbial population in wetlands during the waste water treatment (Karim et al. 2004). Sediments of the constructed wetlands are able to accumulate significant concentrations of pathogenic microorganisms (Karim et al. 2004). However, the technology of constructed wetlands for waste water treatment is still not fully developed, and various problems are encountered with regard to its best management and sustainability.

7 Conclusions

Wetlands have the potential to sequester carbon. Wetland management becomes necessary in order to avoid the emission of excess greenhouse gases, freshwater wetlands possess the ability to act as a sink for green house gas (CO₂). The microorganisms in wetlands play an important role in carbon turnover and methane emission, but the impact of different species of microorganisms in variable nutrient regimes is yet to be studied. Thus, there is pretty need to restore the wetland ecosystem for the sustainability of the world. Besides, a policy should also be framed which emphasizes the importance of wetland for the enhancement of biodiversity, reducing climate change and energy crisis through education, training or awareness.

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Chapter 13 Bioremediation of Heavy Metals: A New Approach to Sustainable Agriculture



Gereraj Sen Gupta, Garima Yadav, and Supriya Tiwari

Abstract With the advancement in agricultural practices, use of various chemicals for better yield is posing huge threat to the society. These chemical containing variable amounts of heavy metals are the key players that have become threat to plants and human beings. The discharge of various harmful environmental pollutants from different industrial sectors has created a challenge for environmentalists and scientists concerning the sustainable development of mankind. Particularly in plants, heavy metals are essential for its growth and development, but when the concentration of each heavy metal crosses, its threshold concentration becomes harmful for plants itself. These heavy metals possess specific density of more than 5 g/cm³ (Cr-7.2, Co-8.9, Ni-8.7, Cu-8.9, Zn-7.1, Mo-10.2, Cd-8.2 etc.). Various survey studies reveals intense exposure of heavy metals still continues in different parts of the world though its ill-effects are well documented. Some of the well-known heavy metals include arsenic, cadmium, copper, lead, nickel, zinc, etc., all of which cause risks for the environment and human health. Considering heavy metals as potential threat to different life forms, it has become an important and interesting issue since last few decades. This chapter attempts to review different strategies for remediating heavy metal contamination with the plants and microorganisms. An attempt has also been made to review and promote the sustainable development with the involvement of phytoremediation and micro-remediation technologies.

Keywords Phytoremediation · Micro-remediation · Heavy metals

1 Introduction

Heavy metals are natural constituents of the environment but with rapid industrialization and development; there has been a considerable increase in the discharge of pollutants in the environment (soil, air and water) (Nagajyoti et al. 2010). Unfortunately contamination of the environment with heavy metals has reached

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beyond the recommended limit (Chibuike and Obiora 2014). As compared to other pollutants, heavy metals are non-biodegradable, and so they persist for long time in the environment (Tak et al. 2013; Kumari et al. 2016; Yadav et al. 2016). Highly reactive heavy metals can enter soil and groundwater, bioaccumulate in food web and adversely affect biota. In the food chain, the non-biodegradable heavy metals get accumulated and cause damage to vital organs such as lungs, liver, kidney and nervous system (Kumar et al. 2015).

Thus, there is a need to remove these hazardous heavy metals from the environment. To seek solution to this problem, bioremediation is applied as a tool. The term bioremediation implies use of microorganisms and plants to degrade the environmental contaminants to less toxic forms (Mani and Kumar 2014; Upadhyay et al. 2016). The reason that bioremediation is used as a potential tool for this problem is because it helps to restore the natural state of the polluted environment. It has longterm environmental benefits and is cost-effective (Dixit et al. 2015). There are two strategies of bioremediation, viz. in situ and ex situ. In in situ bioremediation, the treatment of contaminated soil or water is done at the site in which it is found. It is more convenient and less expensive as compared to ex situ type. In ex situ bioremediation, the contaminated soil or water is excavated or pumped out of the location at which it is found. It is faster, easier to control and usually more able to treat a wide range of toxins from soils. Microorganisms have metabolic pathways which utilizes toxic heavy metals as a source of energy for growth and development. They possess characteristic enzymes for a particular contaminant which provide resistance against heavy metals. The microbes have cell wall which is anionic in nature and thus enables them to bind metal cations through electrostatic forces (Siddiquee et al. 2015). Not only microorganisms but plants also have the potential for remediation of environmental pollutants (Upadhyay et al. 2019). The various processes used by plants under phytoremediation are phytodegradation, phytovolatilization, phytostimulation and phytostabilization.

Bioremediation is less expensive as compared to other technologies. Blaylock et al. showed the cost-effectiveness of bioremediation. They made use of bioremediation for treatment of one acre of lead (Pb)-polluted soil and were able to save 50–60% of cost. The effectiveness of bioremediation depends on the wise selection of the microorganism, identification of the polluted environment and the technique chosen. The ability of the microorganism to degrade pollutants depends on the suitability of the environmental conditions such as temperature, pH and moisture (Verma and Jaiswal 2016). The objective of this chapter is to discuss the heavy metal pollution, its causes and effects along with the bioremedial potential to tackle this problem. A detailed account of bioremediation, various strategies employed, mechanisms, microorganisms used and merits and demerits associated with it has also been covered.

2 Heavy Metal Pollution

The heavy metals are defined as naturally occurring elements that have a high atomic weight and density five times higher than that of water and is toxic or poisonous even at very low concentration (Lenntech 2004). Due to rapid industrialization, the concentrations of heavy metals have reached beyond the threshold value (Dixit et al. 2015; Yadav et al. 2017). Some of the essential heavy metals exert biochemical and physiological functions in plants and animals. They make remarkable effects on plant physiology (Dixit et al. 2015). Pollution of heavy metals is a global concern. Many metallic elements are necessary for growth of plants and animals, but they are required in low concentration; if their amount in soil exceeds above the threshold value, it causes toxicity. Heavy metal toxicity in plants is a function of the bioavailability of these elements in the soil solution. According to Comprehensive Environmental Response Comprehension and Liability Act (CERCLA) USA, the permissible limit of some heavy metals Ar, Cd, Cr, Pb, Hg and Ag in water is 0.01, 0.05, 0.01, 0.015, 0.002 and 0.05 mg/l, respectively (Chaturvedi et al. 2015). According to Indian standards, the standard for soil heavy metal is 3-6, 135-270, 75-150, 250-500, 300-600 mg/kg for Cd, Cu, Ni, Pb and Zn (Dixit et al. 2015).

Heavy metals are naturally occurring element in soil. The naturally occurring heavy metals have a great adsorption capacity in soil, whereas heavy metals from anthropogenic sources are soluble and mobile and thus have a higher bioavailability as compared to naturally occurring heavy metals (Olaniran et al. 2013). Heavy metal accumulation in soil consequently in food items can pose health risks to the human beings. Many recent studies conducted at national and international levels reported heavy metal contamination in the soil and food crops. Agricultural soils have become a big reservoir of heavy metals due to extensive uses of different agrochemicals like fungicides, herbicides and phosphate fertilizers, organic manure and decaying plant and animal residues (Uwah et al. 2011). Table 13.1 below shows sources of some important heavy metals.

Metal	Source	References
Arsenic	Mining, pesticides, smelting ores	Wahab et al. (2015) and Bissen and Frimmel (2003)
Cadmium	Fertilizer, pesticide, wielding, mining	Nagajyoti et al. (2010)
Chromium	Dyes and paints, steel fabrication	Barakat (2011) and Cervantes et al. (2001)
Copper	Copper polishing, mining, paint, plating, printing	Dixit et al. (2015), Nagajyoti et al. (2010) and Salem et al. (2000)
Mercury	Batteries, paint, paper industries, rock weathering, coal combustion	Fashola et al. (2016) and Ali et al. (2013)
Lead	Electroplating, batteries, coal combustion, mining, paint industries, water pipes	Fashola et al. (2016), Nagajyoti et al. (2010) and Ali et al. (2013)
Nickel	Electroplating, porcelain enamelling	Fashola et al. (2016)
Zinc	Brass manufacturing, mining, oil refining, plumbing	Gumpu et al. (2015)

 Table 13.1
 Important heavy metals and their sources

3 Effects of Heavy Metals

Though some heavy metals have biological functions in living organisms, majority of them have no biological function and are extremely toxic even at very low concentration (Fashola et al. 2016). These heavy metals bind with protein sites by displacing original metals from their natural binding sites and thus causing toxicity. Research has indicated that deterioration of biological macromolecules is mainly due to binding of heavy metals to DNA and nuclear proteins (Flora et al. 2008).

In humans, heavy metals lower the energy levels and damage the functioning of vital organs such as the brain, heart, kidney, lungs and cause deterioration of physiological activities (Mupa 2013). They are also responsible for muscular and neurological degenerative processes that imitate diseases such as Alzheimer's disease and muscular dystrophy; long-term exposure can also lead to cancer. One such example of heavy metal toxicity was the "Minamata disease" caused by mercury poisoning in Japan. Lead is a heavy metal which can leach into drinking water and enter food items. Children are highly susceptible to lead and mercury, exposure of lead and mercury in children during their growing years leads to reduced intelligence and impaired development (Wuana and Okieimen 2011). Plants require some heavy metals for their growth and development, but their excess amount becomes toxic. Plants are capable of absorbing the heavy metals; they absorb toxicants either directly from the atmosphere through leaves or from soil and water through roots (Gaur et al. 2014). The excess amount of heavy metals in soil, water and air may lead to various direct or indirect effects on plants and human being. Direct toxic effects include inhibition of the cytoplasmic enzymes and damage to cell structure due to oxidative stress. Indirect toxic effects include replacement of essential nutrients at cation exchange sites of plants. Loss of fertility in plants, yield and food production. Destruction of chlorophyll pigments (Pichhode and Nikhil 2015). Some heavy metals have adverse effects on soil microorganisms. Heavy metals and microorganisms have a strong affinity; many of the heavy metals disrupt the normal metabolic functioning by competing with the essential elements due to their similar chemistry with the essential elements like similar size, charge and oxidation state. Secondly heavy metals pose a restriction on the biodegradation of majority of metallothionein which then accumulate and are harmful for the cells (Ahluwalia and Goyal 2007). Heavy metals have significant effect on soil environment also. It disturbs the buffering capacity of the soil. Heavy metal-contaminated soil limits plant habitat due to toxicity resulting in ecological, evolutionary and nutritional problems as well as severe selection pressure (Abdul-Wahab and Marikar 2012). Table 13.2 shows the hazardous effects of heavy metals on all life forms.

The entire bioremediation process can be studied under micro-remediation (remediation technique using microorganisms) and phytoremediation (remediation of soil and water by using plants) strategies.

Heavy				
metal	Human	Plants	Microorganisms	References
Arsenic	Brain damage, respiratory disorder, skin cancer	Cell membrane damage, inhibition of growth, interferes with critical metabolic processes, loss of fertility in plants and fruit yield, oxidative stress	Enzyme deactivation	Wahab et al. (2015) and Bissen and Frimmel (2003)
Cadmium	Bone disease, emphysema, kidney and lung disease, prostate cancer, testicular atrophy, anaemia	Chlorosis, plant nutrient content decrease, growth inhibition and reduced seed germination	Denaturation of proteins, nucleic acid damage, transcription inhibition and inhibition of carbon and nitrogen mineralization	Nagajyoti et al. (2010) and Fashola et al. (2016)
Chromium	Chronic bronchitis, emphysema, headache, skin itching liver and lung disease, renal failure, cancer and loss of reproductive ability	Delayed senescence Wilting, chlorosis, reduced growth, oxidation stress, biochemical lesions	Elongation of lag phase, i.e. slow growth, inhibition of growth and oxygen uptake	Barakat (2011) and Cervantes et al. (2001)
Copper	Abdominal pain, headache, vomiting, anaemia, liver and kidney damage, metabolic disorder	Oxidative stress and retarded growth	Cellular function disruption and inhibition of enzyme activities	Dixit et al. (2015), Nagajyoti et al. (2010), Fashola et al. (2016) and Salem et al. (2000)
Mercury	Blindness, deafness, dizziness, loss of memory, kidney problems and reduced immunity	Inhibition of photosynthesis, enhanced lipid peroxidation, inhibition of plant growth and yield	Denaturation of nucleic acids and proteins, inhibition of enzyme activities	Fashola et al. (2016), Ali et al. (2013) and Wang et al. (2012)
Lead	Neuronal damage, hyperactivity and high blood pressure, insomnia (lack of sleep), reduced fertility	Reduced photosynthesis and growth inhibition, inhibits enzyme activity and oxidative stress	Inhibition of enzyme activities and transcription	Nagajyoti et al. (2010), Fashola et al. (2016), Wuana and Okieimen (2011) and Mupa (2013)

 Table 13.2
 Effects of heavy metals on different life forms

(continued)

Heavy				
metal	Human	Plants	Microorganisms	References
Nickel	Cardiovascular diseases, kidney and lung diseases, chest pain and shortness of breath, nasal cancer	Decreased chlorophyll content, inhibition of enzymatic activities and reduced nutrient uptake	Cell membrane disruption and oxidative stress	Fashola et al. (2016) and Chibuike and Obiora (2014)
Zinc	Gastrointestinal irritation, kidney and liver failure, lethargy and metal fume fever, prostate cancer	Affects photosynthesis, inhibition of growth rate, chlorophyll reduction and reduced germination	Decrease in biomass and growth inhibition	Chibuike and Obiora (2014) and Gumpu et al. (2015)

Table 13.2 (continued)

4 Bioremediation by Microorganisms

Microorganisms are considered as most cosmopolitan organisms as they have the ability to thrive in wide range of environmental conditions due to their amazing metabolic ability. Further, they are highly versatile in their nutrition uptake, which that this property makes them very useful for decontaminating the immediate environment. Rock-bottom and economic growth requirements (such as carbon dioxide and sunlight) and the advantage of being utilized simultaneously in for multiple technologies (e.g. biofuel production, carbon mitigation and bioremediation) make microorganisms a perfect candidate for many environment-friendly technologies that may be useful for remediation of soil and water (Kumar et al. 2015). In due course of development, these microorganisms have developed substantial array of mechanisms (extracellular or intracellular) to survive the contaminations led by the heavy metals in soil and waterbodies (Kumar et al. 2015). The microbes that are responsible for acting as an agent for bioremediation are called as bioremediators. Bacteria, archaea and fungi are considered as the classic prime bioremediators (Strong and Burgess 2008). Classic bioremediators are those that can convert, modify and then utilize the converted product to obtain energy and biomass (Tang et al. 2007) and thereby cleaning up the environment and restoring the original natural conditions (Demnerova et al. 2005).

Bacteria, microalgae and fungi employ several methods to decontaminate the soil, and these modern techniques are considered to be more efficient than the conventional techniques. The older conventional techniques for removal of heavy metal toxicity includes hydroxide precipitation, carbonate precipitation and sulphide precipitation, chemical oxidation or reduction, lime coagulation, ion exchange (using resins, starch xanthate, etc.), reverse osmosis, solvent extraction, evaporation recovery, cementation, adsorption (involving use of activated carbon), electrodepo-

sition, reverse osmosis and electrodialysis (Rich and Cherry 1987; Ahalya et al. 2003; Gray 1999; Ahluwalia and Goyal 2007). These conventional methods are also able to remove heavy metals but up to a limited extent. But once the heavy metal concentration reaches the range of 1-100 mg/l, these conventional processes become ineffective (Nourbakhsh et al. 1994). Furthermore, the conventional methods are less efficient and require high expenditure of energy and reagents (Ahalya et al. 2003), have low metal uptake selectivity, generate pernicious wastes or sludge (Ahalya et al. 2003; Ahluwalia and goyal 2007) and bear high investment and regeneration cost (Oboh et al. 2009). So, for more efficient removal of contaminants, introduction of new approaches and techniques that are sustainable becomes a must phenomenon of the era. The main reasons behind the need for enforcement of new technologies are to reduce the heavy metal contamination content below its permissible limit. According to Khan et al. (2008), the contamination beyond the permissible limit in aquatic environment can lead to direct toxicity to aquatic life forms and human beings too. Therefore, the need of the hour is to look for better technologies that are much efficient and capable of removing heavy metal toxicity to satisfy the requirements (Sheng et al. 2004). Moreover, the modern and new technologies to be introduced for removal of heavy metal contamination should be cost-effective and consistent and are able to reduce the contamination to such levels that are acceptable to natural field conditions (Kumar et al. 2015).

Among all different kinds of microorganisms such as bacteria, fungi, algae or microalgae, it is the microalgae that possess immense capability to remediate the contaminated waterbodies. Moreover, these microalgae are thought to be more superior to the prevalent physicochemical processes used for eradication of heavy metal toxicity (Kumar et al. 2015). Microalgae are fresh and marine water dweller organisms that can photosynthesize in very similar way as land plants does. They are considered to be the world's largest group of organisms in terms of biomass that can photosynthesize and thus are responsible for at least 32% of global photosynthesis (Priyadarshani et al. 2011). They are well equipped with proper and systematic molecular mechanisms that have the ability to discriminate the essential heavy metals from non-essential ones (Perales-Vela et al. 2006), and as being the renewable natural biomass, they exhibit distinct affinities towards different kinds of heavy metals. This distinctive ability makes them eligible for acting as biosorbent materials (Doshi et al. 2006; Mallick 2002). According to Monteiro et al. (2012), living and non-living microalgal biomass have the ability to remove the heavy metal contamination present at very low concentration. These microalgae are also having the affinity for polyvalent metals and so can be efficiently employed for cleaning waste water containing dissolved metal ions (de Bashan and Bashan 2010). Apart from all these capabilities, they are very eco-friendly and user-friendly too and can be established easily in polluted area as well. Table 13.3 shows heavy metal removal efficiency of different microalgae (living and non-living) at different pH.

Metal	Organism	pН	Type of biomass	References
Copper (Cu ²⁺)	Anabaena cylindrica	4.0– 5.0	Live	Tien et al. (2005)
Copper (Cu ²⁺)	Chlamydomonas reinhardtii	5.5	Cells without cell wall	Macfie and Welbourn (2000)
Copper (Cu ²⁺)	Chlamydomonas reinhardtii	5.5	Cells with cell wall	Macfie and Welbourn (2000)
Copper (Cu ²⁺)	Ceratium hirundinella	4.0– 5.0	Non-living	Tien et al. (2005)
Copper (Cu ²⁺)	Ceratium hirundinella	4.0– 5.0	Live	Tien et al. (2005)
Copper (Cu ²⁺)	Aulosira fertilissima	5	Non-living	Singh et al. (2007)
Copper (Cu ²⁺)	Aulacoseira varians	4.0– 5.0	Non-living	Tien et al. (2005)
Copper (Cu ²⁺)	Aulacoseira varians	4.0– 5.0	Live	Tien et al. (2005)
Copper (Cu ²⁺)	Asterionella formosa	4.0– 5.0	Non-living	Tien et al. (2005)
Copper (Cu ²⁺)	Asterionella Formosa	4.0– 5.0	Live	Tien et al. (2005)
Copper (Cu ²⁺)	Anabaena spiroides	4.0– 5.0	Live	Tien et al. (2005)
Mercury (Hg ²⁺)	Chlorella vulgarisCCAP211/11B	7	Non-living	Inthorm et al. (2002)
Mercury (Hg ²⁺)	Chlorella vulgaris BCC 15	7	Non-living	Inthom et al. (2002)
Mercury (Hg ²⁺)	Chlamydomonas reinhardtii	6	Non-living	Tüzün et al. (2005)
Iron (Fe ³⁺)	Chlorella vulgaris	2	Non-living	Romera et al. (2006)
Nickel (Ni ²⁺)	Aulosira fertilissima	5.0– 5.5	Non-living	Ferreira et al. (2011)
Nickel (Ni ²⁺)	Arthrospira (Spirulina) platensis	5	Non-living	Singh et al. (2007)
Nickel (Ni ²⁺)	Chlorella spp.		Live	Doshi et al. (2006)
Nickel (Ni ²⁺)	Chlorella spp.		Non-living	Doshi et al. (2008)
Lead (Pb ²⁺)	Microcystis novacekii	5	Non-living	Ribeiro et al. (2010)
Lead (Pb ²⁺)	Oscillatoria laetevirens	5	Live	Miranda et al. (2012)
Lead (Pb ²⁺)	Pseudochlorococcum typicum	7	Live	Shanab et al. (2012)
Lead (Pb ²⁺)	Spirogyra hyaline		Non-living	Kumar and Oommen (2012)
Zinc (Zn ²⁺)	Arthrospira (Spirulina) platensis	5.0– 5.5	Non-living	Ferreira et al. (2011)
Zinc (Zn ²⁺)	Planothidium lanceolatum	7	Live	Sbihi et al. (2012)

(continued)

Metal	Organism	pН	Type of biomass	References
Zinc (Zn ²⁺)	Chlorella vulgaris	5.0-	Non-living	Ferreira et al. (2011)
		5.5		
Zinc (Zn ²⁺)	Desmodesmus pleiomorphus	5	Non-living	Monteiro et al. (2009)

Table 13.3 (continued)

4.1 Mechanism of Uptake of Heavy Metals by Microalgae

The common pathway taken by microorganisms such as microalgae to remove heavy metals from solutions include (i) use of viable microorganisms in accumulation or precipitation of metals in extracellular space; (ii) cell-surface sorption which can be accomplished with both the community of microbes, i.e. living as well as dead microorganisms; and (iii) and the accumulation of heavy metals in intracellular spaces that requires microbial activity (Cossich et al. 2002). Here, both living and dead cells are more or less much efficient in metal accumulation, but the main difference lies in the mechanism that they involve. So, the mechanism of remediation with the help of microalgae could be mainly listed into two categories: (i) bioaccumulation by living cells and (ii) biosorption by non-living, nongrowing biomass. This first process (comprising bioaccumulative uptake) forms the principle involving the process for detoxification of waste materials (e.g. biological fluidized beds employing continually growing biofilms) (Kumar et al. 2015). On the other hand, the dead (heat-killed, dried, acid and/or otherwise chemically treated) cells can accumulate heavy metal in much a similar way, rather to greater extent as compared to the growing or resting cells (Aksu 1998).

Although both living and non-living biomass have the potential to accumulate the heavy metals in them, the living biomass have much interesting mechanism of the same due to different barriers provided by cell walls, plasma membrane, cell organelles, etc. (Kumar et al. 2015). Initial barrier provided by cell wall of microalgae stands to be less effective as the wall comprise mainly of polysaccharides, proteins and lipids, which offer several functional groups (e.g. carboxyl, -COOH; hydroxyl; -OH; phosphate; -PO₃; amino; -NH₂; and sulfhydryl-SH) that provides net negative charge to the wall. This galaxy of negative charges proves profitable for the positively charged cations such as cadmium, chromium, copper, etc. (Chojnacka et al. 2005). Much in the similar way, the plasma membrane also provides the second barrier to the heavy metals. In microalgae there exist two kinds of transport proteins, that is, Group A and Group B transporter proteins, where Group-A transporters {such as NRAMP (natural resistance-associated macrophage proteins), ZIP (Zrt-, Irt-like proteins), FTR (Fe transporter) and CTR (Cu transporter) families} help in moving metals inside the plasma membrane and Group-B transporters {such as CDF (cation diffusion facilitator), P1B-type ATPases, FPN (FerroPortiN) and Ccc1 (Ca (II)-sensitive cross-complementer 1)/VIT1 (vacuolar iron transporter 1) families} help in the exocytosis of excess metals (Blaby-Haas and Merchant 2012). Apart from these two ways of uptake of heavy metals by microalgae, some more ways are possible such as ion exchange concept (very similar to the concept of cell wall uptake), sequestration and compartmentalization in vacuoles (Monteiro et al. 2012) and sequestration to the chloroplast and mitochondria (Perales-vela et al. 2006; Shanab et al. 2012).

Microalgae being apt for the bioremediation are widely used in the environment, but the expertise exhibited by other microbes such as bacteria and fungi cannot be overlooked or underestimated. In environment, different types of contaminants are present in intermingled nature. So, the contaminants that exist in coordination with others are called as co-contaminants, for example, association of PAH (polycyclic aromatic hydrocarbons) with heavy metals (Liu et al. 2017). Different of microbes are thought to be used in treatment of these co-contaminants such as bacteria and fungi. Some commonly found bacteria that are used for PAHs and heavy metals bioremediation are *Bacillus, Escherichia* and *Mycobacterium*. They have the capability to breakdown the PAHs such as anthracene, naphthalene, phenanthrene, pyrene and benzopyrene in the presence of heavy metals and can diminish the repression brought about by some heavy metals such as Cd, Cu, Cr and Pb occurring together with PAHs (Table 13.4).

4.2 Factors Affecting Microbial Bioremediation

The efficiency of bioremediation depends on many factors including the chemical nature and concentration of pollutants, the physicochemical characteristics of the environment and their availability to microorganisms (Fantroussi and Agathos 2005). The rate of degradation of contaminants by bacteria is more or less retarded due to less frequency of interaction between them. In addition to this, microbes and pollutants are not uniformly spread in the environment. The controlling and optimizing of bioremediation processes is a complex system due to many factors such as existence of microbial population capable of degrading the pollutants, the availability of pollutants, availability of contaminants to the microbial population and environmental factors such as the soil type and texture, temperature and pH, the presence of oxygen and other electron acceptors and nutrients (Abatenh et al. 2017).

4.3 Advantages and Disadvantages of Bioremediation by Microbes

Microorganisms are found naturally in the environment whether it is beneficial or non-beneficial. And the beneficial microorganisms are necessary for sustaining the natural connectivity of the food chain. In nature they exist as simple organisms, with less labour intensive to culture and are cheap due to their natural role in the environment (Abatenhet al. 2017). According to Dell anno et al. (2012), microorganisms used for bioremediation are environment-friendly and helps in maintaining

Microorganisms	Compounds	References
Penicillium chrysogenum	Monocyclic aromatic hydrocarbons, benzene, toluene, ethyl benzene and xylene, phenol compounds	Pedro et al. (2014) and Abdulsalam et al. (2013)
P. alcaligenes, P. mendocina and P. putida P. veronii, Achromobacter, Flavobacterium, Acinetobacter	Petrol and diesel polycyclic aromatic hydrocarbons toluene	Safiyanu et al. (2015) and Sani et al. (2015)
Pseudomonas putida	Monocyclic aromatic hydrocarbons, e.g. benzene and xylene	Safiyanu et al. (2015) and Sarang et al. (2013)
Phanerochaete chrysosporium	Biphenyl and triphenylmethane	Erika et al. (2013)
A. niger, A. fumigatus, F. solani and P. funiculosum	Hydrocarbon	AI-Jawhari (2014)
Coprinellus radians	PAHs, methylnaphthalenes and dibenzofurans	Aranda et al. (2010)
Alcaligenes odorans, Bacillus subtilis, Corynebacterium propinquum, Pseudomonas aeruginosa	Phenol	Singh et al. (2013)
Tyromyces palustris, Gloeophyllum trabeum, Trametes versicolor	Hydrocarbons	Karigar and Rao (2011)
Candida viswanathii	Phenanthrene, benzopyrene	Hesham et al. (2012)
Cyanobacteria, green algae and diatoms and Bacillus licheniformis	Naphthalene	Hesham et al. (2012) and Lin et al. (2010)
Acinetobacter sp., Pseudomonas sp., Ralstonia sp. and Microbacterium sp.	Aromatic hydrocarbons	Hesham et al. (2012)
Gloeophyllum striatum	Striatum pyrene, anthracene, 9-metilanthracene, dibenzothiophene lignin, peroxidase	Yadav et al. (2011)
Acinetobacter sp., Pseudomonas sp., Ralstonia sp. and Microbacterium sp.	Aromatic hydrocarbons	Hesham et al. (2012)
Gloeophyllum striatum	Striatum pyrene, anthracene, 9-metilanthracene, dibenzothiophene lignin, peroxidase	Yadav et al. (2011)
Acinetobacter sp., Pseudomonas sp., Ralstonia sp. and Microbacterium sp.	Aromatic hydrocarbons	Hesham et al. (2012)
Fusarium sp.	Oil	Hidayat A and Tachibana (2012)
Alcaligenes odorans, Bacillus subtilis, Corynebacterium propinquum, Pseudomonas aeruginosa	Oil	Singh et al. (2013)
Bacillus cereus A	Diesel oil	Maliji et al. (2013)

 Table 13.4
 Microorganisms, especially fungi and bacteria, capable of remediating heavy metals, oils, dyes, pesticides and many hydrocarbons

(continued)

Microorganisms	Compounds	References
Aspergillus niger, Candida glabrata, Candida krusei and Saccharomyces cerevisiae	Crude oil	Burghal et al. (2016)
B. brevis, P. aeruginosa KH6, B. licheniformis and B. sphaericus	Crude oil	El-Borai et al. (2016)
Pseudomonas aeruginosa, P. putida, Arthrobacter sp. and Bacillus sp.	Diesel oil	Sukumar and Nirmala (2016)
Citrobacter koseri and Serratia ficaria, Pseudomonas cepacia, Bacillus cereus, Bacillus coagulans	Diesel oil, crude oil	Kehinde and Isaac (2016)
B. subtilis strain NAP1, NAP2, NAP4	Oil-based based paints	Phulpoto et al. (2016)
Myrothecium roridum IM 6482	Industrial dyes	Jasin et al. (2012, 2013, 2015)
Pycnoporus sanguineus, Phanerochaete chrysosporium and Trametes trogii	Industrial dyes	Yan et al. (2014)
Penicillium ochrochloron	Industrial dyes	Shedbalkar and Jadhav (2011)
<i>Micrococcus luteus, Listeria</i> <i>denitrificans</i> and <i>Nocardia atlantica,</i> <i>Textile</i>	Azo dyes	Hassan et al. (2013)
Bacillus spp. ETL-2012, Pseudomonas aeruginosa, Bacillus pumilusHKG212	Textile dye (Remazol black B), sulfonated diazo dye, Reactive Red HE8B, RNB dye	Yogesh and Akshaya (2016) and Das et al. (2015)
Exiguobacterium indicum, Exiguobacterium aurantiacums, Bacillus cereus and Acinetobacter baumannii	Azo dyes effluents	Kumar et al. (2016)
Bacillus firmus, Bacillus macerans, Staphylococcus aureus and Klebsiella oxytoca	Vat dyes, textile effluents	Adebajo et al. (2017)
Cunninghamella elegans	Heavy metals	Bahobil et al. (2017)
Pseudomonas fluorescens and Pseudomonas aeruginosa	Fe ²⁺ , Zn ²⁺ , Pb ²⁺ , Mn2+ and Cu2	Paranthaman and Karthikeyan (2015)
Lysinibacillus sphaericus CBAM5	Cobalt, copper, chromium and lead	Peña-Montenegro et al. (2015)
Microbacterium profundi strain Shh49T	Fe	Wu et al. (2015)
Fumigatus, Paecilomyces sp., Paecilomyces sp., Trichoderma sp., Aspergillus versicolor, A. Microsporum sp., Cladosporium	Cadmium	Soleimani et al. (2015)
Geobacter spp.	Fe (III), U (VI)	Mirlahiji and Eisazadeh (2014)

Table 13.4 (continued)

(continued)

Microorganisms	Compounds	References
Bacillus safensis (JX126862) strain (PB-5 and RSA-4)	Cadmium	Priyalaxmi et al. (2014)
Pseudomonas aeruginosa, Aeromonas sp.	U, Cu, Ni, Cr	Sinha et al. (2011)
Aerococcus sp., Rhodopseudomonas palustris	Pb, Cr, Cd	Sinha and Paul (2014) and Sinha and Biswas (2014)
Saccharomyces cerevisiae	Heavy metals, lead, mercury and nickel	Chen and Wang (2007), Talos et al. (2009) and Infante et al. (2014)

Table 13.4 (continued)

sustainability in the environment by destroying the contaminants, thus maintain the cycle of nature. Moreover, the contaminants that are destroyed by these microorganisms are not simply transferred to different environmental media. Further, they are nonintrusive, potentially allowing for continued site use. According to Kumar et al. (2011), they are relatively easy to implement in ground-level experiments. Thus, the use of microorganisms stands to be the most effective way of remediating natural ecosystem from a number contaminates and acts as environment-friendly options (Singh et al. 2013). Although there are many advantages of using microorganisms for remediating the natural environment from various heavy metal contaminants, the benefits are limited to those compounds that are biodegradable in nature. In addition to this, not all compounds are susceptible to rapid and complete degradation (Abatenh et al. 2017). Also, there are some concerns that the products of biodegradation (in some cases) may be more persistent or toxic than the parent compound (Abatenh et al. 2017). In nature, biological processes are often highly specific and the site factors are quite important requisites. Important site factors required for success includes the presence of metabolically capable microbial populations, suitable environmental growth conditions and appropriate levels of nutrients and contaminants (Abatenh et al. 2017). A very high-profile research is needed to develop and engineer bioremediation technologies that are appropriate for sites with complex mixtures of contaminants (solids, liquids or gases) that are not evenly dispersed in the environment. Contaminants may be present as solids, liquids and gases.

5 Phytoremediation

An unequalled and rapid emerging branch of bioremediation that fits best as ecofriendly approach and employs natural properties of plants for removal of contaminants from soils is phytoremediation (Oh et al. 2014). This phytoremediation process has gained its importance due to its cost-effective, efficient and
non-invasive way of decreasing the pollutants from water and soils (Mojiri 2012) without showing any negative effect on the environment. This technology is widely applicable in remediating inorganic contaminants such as heavy metals and radionuclide, as well as organic contaminants such as polyaromatic hydrocarbons, chlorinated solvents, etc. (Wang et al. 2003; Oh et al. 2013a, b). The urge for the enforcement of this process is due to continuous contamination of heavy metals beyond its threshold limit which is harmful to all forms of life (Gaur et al. 2014; Dixit et al. 2015; Tak et al. 2013). Earlier it was natural sources which were dominating over anthropogenic sources for heavy metal pollution, but nowadays due to rapid urbanization and industrialization, the anthropogenic sources of pollution left the natural sources way beyond the expectations. Industries that are energy intensive has been established for power an electricity production such as thermal power plants, coal mines, etc. pose to be major sources of anthropogenic pollution (Rai et al. 2007). Many large agrochemical industries such as chlor-alkali industries release large amount of range of heavy metals into the lakes and reservoirs thereby deteriorating the water quality (Rai et al. 2007). Different standards have been set for different heavy metals in water as well as soil to regulate its concentration. According to Comprehensive Environmental Response Compensation and Liability Act (CERCLA), USA, the maximum permissible concentration of heavy metals in water was given as 0.01 for Ar, 0.01 for Cr, 0.02 for Hg, 0.05 for Cd, 0.05 for Ag and 0.15 for lead (mg/litre) (Chaturvedi et al. 2015). Similarly, according to Indian Standards, the maximum concentration should be 3-6 for cadmium, 75-150 for nickel, 135–270 for copper, 250–500 for lead and 300–600 for zinc (in mg/kg) (Nagajyoti et al. 2010). Phytoremediation proves to be very modern and costeffective technology as compared to old conventional techniques, viz. vapour extraction, soil washing, thermal desorption, etc., that leads to other problems such as air and groundwater pollution (Oh et al. 2013a, b). Among the conventional techniques, onsite management or excavation and then dumping of the same waste containing heavy metals pose to be a great threat as it just changes the site of contamination and are often act as a reason for hazard associated with transportation throughout the path of travel to dump area (Tangahu et al. 2011). There are chemical technologies and physical methods too that help in remediating the heavy metal contamination, but they are technically difficult to use and are too expensive and generate large volumetric sludge thereby contributing pollution to the environment again (Rakhshaee et al. 2009). On the other hand, phytoremediation stands to be very useful as it uses sunlight as its energy source and natural green plants for remediation of soil contaminants which can be done in situ. Moreover, this process has least or no secondary contaminants as it immobilizes them, thereby preventing their entry into the groundwater thus protecting the soil profile and enhancing the quality of soil and prevents the soil resources (Oh et al. 2013a, b). According to some workers, phytoremediating plants could metabolize large and highly toxic substances into small and non-toxic ones, but this capability greatly varies from species to species (Oh et al. 2013a, b). Phytoremediating plants have variable capabilities due to difference in their growth rates, their biomass, depth of root zone and their potential to transpire groundwater into the atmosphere (Oh et al. 2013a, b). Besides all the advantages, phytoremediation has some shortcoming as it takes a long time to remediate the soil contamination and is limited by the climatic, geological conditions and the type of soil of that area.

Worldwide, dedicated research is going on to find different ways for remediating heavy metals from soil and water, and till date the phytoremediation process proved to be the best technique and only sustainable alternative to all kinds of remediation. Different plants species have been used to evaluate the phytoremediation capability of plants by varying the type of plant species, properties of medium (pH adjustment, fertilizer) (Prasad and Freitas 2003) and addition of chelating agent such as EDTA (Ginneken et al. 2007), etc. Tables 13.5 and 13.6 enlist some phytoremediating plants that can be used for phytoremediation of heavy metals (Table 13.5) and hydrocarbons (Table 13.6).

6 Different Processes of Uptake of Heavy Metals by Plants in Contaminated Soils

Plants are the amazing creation of nature being always help in bringing up the environment to stabilize itself by various means. Much on the same way, various plant parts absorb heavy metal contaminants present in soil and water leaving the environment pollution-free. Root, shoot and leaves accumulate the metals inside their tissues by many different processes leading to decontamination of important abiotic resources such as soil and water. The urgency of the process is due to the nasty property of heavy metals off being long time persistent and its non-biodegradable nature which increases the threat to human beings and other animal's health (Gisbert et al. 2003). Figure 13.1 depicts various areas of plants for uptake, absorption and evaporation of contaminants. Various processes are involved in the process of phytoremediation which are discussed below.

6.1 Phytoextraction

Phytoextraction is the process of absorption of soil contaminants by plants where it stores or concentrates them in the shoots and harvestable parts of the root. Nickel, copper and zinc are the best members to be absorbed by plants, and over 400 plants can absorb them easily, and they can be "removed permanently" from the soil and water (Etim 2012; Upadhyay et al. 2019). The plants that are selected for this process exhibit excellent property to produce high biomass. But, according to Evangelou et al. (2007), most of the metal accumulating plants are generally found to be slow growing and are having very low capacity to produce considerable amount of biomass. So, the plants with these properties are supposed to discourage the process of phytoextraction as it wholly and solely depend on tissue metal concentration and

Name of plant	Metal	Process	References
<i>Cerastium arvense</i> (field chickweed)	Cadmium	Uptake/accumulation	Institute for environmental research and education (2003)
Claytonia perfoliata (miner's lettuce)	Cadmium	Uptake/accumulation	Institute for environmental research and education (2003)
Lupinus albus (white lupin)	Arsenic	Rhizoaccumulation	Esteban et al. (2003)
Vicia spp. (vetch)	Nutrients/ metals	Uptake	McCutcheon and schnoor (2003)
<i>Thlaspi caerulescens</i> (alpine pennycress)	Cadmium, zinc, nickel	Hyperaccumulation	McCutcheon and schnoor (2003)
Solidago hispida (hairy goldenrod)	Metals	Hyperaccumulation	McCutcheon and schnoor (2003)
Gleditsia triacanthos (honey locust)	Lead	Phytoextraction	García et al. (2003)
Populus tremula (Aspen)	Lead	Extraction	McCutcheon and schnoor (2003)
Viola spp. (violets)	Metals	Phytoextraction/ hyperaccumulation	Institute for environmental research and education (2003)
Water bloom/algal bloom (<i>Microcystis</i> sp.)	Metals	Uptake	Rai et al. (2007)
Reed (Phragmites australis; Phragmites karka)	Metals	Uptake	Bragato et al. (2006) and Vymazal (2007)
Water fern, water velvet (Azolla caroliniana, Azolla pinnata)	Metals	Uptake	Rai et al. (2007)
Bulrush/cattail (Typha latifolia, Typha angustata, Typha domingensis)	Metals	Uptake	Manios et al. (2003) and Hadad et al. (2006)
Poplar trees (<i>Populus deltoids</i>)	Metals	Uptake	Robinson et al. (2000)
Pond weed/curly leaf pond weed (<i>Potamogeton natans</i> ; <i>Potamogeton crispus</i>)	Metals	Uptake	Fritioff and Greger (2006)
Parrot's feather (Myriophyllum spicatum)	Metals	Uptake	Lesage et al. (2007)
Umbrella plant (<i>Cyperus alternifolius</i>)	Metals	Uptake	Qian et al. (1999)
Duckweed (Lemna minor)	Metals	Uptake	DeBusk et al. (1996)

Table 13.5 Table showing phytoremediating plants capable of heavy metal uptake

biomass production (Chaney et al. 2007). Different species of plants differ in their capability of concentrating metals in them, and the species that can accumulate 100 mg kg⁻¹f cadmium (Cd), 1000 mg kg-1 of arsenic (As), cobalt (Co), copper (Cu), lead (Pb) or nickel (Ni) or >10,000 mg kg⁻¹ of manganese (Mn) and zinc (Zn) are considered as hyperaccumulator plants. There are several steps that are

Canadian wild rye (<i>Elymus canadensis</i>)	Hydrocarbons	Rhizodegradation/ accumulation	McCutcheon and Schnoor (2003)
(Red fescue <i>Festuca rubra</i>)	Hydrocarbons	Rhizodegradation	McCutcheon and Schnoor (2003)
(Tall fescue) (Festuca arundinacea)	Pyrene, PAHs and NPK	Rhizodegradation/ phytoextraction	Christensen-Kirsh (1996) and McCutcheon and Schnoor (2003)
English ryegrass (Lolium perenne)	Hydrocarbons/ nutrients	Rhizodegradation/ uptake	McCutcheon and Schnoor (2003)
(Yellow sweet clover) Melilotus officinalis	Hydrocarbons and NPK	Rhizodegradation	Christensen-Kirsh (1996) and McCutcheon and Schnoor (2003)
Switchgrass (Panicum virgatum)	Hydrocarbons	Rhizodegradation	McCutcheon and Schnoor (2003)
Mulberry (Morus rubra)	PAHs and PCBs	Rhizodegradation	McCutcheon and Schnoor (2003)

Table 13.6 Table showing some phytoremediating plants capable of hydrocarbon accumulation



Fig. 13.1 Different methods of remediation of heavy metals contamination in soil by plants. (Modified from Oh et al. 2014)

necessary for hyperaccumulation of heavy metals by plants which includes absorption and transportation of metals across the membranes of root cells followed by uploading of metals into xylem for its transportation and then the translocation of these metals to the shoots and thus sequestration and detoxification of metals within plant tissues (Yang et al. 2005). According to Rascio and Navari-Izzo 2011, the plant epidermis, its trichomes and cuticle are the favourable lodging sites for detoxification of metals, and in several instances, the subsidiary and stomatal cells are protected against metal toxicity.

Since this process generally indulge in accumulation of metals in lower concentration due to inefficiency of plants to produce larger biomass, therefore these hyperaccumulator plants discourages their adoption in larger scale or for commercial purpose. But few plants with metal tolerable capacity can be thought to be effectively used for commercial scale (Saifullah et al. 2009). However, these species have an inherently low ability to absorb metals but can accumulate higher concentrations of metals if grown in the soils treated with chemical amendments to increase metal phytoavailability and plant uptake (Meers et al. 2005).

6.2 Phytostabilization

Sites with high concentration of contamination of heavy metals are difficult to remediate. So, this level of contamination is so much so that the phytoextraction of metals from such soils would take a considerably longer period of time which is neither economical nor suitable. In such cases if remediation technology is not applied quickly and effectively then, these could be a major source of metal dispersion into the environment. The risk posed by such soils can be decreased by using plants to stabilize or immobilized the metals in the soil (Margues et al. 2009). Such process of immobilization of soil contaminants by accumulating or precipitating it with the help of root and its exudates within rhizospheric region, to limit its spread to the food chain is called as phytostabilization. In the process of phytostabilization, plants readily immobilizes the metals present in the rhizospheric zone thereby leaving them less bioavailable and less toxic to plants, animals and humans or retain the metals in the roots by restricting their translocation to above-ground parts (Mendez and Maier 2008; Wong 2003). This technology is quite useful in treatment of lead (Pb), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu) and zinc (Zn) (Etim, 2012).

The main mechanism of phytostabilization is the precipitation and adsorption of heavy metals near the rhizospheric zone where these metals are converted into less soluble forms like carbonates and sulphides of metals, metal complexes with organic compounds, metal adsorption on root surfaces and metal accumulation in root tissues (Mendez and Maier 2008; Wong 2003). The presence of plants in metalcontaminated soils promotes heterotrophic microbial communities which may, in turn, promote plant growth and participate in metal stabilization. Metal-tolerant plants with the capacity to keep the metals out of metabolic sites (shoots) are the best candidates for phytostabilization. Although such plants have developed mechanisms to restrict the metals in the rhizosphere or roots, even then concentration of metals in shoots must be monitored (Mendez and Maier 2008). Among many phytoextracting plant species the Cynodon dactylon was found to be the best accumulator of As in roots and thus a promising candidate for phytostabilization and have wide adaptations in Pb- and Zn-contaminated soils also (Leung et al. 2007). Moreover, the mycorrhizae (interaction of fungi with the roots of higher plants) play an important role in stabilization by binding the metals with hyphae, and some mycorrhizae like ericoid and ectomycorrhizal fungi colonizing in Cynodon dacty*lon* can modify the rhizosphere by excreting organic acids and thus stabilizing metals in the rhizosphere (Meharg 2003). Vetiveria zizanioides, Sesbania rostrata, herb legume and Leucaena leucocephala have been successfully grown in metalcontaminated soils for metal stabilization (Shu et al. 2002; Zhang et al. 2001). This phytostabilization technique is effective only when the phytoextraction method is not efficient (Sabir et al. 2014), and the efficiency of this process can be enhanced by performing and applying soil amendments like zeolites, beringite, steel shot and hydroxyapatite (Lothenbach et al. 1998).

6.3 Phytodegradation

Breakdown of organic contaminants by plants either internally through its metabolic pathway with the help of secreted enzymes or externally by root exudates and incorporation of these contaminants into plant tissues (Trap et al. 2005). This process is mainly used to degrade complex organic molecules and convert it into simpler forms in soils, groundwater medium and sledges. Some complex organic compounds that are reported to be degraded by this process are tetra-chloroethane by poplar species, 2, 4-dichlorophenol by *Brassica*, benzotriazoles by *Helianthus*, trifluralin and lindane by rye, gasoline by pothos, diesel and heavy oil by grasses native to California (Newman and Reynolds 2004).

6.4 Rhizodegradation (Phytostimulation)

Disintegration of contaminants in the soil through the activity of microorganisms, enhanced by the presence of root zone, is known as rhizodegradation (Tangahu et al. 2011). According to USEPA, 2000, the rhizospheric region contains at least 100 times more number of microbes as compared to non-rhizospheric region. This process mainly helps in remediating organic hydrocarbons such as petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), chlorinated solvents, pesticides, polychlorinated biphenyls (PCBs), benzene, toluene, ethylbenzene and xylenes (EPA 2000).

6.5 Phytovolatilization

In phytovolatilization contaminants such as selenium, mercury, arsenic, etc. that are absorb by the root of the plants are converted to more simple forms and are then volatilized through stomata of the leaves to the atmosphere. In phytostabilization metals are assimilated into organic compounds which are volatile in nature and ultimately released into atmosphere as biomolecules (Marques et al. 2009). This process is primarily used for removal of mercury (Hg) contamination from the soil along with other metals such as Se and As. During the course of development, molecular technology reveals the presence of a gene that is responsible for reducing mercuric ion into elemental mercury through enzyme mercury reductase (Rugh et al. 1996). The gene, merApe9, has been introduced into Arabidopsis thaliana which ultimately volatilizes large amounts of Hg into the atmosphere (Rugh et al. 1996). Although the advantage of this process is that the mercury ion can be easily transformed to the less toxic elemental form, unfortunately the disadvantage associated with it is much greater as there is huge probability of recycling of mercury by precipitation and thus its accumulation in lakes and oceans with pose a great threat to aquatic life forms (USEPA 2000). A very similar phenomenon is observed in case of selenium. Brassica juncea has been shown to volatilize Se into the atmosphere through assimilation of Se from the soil into organic seleno-amino acids, selenocysteine and seleno-methionine which later can be biomethylated to form the volatile compound dimethylselenide (Banuelos et al. 1993; Terry et al. 2000). These processes have not gained much importance as the probability of recycling of volatile metallic compound is very high.

Thus, different plant species employing different processes of uptake of heavy metals from metal-contaminated soils can be depicted in Table 13.7 which shows plant species remediating different heavy metals by different mechanisms.

7 Advantages and Limitation of Phytoremediation

Phytoremediation have some significant advantages in terms that they help in reducing the heavy metal ion concentration either by changing its form or by reducing them to low levels with the help of inexpensive biosorbent materials (Rakhshaee et al. 2009). According to Rodrigues (2005), there are various methods that are used for phytoremediation which lead to degradation of heavy metal contents in soil. Moreover, phytoremediation shows its transparency towards lowest remediating capacity, that is, a cost-effective method accompanying least expensive approach for remediation of the environmental media, mainly appropriate for large sites containing relatively low levels of contamination (Ginneken et al. 2007). Furthermore, the phytoremediation technology can also be used for remediating wide range of toxic metals and radionuclides and are equally useful for detoxifying organic as well as inorganic contaminants to a level that are acceptable to the society and

	Phytoremediation			
Plant	type	Metal	Mechanism	References
Sedum alfredii H	Phytostabilization	Pb and Cd	Induction of glutathione biosynthesis that bind metals in roots	Anjum et al. (2012), Gupta et al. (2010) and Sun et al. (2007)
Athyrium wardii	Phytostabilization	Pb and Cd	Root retention of metals	Zou et al. (2011)
Ceratophyllum demersum	Phytoextraction	Cd	Production of phytochelatin for metal binding in shoots	Mishra et al. (2009)
			Activation of cysteine synthase, glutathione-S- transferase, glutathione	
Pteris vittata	Phytoextraction	As	Increased colonization	Leung et al. (2007)
			Exploring more soil	
Sedum alfredii	Phytoextraction	Zn	Metals loaded into leaf sections and protoplast	Yang et al. (2005)
Imperata cylindrical, Miscanthus floridulus	Phytostabilization	Cd, Zn, Cu, Pb	Fibrous root system retaining the metals	Peng et al. (2006)
Cynodon dactylon	Phytostabilization	As, Zn, Pb	Binding with hyphae of mycorrhizae	Leung et al. (2007)
			Release of organic acids	

 Table 13.7
 Plants species with different processes for heavy metal remediation from contaminated soil

environment (Liu et al. 2017; Mwegoha 2008). Vivid researches on phytoremediation technique also help in improving the soils that are enriched with high aluminium and soil level (US Department of energy 1994). Although phytoremediation is good, reliable and cost-effective technique, it can be very a time-consuming process, i.e. it may take several growing season for completion of the process (Mwegoha 2008). It may take weeks to months for excavation and disposal of wastes, or it may extend up to several years to accomplish process exquisitely (Tangahu et al. 2011). Once the process is done, the by-products or the intermediate formed during the remediation process, which is either organic or inorganic in nature, may be cytotoxic to plants itself (Mwegoha 2008).

8 Mechanism of Uptake of Heavy Metals in Plants

Accumulation of heavy metals in small quantities is essential for plant growth and metabolism; however, at higher concentration they stand to be potentially toxic to plants and thus the soil ecosystem (Nagajyoti et al. 2010). Living organism absorbs

heavy metals directly or indirectly, and the over-accumulation of metals ultimately leads to the production of reactive oxygen species (ROS) followed by apoptosis (Shi et al. 2004). These heavy metals are initially encountered by the macromolecules such as proteins. So, to understand the real mechanism or the pathway taken by the heavy metals to get absorbed inside the tissues, we need to search for the proteins that bind these metals or metal ions to it. In fact, these heavy metal-binding proteins are encoded by specific genes. If these genes are properly searched out and thorough analysis is done, then it would be the answer to the mechanism of action of the heavy metals.

According to Trivedi and Ansari (2015), the expressed sequence tags (ESTs) analysis is the best technique that would help to elucidate the sites of accumulation or hyperaccumulation of the heavy metals. With the help of biotechnological techniques and immobilized metal ion affinity chromatography or IMAC, the metal ions are finally immobilized (Trivedi et al. 2003). Following the immobilization of the heavy metals, it initially binds with the cell walls or the membrane, which acts as an ion exchange agent of comparatively low selectivity. Further, the transport systems, with activation and deactivation of intracellular high-affinity binding sites, help in the uptake of these metals across the plasma membrane through secondary transporters such as channel proteins and/or H⁺ -coupled carrier proteins (Chaney et al. 2007). These transporters act through a series of signalling events like phosphorylation cascades, hormones, mitogen-activated protein kinases and calcium-calmodulin systems (Shi et al. 2004).

In the last few years, extensive studies have been done on membrane transporter genes, and few membrane transporter gene families have been identified. After their identification they are characterized by heterologous complementation screens and sequencing of ESTs and plant genome studies. Many cation transporters have been identified in recent years, most of which are Zn-regulated transporter (ZRT), Fe-regulated transporter (IRT), natural resistance-associated macrophage proteins (NRAMP), Al-activated malate transporter (ALMT), cation diffusion facilitator (CDF), P-type ATPase (heavy metal associated), yellow stripe-like (YSL), copper transporter and nicotianamine synthase (NAS) (Guerinot 2000; Williams et al. 2000; Talke et al. 2006; Memon and Schroder 2009; Maestri et al. 2010). Once these heavy metals enter the plant tissues, the subsequent movement of metal takes place through the plant sap with the help of root pressure and by the process called transpirational pull (Robinson et al. 2003). Further the responsibility of transporting these heavy metals to the shoot parts are completed by the xylem cells. Since heavy metals at its higher concentration inside the cell become very much toxic to plants, they start an enzymatic process catalysing oxidation reduction reactions and thereby alter their chemistry from toxic to non-toxic forms. Two such examples are reduction of Cr⁶⁺ to Cr³⁺ in *Eichhornia crassipes* (Lytle et al. 1998) and reduction of As⁵⁺ to As³⁺ in *B. juncea* (Pickering et al. 2000). Besides this, some of the intracellular metals are detoxified by some different mechanism such as they either binds to low molecular mass organic compounds or they may get localized in the vacuoles as a metal-organic acid complex, or they may bind to histidine itself (Persans et al. 1999; Kramer et al. 2000). Heavy metal concentration in the cytoplasm can be regulated in many ways, and among many metals, Zn shows most diversified ways in regulating its concentration, which involves sequestration in a subcellular organelle to low molecular mass organic ligands, low uptake across the plasma membrane and precipitation as insoluble salts and active extrusion across the plasma membrane into the apoplast (Brune et al. 1994). There have been many investigations done in different disciplines of science to understand the mechanism of accumulation and tolerance of heavy metals. Finally, the molecular and genetic engineering technologies led to the well understanding of mechanisms of heavy metals in plants. Furthermore the information, of mechanism of remediation, the rate-limiting steps for uptake, translocation and detoxification of metals in hyperaccumulating plants can be thought to be used in the development of many transgenic plants with increased resistance and uptake of heavy metals and thus improving the applicability of the phytoremediation technology (Yang et al. 2005).

9 Remedial Technologies for Metal-Contaminated Soil

In today's era of scarcity of land under farming and the invariable increase in population size, there is always an urge of fertile land for cultivation and clean water for irrigation. Thus it has become very important for remediating the contaminants from soil and water by generating certain remediation technologies.

Remediation technologies can be classified according to (1) the nature of action that is applied on the metals immobilization or extraction, (2) the location where the process is applied in situ or ex situ and (3) technology type, i.e. containment/disposal methods, or chemical, physical, thermal and biological treatments or monitored



Fig. 13.2 Shows certain remedial technologies which can be useful in removal of metals from the metal-contaminated soil. (Taken from: Dermont et al. 2008)

natural attenuation (Dermont et al. 2008). Figure 13.2 shows certain remedial technologies which can be useful in removal of metals from the metal-contaminated soil.

10 Conclusions

Bioremediation is a powerful tool available to clean up contaminated sites. However, other applications are relatively new, and many other applications are emerging or being developed. Bioremediation occurs when the microorganisms can biodegrade the given contaminant and the necessary nutrients such as nitrogen, phosphorus, electron acceptors and trace elements. This process can be aerobic or anaerobic depending on the microorganisms and the electron acceptors available. This process may be natural (intrinsic bioremediation), or it may be enhanced by man (engineered bioremediation). Regardless of which aspect of bioremediation that is used; this technology offers an efficient and cost-effective way to treat contaminated groundwater and soil. But the effects for increasing the scope and efficiency of phytoremediation and for developing phytoremediation systems for sites contaminated with multi-contaminants are urgently necessary. Although some companies have started their business in phytoremediation, phytoremediation has not been fully commercialized. Further research is still needed, and the priorities on phytoremediation for the future should focus on establishing stable and efficient phytoremediation systems through finding more efficient remediating plants and microbes, monitoring current field trials to obtain thorough understanding, developing microbe-plant combination systems and using genetic engineering technology. Phytoremediation are expected to be used as a vital tool in sustainable management of contaminated soils. Contaminated site managers should consider phytoremediation when evaluating remedial alternatives.

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Chapter 14 Wastewater Treatment Through Nanotechnology: Role and Prospects



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Abstract Water is a most crucial and limited resource on the Earth, which has contaminated due to the addition of heavy metals, pathogens, pesticides, and many organic and inorganic substances. Currently, the research has been focused on the sustainable remediation approach for waste reclamation. Therefore, an affordable technology of wastewater treatment could tackle the problem of water. Nanotechnology is an efficient, affordable, effective, and durable method for water treatment. Nanomaterials have several properties such as specific surface area, high reactivity, high degree of functionalization, size-dependent properties, etc., which make them appropriate materials in wastewater treatment. The present chapter comprehensively describes the characteristics of different nanomaterials and their role in the restoration of aquatic ecosystem.

Keywords Nanotechnology \cdot Environmental pollution \cdot Wastewater \cdot Nanofiber membrane \cdot Nanoadsorbents \cdot Fullerenes

1 Introduction

Nanotechnology is an emerging technology of the twenty-first century used to solve the problem of water shortages and water pollution (Mueller and Nowack 2008). Nanotechnology provides new opportunities in technological developments for better wastewater treatment over the traditional physical, chemical, and biological process. Nano is derived from a Greek word which means "dwarf." Nanomaterials are employed for the expulsion of toxic materials and wastages from water; therefore it plays a major role in the abstraction of water contamination (Amin et al. 2014).

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Water pollution is one of the main crises causing negative impact on plants and human health. Therefore, amplification of technologies for the betterment of the environment is the major need of the hour. Nanotechnology atop the traditional approaches propounds up to the minute opportunities in the technological upgradation for better wastewater technology scheme by employing antimicrobial nanomaterials (Pendergast and Hoek 2011). In this chapter, we enlighten the issue of fresh water and the cost-effective techniques of nanomaterials along with its interactions with several related biological systems (Theron et al. 2008) to treat the wastewater.

The Earth is the only planet of solar system where water (97%) exists (Grey et al. 2013; Pradeep 2009). However, due to its unprecedented utilization, mismanaged remediation of wastewater and high pollution level causes the water unfit for drinking and other agriculture activities. In a report of WHO, it was assumed that by 2025, half of the world's population will be living in water-deficient areas (WHO 2015). The water contains a number of toxic metals such as Hg, Cr, Pb, Co, Ni, As, and Ag, which damage the human health as well as the environment (Mishra et al. 2018; Theron et al. 2008; Yadav et al. 2017). Various traditional techniques are available for the treatment of wastewater, i.e., through a chemical and physical agent such as chlorine and its derivatives, ultraviolet light, boiling, low-frequency ultrasonic irradiation, distillation, reverse osmosis, water sediment filters, activated carbon, etc. This traditional technique of pollutants' removal from wastewater as well as drinking water suffers many disadvantages such as high cost, uses and disposal, and high energy requirement. So, there is an urgent need for the treatment of wastewater in a cost-effective and sustainable manner (Table 14.2).

Nanotechnology is a branch of nanoscience in which nanometer scale (1–100 nm)sized particles are studied. Nanoparticles (NP) play an important role in willingness to numerous pollutants which is challenged to the environment due to their nonbiodegradable and toxicity nature (Fig. 14.1) (Theron et al. 2008). Recently, a variety of approaches have been developed for the synthesis of high-quality nanoparticles (Kumari et al. 2015), nano-ovals, nanobelts (Fu and Wang 2011), and nanorings or other nanostructures. Nanostructured materials such as magnetic nanoparticle, carbon nanotubes, silver-impregnated cyclodextrin nanocomposites, nanostructured iron zeolite, carbon-iron nanoparticles, photocatalyticitania nanoparticles, nanofiltration membranes, and functionalized silica are able to treat the heavy metals, sediments chemical effluents, charged particles, and other pathogen like bacteria, viruses, as well as fungi (Table 14.1) (Amin et al. 2014; Chaturvedi et al. 2018).

Nanoparticles (NPs) are one dimensional structure with less than 100 nm (Amin et al. 2014) in size. Different type of nanoparticles are used for wastewater treatment but among them, metal oxide nanoparticles like titanium dioxide (TiO_2), zinc oxide (ZnO), and cerium oxide (CeO_2) show high reactivity and photolytic properties against wastewater. They act as a good adsorbent for water purification because they have a large surface area and their affinity can be enhanced by using various functionalized groups (Lu et al. 2016). ZnO nanoparticles have been used



Fig. 14.1 Nanotechnology based wastewater treatment

to get rid of arsenic from water (Muñoz-Fernandez et al. 2016). Ag NPs has high antibacterial activity so that it fixed to filter materials for treatment of water waste. It is cost-effective and considered as the best NP for water purification. Several investigators reveal about fabricated nanostructured ceramic membrane containing zinc oxide and titanium involving in degradation of photo catalytically pollutants and check the growth of microorganisms (Reinhart et al. 2010). Since nanoparticle-based wastewater treatment has high in demand, its usage cost should be managed according to competition in the market (Crane and Scott 2012). A number of nanomaterials such as nanocatalysts, nanostructured catalytic membranes, biomimetic membrane, nanosorbents, bioactive nanoparticles, and molecularly imprinted polymers (MIPs) are also used for removing toxic metal ions, disease-causing microbes, organic and inorganic solutes from water waste (Anjum et al. 2016).

2 Role of Inorganic Nonmaterials in Wastewater Treatment

Inorganic nanomaterials are made of up inorganic compound which is used in the wastewater treatment (Fig. 14.2). Here, we described different type of inorganic nanomaterials and their role in a wastewater treatment.

S.N. 1.	Zero valent iron (ZVI) Z-nZVI	Removal of heavy metal ions from water Pb(II)	Summary More than 96% of the Pb(II) was removed	References Kim et al.
			from 100 mL of a solution containing 100 mg Pb(II)/L within 140 min of mixing with 0.1 g Z–nZVI	(2013)
2.	nZVI	Cd(II)	Simultaneous removal of cadmium and nitrate in aqueous media by nanoscale zero valent iron (nZVI) and Au doped nZVI particles	Su et al. (2014)
3.	K-nZVI	Pb(II)	More than 96% of Pb(II) was removed from aqueous solution using K-nZVI at an initial condition of 500 mg/L Pb(II) within 30 min under the conditions of 10 g/L of K-nZVI, pH 5.10, and a temperature of 30 °C	Zhang et al. (2011)
4.	Ferragels	Cr(VI) and Pb(II)	Quick removal of Cr(VI) and Pb(II) from aqueous solution using supported nZVI ("Ferragels"). The result indicates supported nZVI, while oxidizing the Fe to goethite (R-FeOOH) reduced the Cr to Cr^{3+} and the Pb to Pb°	Ponder et al. (2000)
5.	nZVI	Cd(II)	They reported NZVI for the removal of Cd(II) (conc. range 25–450 mg/L). The results recommend the competent removal of Cd(II) from contaminated water	Boparai et al. (2011)
6.	P-NZVI	Hg(II) and Cr(VI)	They investigated NZVI supported on pumice (P-NZVI) successfully removed Hg (II) and Cr (VI) from wastewater. The maximum uptake of Hg(II) and Cr(VI) onto P-NZVI was 332.4 and 306.6 mg/g, respectively	Liu et al. (2014)

Table 14.1 Summary of the removal of heavy metals from wastewater

2.1 Iron Oxide Nanomaterials

Colloidal and particulate forms of iron metals are constitutes in hydroxides, oxides, silicates, sulfides, or grab to adsorbed on clay, silica, or organic matter (Boparai et al. 2011). Iron oxides exist in various forms in nature out of which magnetite (Fe_3O_4), maghemite (Fe_2O_3), and hematite (Fe_2O_3) abide the uttermost prevalent forms (Ferroudj et al. 2013; Wang et al. 2013). In recent years scientist focuses on the preparation of iron oxide nanomaterials for wastewater treatment due to their high surface area to volume ratio and superparamagnetism (Mahdavian and Mirrahimi 2010; Oliveira et al. 2003; Ponder et al. 2000; Pendergast and Hoek 2011). Furthermore, iron oxide nanoparticles show lesser toxicity, chemical inertness, and biocompatibility and exhibit outstanding potential in consolidation with biotechnology (Morones et al. 2005; Nakamura and Isobe 2003). For removal of toxic heavy metals from groundwater, the surface functionalized iron oxide nanomaterials have been used as a nanosorbent. Improvement in iron oxide nanomaterial



Fig. 14.2 Schematic illustration of nanomaterials used in the removal of wastewater treatment

development, along with the achievement of monodisperse, shape formation is validated on the basis of surface active sites (Li et al. 2016). The removal of water waste by iron oxide nanomaterials is worked at the micro- or macro-scale level, which allows nanoparticles to exhibit their reactivity while being complemented by the adsorbent properties of the accompanying materials. Chitosan is a well-known example of iron oxide nanomaterial. Chitosan is a natural substance and hydrophilic in nature and contains active sites along its polymeric chain due to $-NH_2$ groups. Hence, chitosan regarded as a novel biosorbents for water and wastewater treatment (Ahmaruzzaman 2008; Ngah et al. 2011).

Iron oxide nanoparticles have magnetic property and can react with a various functional groups so that researchers approached toward modification of iron oxide nanomaterials by incorporation of various functional groups. To accelerate iron oxide nanoparticle stabilizer, electrostatic surfactant and steric polymers had been used with non-specific moieties and group-specific or highly specific ligands. Durability and sustainability of iron oxide colloid suspensions could be achieved by surface modification through the implementation of suitable functional groups, such as phosphoric acids, carboxylic acid, and amine (Liu et al. 2010). We know that the in vitro modifications of nanomaterial are medium specific, and a series of the

medium can be needed to introduce functional groups in iron oxide nanoparticle. For this, a robust protocol is needed to achieve alteration of nanomaterials. The iron oxide nanomaterials are well dispersed even in industrial application. It should be noted that the application of iron oxide nanomaterials is related to their intrinsic properties, which depend on the preparation method and modification mediums (Neyaz et al. 2014)

Selection of the best method and material for wastewater treatment is a highly complex and tough task, considering a number of factors, such as the quality standards to be met and the efficiency as well as the cost. Therefore, the following four criteria must be considered for preparation of nanomaterials on wastewater treatment technologies: (1) treatment flexibility and final efficiency, (2) reuse of treatment agents, (3) environmental security, and (4) low cost (Xu et al. 2012; Zhang et al. 2013). Magnetism is a distinctive property that helps in water purification by influencing the physical properties of contaminants in water. Therefore, for water treatment and environmental clean-up adsorption procedure, the magnetic separation has been extensively used. At industrial level wastewater treatment, iron oxide nanomaterials show promising results because of their low-cost, simple separation, strong adsorption capacity, and increased stability. The ability of iron oxide nanomaterials to remove contaminants has been demonstrated at both laboratory and field scale tests (Boparai et al. 2011). Current applications of iron oxide nanomaterials in contaminated water treatment can be divided into two groups: (a) technologies which use iron oxide NMs as a kind of nanosorbent or immobilization carrier for removal efficiency enhancement (referred to here as adsorptive/immobilization technologies) and (b) those which use iron oxide nanomaterials as photocatalysts to break down or to convert contaminants into a less toxic form (i.e., photocatalytic technologies) (Oliveira et al. 2003; Ponder et al. 2000). Water contamination with heavy metals not only is a threat to the aquatic organisms but also causes severe health disorder in humans by accumulation through precipitation and adsorption and transferring through the food chain. The toxicities of heavy metals may be caused by the inhibition and reduction of various enzymes, a complication with certain ligands of amino acids and substitution of essential metal ions from enzymes (Zhang et al. 2011; Oliveira et al. 2003).

2.2 TiO₂ Nanoparticles

Titanium (Ti) is the seventh most abundant metal in the Earth's crust with significant worldwide reserves >600 million tons, with the annual production, approximately 4.3 million tons titanium dioxide (TiO₂) (Wang et al. 2012). Ti has multifarious industrial applications such as in metal alloying, in aerospace applications, and in biomedical devices (Ghaly et al. 2011). Food-grade TiO₂ ranges in size from tens to hundreds of nanometres; the typical mean diameter is proximately 200 nm. Approximately, 95% of mined Ti is refined to pure TiO₂ by extraction of Ti-bearing ores along with carbon, chlorine, oxygen, or sulfuric acid. In the current period, a number of TiO₂ nanoparticle aggregates are deployed (i.e., bulk TiO₂ products), and industrial trends have been suggested that much higher amount of TiO₂ will be deployed in the near future because of its inert nature, somewhat opaque, and resist fading nature (Kiser et al. 2009). Active and passive depletion of consumer products comprise of nanomaterials (e.g., food additives, pharmaceuticals, and clothing) cause to excretion of engineered nanomaterials into domestic sewage (Khin et al. 2012; Malato et al. 2009). A recent study presented the evidence of the release of synthetic TiO₂ nanoparticles from paints on building facades and measured a significant amount of TiO₂ nanosilver, and carbon nanotube) have been studied, in which, nano-TiO₂ in WWTP effluents (0.7–16 μ g/L) were close to or higher than the permissible level (1 μ g/L) (Kiser et al. 2009; Lu et al. 2016).

Nanocrystalline titanium dioxide shows several activities. It is a photocatalyst which works in water splitting to produce hydrogen fuel as energy catalyst and behaves as an environmental catalyst for water and air purification or an electron transport medium in dye-sensitized solar cells (Chong et al. 2010; Khin et al. 2012; Pelaez et al. 2012). Water purification by nanocrystalline titanium dioxide worked as an advanced oxidation process because of its high efficiency and eco-friendliness with the ecosystem. Photocatalytic decomposition of wastewater by nanocrystalline titanium dioxide is mainly carried by a series of hydroxylation reactions initiated by hydroxyl radicals which attack the contaminant present in the wastewater, and water get purified (Lu et al. 2009; VanGrieken et al. 2009). Scientists made efforts to increase the photocatalytic activity of nanocrystalline titanium dioxide which includes the synthesis of mesoporous titanium dioxide (Nakata et al. 2012; Wang and Lewis 2005); the utilization of different morphologies of titanium dioxide such as nanowires, nanotubes, and nanospheres (Sun et al. 2011); and surface treatments of nanocrystalline titanium dioxide (Monllor-Satoca et al. 2011).

2.3 Silver Nanoparticles

The applications of silver nanoparticles are abundant during the recent periods. It is also applied to an open wound and burn treatment along with wastewater treatment (Pradeep 2009). The elementary studies exhibit that ~20 ppm silver colloidal solution (~30 nm diameter) in pure water circumscribed the 100% cure rate for malaria (Politano et al. 2013). In the wastewater treatment, spherical aggregates of nanoparticles (Pradeep 2009) able to form resin beads were usually employed. Ag and gold nanoparticles had been widely used for detection of trace level of organic contaminants in view of their unique optical properties (Sajanlal and Pradeep 2008). Raman spectra reveal the optical properties of silver nanostructures (Amin et al. 2014). Several Ag/Pt, Au/Pt, or Ag/Au bimetallic nanoparticle-based electrodes were studied for contaminant sensing, monitoring, as well as photocatalysis (Kumari et al. 2015; Zhang et al. 2016). The biocidal activity of silver nanoparticles was deployed in regard to water purification. The water inhabitable microorganisms like *E. coli*

become inactivated when reaching in the influence of Ag nanoparticles (Xiu et al. 2011). It has been shown that Ag nanoparticles provoke destruction to the cellular membrane when it comes in direct contact of the microorganism (Morones et al. 2005). Ag nanoparticle is also used as a disinfectant for surgical masks and textile fibers. Nanoparticles, derived from noble metals, were also exploited for photocatalytic degradation of several water pollutants such as pesticides, dyes, and halogenated organic matters. These metals are able to act as electron sinks, inhibiting the photo-generated e -/h + recombination, at the time of promotion of surface charge separation (Pradeep 2009). A number of noble metal-based nanocomposites, e.g., Ag/ZnO and Pt/ZnO nanocomposites (Muñoz-Fernandez et al. 2016), Au-CuS-TiO₂ nanobelts (Chen et al. 2016), and Ag/AgBr/graphene oxide nanocomposites (Esmaeili and Entezari 2016), have been developed and exhibited upgraded photocatalytic performance against certain organic contaminants.

2.4 Carbon-Based Nanomaterials

Carbon-based nanomaterials depend on various factors like size, length, chirality, and the number of layers in the fullerene cage. The current fabrication techniques for synthesis of carbon nanomaterial lacks complete exactness and uniformity between growth conditions. To overcome these problems, scientists modified the synthesis technique of carbon nanomaterial. The modification takes place in various factors such as temperature, pressure, catalyst, purity, and physical orientation for specific applications (Tofighy and Mohammadi 2011). There are various carbon-based nanomaterials available which are used in wastewater treatment, e.g., activated carbon, graphene, carbon nanosorbent, and fullerene.

Activated carbon reduced the organic wastes and odor from water and wastewater treatment (Liu et al. 2012). Carbonaceous nanosorbents are also very effective in wastewater treatment because toxicity has prevented in water. In 2005 Savage and Diallo have proposed the incorporation of nanosorbents into traditional packed bed reactors, but the details of the immobilization strategies have not been presented (Savage and Diallo 2005). Several types of research show that nanosorbents have used for the removal of specific contaminants such as trihalomethanes, polycyclic aromatic hydrocarbons, or naphthalene (Chen 2004). Moreover, most of the literature focuses on the physical properties of nanomaterials and demonstrated that they are dependent upon aggregation state and solvent chemistry. Various types of impurities such as vapor, biomolecules, and metals adsorb to the surface of nanomaterials and change the aggregation behavior and thermal and physicochemical properties of the nanomaterials. Hence, it is necessary to resolve these problems for widespread use of carbonaceous nanomaterials for wastewater treatment. To target the low concentration contaminant and specific micropollutant, functionalized nanosorbents may provide an optimized approach for removal of this contaminant and improve subsurface mobility (Lecoanet et al. 2004).

2.4.1 Classification of Carbon-Based Nanomaterials

The classification of carbon-based nanomaterials (Yu et al. 2011) is mostly based on their geometrical structures. Carbon nanostructures possess particles having tubeshaped, horn-shaped, spherical, or ellipsoidal. On the basis of the shape, nanoparticles having tube-like shape are called as carbon nanotubes; spheres or ellipsoids belong to the set of fullerenes; and horn-shaped particles are called nanohorns (Das et al. 2014). Carbon nanomaterials have been widely used technically as micro- and nano-electronics, production matter of conductive plastics, gas storage, composites, displays, textiles, antifouling paints, batteries with improved sturdiness, gas biosensors, etc. (Ramnani et al. 2016).

Fullerenes

Fullerenes are an allotropic modification of carbon discovered by Kroto et al. (1985) who were later awarded the Nobel Prize for chemistry in 1996. A number of atomic C_n clusters (n > 20), constitutes from carbon atoms on a spherical surface, are considered as fullerene family (Pyrzyńska and Bystrzejewski 2010; Wang et al. 2012). One of the best-inquiries of fullerenes is its C60 isoform also called as buckminsterfullerenes (Das et al. 2014; Lam et al. 2006). A spherical molecule of a fullerene is comprised of 60 carbon atoms that have great symmetry and are occupied with the vertices of 12 pentagons and 20 hexagons. The diameter of fullerene C60 is 0.7 nm (Fu and Wang 2011). C60 is a powerful photocatalyst, used in wastewater treatment, in UV and solar disinfection reactors, and in advanced oxidation process reactors. It augmented the oxidative processes which destroy a variety of contaminant including carcinogens and endocrine disruptors, simultaneously with disinfection (Tsydenova et al. 2015).

Carbon Nanotubes and Surface-Modified Nanotube (CNT)

CNTs are one of the well-known carbon allotropes with unprecedented virtue relevant for technical implications upon carbon-based nanomaterials. CNT was discovered by the Japanese researcher Iijima (1991). CNTs are specified cylindrical structures having a diameter of several nanometres, comprised of rolled graphene sheets (Lam et al. 2006). It varies in diameter, length, chirality, as well as a number of layers. Based on their structure, they can be classified into two main groups: single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs) (Tasis et al. 2006). Further a distinct class of CNTs had been introduced by some researchers as they have a different framework of double-walled carbon nanotubes (DWCNTs) (Thostenson et al. 2001). Single-walled nanotubes (SWNT) are of 1–3 nm in diameter along with the length of a few micrometers, whereas multi-walled CNTs hold a diameter of 5–40 nm and proximately 10 µm length (Bahgat et al. 2011). CNTs structure prevails upon notable features amidst a privileged

composite of rigorousness, stability, and elasticity in comparison with other fibrous materials (Kumar et al. 2014; Yu et al. 2011). For instance, in comparison to other materials, CNTs exhibit considerably higher aspect ratios (length to diameter ratios) and larger aspect ratios for SWCNTs as compared with MWCNTs due to their smaller diameter (Pyrzyńska and Bystrzejewski 2010). On the other hand, CNTs show high thermal and electrical conductivity in comparison with other conductive materials (Thostenson et al. 2001).

CNTs have shown higher efficiencies for adsorption of bacteria and other microorganisms than other adsorbents such as granulated activated carbon (GAC) and powdered activated carbon (PAC) which are used in the wastewater treatment processes (Kang et al. 2008) Several studies reveal that pH level plays an important role in removing heavy metals contaminant in wastewater through CNTs (Ye et al. 2007). One of the studies demonstrated the efficiency of removal of lead from water can be augmented by optimizing the pH level. In the case of chromium contaminant, it was seen that by maintaining the pH higher than 4, it can efficiently remove chromium from wastewater. This study deduced that CNTs can behave as an effective adsorbent for removal of heavy metals from wastewater by increasing the pH, resulting in decreased protonation of the surface which increases the adsorption capacity of CNTs (Addo Ntim and Mitra 2011). CNT membranes are considered as a model water distillation tool. It consists of open-end single empty structure which is settled upright with resistant filter media. CNT-based membrane shows several advantages over CNTs such as these membranes are hard-like ceramic membrane and soft-like polymeric membranes. The second major advantage of CNT membrane is it permits fast infiltration of water. Scientist demonstrated that graphene membrane produced more precise results than CNTs membranes (Das et al. 2014). Nowadays, the detection of the pathogen in wastewater is a major challenge due to the low quantity of some pollutants that are present in water and the high difficulty of the wastewater mediums. Hence, advanced sensors technologies are used to detect the pathogen in the wastewater. So, high discrimination and sensitivity, with fast kinetics, are needed for sensing contaminant detection in wastewater (Savage and Diallo 2005; Theron et al. 2008; Upadhyayula et al. 2009)

Graphene Nanoparticles

A two-dimensional allotropic form of carbon is known as graphene, constitutes of a single layer of carbon atoms (Zhao et al. 2011). Graphene is a carbon allotrope like graphite, carbon nanotubes, and fullerenes (Chen et al. 2012; Gao et al. 2012; Georgakilas et al. 2012). From the ancient time period, the theoretical studies on graphene began. The Canadian theoretical physicist P. R. Wallace first explored the theory of graphene in 1947, while the first graphene samples were described 57 years later (in 2004) by A. Geim (Dutch-British physicist) and K. Novoselov (Russian-British physicist), awarded with a Nobel prize in 2010 (Allen et al. 2009) (Table 14.2).

C N	Nanomaterials/	Amiliantian	A deconto ano	Disadaanta aaa
<u> </u>	Carbon nanotubes	Application Contaminant preconcentration/detection, adsorption of recalcitrant contaminants, ultralong carbon nanotubes with extremely high specific salt adsorption	Highly assessable sorption sides, bactericidal, reusable	High production costs, possibly health risk
2.	Nanoadsorbents	Point-of-use, removal of organics, heavy metals, bacteria	High specific surface, higher adsorption rates, small footprint	High production costs
3.	Membranes and membrane processes	All fields of water and wastewater treatment processes	Reliable, largely automated process	More energy demand
4.	Nanometals and nanometal oxides	Heavy metals (arsenic) and radionuclides removal, media filters, slurry reactors, powders, pellets	Short intraparticle diffusion distance compressible, abrasion-resistant, magnetic photocatalytic	Less reusable
5.	Polymeric nanoadsorbents (dendrimers)	Expulsion of organics and substantial metals biodegradable, biocompatible, nontoxic bioadsorbent	Bifunctional (inner shell adsorbs organics, outer branches adsorb heavy metals), reusable	Complex multistage production process
6.	Magnetic nanoparticles	Forward osmosis, groundwater remediation	Simple recovery by magnetic field	Stabilization is required
7.	Nanosilver and nano-TiO2	Point-of-use water disinfection, anti-biofouling surfaces, decontamination of organic compounds, remote areas, TiO2 modification for activation by visible light, TiO2 nanotubes	Bactericidal, low human toxicity nano-TiO2: high chemical stability, very long life time	Nanosilver, limited durability nano- TiO ₂ requires ultraviolet activation
8.	Zeolites	Disinfection processes, nanozeolites by laser- induced fragmentation	Controlled release of nanosilver, bactericidal	Reduced active surface through immobilization of nanosilver particles

Table 14.2 Potential applications, advantages and disadvantages of nanotechnology in the wastewater treatment

(continued)

	Nanomaterials/			
S.N.	nano-objects	Application	Advantages	Disadvantages
9.	Nanocomposite membranes	Highly dependent on the type of composite, e.g., reverse osmosis, removal of micropollutants Bionanocomposite membranes	Increased hydrophilicity, water permeability, fouling resistance, and thermal/ mechanical robustness	Resistant bulk material required when using oxidizing nanomaterial, possibly release of nanoparticles
10.	Nanofiber membranes	The filter cartridge, ultrafiltration, prefiltration, water treatment, stand- alone filtration device Composite nanofiber membranes, bionanofiber membranes	High porosity, tailor-made, higher permeate efficiency, bactericidal	Pore blocking, possibly release of nanofibers

Table 14.2 (continued)

3 Organic Polymer Nanomaterials in Remediation of Wastewater

3.1 Organic Polymer Nanomaterials

Hazardous and recalcitrant pollutants can be removed from the wastewater through the process of adsorption, which is the most effective and simplest approach (Wan et al. 2010). Activated carbon is used for the adsorption purpose, but it is highly costly and didn't adsorb the functional group. Therefore, organic polymers have been used to the uptake of heavy metals. Organic nanosorbents having properties such as large surface area and polyfunctional groups are highly rigid, and it is easily regenerate under the mild condition (Jain et al. 2018). The large surface area of nanosorbents provides a good contact between the solid sorbent and metal ions. On the other hand poly functional groups provide a large number of active sites for the adsorption reaction (Huang et al. 2011). Polyphenylenediamine, organic polymers, have polyfunctional groups such as amino and imino groups which can effectively adsorb the heavy metal ions. However, due to their relative small specific area, their adsorption rate is slow (Huang et al. 2011). In 2006, Huang et al. reported that poly (p-phenylenediamine) (PpPD) and poly(m-phenylenediamine) (PmPD) were directly synthesized by a facile oxidative precipitation polymerization and their strong ability adsorbs lead ions from aqueous solution (Huang et al. 2006). The strong adsorption of the lead ion on the microparticles makes them suitable adsorbents candidate for wastewater treatment. Some thiol-functionalized mesoporous silica microspheres showed the behavior in mercury ion adsorption (Bibby and Mercier 2002), while humic acid (HA)-coated Fe_3O_4 nanoparticles (Fe_3O_4/HA) were developed for the removal of toxic Hg, Pb, Cd, and Cu from water (Liu et al. 2014). In 2010, Liu et al. documented that new hybrid polymers were prepared from the ring-opening polymerization of pyromellitic acid dianhydride (PMDA) and phenylaminomethyltrimethoxysilane (PAMTMS) and are capable for the removal of Pb (II) ions from Pb(II)/Cu(II)-mixed aqueous solution and can be applied to separate and recover the heavy metal ions from contaminated wastewater (Liu et al. 2010). In 2010, Cai et al. reported an efficient method for synthesis of poly (acrylic acid) stabilized amorphous calcium carbonate nanoparticles (ACC) and their application for removal of toxic heavy metal ions from aqueous solutions. The maximum removal capacities for Cd, Pb, Cr, Fe, and Ni ions were found to be 514.62, 1028.21, 258.85, 320.5, and 537.2 mg g^{-1} , respectively. The unique characteristic of the ACC nanoparticles in wastewater treatment involves not only high removal capacities but also decontamination of trace ions (Cai et al. 2010). Zhang et al. (2013) demonstrated that thiolmodified Fe₃O₄-SiO₂ as a robust, highly effective, and recycling magnetic sorbent for Hg removal. In 2013, Wang and their coworker developed the rhodamine hydrazidemodifying Fe₃O₄ microspheres (Fe₃O₄-R6G) for detection and removal of mercury (Hg) from wastewater. The maximum adsorption capacity of the Fe_3O_4 -R6G for Hg was 37.4 mol g⁻¹ (Huang and Chen 2009; Zhang et al. 2013). In 2016, Chen and their coworker prepared the magnetic Fe₃O₄ nanoparticles (MNP) coated with 3-aminopropyltriethoxy-silane (APTES), and magnetic absorbent was formed (Fe_3O_4 .SiO2-NH-HCGs) by grafting of different heterocyclic groups (HCG) on amino groups through the substitution reaction. This magnetic absorbent was used for the removal of heavy metal cations such as Cu, Hg, Pb, and Cd. Results showed that 96% heavy metals were removed from the wastewater within 20 min at normal temperature and have good stability and reusability (Chen et al. 2016). Mahdavian et al. developed magnetic iron oxide nanoparticles by modification with APTES and acryloyl chloride (AC). Further, the surface of these nanoparticles was modified by graft polymerization with acrylic acid. Then the grafted magnetite nanoparticles were used for separation of heavy metal cations such as Cd, Pb, Ni, and Cu from the wastewater. Huang et al. (2011) reported that poly (5-sulfo-1-aminoanthraquinone) nanoparticles were synthesized by a chemical oxidative polymerization of 5-sulfo-1aminoanthraquinone. In particular, a large amount of-SO3- -NH2/-NH-/-N=/=O groups are added which shows high specific area with fast and strong adsorb ability toward heavy metal ions from the wastewater (Mahdavian and Mirrahimi 2010).

3.2 Organic Polymer-Supported Nanocomposites

Wang et al. (2011) prepared a multifunctional inorganic–organic hybrid nanomaterial (MMS–Py) by immobilization of a pyrene-based receptor (Py) within the channels of magnetic mesoporous silica nanocomposites (MMS) which is used for the removal of Hg ions from the wastewater. Polymer-layered silicate nanocomposites made nanocomposite material catching the attention of both academic and industries because they exhibit dramatic improvement at very low filler contents (Pavlidou and Papaspyrides 2008). Eisazadeh (2007) demonstrated the polyaniline (PAn) and its nanocomposites for the removal of Cr ions from wastewater. Huang et al. (2014) reported that conjugated polymers based nanocomposites for polyaniline (PAn), polypyrrole (PPy), and polythiophene (PT) have been widely used in wastewater purification. Poly (N-ethylaniline)/chitosan composite exhibited the highest removal ability to Cr (229.8 mg/g) from wastewater. However, other conjugated polymers such as polyacetylenes, poly(phenylenevinylene) (PPV), poly(p-phenylene) (PPP), etc. may also be applied as composites in wastewater treatment, but due to the absence of heteroatom for the functional group, their practical applications are not reported till date (Huang et al. 2014).

4 Patented Products of Nanomaterials for Purification of Water

There are various patented product of nanomaterials that are present such as wastewater treatment method and wastewater treatment apparatus invented by Yamasaki et al. (2007) (Table 14.3).

5 Conclusions

In a current scenario, there is a significant need for advanced water technologies to ensure a high quality of water, elimination of chemical, and biological pollutants and intensify industrial production processes of wastewater. The universal solvent water is one the most crucial for all living organisms exist on Earth. Contaminated water is the major challenge of the current era, and there are several reasons which are responsible for water contamination. The contaminants contain undesired substances such as microorganisms and unnecessary elements, as well as chemicals, that leads to water pollution and water becomes unsafe for all purposes. Untreated water creates a great threat to living beings and the environment. In this regard, nanotechnology is one of the ideal technologies to advance wastewater treatment processes. Various nanomaterials have been developed and investigated successfully for wastewater treatment. Nanotechnology has a significant prospective in magnifying water quality by wastewater management as it profound potential supremacy such as cost-effective, reiterate, and highly proficient in expelling and recuperating the pollutants. The efficiency of nanomaterials as anti-pollutant is due to its size in nano-range which makes it worth working as it has a large surface to volume ratio, high reactivity, rapid dissolution, and high adsorption. For the development of antimicrobial nanomaterials, knowledge of biotechnology is employed for removal of microbes from water. Moreover, further work is required on developing cost-effective methods of synthesizing nanomaterials and testing the efficiency of nanomaterials at large scale for successful field application on purification of wastewater treatments.

	Claimed title/patent		Nanomaterials claimed	
S.N.	name	Patent No.	activity	Inventers
1.	Wastewater treatment method and wastewater treatment apparatus	US 20070068869	Micro-nano, nanomaterials used to decompose organic compound and microorganism	Yamasaki et al. (2007)
2.	Process for biochemical treatment of wastewater using nanomaterials	US 20030010712	Nanomaterial used such as carbon black to induce micropores to degrade organic pollutants and enhance the effect of biological cleaning of wastewater	Gao et al. (2003)
3.	Drinking water filtration device	US20070175196	Nano-alumina fibers shows antimicrobial for sterilization of retained microbes for purifying drinking water	Tepper and Kaledin (2008)
4.	Water treatment by dendrimer enhanced filtration	US20080185341	Cation-binding dendrimers, anion- binding dendrimers, and organic compound- binding dendrimers used in filtration of wastewater	Diallo (2008)
5.	Adsorption filter	US20060123991	An adsorption activated carbon particles used as simple and cost-effective filters	Braeunling et al. (2006)
6.	Reduced graphene oxide-based- composites for the purification of water	US20130240439	A nanocomposite is disclosed comprising reduced graphene oxide (RGO) an adsorbent comprising the nanocomposite and an adsorbent comprising the nanocomposite bound to silica by using chitosan	Pradeep et al. (2013)
7.	Portable drinking water purification device	US20100102002	Activated carbon or nano-filter in portable water chamber and having a very small pore size	O'Brien et al. (2013)
8.	Purification of fluids with nanomaterials	US 20080041791	Nanostructured material carbon nanotubes	Cooper et al. (2008)

 Table 14.3
 Some examples of patented products of nonmaterial for the purification of water

(continued)

a	Claimed title/patent		Nanomaterials claimed	_
S.N.	name	Patent No.	activity	Inventers
9.	Water purification device	US20170203244	A water purification device includes a heavy metal removal layer configured to remove heavy metal ions and perfluorinated compounds from contaminated water	Chen et al. (2017)
10.	Method for biological disposal of organic wastewater and biological disposal apparatus	US 20090277832	A biological treatment method and device for organic wastewater, whereby the amount of minute organisms which reduce the amount of excess sludge	Fujishima and Kurita Water Industries Ltd (2009)
11.	Water purification and disinfection device and method	US 20060151393	Purify and filter water, particularly brackish water, so that it is made potable. The system includes the use of physical and chemical treatment means, including carbon, reverse osmosis, and antimicrobial media	Badger (2006)
12.	Double chamber water purification device	US 8425771	A portable device for filtering and purifying water comprised of an outer chamber and an inner chamber that is activated carbon bed, removing any remaining contaminants before the potable water exits through a mouthpiece	O'Brien et al. (2013)

Table 14.3 (continued)

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