Chapter 10
Removal of Organic Pollutants from Contaminated Water Bodies by Using Aquatic Macrophytes Coupled with Bioenergy Production and Carbon Sequestration

Ankit, Lala Saha, Khushbu Kumari, Sagarika Sinha, Nirmali Bordoloi, Jaya Tiwari, John Korstad, and Kuldeep Bauddh

Abstract The burgeoning population and continuous increase in developmental activities are the major cause of rampant release of numerous environmental contaminants. These contaminants pollute the soil, air and water and ultimately enter the food chain. Several physical, chemical and biological techniques have been developed to remove these contaminants; however, these methods are quite costly and not environmentally sound. Specifically, organic contaminants like pesticides, phenols, oils, pharmaceuticals and dyes are entering aquatic habitats and damaging these ecosystems. Application of aquatic macrophytes for the removal of organic contaminants has proved to be an eco-friendly and efficient tool to remediate aquatic ecosystems. Aquatic macrophytes such as *Eichhorn crassipes, Elodea canadensis, Lemna minor, Pistia stratiotes,* and *Trapa natans* can be used for reclamation of contaminated waste and wastewater systems. In addition, these plants help in carbon sequestration, and the biomass of these plants may be used to produce bioenergy (biofuel) at the same time. In this chapter, the potential of aquatic macrophytes for phytoremediation and bioenergy production along with carbon sequestration have been thoroughly discussed.

Ankit and Lala Saha contributed equally to this work.

Ankit · L. Saha · K. Kumari · S. Sinha · N. Bordoloi · K. Bauddh (✉)
Department of Environmental Sciences, Central University of Jharkhand Ranchi,
Ranchi, India
e-mail: kuldeep.bauddh@cuj.ac.in

J. Tiwari
School of Biological Sciences, AIPH University, Bhubaneswar, Orissa, India

J. Korstad
Department of Biology and Renewable Energy, Oral Roberts University, Tulsa, OK, USA

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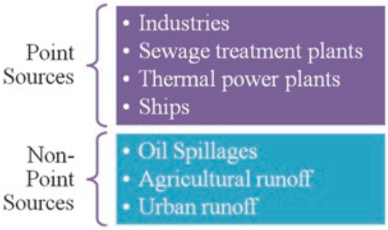
10.1 Introduction

Environmental contamination due to anthropogenic sources is widespread and occurs through point as well as diffused sources (Fig. 10.1). However, most of the ecotoxicological implications are often obscure. Environmental contamination is a serious issue grappling the world. The introduction of chemicals, wastewater, wastes, toxic substances, or microorganisms into the air, water, and soil often contributes to areas being unsafe for human habitation, crops being contaminated, water being unpotable, and food being unfit for consumption. Increased concentrations of several organic contaminants like polycyclic aromatic hydrocarbons (PAHs) in the ecosystem have been of great concern owing to its hydrophobicity, toxicity, bioaccumulation, and prolonged presence in living organisms (Yadav et al. 2016; Saxena and Bharagava 2017; Keshavarzifard et al. 2019).

Aquatic ecosystems can be contaminated with hazardous substances such as petroleum hydrocarbons, pesticides, and/or heavy metals that may be toxic to aquatic animals and plants (Fleeger et al. 2003; Singh 2009; Yadav et al. 2017; Mishra and Bharagava 2016). Over consumption of chemicals, fossil fuels, minerals, industrial effluents, and other anthropogenic substances lead to contamination of ecosystems with pesticides, petroleum hydrocarbons, dyes, heavy metals, metal nanoparticles, radionuclides, pharmaceutical products, etc. Aquatic ecosystems are at greatest risk mainly due to imprudent human activities (Borgwardt et al. 2019).

A sustainable technique to remediate polluted aquatic ecosystems is rhizofiltration (Tiwari et al. 2019). It is a type of phytoremediation which involves the use of hydroponically cultivated roots of the plant for remediating contaminated water by absorbing, concentrating, and precipitating the pollutants. Phytoremediation is a green clean technology available for restoring contaminated aquatic ecosystems (Bauddh and Singh 2015a, b; Bauddh et al. 2016a, b; Bharti et al. 2017; Chakravarty et al. 2017; Ashraf et al. 2019; Saxena et al. 2019). Using aquatic plants for the removal of contaminants is proven to be a win-win situation, because first, they are often weeds (not desirable) and second, they are good at extracting contaminants. Macrophytes used for phytoremediation include *Pistia stratiotes, Potamogeton*

Fig. 10.1 Sources of aquatic ecosystem contamination



pectinatus, Trapa natans, Eichhorn crassipes, Potamogeton lucens, Potamogeton perfoliatus, and Ceratophyllum demersum. The studied macrophytes can efficiently remove heavy metals like Ni, Pb, As, Cu, Cd, and other cations (Kumar et al. 2012; Sood et al. 2012; Sweta et al. 2015; Materac and Sobiecka 2017; Neha et al. 2017; Riaz et al. 2017; Wang et al. 2017).

Carbon sequestration is another ecological service that is provided by aquatic macrophytes. This service is of immense importance because greenhouse gas concentrations are increasing globally. Macrophytes are comparatively bigger in size and have larger biomass than many other aquatic plants and thus have tremendous potential to sequester CO_2. *Typha latifolia* and *Scirpus acutus* are known to have promising potential to sequester carbon (Burke 2011). Aquatic macrophytes also supply biomass for our energy demands. It is a renewable energy that is obtained from living organic material called biomass, which can be used to produce heat, transportation fuels, bio-products and electricity. Using bioenergy can reduce dependency on foreign oil, revitalize rural economies, and supply clean energy, which are all serve vital needs, especially for underdeveloped and developing nations. Aquatic macrophytes like *Lemna* spp. are supportive for producing biofuel (Xu et al. 2011).

10.2 Types of Contaminates Present in Aquatic Ecosystems

Contamination of aquatic environments can be attributed to organic, inorganic and other anthropogenic substances (Fig. 10.2). Industrial sources may be in the form of hot water discharged form a thermal power plant, mine tailings and discharge of heavy metals like Cd, Hg, U, As, and other metals. Agricultural waste can be broadly categorized into organic and inorganic compounds (Milovanovic 2007). Organic compounds include pesticides and oils. There are several classes of pesticides as well, like organochlorine which includes chlordane, methoxychlor, lindane, aldrin,

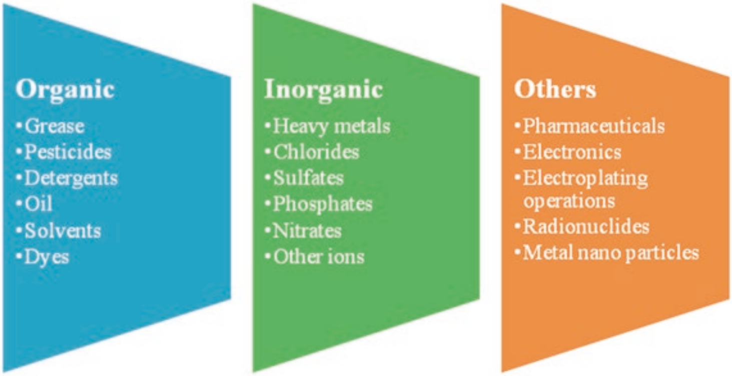


Fig. 10.2 Different classes of aquatic ecosystem contamination

toxaphene, dichloro diphenyl trichloroethane (DDT), heptachlor, endosulfan, and dieldrin. Organophosphates include parathion, malathion, dimethoate and diazinon and carbamates like aldicarb, carbofuran, and carbaryl. Inorganic compounds consist of phosphates, nitrates, and other chemicals (Tiwari et al. 2019). Heavy metals include As from insecticides; chromate and cadmium from electroplating industries; Pb from paint manufacturing pipes and pottery; Hg from combustion of fossil fuels; Cr from leather tanning industry; and Zn from smelting.

10.3 Sources of Organic Pollution

Organic pollutants are mainly emanated from agricultural practices, industrial activities and military waste. Agriculture is mainly based on seed, water, fertilizer and pesticides. Use of pesticides in agricultural activities plays a major role in organic pollution in some urban areas (Ratnakar et al. 2016). Organic pollutants are generally categorized into three groups: (1) organometallic compounds; (2) oxygen, nitrogen, and phosphorus compounds; and (3) hydrocarbons. Hydrocarbons like dioxins, PAHs, and DDT are considered to be the most toxic compounds. Automobiles are a major source of organic pollutants like dioxins, petroleum hydrocarbons, and PAHs and are discharged into the environment in particulate form. Direct disposal of industrial and urban waste into dug pits and improperly constructed landfills contributes to contamination of soil and groundwater adjacent to disposal sites.

Increasing concentration of harmful organic chemicals is mostly due to anthropogenic reasons and is termed persistent organic pollutants (POPs). POPs are toxic organic compounds that are persistent in soils, sediments and biota, have long residence times, and are bioaccumulative (Jacob 2013). POPs like dioxins and dibenzofurans originate from natural sources like volcanic eruptions and forest fires. Some of the major anthropogenic sources of POPs are industrial-based such as agricultural sprays, power stations, heating stations, and evaporation from soil and landfills. Based on application and source, POPs are classified into three groups: pesticide, industrial, and technical chemicals, and also unintended by-products from various industrial activities.

Different types of pesticides such as DDT, aldrin, endrin, dieldrin, chlordane, hexachlorocyclohexane, and toxaphene are used to control weeds, fungi, bacteria, insects, and other organisms. Although agricultural activity is considered to be one of the major sources of pesticide, they are not restricted to agricultural fields. Pesticides are also used as household commodities in the form of powders, sprays, and poisons to kill mosquitoes, cockroaches, fleas, other insects, ticks, and rats. Organic pesticides are semi-volatile in nature and can be dispersed by air and are frequently found in edible items (Jacob 2013). Globally, POPs continue their cycle due to revolatilization from contaminated water bodies, soils, and vegetation.

The most common industrial chemicals are hexachlorobenzene (HCB) and polychlorobiphenyls (PCBs). In the environment, HCB is released from some chlorinated pesticides and chlorinated aromatics, incomplete combustion, waste material, and old disposal sites. PCBs are stable and human-made chlorinated hydrocarbons. PCBs are used in pigments and dyes, plastics and rubber products, fluorescent lighting, floor finish. They enter air, water, and soil during production, use, and improper disposal. Polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzodioxins (PCDDs) are unintentional by-products of various chemical processes and combustion which contain chlorine. Important sources of PCDDs and PCDFs are classified into three groups: (1) stationary, which includes chemical industries and thermal processes; (2) diffused, which includes burning of fossil fuels; and (3) secondary, which includes sewage sludge and bio-compost.

10.4 Toxicity of Organic Pollution to Plants and Animals

Persistent organic pollutants generally are low water soluble but highly soluble in lipid and are not naturally degradable. Exposure to POPs can be through food items and environmental exposure; they are highly toxic to plants and animal including humans. POPs are persistent in the environment and contaminate at the origin and also at remarkable distances from the original source of discharge. The negative or unpleasant effects of pesticides include injury to non-target plants and animals. Based on the exposures and time taken for the appearance of toxic symptoms, pesticide toxicity is classified as: (1) acute toxicity, (2) sub-chronic toxicity, (3) chronic toxicity, and (4) delayed toxicity. Excessive application of pesticides in soil may hamper seed germination, crop growth, plant metabolic pathways and interfere with photosynthesis, resulting in subsequent reduction of yield. Fat-soluble pesticides enter animal bodies through the process of biomagnification and accumulate in fatty tissues and remain in food chains for a considerable period of time. Potential health impacts of pesticides include negatively impacting immune, hormonal, nervous, and reproductive system and may cause deformity (DeSolla et al. 2008).

HCB is mobile, persistent, distributed throughout the environment and bioaccumulate and toxic to both humans and biota. HCB can bioaccumulate in fish and other marine animals; a high dose of HCB can lead to birth defects because it affects the reproductive system of animals. Exposure to HCB can occur dermally, through inhalation of polluted air at industrial sites, or by contaminated food. HCB has low to moderate acute toxicity, is immunotoxic and may cause ovarian toxicity; prolonged oral exposure to HCB may cause liver diseases resulting in enzyme induction and porphyria. HCB also affects skin, thyroid glands, bones and nervous systems. HCB toxicity commonly leads to abnormal physical development in young children.

Polychlorinated biphenyls are human-made organic compounds and were first reported as environmental pollutants in 1996. PCBs are released into the environment from hazardous waste sites, burning municipal and industrial waste, and electrical transformers. PCBs tend to bioaccumulate in plant and animal tissues due to their lipophilic nature and can persist in air, water and soil for long periods of time.

Sediments, water, fish and bird tissue have been contaminated by PCB compounds. Plants represent the main entry route of PCBs in food chains. PCBs accumulate in leaf surfaces and other above-ground parts of plants (Campanella et al. 2002). Chronic exposure to PCBs may cause serious immunological, reproductive, neurobehavioral, and endocrine disorders in children. PCBs are suspected to be carcinogenic for animals, including humans (Department of Health and Human Services (DHHS); U.S. Environmental Protection Agency; Pieper and Seeger 2008).

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF) are ubiquitous in the environment; human exposure is mainly through diet, inhaling polluted air, and skin contact. PCDD/PCDF comes from air and dust from soil erosion and accumulates in plant above-ground parts. Chronic exposure of PCDDs and PCDFs leads to carcinogenesis; acute toxicity may lead to progressive loss of body weight and hypophagia, gastrointestinal hemorrhage, thymic atrophy, and delayed lethality in tested animals. Chronic exposure of PCDD/PCDF increases the chances of infertility in animals and humans. It can also damage the immune system, causing reproductive and developmental problems, interfere with hormonal functions, and cause kidney and hepatic lesions, which is cancerous (Marcia de 2004).

10.5 Abundance and Ecology of Aquatic Macrophytes

Macrophytes are important biotic components of aquatic ecosystems. Other aquatic life depends on them for food and habitat. Aquatic macrophytes help to control sediment erosion, buffer temperature variation, wave action, stabilize dissolved oxygen, absorb pollutants such as heavy metals and POPs and sequester nutrients. Thus, aquatic macrophytes help maintain healthy aquatic ecosystems.

Aquatic plants can be categorized into seven different groups: Bryophyta (mosses and liverworts), Chlorophyta (green algae), Cyanobacteria (blue–green algae), Pteridophyta (ferns), Rhodophyta (red algae), Spermatophyta (seed-bearing plants), and Xanthophyta (yellow–green algae) (Chambers et al. 2007). Aquatic macrophytes may be floating on the water surface, submerged, or emergent. They can complete their whole life cycle in water or on hydric soils (inundated and non-inundated) (Gecheva et al. 2013). Local habitat determines which macrophytes will grow; it also depends on the availability of light, current velocity, sediment composition and nutrient supply (Hrivnák et al. 2006; Birk and Willby 2010). However, human-impacted land use changes and hydrological dynamics are responsible for aquatic macrophyte diversity (Otahelová et al. 2007). Scarlett and O'Hare (2006) showed that coarse substrate with variable flow of water is suitable for the growth of bryophytes and excludes vascular hydrophytes. Bryophytes are dominant in lotic (moving water) ecosystems, specifically in undisturbed areas (Suren et al. 2000; Scarlett and O'Hare 2006). Thus, bryophytes are good candidates for running water remediation of pollutants.

In many cases, these plants have developed anatomical and morphological adaptations to different habitats. For example, many species like *Nymphaea nouchali*, *Myriophyllum brasiliense*, *Eichhornia crassipes*, *Equisetum fluviatile, Hippuris vulgaris,* and *Potamogeton amplifolius* have floating and aerial leaves to absorb CO_2 directly from the atmosphere. Some species use their root to absorb the high concentration of CO_2 available in the sediments (e.g., *Lobelia* and *Littorella*). These species have modified transport vessels for easy movement of CO_2 from root to leaves, having high root: shoot ratios (Thomaz et al. 2009).

The excessive load of pollutants, such as high nutrient level and essential and nonessential metals, results in booming the macrophytes in aquatic ecosystem. The most common species found in these ecosystems are *Hydrilla verticillata, Eichhornia crassipes*, *Salvinia* sp., *Pistia stratiotes,* and *Phragmities* sp. Although aquatic macrophyte has been utilized in various purposes, their use in eutrophication and for control of the pollution level in water is spreading rapidly. Aquatic macrophyte is used as an environmental filter for treatment of wastewater because of its high growth rate and rapid nutrient assimilation rate. Number of studies have been conducted to find the purification potential of macrophytes and found that there are significant differences among plant species and plant biotopes (e.g., floating leaves, submerged, emergent) (Keskinkan et al. 2003; Kamal et al. 2004; Maine et al. 2004; Victor et al. 2016).

Mostly, the floating macrophytes such as *Pistia stratiotes, Eichornia* spp*.,* and *Salvinia* spp. are used for remediating wastewater, because plant nutrient assimilation and photosynthetic activity are not affected by water turbidity. In addition, floating macrophytes are easier to manage and harvested when needed. The emergent plants such as *Juncus* spp. *and Typha* spp. are efficient enough to adsorb heavy metals to organic matter due to the fast adsorption and their post precipitation as particulate form in the sediment (Thomaz et al. 2009).

10.6 Removal of Organic Contaminants

Removal of organic contaminants by traditional technologies like filtration with coagulation, adsorption, ion exchange, precipitation, coagulation, ozonation, reverse osmosis and oxidation is time taking and costly as well as non-eco-friendly (Chandra et al. 2011; Saxena et al. 2017). Phytoremediation is an important and natural technique for the removal of organic contaminants. Organic contaminants available in the aquatic ecosystem have the potential to remove, sequester, and transform using microphytes (Day and Saunders 2004; Dosnon-Olette et al. 2009; Zhao et al. 2011). Several studies confer that application of aquatic macrophyte to degrade or uptake the organic components organophosphorus, organochlorine compounds, and chlorobenzenes present in water bodies is a cheap and sound technique (Gobas et al. 1991; Gao et al. 2000; Mercado-Borrayo et al. 2015).

The amount of organic compound removed by the macrophytes depends on the availability and composition of contaminates, the biochemical composition of plant tissue and physio-chemical properties of contaminants, as well as aqueous medium (Gao et al. 2000; Gao et al. 2003; Greenway 2007; Rezania et al. 2015). Studies show that halogenated organic compound sequestration by plant occurs through rapid physical and chemical process such as absorption, adsorption, complexation, and reaction with cuticular and membrane components (Nzengung and Jeffers 2001). The capacity to sequester organic contaminants of aquatic plants depends upon the plant's lipid-rich cuticle, which is responsible for sequestration of oils, fats, and hydrocarbons which comes under lipophilic organic compounds (Garrison et al. 2000; Gao et al. 2000; Gao et al. 2003).

10.7 Phytoremediation of Organic Pollutants Using Aquatic Macrophytes

Several common aquatic macrophytes like *Lemna minor, Elodea canadensis, Cabomba aquatica*, *Eichhornia crassipes* are used for the remediation of organic pollutants as shown in Table 10.1. According to Russell (2005), rhizodegradation and phytodegradation are the most suitable and effective removal techniques for organic pollutants, while phytoextraction is best for the removal of inorganic pollutants. Some mechanisms, like phytovolatilization, are equally effective with inorganic and organic contaminants. Phytodegradation process involves various enzymes (e.g., laccase, peroxidase, dehalogenase nitrate reductase, and nitrilase) excreted from the plant roots into rhizosphere which degrade organic molecules, e.g., PAHs (McCutcheon and Schnoor 2003).

However, the uptake of lipophilic large molecules by narrow channels in plant cell wall is difficult. In this case, the oxygenation process serves to enhance the solubility of water and provides an opportunity for conjugation through glycosidic bond formation. Peroxidases, peroxygenases and Cytochrome P450 are involved in plant oxidation of xenobiotics. Other classes of enzymes like carboxylesterases, gluthathione S-transferases are also associated with xenobiotic biotransformation in plant cells (Macek et al. 2000). In addition, the aquatic plant rhizosphere serves as a habitat for many biodegrading microbes and degrades organics much faster.

The organochlorine pesticides (OCPs) are one of the greatest threats to living organisms due to their acute effect and dispersion to long distances and bioaccumulation in the living tissues. Cleaning of the pesticides through conventional methods is expensive and not practical for less contaminated areas specifically in aquatic medium. To overcome the problem, scientist and researchers find that the phytoremediation technique to be more suitable. A number of studies have been conducted to know the phytoremediation potential of different aquatic macrophyte, which has been summarized in Table 10.1. Many studies have been made using *Lemna* spp. to remediate contaminants due to its tolerance in cold, fast growth rate, ease of harvesting, and cost-effectiveness (El-Kheir et al. 2007). A recent study by Xu et al. (2018) found that *P. australis* is a good candidate for remediating chlorpyriphos contamination from the eutrophic water and also indicated that suitable plant combination is needed for treatment of polluted water. Macrophytes like *Eichhornia crassipes* have

Table 10.1 Macrophytes used for removal of different pesticides from aquatic ecosystems

Pesticides	Concentration	Plants used	Removal/accumulation	References
Dimethomorph, copper sulfate, flazasulfuron	Five different conc. Between 0 and 1 mgL^{-1} were exposed to plants	*Cabomba aquatica, Lemna minor, Elodea canadensis*	Order of uptake was *L. minor* > *E. canadensis* > *C. aquatica*. Maximum removal rate as copper sulfate, flazasulfuron, and dimethomorph with 30, 27, and 11 $\mu g\ g^{-1}$ fresh weight day^{-1}	Olette et al. (2008)
2,4-D	10 µM concentration used in the experiment	*Lemna minor*	Plants helped in enhancing the microbial degradation process. Sorption also took place passively which helped in depletion of fluoxetine and triclosan	Reinhold et al. (2010)
Chlorpyrifos	The experimental concentrations were 0.0, 0.1 and 0.5 $mg\ L^{-1}$	*Pistia stratiotes* *Lemna minor*	The removal conc. was 82 and 87% for *P. stratiotes* and *L. minor* at 0.5 $mg\ L^{-1}$ conc. level. *L. minor* has high bioconcentration factor than *P. stratiotes*	Prasertsup and Ariyakanon (2011)
Nutrients and chlorpyriphos	The eutrophic water contents 1 $mg\ L^{-1}$ chlorpyrifos, 10 $mg\ L^{-1}$ total phosphorus And 30 $mg\ L^{-1}$ total nitrogen (TN)	*Phragmite australis,* *Nymphaea alba,* *M. verticillatum*	*P. australis* found to be suitable for clearing the sediment chlorpyriphos	Xu et al. (2018)
Ethion	The treatment ethion conc. was 1 $mg\ L^{-1}$ (purity 95%)	*Eichhornia crassipes*	Plant uptake and phytodegradation up to 69%	Xia and Ma (2006)
KHP, sodium tartrate, malathion, 2,4-D	The conc. of organic pollutant present in terms of COD (200, 100, 50, and 25 mg COD L^{-1})	*Eichhornia crassipes*	Study found that maximum absorbance of malathion, 2,4-D, and piroxicam was 67.6%, 58.3%, and 99.1%, respectively	Rodríguez-Espinosa et al. (2018)
Aldrin, Endosulfan γ–HCH DDTs	The available total organochlorine pesticides (OCPs) conc. in the sediments was in the range 3.60–11.12 $ng\ g^{-1}$	*Ceratophyllum demersum, Phragmites, Typha*	The OCPs conc. in the plant tissues in between 4.72 and 11.19 $ng\ g^{-1}$. The highest conc. is found in *Phragmites* leaves	Guo et al. (2014)

the ability to uptake toxic insecticide like ethion and malathion and degrade up to 68% (Xia and Ma 2006; Rodrigue-espinosa et al. 2018).

The extensive medical facility uses diverse range of medicines and personal care products which have triggered large amount of chemicals. Several studies have demonstrated that with the help of aquatic plants, cleaning of PPCPs is very effective (Table 10.2). Medicinal constituents like ibuprofen, naproxen, and carbamazepine were successfully removed by *Typha* spp. from the contaminated medium with greater than 90% efficiency (Dordio et al. 2010; Zhang et al. 2011). Most of the aquatic plants degrade pharmaceutical products with the help of available microbe.

Apart from the pesticides and pharmaceutical contaminants, there are other types of organic pollutant such as dyes, perchlorate salts (used in food packaging), and phenols which are potentially toxic to living organisms. There are a number of physicochemical methods available like coagulation, adsorption, electrolysis to decolorize and remediate the contaminants from wastewater (Robinson et al. 2001; Aksu 2005), but these methods have drawback because they produce large amount of sludge which results in production of secondary pollutant (Zhang et al. 2004; Al-Degs et al. 2008). Studies have shown that macrophytes like *Lemna minor* and *Eichhornia* can remove up to 90% of organic dyes from the water medium as shown in Table 10.3 (Muthunarayanan et al. 2011; Török et al. 2015; Torbati 2015).

Organic pollutant like phenols which is being released by various manufacturing industries such as fertilizers, plastics, pesticide, and oil refineries into the aquatic ecosystems are said to be extremely dangerous (Huang et al. 2014). A study found that plant degrades phenol by catechol-cleavage pathways where catechol forms (Jha et al. 2013). Catechol further cleaves to produce fumaric and muconic acid which passes to Krebs cycle and finishes the phenol degradation pathway. Recent research found that *Ipomoea aquatica* can be helpful for complete removal of lower concentration (up to 0.05 g/ L^{-1}) of phenol from the water (Lee et al. 2017). Macrophytes sometimes are unable to degrade the contaminant completely, but can transform the toxicants into less harmful compounds (Table 10.4).

10.8 Factors Affecting Phytoremediation of Organic Contaminants by Using Macrophytes

Ecological and physicochemical factors of water, such as light, dissolved oxygen, salinity, temperature, pH, are known to affect the uptake of nutrients or metals or organic pollutants. However, environmental conditions, especially temperature, macronutrients, micronutrients, and non-mineral nutrients significantly affect the macrophytes biochemical composition, which affects the phytoremediation potential (Kalacheva et al. 2002; Juneja et al. 2013). Moreover, the energy derived from photosynthesis and the oxygen released can improve conditions for the absorption of elements.

Table 10.2 Showing PPCPs remediation capacity of different aquatic macrophytes

Pharmaceutical and personal care products (PPCPs)	Concentration	Plant use	(Removal/accumulation)	References
Carbamazepine (CB), ibuprofelinn (IB), sulfadiazine (DIA), sulfamethoxazole (SMX), sulfamethazone (SMZ) and triclosan (TRI)	High (10 mg L^{-1}) and low (0.8 mg L^{-1}) conc. were considered for the experiment	*Eichhornia crassipes, Pistia stratiotes*	Biodegradation, photodegradation, adsorption and plant uptake occurred synergistically. Removal efficacy was lower in high conc.	Lin and Li (2016)
Ibuprofen, carbamazepine and clofibric acid (CA)	CA, IB, and CB having 97%, 99.8% and >99% purity and wastewater Samples conc. Levels were 0.5,1.5 and 2.5 μg mL^{-1}	*Typha* spp.	Total removal efficiencies of 96%, 97%, and 75% for IB, CB and CA, respectively. It was achieved under summer conditions after 7 days retention time	Dordio et al. (2010)
CB, declofenac, IB and naproxen	Hydraulic residence time of 2–4 days	*Typha angustifolia*	For IB and naproxen removal efficiencies 80% and 91%, in planted beds compared to unplanted beds 60% and 52%, respectively	Zhang et al. (2011)
Tetracycline (TC), and oxytetracycline (OTC)	Plant were put in the experimental flasks/jars, after 8–10 days stock solutions were added	*Myriophyllum aquaticum, Pistia stratiotes*	Both plants have high antibiotic modification rates. Result showed modification rates decreased with increasing OTC concentrations	Gujarathi et al. (2005)
Fluoroquinolones (FQs) (ciprofloxacin (CIP) and norfloxacin (NOR))	CIP and NOR purity of 98.8%. The FQs conc. added for experiment was (10 mg L^{-1})	*Acrostichum aureum L., Rhizophora apiculata*	The antibiotics accumulation occurred in the root parts. Results showed translocation from root to stem and leaves happened at a low rate. Overall a good candidate for phytoremediation	Hoang et al. (2013)
Methyl (MeP) and propyl parabens (PrP)	___	*Landoltia punctate, Lemna minor*	For MeP and PrP average removal efficiency was 90 and 89%, respectively	Anjos et al. (2018)

(continued)

Table 10.2 (continued)

Pharmaceutical and personal care products (PPCPs)	Concentration	Plant use	(Removal/ accumulation)	References
Fluoxetine, ibuprofen and triclosan	10 μM concentration used in the experiment	*Lemna minor*	Plants helped in enhancing the microbial degradation process. Sorption also took place passively which helped in depletion of fluoxetine and triclosan	Reinhold et a. (2010)
Atrazine	Atrazine used conc. was 4.0 mg L^{-1} in the study	*Acorus calamus, Iris pseudacorus, Lythrum salicaria*	The degradation capacity of *A. calamus, I. pseudacorus,* and *L. salicaria* were recorded 61.8, 75.6, and 65.5%	Wang et al. (2012)

Table 10.3 Macrophytes used for removal of dyes

Dyes	Concentration	Plant use	Removal/ accumulation)	References
Azo dye (AB92)	The conc. of dye used for the study was between 5 and 20 mg L^{-1}	*Lemna minor*	Study confirmed that *L. minor* had considerable potential for remediate AB92	Khataee et al. (2012)
Triphenylmethane dyes (crystal violet and malachite green)	The experimental conc. was 1 g dye/1 L	*Lemna minor*	Crystal violet removed by 80% and malachite green by 90%	Török et al. (2015)
Malachite green	Dye concentrations use between 5 and 40 mg L^{-1}	*Lemna minor*	Decolorization ability of the plant was 88%	Torbati (2015)
Red RB and black B (dye)	The test conc. was ranging from 10, 20, 30, 40 and 50 ppm	*Eichhornia crassipes*	Successfully degrade the red RB (95%) and black B (99.5%)	Muthunarayanan et al. (2011)

10.8.1 pH of Growing Medium

Growth and biomass of the plants are two important factors for a phytoremediator species. The pH is one of the most important factors for cultivating macrophytes because it can control the solubility and availability of CO_2 and essential nutrients which affect the growth of plants. The change in pH lowers the plant growth and metabolic inhibition (Juneja et al. 2013). Shah et al. (2014) conducted a study to see the effect of pH on the performance of aquatic macrophytes at different pH values

Table 10.4 Macrophytes used to remove other organic contaminants

Others organic pollutants	Concentration	Plant use	(Removal/accumulation)	References
Organic matter and nutrients	Maximum organic load was 6.16 g BOD/ m^2day	*Phragmite karka, Vetiveria zizanioide*	*V. zizanioide* had better removal capacity (TSS: 92.3%; BOD5: 92.0%; PO4 3−: 86.7%) than *P. karka* (91.3%, 90.5%, 85.6%). In addition, *P. karka* removal efficiency was better of NH4 $^+$ (86%), NO3 − (81.8%) and SO4 2− (91.7%) than *V. zizanioide* (83.4%, 81.3%, 90.5%)	Angassa et al. (2018)
Phenols	The test medium conc. of phenol was 0.05, 0.10, 0.20, 0.30 and 0.40 g/L^{-1}	*Ipomoea aquatica*	Plants completely removed the phenol conc. 0.05 g/L^{-1} after 12 days of growing. Plant extract test showed *I. aquatica* was able to degrade the absorbed phenol	Lee et al. (2017)
Perchlorate	Examined in sand and aqueous medium with test sample conc. between 0.2 and 20 ppm	*Myriophyllum aquaticum*	Five times higher uptake rates in aqueous medium than in sand medium. Phytotransformation occurred with accumulation of perchlorate in the plant tissues (1.2 g/kg) was recorded	Susarla et al. (1999)
Phenanthrene	The contaminants conc. was 0.385 mg L^{-1}	*Scirpus lacustris, Typha* spp.	99.9% phenanthrene adsorption took place	Machate et al. (1997)

and found almost very poor performance at pH below 5 and above 10. Maximum performance was observed at pH 7.5. Therefore, pH between 6 and 9 was recommended as the most suitable pH for better growth of the macrophytes. Lu et al. (2004) observed the best growth of water hyacinth in the pH range of 5.5–7.0 (El-Gendy et al. 2006).

10.8.2 Temperature

Temperature is another most important environmental factor that influences the macrophytes' growth pattern, biochemical composition, cell size, and nutrient supplies (Table 10.5). Studies have been conducted to know the performance of macrophytes under different temperature conditions. Shah et al. (2014) conducted an experiment on three macrophyte species (Water hyacinth, Duckweed and Water lettuce). These macrophytes were found to be temperature sensitive and showed no

Table 10.5 Impact of temperature on different macrophytes

Aquatic plants	Results	References
Water hyacinth (*Eicchornia crassipes*)	Water hyacinth was reported to be very sensitive to temperature, and 15–25 °C was found to be the most favorable temperature for their optimum growth	Wang et al. (2013)
Salvinia natans, Ceratophyllum demersum	In this experiment, *ceratophyllum demersum* was found to be more tolerant to temperature change than *salvinia natans* which renders it more effective in phytoremediation	Hreeb (2017)
Eelgrass *(Zostera marina)*	The optimum water temperature for eelgrass appeared to be between 10 and 20 °C. These results show that extreme conditions may affect the fitness and ecological performance of eelgrass	Nejrup and Pedersen (2008)

growth and removal of pollutant at temperature below 10 °C. Almost all three species ceased to survive at such low temperature. There was no growth of these macrophytes; therefore, there was negligible uptake of nutrients (N and P) by the plants. It was also observed that the temperature between 15 and 38 °C is suitable for the treatment of municipal wastewater by macrophytes as optimum growth was observed in this temperature range. Majority of the aquatic macrophytes are temperature sensitive and not suitable for temperate or frigid areas.

10.8.3 Plant Species

Albers and Camardese (1993) found submerged species to be more efficient in phytoremediation because of high accumulation of the contaminants as compared to emerged species. This might be due to degradation and disappearance of plant's roots such as *Ceratophyllum demersum*, which do not have profound root system but develop modified leaves with a root-like appearance and their waxy coat inhibits absorption by epidermal cells (Yurukova and Kochev 1994). In another study, due to specific morphology and higher growth rate, free-floating plants were more efficient to heavy metal uptake in comparison with submerged and emergent plants. However, the removal efficiency is highly correlated with growth rate, tolerance to higher concentration of metals, and adaptability to different environmental conditions (Rezania et al. 2016).

10.9 Carbon Sequestration Potential of Macrophytes

For the last 200 years, the levels of greenhouse gas (GHGs) especially CO_2 has increased palpably in the atmosphere. The global desire to reduce GHGs levels has led to an increase in the number of researches in the field of carbon sequestration.

Macrophytes being greater in size and obviously having larger biomass than other aquatic plants have comparatively greater potential to sequester carbon especially in the form of CO_2.

Some of the emergent macrophytes like *Typha latifolia* and *Scirpus acutus* are seen to have good potential to promote the process of carbon sequestration (Burke 2011). Biological fixation of light energy into chemical energy, the process known as photosynthesis is the process by which plants transform atmospheric carbon as CO_2 into the carbon of biomass or plant tissue. Accurate knowledge of species-specific carbon contained in biomass of plant is indispensable for better understanding of carbon stock of a particular ecosystem (Thomas and Martin 2012). A study was done by Maqbool and Khan (2013), by taking into account several macrophytes for their organic carbon percentage. The percentage of carbon varied between 34.97 and 50.92% as shown in Fig. 10.3.

Wetland ecosystems are really unique because they are biologically diverse and have local economic benefits (Goswami et al. 2010). This is supported by the fact that even a eutrophic system colonized by only water hyacinth can trap significant amount of carbon. The net primary productivity (NPP) of a wetland is remarkably higher than many terrestrial ecosystems (Reddy and DeLaune 2008), and so, wetlands are very important as sinks of carbon sequestration.

A number of factors affect the rate of carbon sequestration. With increase in temperature, the rate of respiration is increased, which in turn can decrease the rate of carbon sequestration (Turnbull et al. 2001), also shorter day length, lower temperature, and low light intensity, the rate of photosynthesis (Yamasaki et al. 2002) as well as enzyme activity (Khodorova and Boitel-Conti 2013) may go down, all these factors might be limiting the efficiency of carbon capture by the plants. It can

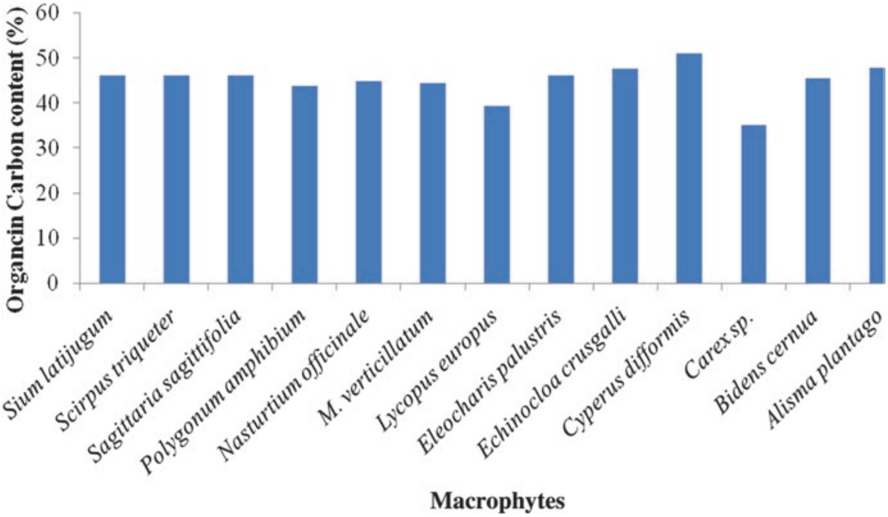


Fig. 10.3 Organic carbon content (percentage) of different species of macrophytes in Lake Manasbal. (*Source*: Maqbool and Khan 2013)

be concluded that macrophytes are an inseparable constituent of aquatic ecosystems. Besides playing several important roles in numerous accessory resilience, restoration capacity, etc., it also plays an important role in carbon capture, and they also are significantly sustainable and promising means of sequestering atmospheric carbon.

10.10 Biofuel Production by Macrophytes

Like algae, macrophytes also perform the dual role of wastewater treatment along with the production of renewable fuels. Macrophytes are known to absorb important wastewater nutrients like phosphorus and ammonium. On analyzing the pyrolysis products, it was found that algae and Azolla produce bio-oils of similar range which consist of a wide spectrum of photochemicals that include C_{10}–C_{21} alkenes that can be directly utilized as supplement for biodiesel fuel as given in Table 10.6 (Muradov et al. 2014).

Lemna spp. or duckweeds have comparatively high level of starch, lower lignin level, and the composition of cell wall carbohydrates help improve the production of bioethanol, in an economical way. Its production is 50% more as compared to production of ethanol based on maize, and this makes duckweed more competitive for the production of ethanol (Xu et al. 2011). Aquatic macrophytes like *Eichhornia crassipes, Nymphaea* spp., and *Eichhornia azurea* have double whammy, as they are invasive as well as they cause environmental problems like excessive growth (Villamagna and Murphy 2010; Luo et al. 2011; Pal et al. 2017), thereby obstructing the passage of light for submerged plants and reducing the level of oxygen in water.

Table 10.6 Different methods of bioenergy production from various macrophytes

Source of bioenergy	Process of bioenergy production	References
Bioethanol production	1. Hydrolysis 2. Fermentation	Patel and Patel (2015), Randive et al. (2015)
Lipid production	1. Solvent extraction (a) Chloroform based (production at laboratory scale) (b) Hexane based (production at industrial scale)	Halim et al. (2012)
Biogas production	1. Biomass conversion into slurry followed by anaerobic digestion	Malik (2007)
Biohydrogen production	1. Biological water–gas shift reaction 2. Photo fermentation 3. Dark fermentation 4. Direct photobiolysis 5. Indirect photobiolysis	Gaudernack (1998), Lin and Jo (2003), Levin et al. (2004), Bridgwater (1999)

However, these plants can be effectively used for the production of second-generation biofuel by pyrolysis. The fuel thus obtained is mainly composed of alkanes (~26%) (Lu et al. 2009).

Using aquatic invasive plant species for the production of biofuels have multiple ecological benefits; some of them have been enumerated below:

(a) They grow and accumulate rapidly thus producing enormous biomass (Wilkie and Evans 2010).
(b) As they are invasive, they do not have an impact on the production of food.
(c) Energy dispersive X-ray fluorescence spectrometry (EDX) analyses of ashes show significant levels of micro and macronutrients, which may be incorporated in biochars, indicating that they can also be used in soil management (Santos et al. 2018).

Using different invasive aquatic species have unique benefits, such as water hyacinth has the following ecological benefits: (1) no/low maintenance cost, (2) its biomass is of non-food nature, (3) rapid reproduction rate, (4) does not require land use change, (5) highly energetic biomass (Das and Jana 2003), (6) low lignin and high cellulose and hemi cellulose content (Bergier et al. 2012), (7) resistant to insect, pests, and diseases (Bhattacharya and Kumar 2010).

Using Azolla has a different set of ecological benefits altogether, which has been enumerated below: (1) it has high productivity, (2) it can grow abundantly even in wastewaters, (3) unique chemical composition makes Azolla sustainable, attractive, and universal feedstock, (4) low energy demand for proliferation, (5) almost zero maintenance system makes it a renewable biofuel source of choice (Miranda et al. 2016). Using invasive species like *Eichhornia crassipes, Nymphaea* spp., *Eichhornia azurea,* for the production of biodiesel is thus a win-win situation.

Apart from this, the biomass of *Eichhornia azurea, Eichhornia crassipes, Salvinia,* and *Pistia stratiotes* can also be used to produce biogas. The biogas may be obtained by the process of anaerobic digestion. The biogas thus obtained has significant amount of methane (CH_4). The amount of methane in the biogas obtained from the mixture of these plants in volume percentages on 7 days, 14 days, 21 days, and 28 days are 40.9%, 49.7%, 48.0%, and 48%, respectively (Pereira and de Jesus 2011).

The most common method for the production of biogas from aquatic plants includes the processing of wet biomass into slurry that is ultimately loaded into an anaerobic digester (Malik 2007). Some factors that generally affect biogas yield from aquatic plant biomass are as follows (Wilkie and Evans 2010): (1) particle size, (2) volatile solid content, (3) trace nutrients, and (4) inoculation—need of the hour is to develop harvester machines and processing infrastructure that can transport these aquatic plant biomasses to refineries in timely and cost-effective manner.

10.11 Conclusion

The presence of organic contaminants in aquatic ecosystems are a global concern and their safely removal is a pivotal task. Application of aquatic macrophytes for the removal of these contaminants may be done in an environmentally manner through the process, phytodegradation/phytovolatilization. The macrophytes like *Elodea canadensis, Lemna minor, Eichhorn crassipes, Trapa natans*, *Pistia stratiotes* may be used for the removal of organic contaminants. Majority of macrophytes are high biomass-producing plants, and therefore, the biomass may be used for the energy production (as biofuel). Several potential phytoremediator macrophytes like *Eichhornia crassipes*, *Typha angustifolia* are also considered as significant carbon sequesters (Pal et al. 2017). Therefore, the application of aquatic macrophytes for the remediation of organic pollutants may also help in management of another two major environmental issues, i.e., energy crisis and global climate change.

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