# **Chapter 10 Municipal and Industrial Wastewater Treatment Using Constructed Wetlands**



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**Abstract** High rate of urbanization and industrialization in recent years is generating very large amount of wastewater. Inadequate wastewater treatment options may lead to the discharge of untreated wastewaters (containing organic matter, inorganic and organic chemicals, toxic substances, and disease-causing agents) into the aquatic environment, thereby deteriorating their quality. These toxic chemicals such as heavy metals draw our concern towards their remediation due to their harmful effect on human metabolism and ecosystem as a result of their high persistence in the environment. Constructed wetlands are being widely used for treating many classes of contaminants such as heavy metals, domestic and industrial wastewater, textile dye effluents, pesticides, petroleum hydrocarbons, explosives, radionuclides, etc. This treatment method overcomes the shortcomings of conventional wastewater treatment methods as it is a cost-effective, non-intrusive and eco-centric technology. This chapter reviews and provides an insight into constructed wetland technology employed for efficient remediation of difficult-to-treat wastewaters.

**Keywords** Constructed wetlands · Environmental pollution · Industrial wastewater treatment · Phytoremediation

## **Abbreviations**

- BOD Biochemical Oxygen Demand
- COD Chemical Oxygen Demand
- CW Constructed Wetlands

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## **10.1 Introduction**

Wetlands are defined as areas that are inundated or saturated with surface or groundwater, saline or fresh, which support vegetation typically adapted for living in saturated soil conditions (Metcalfe et al. [2018\)](#page-34-0). They are characterized by distinguished vegetation (aquatic plants) and are adapted to the unique hydric soils. Wetlands exist in every climatic zone (from polar to tropical regions) and include marshes, peatlands, mangrove forests, rivers, lakes, deltas, and floodplains. Being an important component of the ecosystem, urban wetlands offer vital services such as water purification, filtration, retention of nutrients, flood control, groundwater recharge, and providing habitat for a variety of species (Gibbs [1993;](#page-32-0) Boyer and Polasky [2004;](#page-31-0) Rana et al. [2016\)](#page-35-0). They play an important role in regulating biogeochemical cycles (carbon, nitrogen, and sulfur cycles) in the atmosphere. With increasing population and industrialization, the total area covered by wetlands has decreased substantially due to anthropogenic activities (Hansson et al. [2005\)](#page-33-0). Wetlands act as "sinks" to metals, as they offer processes such as sedimentation and adsorption of pollutants. The metals in dissolved and particulate form are reduced in wetlands due to the presence of organic matter, divalent ion (Fe), and clay. In addition, carbonates, phosphates, and Fe/Mn oxides also promote the immobilization of metals.

The economic value of a wetland depends upon its functioning. Wetland functions are not necessarily of economic worth but the value derives from the existence of a demand for wetland goods and services due to these functions. *Use-value* of a wetland means indirect or direct utilization of wetland goods and services by humans. However, *non-use* value of a wetland is associated with benefits derived simply from knowledge that a resource such as an individual species or an entire wetland is maintained (Turner et al. [2000\)](#page-36-0). It is independent of use, although it is dependent upon the essential structure of the wetland and functions it performs.

The diversity of wetlands depends upon their method of formation, geographical location, and altitude. The flow of water in to and out of the wetland system is driven by the climate and configuration of its catchment area. The storage capacity of the system is regulated by landscape and geology. This hydrological cycle influences the rates at which gases diffuse through water, the reduced or oxidized (redox) state of

<b>Treatment level</b>	Description
Preliminary	Removal of was tewater constituents such as rags, sticks, floatables, grit, grease that may hamper operation and maintenance of various treatment processes
Primary	Removal of a portion of the suspended solids and organic matter from the wastewater
Advanced primary	Enhanced removal of suspended solids and organic matter from the wastewater, typically accomplished by chemical addition and filtration
Secondary	Removal of biodegradable organic matter and suspended solids. Disinfection is also included in the definition of conventional secondary treatment
Secondary with nutrient removal	Removal of biodegradable organics, suspended solids, and nutrients (nitrogen, phosphorus, or both)
Tertiary	Removal of residual suspended solids (after secondary treatment), usually by granular medium filtration or micro-screens. Disinfection is also a type of tertiary treatment. Nutrient removal is often included in this definition
Advanced	Removal of dissolved and suspended materials remaining after normal biological treatment when required for various water reuse applications

<span id="page-2-0"></span>**Table 10.1** Different levels of wastewater treatment (Adopted from Metcalf and Eddy [2003\)](#page-34-1)

nutrients and their solubility which thereby affecting the salinity of the water. These factors indicate the diversity of flora and fauna that sustain in a wetland and species diversity and composition, in turn, regulates the recycling of nutrients and pollutants in wetlands (Gupta et al. [2020\)](#page-33-1).

Municipal wastewater represents the spent water supply of communities. Before discharging the wastewater into natural water streams, it undergoes various levels of treatment which are enlisted in Table [10.1.](#page-2-0)

## *10.1.1 Phytoremediation: A Green Technology*

Phytoremediation refers to the use of plants to remove, destroy, or sequester hazardous contaminants from media, such as soil, water, and air (Prasad [2003;](#page-35-1) Rana and Maiti [2018a\)](#page-35-2). It encompasses the use of various technologies to reduce, degrade, or immobilize harmful intoxicants in the environment, primarily of anthropogenic origin, with an objective to remediate contaminated sites and wastewater treatment by employing plants (Mukhopadhyay and Maiti [2010\)](#page-35-3). Phytoremediation is being used in different decentralized wastewater treatment systems such as constructed wetlands for treating municipal and various industrial wastewater efficiently (Daverey et al. [2019\)](#page-32-1).

Phytoremediation operates through various processes: phytoextraction, rhizofiltration, phytostabilization, phytodegradation, and phytovolatilization. The remediation of pollutants can take place either individually or in combination by these processes (Ali et al. [2013\)](#page-31-1). Phytoremediation is being widely used for treating many classes of contaminants such as metals, pesticides, petroleum hydrocarbons, explosives, and radionuclides (McCutcheon and Schnoor [2003\)](#page-34-2). Phytoremediation overcomes the shortcomings of conventional wastewater treatment methods as it is a solar-driven, cost-effective, non-intrusive, and environment-friendly technology.

### **10.1.1.1 Phytoextraction**

Phytoextraction (also known as phytoaccumulation, phytoabsorption, or phytosequestration) is defined as the process that utilizes plant roots for the uptake of pollutants from soil or water and their translocation to and subsequent accumulation in above-ground biomass, e.g., shoots or any other harvestable part of the plant (Bhargava et al. [2012\)](#page-31-2). Microbe-assisted phytoextraction enhances the uptake of metal ions by plants.

### **10.1.1.2 Rhizofiltration**

Rhizofiltration is the technique of utilizing plant roots to absorb, precipitate, and concentrate toxic metals from polluted effluents. Rhizofiltration technique has been used for the remediation of uranium and metals such as Pb, Cd, and Zn (Lee and Yang [2010;](#page-34-3) Duresova et al. [2014\)](#page-32-2).

### **10.1.1.3 Phytostabilization**

Phytostabilization is the immobilization of pollutants in the soil to dampen the biological availability of the pollutants and to reduce the possibility of further environmental degradation by transportation to other environmental components through the air or by leaching into the underground water table. Phytostabilization mainly focuses on sequestering metal ions and other pollutants near the root area instead of plant tissues (Lee [2013\)](#page-34-4).

### **10.1.1.4 Phytodegradation**

Phytodegradation, also known as phytotransformation, is the uptake, metabolization, and degradation of organic pollutants with the help of enzymes such as dehalogenase and oxygenase generated by plants and is independent of rhizospheric microorganisms. This technique has been used for treating pollutants of organic nature such as dyes (Muthunarayanan et al. [2011\)](#page-35-4).

#### **10.1.1.5 Phytovolatilization**

Phytovolatilization encompasses the release of contaminants into the air through leaves after taking up the contaminated water. This technique could be used for remediation of organic pollutants and the uptake of some metals such as Hg, Se, and As (Ali et al. [2013\)](#page-31-1).

## *10.1.2 Ramsar Convention for Conservation of Natural Wetlands*

Ramsar Convention is an inter-governmental treaty that provides the framework for national action and international cooperation for the conservation and wise use of wetlands and their resources. On February 2, 1971, in the Iranian town of Ramsar, 18 nations signed this remarkable treaty. It was the first of the modern instruments seeking to conserve natural resources on a global scale. The need to sign this treaty on an international level was because: (i) many wetlands shared international boundaries, thus the circulation of water in atmosphere was truly international; (ii) fish hatching in wetlands included shares in two or more countries; (iii) migratory birds crossed international boundaries to rest, feed, and breed; and (iv) there must be international arrangements for the provision of technical and financial aid to conserve wetlands in developing countries (Matthews [1993\)](#page-34-5). As of 2016, the Ramsar Convention included 2266 sites of international importance. The country with the highest number of sites is the United Kingdom with 170 wetland sites, and the country with the greatest area covered with wetlands is Bolivia, with over  $140,000 \text{ km}^2$ . The countries signing this treaty commit to (i) work towards the wise use of the wetlands to be conserved under this treaty; (ii) include suitable wetlands in the list of Wetlands of International Importance (Ramsar list) and ensure their effective management; and (iii) cooperate on transboundary wetlands, shared wetland systems, and shared species. In India, there are 26 wetland sites which are designated as Ramsar sites.

## *10.1.3 Flora in Natural Wetlands*

Macrophytes are large plants that may dominate in wetlands or littoral zones of lakes and streams. Lakes, rivers, and marshes comprise of two types of macrophytes: (i) free-floating and (ii) rooted (Fig. [10.1\)](#page-5-0).

Rooted macrophytes divide the shoreline into distinct zones and assist in removing nutrients from the sediments and water column. From the shallow to the deeper water, three different types of plants are there: (i) floating-leaved plants, with leaves that grow from the vegetative portions near the bottom of the wetland until floating at the surface; (ii) emergent plants, with all or part of their vegetative and sexually



<span id="page-5-0"></span>**Fig. 10.1** Different types of macrophytes found in littoral zone of wetlands (Courtesy of the Minnesota Department of Natural Resources, the USA)

reproductive parts above the water surface; and (iii) submerged plants, that have all portions of the plant underwater, or the weed is dependent upon water for support. The list of some of the macrophytes which are commonly found in wetlands is shown in Table [10.2.](#page-6-0)

### *10.1.4 Biogeochemical Cycles in Natural Wetlands*

### **10.1.4.1 Carbon Cycle**

Wetlands are one of the largest biological pools of carbon and play a vital role in driving global carbon cycles by acting as natural carbon sinks (Mitra et al. [2005\)](#page-34-6). Wetlands cover a mere  $6-8\%$  of the land and freshwater surface; however, they contribute about 12% of the global carbon pool (Mitsch and Gosselink [2007\)](#page-34-7). Carbon in wetlands exists as plant biomass carbon, dissolved carbon, particulate carbon, microbial biomass carbon, and gaseous products such as  $CH_4$  and  $CO_2$ . The mass balance of carbon in wetlands depends on the (i) carbon input contributed by organic matter production and (ii) carbon output contributed by decomposition of organic matter, methanogenesis, etc. The storage of carbon in the wetlands is dependent on its topography, landscape, morphology, hydrologic regime, vegetation, temperature and pH, salinity and moisture of the soil.

Methane is generated through different pathways: (i) diffusion, which includes the transmission of  $CH_4$  through the soil and water to the atmosphere; (ii) plant mediated, which encompasses aerenchyma possessing tissues for direct transport of gases between atmosphere and plant roots; (iii) ebullition, which encompasses the

<b>EXAMPLE 2</b> Last of some macrophytes commonly round in weithing Scientific name	Family	Common name
<b>Floating macrophytes</b>		
Commelina benghalensis L.	Commelinales	Benghal dayflower, tropical spiderwort
Enhydra fluctuans Lour	Asteraceae	Water spinach, watercress
Hydrocharis dubia (Blume) Backer	Hydrocharitaceae	
Ipomoea aquatic Forssk.	Convolvulaceae	Water spinach, water convolvulus
Pistia stratiotes L.	Araceae	Water cabbage, water lettuce
Salvinia auriculata Aubl.	Salviniaceae	Eared watermoss, butterfly fern
Salvinia molesta D.Mitch.	Salviniaceae	Giant salvinia
Salvinia natans (L.) All.	Salviniaceae	Floating fern, floating moss
Trapa natans L.	Lythraceae	Buffalo nut, devil pod
<b>Emergent macrophytes</b>		
Cabomba aquatica Aubl.	Cabombaceae	Aquarium plant
Colocasia esculenta (L.) Schott	Araceae	Taro
Cyperus alternifolius Rottb., 1772	Cyperaceae	Umbrella papyrus, umbrella sedge
Cyperus esculentus L. Euryale ferox Salisb.	Cyperaceae Nymphaeales	Hufa sedge, nut grass Fox nut, gorgon nut
Leersia hexandra Sw.	Poaceae	Southern cutgrass, club head cutgrass
Monochoria hastata (L.) Solms	Pontederiaceae	
Scirpus grossus L.f.	Cyperaceae	Bulrush, deer grass
Typha latifolia L.	Typhaceae	Broad-leaf cattail
Typha angustifolia L.	Typhaceae	Narrow-leaf cattail
<b>Submerged macrophytes</b>		
Cabomba caroliniana A. Gray	Cabombaceae	Carolina fanwort, fish grass
Elodea canadensis Michx.	Hydrocharitaceae	Canadian waterweed or pondweed
Hydrilla verticillata (L.f.) Royle	Hydrocharitaceae	Waterthyme, hydrilla
Najas graminea Del.	Hydrocharitaceae	Rice-field water-nymph
Ottelia alismoides (L.) Pers.	Hydrocharitaceae	Duck-lettuce
Potamogeton crispus L.	Potamogetonaceae	Curled pondweed, curly-leaf pondweed
Ruppia maritima L.	Ruppiaceae	Beaked tasselweed, widgeon grass
Utricularia vulgaris L.	Lentibulariaceae	Greater bladderwort, common bladderwort
Vallisneria Americana Michx.	Hydrocharitaceae	Wild celery, water celery

<span id="page-6-0"></span>**Table 10.2** List of some macrophytes commonly found in wetlands

release of trapped  $CH_4$  in the vacuoles of the soil through popping up the  $CH_4$  pockets as a result of the built-up pressure over the time (DelSontro et al. [2016\)](#page-32-3).

The consumption of  $O_2$  by microorganisms living in warm, moist conditions is more than its diffusion from the atmosphere leading to the characterization of wetlands as an anaerobic platform for fermentation. Two types of bacteria belonging to the domain *Archaea* play a significant role in the global carbon budget: (i) methanotrophs and (ii) methanogens. Methanogens are obligate microorganisms degrading the organic matter by utilizing  $CO<sub>2</sub>$  as the energy source in the absence of alternative electron acceptors (Fe<sup>3+</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>). The reduction of CO<sub>2</sub> is carried out either with molecular  $H_2$  or through fermentation by acetoclastic methanogenesis encompassing the fermentation of acetate and  $H_2$ –CO<sub>2</sub> into CH<sub>4</sub> and CO<sub>2</sub> as shown in Eqs. [\(10.1\)](#page-7-0) and [\(10.2\)](#page-7-1). Active methanotrophs in aquatic environments including wetlands are quantified using various conventional and novel techniques such as determination of gene transcripts, DNA-based stable-isotope probing (SIP), quantitative PCR (Q-PCR), pyrosequencing (Deng et al. [2016\)](#page-32-4).

<span id="page-7-1"></span><span id="page-7-0"></span>
$$
CO2 + 4H2 \rightarrow CH4 + 2H2O
$$
 (10.1)

$$
HC_3 - COOH \rightarrow CH_4 + CO_2 \tag{10.2}
$$

The methane flux in wetlands is a function of the relative activities of methanotrophs and methanogens. Methane flux is also dependent upon several other factors such as the water table of the area, temperature, plant community composition, and substrate availability (Yun et al. [2015\)](#page-37-0). The decaying plant organic matter and root exudates released in the rhizosphere increases the substrate pool for the methanogens. Moreover, the  $O_2$  transferred to the rhizosphere through the aerenchyma of the plants growing in the wetlands increases the oxidation of CH4 by methanotrophs (Whalen  $2005$ ). Contrary to that, the aerobic methanotrophs can feed upon CH<sub>4</sub> for carbon and energy utilization.

The organic matter content within wetland systems is impacted by processes such as biodegradation, photochemical oxidation, sedimentation, volatilization, and sorption. Some of these mechanisms provide natural organic matter accumulation via microbial and/or vegetative decay. Moreover, the accumulation of organic matter is a potential energy source for microbial communities. Dissolved organic matter degradation is expected to occur via heterotrophic uptake by aerobic and anaerobic bacteria, and degradation by ultra-violet light. Several authors have reported on dissolved organic matter transformations in algae, forest vegetation, wetland plant material, microbial groups, and soils. Dissolved organic matter from plant exudates appears more dominant during warm months with active plant growth.

#### **10.1.4.2 Nitrogen Cycle**

The nitrogen transformation includes the conversion of inorganic to organic compounds and organic compounds back to inorganic form. Bacteria (known as ammonifiers) convert organically bound N to ammonia and the process is known as ammonification (Vymazal [2007\)](#page-37-2). The optimum temperature and pH for ammonification are 40–60 °C and 6.5–8.5, respectively. The ammonification process encompasses oxidative and reductive deamination in oxidized and reduced soil layers, respectively, which can be written as Eqs.  $(10.3)$  and  $(10.4)$ .

Amino acids 
$$
\rightarrow
$$
 Imino acids  $\rightarrow$  Keto acids  $\rightarrow$  NH<sub>3</sub> (oxidative deamination) (10.3)

$$
Amino acids \rightarrow Saturated acids \rightarrow NH_3 (reductive deamination) \qquad (10.4)
$$

Chemotrophic bacteria (nitrifiers) perform oxidation of ammonium to nitrate with nitrite as an intermediate in the reaction sequence and the reaction is known as nitrification [Eqs.  $(10.5)$ ,  $(10.6)$ , and  $(10.7)$ ]. Nitrification is a twostep process in which the first step includes oxidation of ammonium-N to nitrite-N by strictly chemolithotrophic (strictly aerobic) bacteria such as *Nitrosomonas europaea*. The second step includes oxidation of nitrite-N to nitrate-N by facultative chemolithotrophic bacteria such as *Nitrobacter winogradskyi* and *Nitrococcus mobilis* (Paul and Clark [1996\)](#page-35-5).

$$
NH_4^+ + 1.5O_2 \to NO_2^- + 2H^+ + H_2O \tag{10.5}
$$

<span id="page-8-4"></span><span id="page-8-3"></span><span id="page-8-2"></span><span id="page-8-1"></span><span id="page-8-0"></span>
$$
NO_2^- + 0.5O_2 \to NO_3^-
$$
 (10.6)

$$
NH_4^- + 2O_2 \to NO_3^- + 2H^+ + H_2O \tag{10.7}
$$

After  $O_2$  depletion, the reduction of nitrate is carried out by two processes: nitrate-ammonification in which nitrate is reduced to  $NH_4$ <sup>+</sup> by nitrate-ammonifying bacteria such as *Bacillus vireti* (Mania et al. [2014\)](#page-34-8) and denitrification in which nitrate is reduced to N<sub>2</sub> or N<sub>2</sub>O by denitrifying bacteria such as *Acidovorax*, *Azoarcus*, *Bradyrhizobium*, *Ochrobactrum*, *Paracoccus*, *Pseudomonas*, *Mesorhizobium*, *Ensife*r*,* and *Thauera* via intermediates nitrite, nitric oxide, and nitrous oxide (Song et al. [2000\)](#page-36-1).

Microbial denitrification is considered as the dominant and long-term mechanism of nitrate-nitrogen removal from wastewater especially when the constructed wetland system is subjected to high nitrate loading (Lin et al. [2002\)](#page-34-9). In constructed wetlands, the nitrogen transformation directly/indirectly depends upon the temperature, soil material types, operation strategies, and redox conditions in the wetland bed. Nitrogen fixers such as symbiotic actinomycetes and asymbiotic heterotrophic bacteria convert gaseous  $N_2$  to ammonia in the presence of nitrogenase enzyme. In

anaerobic ammonium oxidation (ANAMMOX), autotrophic bacteria convert ammonia to  $N_2$  gas with nitrite as the electron acceptor. Apart from conventional nitrogen transformation mechanisms in wetlands (natural/constructed), new techniques such as completely autotrophic nitrogen removal over nitrite (CANON), single reactor high-activity ammonia removal over nitrite (SHARON), simultaneous partial nitrification, ANAMMOX and denitrification (SNAD) have also gained attention as novel biological nitrogen transformation processes (Chang et al. [2013\)](#page-31-3).

#### **10.1.4.3 Sulfur Cycle**

The sulfate-reducing bacteria (SRB) present in the wetlands are strict anaerobes and sensitive to low temperatures which utilize on mole of sulfate to generate one mole of sulfide along with alkalinity Eq. [\(10.8\)](#page-9-0).

<span id="page-9-0"></span>
$$
SO_4^{2-} + 2CH_2O + 2H^+ \to H_2S + 2H_2O + 2CO_2
$$
 (10.8)

In constructed wetlands, the sulfur dynamics are dependent on biotic and abiotic factors such as the presence of SRB, availability of organic matter, precipitation as metal sulfides (Wu et al. [2013\)](#page-37-3). The sulfide produced in anoxic zones by SRB is transported to the oxic zones and then may oxidize back to polysulphides, elemental sulfur, thiosulfate, tetrathionate, or sulfate by biological pathways which is evident by the presence of sulfur compounds such as elemental S which can be generated by oxidation, by chemolithotrophic microbes using electron acceptors such as oxygen or nitrate. Moreover, anoxygenic phototrophic bacteria may associate sulfide oxidation with  $CO<sub>2</sub>$  reduction in some micro-zones of constructed wetlands. However, the generated elemental S can again convert back to sulfide by sulfur-reducing bacteria.

## **10.2 Constructed Wetlands: Decentralized Wastewater Treatment Technology**

Phytoremediation is being widely used for treating many classes of contaminants such as metals, pesticides, petroleum hydrocarbons, explosives, and radionuclides. Phytoremediation overcomes the shortcomings of conventional wastewater treatment methods as it is cost-effective, non-intrusive, and environment-friendly (Roongtanakiat et al. [2007\)](#page-36-2).

Constructed wetlands are engineered wastewater treatment systems that have been designed to work on the natural processes encompassing wetland vegetation, soils, and their associated microbial assemblages. They are constructed considering the merits of many of the same processes that work in natural wetlands but bound to

work in a more controlled environment (Vymazal [2013;](#page-37-4) Rana and Maiti [2018b\)](#page-35-6). Constructed wetlands have become a popular alternative to traditional wastewater treatment technologies which accounts for their low cost of installation and maintenance, and optimum climatic conditions for ponds found in tropical areas (Kivaisi [2001\)](#page-33-2). The conventional wastewater treatment technologies lag in the treatment applicability due to expensive installation, power consumption, formation of by-products while using chemical treatment methods (Robinson et al. [2001\)](#page-35-7). Constructed wetlands also have other merits related to environmental safeguards such as advancement of biodiversity, bioaccumulation, and methylation of metals, rendering habitat for wetland organisms and wildlife, rationing climatic and hydrological functions. Constructed wetlands have been used for the: (i) treatment of septic tank and Imhoff tank effluents from housing complexes and (ii) tertiary treatment of effluents from aerated lagoons and conventional STPs. In western countries, constructed wetlands have been used to treat storm waters, industrial, mining, and agricultural wastes. Constructed wetlands were first developed in 1960 by Dr. K Seidel in Germany. By 1995, over 200 units had been installed in Europe (Mainly in Denmark, Germany, and the United Kingdom) and another 200 units in the USA. In India, only 50–60 units were reported to be installed by the year 2005 which existed mostly in Tamil Nadu and Auroville, Puducherry. A schematic diagram of a constructed wetland is shown in Fig. [10.2.](#page-10-0)

They are in wide usage as a recognizable and attractive treatment technology for domestic sewage (El Hamouri et al. [2007;](#page-32-5) Sutar et al. [2019\)](#page-36-3). Moreover, their application has also been extended to various difficult to treat wastewaters such as pharmaceutical wastewater, textile wastewater, sugarcane molasses stillage, landfill leachate, tannery wastewater, pulp and paper mill effluent, and electroplating wastewater (Zainith et al. [2019\)](#page-37-5). Toxic pollutants are released into the aquatic environment by natural and anthropogenic sources which pose a serious threat to



<span id="page-10-0"></span>**Fig. 10.2** Schematic diagram of a constructed wetland

mankind. These pollutants may be organic or inorganic encompassing metals, dyes, and landfill leachate. The presence of metals and its components that are essential for the sustainability of an ecosystem is ubiquitous in the environment but their non-biodegradable, immutable, and almost indefinite persistent nature leads to the presence of these metals in an excess amount which may result in chronic and acute poisoning to the receivers. High concentrations of these metals found in the human body adversely influence nervous, cardiovascular, respiratory, gastrointestinal, hepatic, renal, hematopoietic, immunological, and dermatological systems. The toxic nature of Cd is attributed to its exceptionally high biological half-life in the human body (10–30 years) (Bernard and Lauwerys [1986\)](#page-31-4). Cadmium toxicity affects the immune system, leads to bone deformities accompanying renal dysfunction. Mercury is transported by water into the aquatic ecosystem and is considered relatively lipid-soluble due to its low water solubility. Mercury toxicity devastates the nervous system by interfering with the production of energy and impairing cellular detoxification processes causing cell death or cellular malfunction (Rice et al. [2014\)](#page-35-8). Lead also interferes with a number of body functions and primarily affects the central nervous system, hematopoietic, hepatic, and renal system producing serious disorders in the body. Chromium toxicity affects the immune system and may lead to immunosuppression or immune stimulation. Chromium also causes lung cancer, nasal irritation, and nasal ulcer and hypersensitivity reactions like contact dermatitis and asthma (Shrivastava et al. [2002\)](#page-36-4).

National Environmental Engineering Research Institute (NEERI) at Nagpur (India) developed a constructed wetland that was exclusively designed for the treatment of municipal, urban, agricultural, and industrial wastewater. The treatment system was based on plants such as *Pennisetum purpureum* Schumach, 1827, *T. latifolia*, *Phragmites* sp., and *Iris pseudacorus* L. Moreover, some ornamental and flowering plants such as *Duranta erecta* L. were used for wastewater treatment as well as for aesthetic purposes. Depending upon land availability, NEERI constructed sub-surface Phytorid technology in parallel or series modules. The treatment bed consisted of simple materials such as gravel, stones, and crushed bricks. The treatment system was divided into three zones: (i) inlet zone, which consisted of crushed bricks and stones of different sizes; (ii) treatment zone, which comprised the same media with plantation, and (iii) outlet zone. This technology demonstrated a reduction of 70–80% total suspended solids,  $78-84\%$  BOD,  $70-75\%$  nitrogen,  $52-64\%$ phosphorus, and 90–97% fecal coliform. The treated water was used for various purposes such as municipal gardens, fountains, and irrigation. The total area requirement for the treatment system is approximately  $35 \text{ m}^2$  for a wastewater flow rate of 20  $\text{m}^3$ /day. This technology has been transferred to General Techno Services, Technogreen Environmental Solutions, Pune, BIOUMA, Goa, and Devi Agencies, Aurangabad, and implemented to reuse water and benefit the local people.

The advantages of using constructed wetlands with emergent vegetation are:

i. Rhizomes of the reeds grow vertically and horizontally in the treatment bed (soil, sand, or gravel), opening up "hydraulic pathways";

- ii. Wastewater BOD and nitrogen are removed by bacterial activity; aerobic treatment takes place in the rhizosphere, with anoxic and anaerobic treatment taking place in the surrounding soil;
- iii. Oxygen passes from the atmosphere to the rhizosphere via the leaves and stems of the reeds through the hollow rhizomes and gets out through the roots;
- iv. Suspended solids in the sewage are aerobically composted in the above-ground layer of vegetation formed from dead leaves and stems; and
- v. Nutrients and metals are removed by plant uptake.

Based on the water surface, the constructed wetlands are generally of two types: (i) free water surface type, and (ii) submerged flow type. The submerged flow type constructed wetlands can be horizontal or vertical depending upon the wastewater flow regime. Submerged flow wetlands are preferred over free water surface wetlands due to: (i) relatively easy installation; (ii) inexpensive; and (iii) discouragement to the possibility of mosquito breeding that is likely with a free water surface wetland. Constructed wetlands are composed of media bed and vegetation that grows upon the media. The treatment media is composed of natural materials, such as gravel, sand, soil, etc. A list of materials used in different types of constructed wetlands is shown in Table [10.3.](#page-13-0)

### *10.2.1 Merits and Demerits of Constructed Wetlands*

Constructed wetland systems offer a green and sustainable treatment of wastewaters; however, they are characterized by some disadvantages too (Arceivala and Asolekar [2006\)](#page-31-5). Constructed wetland systems used for wastewater treatment are advantageous in the following ways (Singh et al. [2019\)](#page-36-5):

- i. Installation, operation, and maintenance of constructed wetlands are comparatively inexpensive to other treatment options;
- ii. They constitute simple construction and operation. There is no skilled labor required for the construction, operation, and maintenance of constructed wetlands;
- iii. Only periodic on-site labor is required for operation and maintenance of constructed wetlands, instead of continuous monitoring in other treatment options;
- iv. They utilize natural processes for wastewater treatment;
- v. They reduce excess sludge production; and
- vi. They enable reuse and recycling of water.

However, there are also some limitations to the use of constructed wetlands which are as follows:

i. A large land area requirement is a constraint for constructed wetlands. They require a large land area for the same level of treatment by traditional

Treatment media	Constructed wetland type	Type of wastewater treated	References
Gravel: Rock chips of charnackite type	Sub-surface	Domestic wastewater	Bindu et al. $(2008)$
1. Gravel $(D_{10})$ : $15 \text{ mm}$ ) 2. Composite filling: Round ceramsite $+$ blast furnace granulated slag $+$ $\text{soil} + \text{ sawdust}$ (Ratio 3:3:2:1)	Sub-surface vertical flow	Cadmium-spiked synthetic wastewater	Gao et al. (2015)
Gravel $(\phi: 25 \text{ mm})$ and porosity $(\eta)$ : $38.6\%$	Horizontal sub-surface flow	Synthetic landfill leachate	Madera-Parra et al. (2015)
Fine sand $(\phi: 2 \text{ mm})$	Free-surface flow	Diesel-spiked synthetic wastewater	Al-Baldawi et al. (2013)
1. Fine sand $(\phi)$ : $2 \text{ mm}$ ) 2. Gravel $(\phi)$ : $1-5$ mm) 3. Gravel $(\phi)$ : $10 - 20$ mm)	Sub-surface flow	Diesel-spiked synthetic wastewater	
Gravel $(0.2 - 2.24$ mm)	Vertical flow	Phosphorus-spiked synthetic wastewater	Li et al. $(2013)$
Gravel	Sub-surface flow	Mercury-spiked synthetic wastewater	Gomes et al. $(2014)$

<span id="page-13-0"></span>**Table 10.3** Different types of treatment media used in constructed wetlands

technologies which render them unsuitable for treating large volumes of wastewater;

- ii. Treatment time is comparatively higher than other treatment technologies;
- iii. The performance of constructed wetlands is driven by environmental factors, for example, the efficiency is reduced in colder climate;
- iv. The longer time period is required before the vegetation is fully established and optimum treatment efficiency is acquired;
- v. The dynamics of the treatment process are unclear which leads to inaccurate design and operation criteria;
- vi. They require a minimum base water flow as they can tolerate temporary water level drawdowns but not complete drying; and
- vii. The biological components are intolerant to shock loads due to toxic pollutants.

## *10.2.2 Mechanisms of Pollutant Removal in Constructed Wetlands*

Constructed wetlands resemble natural wetlands and include mineral or organic soil underneath vegetation. The vegetation encompasses emergent or floating macrophytes which, collectively with media bed, assist in removing the pollutants from wastewater. The basic processes driving the removal of pollutants are physical, chemical, and biological. The physical processes include sedimentation and filtration; chemical processes include sorption, photo-oxidation, and volatilization; and biological processes encompass the conversion of organic matter to  $CO<sub>2</sub>$  by using carbon as an energy source. The various pollutant removal mechanisms that are active in constructed wetlands are shown in Table [10.4.](#page-14-0)

Biochars increase plant growth, metal immobilization, and pH reduction in constructed wetlands (Zhang et al. [2013\)](#page-37-6). They sorb metals and increase the metal removal efficiency of constructed wetlands (Cui et al. [2016;](#page-32-7) Kizito et al. [2017\)](#page-34-12). Apart from metals, biochar also improves the overall efficiency of a constructed wetland system. Gupta et al. [\(2015\)](#page-33-4) treated synthetic wastewater and reported that the wetland with biochar was more efficient as compared to the wetland with gravels alone with an average removal rates of  $91.3\%$  COD,  $58.3\%$  TN,  $58.3\%$  NH<sub>3</sub>,  $92\%$ NO3-N, 79.5% TP, and 67.7% PO4. Enhanced nitrogen removal was also observed by using plant-based biochar in constructed wetlands (Li et al. [2018\)](#page-34-13).

Pollutant	Removal mechanism
Total suspended solids	Sedimentation and filtration
Soluble biodegradable organic matter	Microbial degradation (aerobic, anoxic, and anaerobic), adsorption, and plant uptake
<b>Nutrients</b>	
Nitrogen	Ammonification (mineralization), nitrification/denitrification, nitrate-ammonification, plant/microbial uptake, media adsorption/ion exchange, ammonia volatilization, and ANAMMOX
Phosphorus	Media adsorption, plant and microbial uptake, sedimentation, and precipitation
Metals	Adsorption and cation exchange, complexation, precipitation/co-precipitation, oxidation and hydrolysis, plant uptake, microbial oxidation/reduction (microbial-mediated processes), and sedimentation
Pathogens (microbial population)	Sedimentation, filtration, natural die-off, predation, UV irradiation, excretion of antibiotics by roots of macrophytes, and adsorption
Organic xenobiotics	Sedimentation, volatilization, biodegradation, adsorption, plant uptake, photolysis, and chemical reactions

<span id="page-14-0"></span>**Table 10.4** Wastewater pollutant removal mechanisms in constructed wetlands

## *10.2.3 General Design Considerations for Constructed Wetlands*

For the creation of successful constructed wetlands, Mitsch and Cronk [\(1992\)](#page-34-14) suggested the following guidelines: (i) simple designing; (ii) minimum maintenance; (iii) system designing using natural energies (such as gravity flow); (iv) system designing for peak loading condition and not average loading; (v) integrating the design with natural topography of the site; and (vi) designing for performance optimization. Arceivala and Asolekar [\(2006\)](#page-31-5) had given some process design norms for the construction of sub-surface flow constructed wetlands for treating raw domestic wastewaters in India which is shown in Table [10.5.](#page-15-0)

For designing macrophyte beds with the horizontal flow, two key aspects have to be kept in mind: (i) organic removal parameters, and (ii) hydraulic flow considerations.

#### **10.2.3.1 Organic Removal in Constructed Wetlands**

BOD removal has been approximated by first-order plug-flow kinetics. On the basis of the European design and operations guidelines, Green and Upton [\(1994\)](#page-33-5) reported Eqs. [\(10.9\)](#page-15-1) and [\(10.10\)](#page-16-0) based on first-order kinetics as also used in Severn Trent, the United Kingdom, for the design of constructed reed beds for polishing wastewater treated effluents from small communities.

<span id="page-15-1"></span>
$$
C_t = C_0 e^{-Kt} \tag{10.9}
$$

Parameter	<b>Typical values</b>		
	European literature	Recommended for India	
Area requirement, $m^2$ /person <sup>a</sup>	$2.0 - 5.0$	$1.0 - 2.0$	
$BOD_5$ loading rate, $g/m^2$ -day <sup>b</sup>	$7.5 - 12.0$	$17.5 - 35.0$	
Detention time, days	$2 - 7$	$2 - 3$	
Hydraulic loading rate, mm/day	(Must not exceed hydraulic conductivity of the bed)		
Depth of bed, m		$0.6 - 0.9$	
Porosity of bed, % (typical)		$30 - 40$	
First-order reaction constant. $K_T$ /day		$0.17 - 0.18$	
Evapotranspiration losses, mm/day <sup>c</sup>	$10 - 15$	>15	

<span id="page-15-0"></span>**Table 10.5** Process design norms for the construction of sub-surface flow constructed wetlands for treating raw domestic wastewaters in India (Adopted from Arceivala and Asolekar [2006\)](#page-31-5)

aConstructed wetlands may be suitably downsized when wastewater is pre-treated

<sup>b</sup>Based on raw sewage BOD = 50 g/person-day and 30% reduction in pre-setting <sup>c</sup>1.0 mm/day = 10 m<sup>3</sup>/ha-day

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Since *t* is a function of bed area, we can also write

<span id="page-16-0"></span>
$$
A = \frac{Q(\ln C_0 - \ln C_t)}{K_{\text{BOD}}}
$$
 (10.10)

where *A* = bed area, m<sup>2</sup>;  $Q =$  average flow, m<sup>3</sup> day<sup>-1</sup>;  $C_0 =$  inlet 5-day BOD, mg L<sup>-1</sup>;  $C_t$  = outlet BOD<sub>5</sub>, mg L<sup>-1</sup>;  $K_{\text{BOD}}$  = BOD<sub>5</sub> reaction constant, day<sup>-1</sup>.

#### **10.2.3.2 Hydraulic Considerations in Design**

The dimensions of the reed bed can be calculated by two assumptions in applying Darcy's law: (i) hydraulic gradient is equivalent to a slope of 5% and (ii) hydraulic conductivity will stabilize at around  $1 \times 10^{-3}$  m s<sup>-1</sup> (86.4 m day<sup>-1</sup>) as the reed bed is fully established. In India, values up to 500 m day<sup>-1</sup> have been reported.

The cross-sectional area of the reed bed can be calculated as

$$
A_{\rm c} = \frac{Q}{K_{\rm f} \frac{\mathrm{d}H}{\mathrm{d}S} \times 86,400} \tag{10.11}
$$

where  $A_c$  = cross-sectional area of the bed, m<sup>2</sup>;  $Q$  = average flow, m<sup>3</sup> day<sup>-1</sup>;  $K_f$  = hydraulic conductivity, m s<sup>-1</sup>;  $dH/dS =$  slope = m m<sup>-1</sup>.

### *10.2.4 Potential Plants for Wastewater Treatment*

Based on the response of plant species to metal concentrations, they are primarily classified into three categories: (i) metal excluders (which prevent metals from entering their aerial parts over a broad range of metal concentrations); (ii) metal indicators (accumulate metals in their above-ground tissues and the metal levels in the tissues of these plants generally reflect metal levels in the rhizosphere); and (iii) metal accumulators (usually referred to as hyperaccumulators that concentrate metals in their above-ground tissues to levels far exceeding those present in the rhizosphere or in non-accumulating species growing nearby) (Memon and Schroder [2009\)](#page-34-15). Plants act as solar-driven pumps that can extract metals from the environment with which they interact (Garbisu and Alkorta [2001\)](#page-32-8). In addition, constructed wetlands that employ plants for the treatment of wastewater are found effective in treating organic matter, nutrients, and pathogens. Aquatic macrophytes are preferred over terrestrial plants for the treatment of wastewater due to their faster rate of growth, larger biomass production, relatively higher pollutant uptake ability, and better pollutant removal due to direct contact with the wastewater. A number of aquatic plant species encompassing free-floating species such as *Eichhornia* sp., *Lemna* sp., *Spirodela* sp., and *Salvinia* sp., submerged species (*Potamogeton* sp.), and emergent species such as *Typha* sp.,

*Phragmites* sp., *Vetiveria* sp., and *Juncus* sp. are well known to be employed for phytoremediation.

Duckweed belongs to Lemnaceae family that grows in stagnant and slow-flowing water in many parts of the world except Arctic and Antarctic regions (Zhao et al. [2014\)](#page-37-7). Duckweed encompasses four main genera of Lemnaceae: *Lemna, Spirodela, Wolffia, and Wolfiella* and is considered as the smallest and fastest-growing flowering plant on earth. Duckweeds possess high removal efficiency for dissolved nutrients (especially nitrogen and phosphorus), suspended solids, and organic matter. A comparative study between *Lemna gibba* L. and *Lemna minor* L. to accumulate boron from secondary wastewater was carried out by Tatar and Obek [\(2014\)](#page-36-6) and reported that *Lemna gibba* L. is more prone to accumulate boron in comparison with *L. minor.* Moreover, the study carried out by Sekomo et al. [\(2012\)](#page-36-7) revealed that textile wastewater laden with metals such as Cr, Zn, Pb, Cd, and Cu was also treated by duckweeds, making it suitable for metal uptake from contaminated wastewaters. *Typha* sp. is one of the eleven flowering plant species classified under family Typhaceae widely distributed in parts of the northern hemisphere. *Typha* sp. is commonly known as "cattails" which describes its characteristic inflorescence. Cattails are familiar wetland plants used for wastewater treatment and have an ability to adapt to diverse climatic conditions and are particularly found in wet soil, marshes, swamps, and shallow fresh and brackish waters*. T. latifolia* has reduced COD, BOD, total suspended solids, ammoniacal nitrogen, nitrate nitrogen, and phosphorus (Ciria et al. [2005\)](#page-31-8). Similarly, *Typha domingensis* Pers. was found to remediate textile effluents and metals. Species of *T. latifolia* were studied for uptake and removal of various metals such as Cr, Zn, Mn, Co, and Cd and for treatment of effluents generated from aluminum smelters. *Canna indica* L., a perennial rhizomatous herb, belongs to the family Cannaceae*. C. indica* grows naturally along creeks, lakes, and open swamps and is often used as an ornamental plant in parks and streets which makes its use as a phytoremediation species possible. *C. indica* plant was used individually and in combination with other plant species to remediate domestic wastewater. Individually, this species was able to satisfactorily remove total nitrogen, ammonia nitrogen, and BOD5 (Li et al. [2013\)](#page-34-11). *Azolla* sp. is a fast-growing nitrogen-fixing pteridophyte that freely floats on water and is considered as an excellent plant species for removal, disposal, and recovery of metals from polluted aquatic ecosystems (Arora et al. [2006\)](#page-31-9). Reed (*Phragmites* sp.) belongs to gramineous perennial herbaceous plants in aquatic ecosystems possessing the ability to absorb metal pollutants such as Cu, Zn, Pb, and Cd; and thus is important in wastewater treatment. Reeds are large perennial grass found in wetlands distributed throughout temperate and tropical regions of the world.

Shukla et al. [\(2011\)](#page-36-8) evaluated the metal uptake capability of *Terminalia arjuna* (Roxb.) Wight and Arn.*, Prosopis juliflora* (Sw.) DC., *Populus alba* L.*, Eucalyptus tereticornis* Sm., and *Dendrocalamus strictus* (Roxb.) Nees by growing selected plants on tannery sludge dumps of Common Effluent Treatment Plants. After one year of study period, a reduction in the concentration of Cr (70.22%), Ni (59.21%), Cd (58.40%), Fe (49.75%), Mn (30.95%), Zn (22.80%), Cu (20.46%), and Pb (14.05%) in the tannery sludge was observed. Some of the plants, which are generally used for wastewater treatment, are listed in Table [10.6.](#page-18-0)

Plant species	Family	Wastewater treated	Performance	References
Typha sp.	Typhaceae	Pharmaceutical wastewater	80% removal of clofibric acid after 21 days of exposure to a solution spiked with 20 $\mu$ gL <sup>-1</sup> clofibric acid	Dordio et al. (2009)
Typha sp.	Typhaceae	Pharmaceutical wastewater	$82\%$ of carbamazepine (an epilepsy drug)	Dordio et al. (2011)
Cyperus alternifolius Rottb., 1772	Cyperaceae	Urban wastewater	Removal of $652$ kg BOD <sub>5</sub> $ha^{-1}$ d <sup>-1</sup> and 1869 kg COD $ha^{-1} d^{-1}$	Calheiros et al. (2008)
Typha angustifolia L.	Typhaceae	Textile wastewater	$60\%$ color removal was found in 14 days of exposure	Nilratnisakorn et al. (2007)
Canna indica L.	Pontederiaceae	Domestic wastewater	In combination with Pontederia cordeta L., it has shown 62.8% COD removal, $12.8\%$ TN removal, and 51.1% TP removal	Chang et al. (2012)
Colocasia esculenta (L.) Schott	Araceae	Landfill leachate	$\overline{\phantom{0}}$	Madera-Parra et al. $(2015)$

<span id="page-18-0"></span>**Table 10.6** Emergent wetland plants used for treatment of different types of wastewater

Mishra et al. [\(2008\)](#page-34-16) investigated the capacity of aquatic macrophytes [*Eichhornia crassipes* (Mart.) Solms*, L. minor*, and *Spirodela polyrhiza* (L.) Schleid.] for the uptake of metals (Hg and As) for the treatment of open-cast coal mine effluent generated at Northern Coalfields Limited (NCL), Singrauli (India). The results indicated that *E. crassipes* possessed the highest uptake capacity for Hg and As followed by *L. minor* and *Spirodela polyrhiza* (L.) Schleid. Zojaji et al. [\(2015\)](#page-37-8) reported uptake of Cr, Zn, and Cu using *Populus deltoides* W. Baltram ex Marshall*,* with enrichment coefficients of 0.18, 1.11, and 1.35, respectively. Primarily, constructed wetlands are categorized as free water surface constructed wetlands (FWSCW), sub-surface flow constructed wetlands (SSFCW), and hybrid wetlands. SSFCW may be further classified into the vertical sub-surface flow (VSSF) and horizontal sub-surface flow

(HSSF) systems depending upon the flow regimes they follow. Various suitable plant species that are being used in combination or individually in engineered wetlands for the phytoremediation of toxic pollutants present in the wastewater are enlisted in Table [10.7.](#page-19-0)

In a study conducted by Morari and Giardini [\(2009\)](#page-34-17), two vertical flow constructed wetlands (VFCWs) were constructed and planted with *T. latifolia and Phragmites australis* (Cav.) Trin. ex Steud. and the observed treatment efficiency was higher (>86%) for COD, BOD, N, and K while lower (<47%) for Na and Mg. In Czech Republic, a similar study in a horizontal sub-surface flow constructed wetland for the treatment of municipal sewage using *P. australis* demonstrated that highest concentrations in plants were observed for Al, Fe, Mn, Ba, and Zn while the lowest concentrations were those of Hg, U, and Cd (Vymazal et al. [2009\)](#page-37-9). Secondary treated municipal wastewater was also treated by Sharma and Brighu [\(2014\)](#page-36-9) using VFCWs planted with *C. indica* and *Phragmites australis* (Cav.) Trin. ex Steud. resulting in better aerobic conditions and removal of nitrogenous compounds such as NH4-N, TKN, and  $NO<sub>3</sub><sup>-</sup>$  in mesocosms planted with *C. indica* than treatment beds planted with *P. australis*. Moreover, treatment beds having gravel as the media have been

Type of	Removal	Wetland design and operation			References
wastewater	performance	Plant species	Flow regime	HLR	
Winery wastewater	TSS: 86.8%; $BOD5$ : $74.2\%$ ; COD: 73.7%; TKN: 52.4%	Phragmites <i>australis</i> (Cav.) Trin. ex Steud. and <i>Juncus</i> effusus L.	<b>VFCW<sup>a</sup></b> followed by <b>HFCW</b> <sup>b</sup>	$19.5$ mm/d	Serrano et al. (2011)
Olive mill wastewater	$COD: 70\%$ ; TKN: 75%	Phragmites <i>australis</i> (Cav.) Trin. ex Steud	<b>VFCW</b>	$\overline{\phantom{0}}$	Herouvim et al. (2011)
Synthetic wastewater	$TSS: >44\%$ ; $BOD_5$ : >80%	Typha angustifolia L.	<b>HFCW</b>	$\overline{\phantom{0}}$	Weerakoon et al. (2013)
Domestic Wastewater	$NO3-N: 97\%$ ; TN: 46.6%	Cyperus alternifolius Rottb., 1772	<b>VFCW</b>	$20.78$ mm/d	Bilgin et al. (2014)
Polluted river water	COD: $39.3 \pm$ $12.1\%$ ; $NH_4-N: 62.1$ $\pm 8.8\%$ ; TN: $45.8 \pm 15.4\%$ ; TP: $57.7 +$ 8.3%	<i>Iris sibirica</i> L.	<b>VFCW</b>		Gao et al. (2014)

<span id="page-19-0"></span>**Table 10.7** Treatment efficiencies of constructed wetlands for different wastewaters

*VFCW*<sup>a</sup> Vertical Flow Constructed Wetlands, *HFCW*<sup>b</sup> Horizontal Flow Constructed Wetlands

known to show better oxygenation capacity to oxidize the organic matter while superior filtration and adsorption properties were observed while using sand as the media. Nitrogen in wastewater poses a serious threat to the aquatic life due to the potential of eutrophication in aquatic systems. A hybrid constructed wetland was designed by Ye and Li [\(2009\)](#page-37-11) to enhance nitrogen removal during domestic wastewater treatment in China. The designed plant increased the nitrification rate by providing passive oxygen creating a cascade-type current and the reported average removal rates as 89% for total suspended solids, 85% for COD, 83% for ammoniacal nitrogen, 83% for total nitrogen, and 64% for total phosphorus.

Morvannou et al. [\(2014\)](#page-35-10) dealt with the modeling of the fate of nitrogen during the treatment of domestic raw wastewater using a VFCW and demonstrated that the ammonium was adsorbed onto the organic matter during the feeding period and characterized the presence of heterotrophic biomass mainly in the sludge layer (first 20 cm), whereas autotrophic biomass was located in the first 50 cm of the VFCW (sludge and 30 cm biomass).

Advanced oxidation processes can be combined with the constructed wetlands for the treatment of wastewaters to increase their efficiency and foster the reuse of treated water. Horn et al. [\(2014\)](#page-33-7) investigated the combination of constructed wetlands with photocatalytic ozonation for a university sewage treatment plant. The treatment efficiency with the constructed three-stage sub-surface flow sequence planted with *Hymenachne grumosa* (Nees) Zuloaga had the following characteristics: a constructed wetland (CW-1) built inside the greenhouse and another constructed wetland (CW-2) built-in outdoors with a UV/TiO<sub>2</sub>/O<sub>3</sub> reactor in between the two systems to improve the quality of wastewater for reuse. The treatment efficiency after the photocatalytic ozonation of the effluent from CW-1 increased as follows:  $BOD<sub>5</sub>$  (88.7%); COD (62.1%); total Kjeldahl nitrogen (27.6%); ammoniacal nitrogen (27.1%); and total phosphorus (63.4%). A hybrid system encompassing a horizontal sub-surface flow (HSSF) CW preceded by two VSSFCW working in parallel was constructed by Comino et al. [\(2013\)](#page-32-12) to treat gray wastewater and demonstrated that the system was able to bear the subjection to high hydraulic and organic variations and reduced COD efficiently even at three times the pollutant concentration and with an inlet flow four times higher than the designed specifications.

Complex wastewaters emanating from leather industry were treated with five wetland plants by Calheiros et al. [\(2007\)](#page-31-13), namely *C. indica, T. latifolia, P. australis, Stenotaphrum secundatum* (Walter) Kuntze, and *Iris pseudacorus* L. and the treatment performance at hydraulic loading rates of 3 and 6 cm d−<sup>1</sup> was assessed. COD reduction of 41–73% for an inlet organic loading varying between 332 and  $1602$  kg ha<sup>-1</sup> d<sup>-1</sup> and BOD<sub>5</sub> reduction of 41–58% for an inlet organic loading varying between 218 and 780 kg ha−<sup>1</sup> d−<sup>1</sup> was reported. Moreover, *P. australis* and *T. latifolia* were the only plants that were able to establish successfully. Another study conducted by Ong et al. [\(2009\)](#page-35-11) for the treatment of dye wastewater using up-flow constructed wetland reactors planted with *P. australis* reported that COD concentration drastically decreased at the aeration points in the reactor and supplemented aeration led to increased removal of organic pollutants. Tee et al. [\(2015\)](#page-36-11) reported an

increase in dye removal efficiency by incorporating baffles in HSSF constructed wetlands to facilitate up-flow and downflow conditions to achieve aerobic, anoxic, and anaerobic conditions sequentially in the same wetland bed. The planted baffled unit was found to achieve 100, 83, and 69% dye removal against 73, 46, and 30% for the conventional unit at HRT of five, three, and two days, respectively.

The root properties such as root porosity, radial oxygen loss (ROL), and Fe plaque formation are important parameters for the selection of wetland plants. Wetland plants grown in waterlogged conditions own a strategy to cope with the anaerobic environment by forming extensive aerenchyma tissue which provides low resistance to the passage of oxygen from the aerial parts of the plant to their roots. The excessive oxygen diffuses from the roots into the rhizosphere resulting in its oxidation. The oxidation of the rhizosphere leads to the precipitation of As on wetland plant's root surface. Due to the release of oxygen by wetland plants, reduced soluble iron reacts with it to form a smooth regular reddish precipitate on root surfaces. A substantial amount of Fe is transferred to the plaque during the process of ROL and rhizosphere oxidation which develops a well-defined zone of ferric hydroxide accumulation in the rhizosphere. The Fe plaque can sequester metals on root surfaces and so influence metal uptake and tolerance by wetland plants. A study carried out by Yang et al. [\(2014\)](#page-37-12) revealed that wetland plants possessing high porosity and high ROL from their roots tend to have high Fe, Mn, and Zn concentrations on root surfaces and in their rhizosphere. Cheng et al. [\(2014\)](#page-31-14) illustrated that ROL-induced Fe plaque would promote Pb and Cd deposition on root surfaces. Plants improve Fe uptake by excreting protons by a plasma membrane  $H^+$ -ATPase which acidifies the rhizosphere and reduces  $Fe^{3+}$  to more soluble  $Fe^{2+}$ .

### *10.2.5 Textile Wastewater Treatment in Constructed Wetlands*

Widespread use of dyes in the paper, leather, and tannery industries generate a substantial amount of wastewater and their presence in wastewater affects all forms of life. A total of fifteen percent of the dyes produced globally are lost during the dyeing process and are released in the textile effluents. Azo dyes are characterized by strong—N=N—nature which is the most common chromophore of reactive dyes. Azo dyes' structural stability compels their recalcitrant nature toward biodegradability (e.g., activated sludge) or physical/chemical treatment methods (e.g., flocculation and coagulation) and results in the transfer of azo dyes from wastewater to the sludge, leading to additional disposal problems. Various garden plants like *Aster amellus* L.*, Cosmos bipinnatus* Cav., 1791*, Chrysanthemum cinerariifolium* (Trevir.) Vis. pyrethrum*, Cuphea hyssopifolia* Kunth and *Cortaderia selloana* Schult. and Schult.f. Asch. and Graebn. (Pampas grass) effectively treat a wide array of textile wastewater up to varying extents. Hu et al. [\(2010\)](#page-33-8) reported Congo Red dye removal from textile wastewater by cattail roots as they are porous in structure and have a large surface area. The use of cattails for dye wastewater treatment demonstrated that the removal of Congo Red increased with increasing adsorbent dosage, i.e., cattail

roots and decreased with increasing temperature over the operating conditions (20– 40 °C). Adsorption dynamics analysis indicated that pseudo-second-order equation fitted well to the adsorption of Congo Red on cattail root ( $\mathbb{R}^2 > 0.99$ ). The role of sunflower, a flowering garden plant, in removing some azo dyes hydroponically was assessed by Huicheng et al. [\(2012\)](#page-33-9) and demonstrated a decolorization of 62.64% of average percent of three azo dyes (Evans Blue, Bismark Browny, and Orange G) at 100 mg/L within four days. Another study was carried out by Nilratnisakorn et al. [\(2007\)](#page-35-9) using narrow-leaved cattail (*Typha angustifolia* L.) and observed a maximum decolorization of 60% of Reactive Red 141 in 14 days. Moreover, it was reported by Nilratnisakorn et al. [\(2007\)](#page-35-9) that *T. angustifolia* can grow well under caustic conditions and can withstand stress due to salts as they have high plant weight and extensive roots undergoing special mechanisms such as salt accumulation in roots by shedding older leaves and by the formation of metal complexes in the form of Ca, Fe, and Si bonded to dye molecules.

Patil and Jadhav [\(2013\)](#page-35-12) used *Tagetes patula* L. (flowering plant) for the degradation of Reactive Blue 160 (textile dye) and reported 90% decolorization within four days. Inthorn et al. [\(2004\)](#page-33-10) studied the treatment of dye wastewater using narrowleaved cattail (NLC) powder as an adsorption media after pre-treatment with distilled water (DW-NLC), a mixture containing 37% formaldehyde and 0.2 N sulfuric acid (FH-NLC) or 0.1 N NaOH (NaOH-NLC) and reported that the highest removal of dye was observed with FH-NLC treatment. Khandare et al. [\(2011\)](#page-33-11) evaluated the removal of a sulfonated azo dye, Remazol Red, by *Aster amellus* L. and the study revealed a reduction of BOD (75%), COD (60%), and total organic carbon (54%) after 60 h. However, Bulc and Ojstršek [\(2008\)](#page-31-15) reported removal efficiency of COD (84%), BOD<sub>5</sub> (66%), TOC (89%), N<sub>total</sub> (52%), N<sub>organic</sub> (87%), SO<sub>4</sub><sup>2-</sup> (88%), TSS (93%), and color (90%) in a constructed wetland planted with *P. australis*.

Davies et al. [\(2005\)](#page-32-13) constructed a VFCW planted with *P. australis* to remove an azo dye [Acid Orange 7 (AO7)] and reported degradation of AO7 dye and its aromatic amines, after 120 h in contact with  $H_2O_2$ , and removal of 3.2–5.7 mg AO7 g−<sup>1</sup> *P. australis* was obtained for 40 mg AO7 L−<sup>1</sup> (8 mg AO7 g−<sup>1</sup> *P. australis*). The potential of duckweed (*L. minor*) for the degradation of C.I Acid Blue 92 (AB92) has been evaluated by Khataee et al. [\(2012\)](#page-33-12) and observed the considerable potential of *L. minor* for the phytoremediation of AB92 depending upon temperature, initial dye concentration, and weight of the plant. Sekomo et al. [\(2012\)](#page-36-7) constructed a lab-scale system, each system consisting of three ponds in series and seeded with algae (natural colonization) and duckweed (*L. minor*) with a hydraulic retention time of seven days under different light regimes. The observations revealed that both the systems were unsuitable for the removal of metals due to low and negotiable differences in the removal efficiencies of duckweeds and algae for metals.

### *10.2.6 Landfill Leachate Treatment in Constructed Wetlands*

A landfill is one of the most widely adopted methods globally for the disposal of municipal solid waste. A landfill containing a wide range of organic molecules of both natural and xenobiotic origin is highly variable and heterogeneous in nature and landfill leachate is difficult to be co-treated with conventional municipal wastewater treatment plants due to its low biodegradability, high nitrogen content, and other possible toxic components. Phytoremediation of landfills appears economically viable option which has been practiced in many countries with varying degrees of success and found out to be less harmful to human health. As a practice of merging traditional forestry with waste management, the treatment of leachate was conducted by Justin and Zupancic [\(2009\)](#page-33-13) in which irrigation of *Salix purpurea* L. was done by reusing leachate after treatment through a constructed wetland and it was found that these leachate acts as a good fertilizer for landfill vegetative cover if applied under controlled conditions. As an alternative to conventional clay cover on landfills, phytocapping seems to be a sustainable alternative owing to its cost-effectiveness, less technical expertise requirement, prevention of the percolation of water into the piled waste, thus reducing the amount of leachate generation. *Populus* sp. is suitable for phytoremediation because of its high water usage, fast growth, and deep root system, and *Populus* sp. clones irrigated with landfill leachate designed by Zalesny et al. [\(2009\)](#page-37-13) exhibited greater height, diameter, and number of leaves of *Populus* sp. Justin et al. [\(2010\)](#page-33-14) used *Salix viminalis* L. and *Salix purpurea* L. for the treatment of municipal solid waste landfill leachate and demonstrated a 155% increase in above-ground biomass, compared to control water treatments and an average mass load of 2144 kg N ha<sup>-1</sup>, 144 kg P ha<sup>-1</sup>, 709 kg K ha<sup>-1</sup>, 1010 kg Cl ha<sup>-1</sup>, and 1678 kg Na ha−1. *Salix* sp. is an excellent candidate for phytoremediation due to its large biomass, high metal tolerance, and accumulation capacity and demonstrated that a significant clonal difference in Mn tolerance and accumulation among *Salix* clones was observed (Yang et al. [2015\)](#page-37-14). Moreover, the phytoextraction potential of Mn varied 5.8-fold among *Salix* clones due to which a scope for the improvement in Mn removal efficiency can be expected. Willows (*S. viminalis*) are known to have considerable oxygen transfer capacity (195.7 g O<sub>2</sub> m<sup>-3</sup> h<sup>-1</sup> kg<sup>-1</sup><sub>root wet mass</sub>) so that oxidation of the organic matter present below-ground can take place (Randerson et al. [2011\)](#page-35-13). Akinbile et al. [\(2012\)](#page-31-16) also reported significant removal of metals from leachate in a SSFCW planted with *Cyperus haspan* L.

## *10.2.7 Treatment of Organic Pollutants in Constructed Wetlands*

Organic pollutants enter into the environment through various sources such as spills (fuel and solvents), military activities (explosives and chemical weapons), agricultural activities (pesticides and herbicides), industries (chemical and petrochemical),

and wood treatment. The treatment of organic pollutants such as explosives and pesticides through phytoremediation has been a concern among various researchers. Explosives such as research department explosive (RDX) and trinitrotoluene (TNT) have been treated by transgenic plant species *Arabidopsis thaliana* (L.) Heynh. (Rylott et al. [2011\)](#page-36-12). Benzene, toluene, ethylbenzene, and xylene (BTEX), an organic solvent consisting volatile organic compounds released by petroleum derivatives, was removed from wastewater using HSSFCW (offering more than 60% removal for HRT higher than 100 days) planted with *T. latifolia* and *P. australis* (Ranieri et al. [2013\)](#page-35-14). Al-Baldawi et al. [\(2013\)](#page-31-7) carried out the treatment of petroleum hydrocarbons by *S. grossus* and reported a higher remediation potential of SSFCW in comparison with FWSCW. Naphthalene, a polyaromatic hydrocarbon, was found to be reduced by *E. crassipes* (Nesterenko-Malkovskaya et al. [2012\)](#page-35-15).

### *10.2.8 Metal Removal in Constructed Wetlands*

The increasing presence of metal ions in aquatic systems has become a significant environmental problem in both industrialized and developing countries. The various anthropogenic sources of common metals found in wastewater are enlisted in Table [10.8.](#page-24-0)

Metal	Anthropogenic sources	References
As	Tannery, electroplating, pesticides, fertilizers, smelting, landfilling paints/chemicals, and mining	Lievremont et al. $(2009)$
C <sub>d</sub>	Manufacturing of cadmium–nickel batteries, phosphate fertilizers, pigments, stabilizers, alloys, and electroplating industries	Mortaheb et al. $(2009)$
Cu	Electroplating, agricultural run-off, mining, electrical and electronics, iron and steel production, nonferrous metal industry, printing and photographic industries, and metalworking and finishing processes	Nadaroglu et al. (2010)
Hg	Solid waste incineration, coal and oil combustion, and pyrometallurgical processes	Wang et al. (2004)
Ni	Nickel plating, colored ceramics, electroplating, batteries manufacturing, mining, and metal finishing and forging	Sud et al. (2008)
Cr	Electroplating, leather tanning, metal finishing, nuclear power plant, textile industries, and chromate preparation	Tripathi et al. (2011)
Pb	Combustion of coal, processing and manufacturing of lead products, manufacturing of lead additives such as tetraethyllead (TEL) for gasoline	Acharya et al. (2009)
Zn	Mining, smelting, steel making, fossil fuel combustion, phosphate fertilizer, manure, sewage sludge, pesticides, motor vehicles, and galvanized metal	Fuge (2004)

<span id="page-24-0"></span>**Table 10.8** Anthropogenic sources of common metals found in wastewater

Because of their high solubility in the aquatic environment, metals are highly prone to be absorbed by living organisms and lead to their bioaccumulation by entering into the food chain. Their ingestion beyond permissible concentration may lead to serious health problems. Although several treatment methods such as chemical precipitation, coagulation–flocculation, flotation, ion exchange, and membrane filtration can be employed to remove metals from contaminated wastewater, they have inherent limitations in practical application. Hyperaccumulation of metals by plants involves several steps, including metal transport across plasma membranes of root cells, xylem loading, and translocation after facilitative radial symplastic passage through the roots and across the epidermis (Clemens et al. [2002\)](#page-32-15), detoxification, and sequestration of metals at the whole plant and cellular level. The general mechanism for metal detoxification encompasses the distribution of metals to apoplast tissues like trichome and cell walls, reduced uptake or efflux pumping of metals at the plasma membrane followed by chelation of the metals in the cytosol by various ligands such as organic acids, amino acids, and peptides (phytochelatins and metallothioneins). Thereafter, repairing of stress-damaged proteins and sequestration of metal-ligand complex into the vacuole takes place (Yang et al. [2005\)](#page-37-16). An efficient translocation of metal ions from roots to shoots requires mobile metal-binding chelators in cytosol and xylem with efflux activities to pump toxic metals out of the root cells into the xylem (Clemens [2006\)](#page-32-16).

Metal-chelating compounds such as catecholates, hydroxamates, and organic acids were found out to be released by ectomycorrhizal fungi collected from *Pinus radiata* D. Don. Various chemicals secreted in the plant root zone mediate multipartite interactions in the rhizosphere, where plant roots continually respond to and alter their immediate environment. Hyperaccumulator species may release metalchelating root exudates which enhance metal uptake, translocation, and resistance. Plant growth affects the pH, redox conditions, and dissolved organic carbon content in the rhizosphere and thus affects the distribution of metals within the chemical species and their mobility in the plant's rhizosphere. Moreover, they oxidize Fe present in rhizosphere and cause co-precipitation of metals, thereby reducing metal mobility in the rhizosphere. Various plant species are known to successfully remediate metals present in industrial wastewaters as shown in Table [10.9.](#page-26-0) Principal metal chelators in plants such as phytochelatins, metallothioneins, organic acids, and amino acids endow metal detoxification by buffering cytosolic metal concentrations (Shah and Nongkynrih [2007\)](#page-36-15).

#### **10.2.8.1 Siderophores**

Siderophores are high-affinity iron-chelating compounds released by gramineous plants as well as microorganisms to acquire/sequester iron that is accumulated in mineral phases as iron oxides and hydroxides. These form strong complexes with  $Fe<sup>3+</sup>$ , which are highly soluble over a wide pH range and hence can be taken up by active transport. It was reported by Ma et al. [\(2011\)](#page-34-20) that phytosiderophores typically have a lower affinity for iron than microbial siderophores. In their metal-binding

Nature of wastewater	Plants vegetated	Metals removed	References
Industrial effluent	Ecchornia crassipes (Mart.) Solms; Typha latifolia L.	Cd, Pb, Cu, As	Sukumaran (2013)
Municipal wastewater	Phalaris arundinacea L.	Cd, Cr, Cu, Ni, Pb, Zn	Brezinova and Vymazal $(2015)$
Landfill leachate	Typha latifolia L.; Phragmites australis (Cav.) Trin. ex Steud.	As, Cd, Cr, Cu, Pb, Zn, Ni	Grisey et al. $(2012)$
Artificial wastewater	Canna indica L.; Typha angustifolia $L$ .; Cyperus alternifolius Rottb., 1772; Alternanthera hiloxeroides Griseb. Zizania latifolia (Griseb.) Turcz. ex Stapf; Echinochloa $crus$ -galli $(L.)$ Beauv; Polygonum hydropiper L. $(1753)$ ; Isachne globosa (Thunb.) Kuntze; Digitaria sanguinalis (L.) Scop.; Fimbristylis miliacea (L.) Vahl;	Cu, Cr, Co, Ni, Zn Zn	Yadav et al. $(2012)$ Liu et al. (2007)
Swine wastewater	Typha domingensis Pers., Eleocharis cellulosa Torr.	Cu, Zn	Jorge et al. $(2012)$
Synthetic wastewater	Typha domingensis Pers.	Zn, Ni, Cr	Mufarrege et al. (2015)

<span id="page-26-0"></span>**Table 10.9** List of plant species used for metal removal from industrial wastewater

sites, siderophores have either α-hydroxycarboxylic acid, catechol, or hydroxamic acid moieties and thus can be classified as hydroxycarboxylate, catecholate, or hydroxamate-type siderophores. Various phytosiderophores such as mugineic acid, deoxymugineic acid, epi-hydroxymugineic acid, avenic acid are released by plants out of which mugineic acid is the very first detected phytosiderophore. However, many siderophores have shown negative or no increase in the metal uptake capacity of plants which indicates their dependency on the type of plant and other factors affecting metal uptake capability. Metal cation uptake capacity by siderophores varies in accordance with their valency as reported by Dimkpa et al. [\(2009b\)](#page-32-17); in that trivalent metal ions have shown more competitiveness for siderophore binding. Various siderophores produced by rhizospheric microbes that assist in increasing metal availability and mobility are listed in Table [10.10.](#page-27-0)

Microbial metabolites	Microorganisms	Microbial origin	Plant cultivated	Effect on metal uptake by plants	References
Ketogluconates	Pseudomonas aeruginosa	Tannery air environment (Karachi, Pakistan)	$\overline{a}$	Solubilization of Zn	Fasim et al. (2002)
5-ketogluconic acid	Gluconacetobacter diazotrophicus <b>PA15</b>	Center of Advanced Studies in Agricultural Microbiology, Tamil Nadu Agricultural University (India)	$\overline{\phantom{0}}$	Solubilization of Zn	Saravanan et al. (2007)
Desferrioxamine <b>B</b> , desferrioxamine E, coelichelin	<b>Streptomyces</b> tendae F4	Uranium mine, Wismut (Eastern Thuringia, Germany)	Sunflower	Enhanced Cd solubility and availability to plants	Dimkpa et al. (2009a)
Pyoverdine, pyochelin and alcaligin E	Pseudomonas aeruginosa, Pseudomonas fluorescens, Ralstonia metallidurans	VITO, Flemish Institute for Technological Research (Belgium)	Maize	<b>Enhanced Pb</b> and Cr uptake by plants though increasing their mobility	<b>Braud</b> et al. (2009)
Desferrioxamine В, desferrioxamine E, coelichelin	<b>Streptomyces</b> acidiscabies E13	International Max Planck Research School (Munchen)	Cowpea	Enhanced uptake of Al, Cu, Fe, Mn, Ni, U	Dimkpa et al. (2009b)

<span id="page-27-0"></span>**Table 10.10** List of siderophores assisting in increasing metal mobility and availability

### **10.2.8.2 Metal-Binding Cysteine-Rich Proteins**

Plants ubiquitously synthesize cysteine-containing metal-binding ligands namely, metallothioneines, phytochelatins, and glutathione. Metallothioneines are low molecular weight cysteine-rich metal-binding peptides containing thiol group while phytochelatins are naturally occurring cysteine-rich non-ribosomal peptides composed of only three amino acids, namely Glu, Cys, and Gly, with Glu and Cys residues linked through a γ-carboxymide bond. These are produced by glutathione by enzyme phytochelatin synthase PCS (γ-glutamylcysteine dipeptidyl transpeptidase). Glutathione (GSH), L-Glutamyl-L-cysteinyl-glycine, is considered as the most important non-protein thiol present in all living organisms consisting of three amino acids (Glu-Cys-Gly) and the cysteine thiol group of the active site is responsible for its biochemical properties (Mendoza-Cózatl et al. [2005\)](#page-34-22). Metallothioneins and phytochelatins comprise of amino acids and form thiolate complexes through binding with metals which is energy-intensive and requires significant amount of

amino acids (especially cysteine), growth limiting elements sulfur and nitrogen from the plant as the level of metal accumulation rises. Phytochelatins, synthesized using glutathione as a substrate by enzyme PC synthase that is activated in the presence of metal ions, contain strongly nucleophilic sulfhydryl groups and thus can react with many toxic species within the cell, such as free radicals, active oxygen species, cytotoxic electrophilic organic xenobiotics, and metals (Singh and Tripathi [2007\)](#page-36-18). Apart from metal detoxification, phytochelatins facilitate metal homeostasis in plants which are responsible for metal availability in plant cells. Glutathione conjugates with metal ions or electrophilic xenobiotics through nucleophilic cysteine thiol moiety and sequesters in the vacuoles of the leaves of the plants. In addition, histidines are known to have a high affinity for transition metal ions such as  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $Cu^{2+}$ .  $Zn^{2+}$  bears resemblance to  $Cd^{2+}$  because of its position in the periodic table.

#### **10.2.8.3 Organic and Amino Acids**

The organic acids and amino acids such as citric, malic, and histidine are exudated by plants (due to the reactivity of metal ions with S, N, and O) and play an important role in metal detoxification and tolerance (Clemens  $2001$ ). These acids release H<sup>+</sup> ion while the COO<sup>−</sup> binds to the cationic positive charge and forms metal–ligand complex. In addition, organic acids may chelate with metals in the cytosol where the ions can be transformed into non-toxic or less toxic form (Clemens [2001\)](#page-32-20). The Cd- and Zn-citrate complexes are pervasive in leaves; however, malate is more ample. Moving from roots to leaves, citrate, and histidine are the principal ligands present in the xylem sap for Cu, Ni, and Zn. Ethylenediamine disuccinate and nitrilotriacetic acids are natural aminopolycarboxylic acids produced by many microorganisms which play an important role in enhancing the phytoavailability and phytoextraction of metals. The root-induced chemical changes on metal uptake have been observed by Kim et al. [\(2010\)](#page-33-17) using Indian mustard (*Brassica juncea* (L.) Czern.) and sunflower (*Helianthus annuus* L.) and it was found that metal uptake and bioavailability increased with increasing rhizospheric pH and dissolved organic carbon. Moreover, Kim et al. [\(2010\)](#page-33-17) also reported that the influence of root-induced dissolved organic carbon on metal solubility is a function of pH as well as total metal loading. It was reported by Javed et al. [\(2013\)](#page-33-18) that organic acids exudation by the roots of *Eriophorum angustifolium* Honck. increases the rhizospheric pH and is a suitable plant for remediation of acidic metal-polluted soils. High concentrations of citric, malic, and malonic acids were found in the hairy roots of the plants *Thlaspi caerulescens*J. Presl and C. Presl and *Alyssum bertolonii* Desv., which are Cd and Ni hyperaccumulators, respectively. Citric acid has shown an enhancement in Cr uptake by *Parthenium hysterophorus* L. (UdDin et al. [2015\)](#page-37-18). Synthetic acids like ethylenediaminetetraacetic acid increase the mobility of various metals such as Cu, Pb, Cd, and Zn.

#### **10.2.8.4 Biosurfactants**

Biosurfactants are biological complexing agents produced by yeast or bacteria from various substrates including sugars, oils, alkanes, and wastes (Mulligan [2009\)](#page-35-18). They are capable of improving metal mobility, leading to enhanced phytoremediation. They are amphiphilic in nature, having a polar (hydrophilic) and a non-polar (hydrophobic) moiety. The hydrophobic part of the molecule is based on long-chain fatty acids, hydroxy fatty acids, or α-alkyl-β-hydroxy fatty acids while the hydrophilic portion can be a carbohydrate, amino acid, cyclic peptide, phosphate, carboxylic acid, or alcohol. Metals are transferred from one chemical state to another by biosurfactants, which changes their mobility and availability. The anionic biosurfactants form ionic bonds with metals and create complexes and these metal–biosurfactant bonds are stronger than the metal bond with the medium from which the metal is to be removed. As a result, the metal is desorbed from the medium due to the lowering of surface tension and the precipitation of the biosurfactants out of the complexes takes place (Singh and Tripathi [2007\)](#page-36-18). However, the cationic biosurfactants replace the same charged metal ions by competing for some of the negatively charged surfaces (ion exchange). In addition, metal ions can also be removed by the formation of micelles by the biosurfactants in which the hydrophilic portion binds to metals and increases the mobility of metals. The entrapment of metal ions in the micelles increases bacterial tolerance and resistance toward a high concentration of metals. The potential of environmentally compatible di-rhamnolipid biosurfactant produced by *Pseudomonas aeruginosa* strain BS2 to treat metals in soil artificially contaminated with multi-metals was evaluated and di-rhamnolipid selectively removed Cd and Pb in the soil with more uptake of Cd, and the corresponding uptake efficiency was reported as  $Cd = Cr > Pb = Cu > Ni$  (Juwarkar et al. [2008\)](#page-33-19). Various other researchers have evaluated biosurfactant-induced increment in the availability and mobility of metals which are enlisted in Table [10.11.](#page-29-0)

Microorganisms	Microbial origin	References Effect on metal uptake by plants	
Bacillus sp. J119	Nanjing (China)	Enhanced Cd uptake	Sheng et al. $(2008)$
Candida lipolytica	Culture collection (Brazil)	Removal of 96% of Zn and Cu, and reduction in the concentration of Pb. Cd, and Fe	Rufino et al. (2012)
Pseudomonas sp. LKS <sub>06</sub>	Rhizosphere of Cd-hyperaccumulator Solanum nigrum L. grown in tailings	Uptake of Pb and Cd	Huang and Liu (2013)

<span id="page-29-0"></span>**Table 10.11** Biosurfactant-induced increment in the availability and mobility of metals

### **10.3 Recent Development of Constructed Wetlands in India**

According to Central Pollution Control Board, Government of India (CPCB [2009\)](#page-31-20), the total wastewater generation from Class I cities (no. of cities 498, population greater than  $1.0 \times 10^5$ ) and Class II (no. of cities 410, population between  $5.0 \times 10^4$ and 9.9999  $\times$  10<sup>4</sup>) towns in the country is approximately 35,558 and 2696 million liters per day (MLD), respectively. However, the installed sewage treatment capacity in Class I cities and Class II towns is just 11,553 and 233 MLD, respectively, thus leading to a gap of 26,468 MLD in sewage treatment capacity. To reduce this gap, there is a need for a sustainable wastewater treatment alternative against conventional treatment methods. The use of constructed wetlands for the treatment of sewage in India is increasing day by day in rural as well as peri-urban India (Singh et al. [2019;](#page-36-5) Sutar et al. [2019\)](#page-36-3). Several researchers are working on pilot-scale studies to implement constructed wetland technology to a large scale in India. Yadav et al. [\(2018\)](#page-37-19) developed a "French system" vertical flow constructed wetland for domestic wastewater treatment and achieved COD and BOD removal up to 90 and 84%, respectively. Gray water was treated by constructed wetlands and reused for gardening and toilet flushing (Gupta and Nath [2018\)](#page-33-21). Moreover, it is also applied to treat livestock wastewater (Rajan et al. [2019\)](#page-35-19). For nitrogen and phosphorus removal from wastewater, pilot-scale plants are being tested for the development of a fullscale application (Nandakumar et al. [2019\)](#page-35-20). Verma and Suthar [\(2018\)](#page-37-20) treated dairy wastewater and reported that *Typha* biomass can be used as a potential feedstock for renewable energy operations. In India, constructed wetland technology is being studied widely by researchers on pilot-scale but very few large-scale studies are being applied.

### **10.4 Conclusion**

An increase in wastewater generation mandates the utilization of an alternative treatment option to bridge the gap between wastewater generation and its treatment. Domestic and industrial wastewater treatment using constructed wetlands is an increasingly attractive option since it is effective with relatively low energy demands when compared to current physical and chemical alternatives. The efficiency of hyperaccumulators in heavy metal remediation is improved multifold by the secretion of siderophores, organic acids, biosurfactants, and metal-binding cysteine-rich proteins by plants. Despite the critical function of these biomolecules in the treatment of an array of environmental contaminants, the biogeochemical factors that affect their activity are poorly understood. Unraveling the exact mechanisms of how these molecules assist in facilitating heavy metal uptake by plants offers a low-cost and sustainable solution for remediation of toxic and recalcitrant pollutants. Also, in India, the escalation of pilot-scale studies to the large-scale applications may reveal the long-term applicability of constructed wetland technology.

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