Chapter 8
Biosorption Strategies in the Remediation of Toxic Pollutants from Contaminated Water Bodies

P. Senthil Kumar and K. Grace Pavithra

Abstract Heavy metals, radioactive waste, hydrocarbon pollutant, and pesticides are some of the leading toxic pollutants in our environment. Challenges are faced in decontamination of these types of pollutants to soil and water for a long period of time. A number of methods such as membrane technology, electro-Fenton reaction, advanced oxidation process, and nanotechnology played a major role in removing toxic pollutants but difficulties are seen in degradation of toxic sludge, additional side reactions, high cost in initial installment and in maintenance, etc. Biosorption is a physiochemical metaprocess involving solid and liquid phases in which dissolved species to be sorbed. Low cost, high efficiency, and reusability of biosorbent are some of the advantages in biosorption. Biosorption involves removal of toxic pollutants by biomass. Some microorganisms are targeted for the removal of single pollutant alone. Algae, bacteria, fungi, yeast, waste materials from agricultural and food industries, etc., are used as biosorbent. Different mechanisms such as precipitation, absorption, adsorption, and ion exchange are combined with biosorption in order to treat toxic pollutants. This chapter provides collective ideas of various removal techniques in combination with biosorption and their applications to remediate water streams. This chapter also illustrates some of the problems faced during the biosorption activity and highlights the importance of improving the process for bioremediation in toxic pollutants.

Keywords Toxic pollutants · Degradation · Biosorption · Physiochemical Biosorbent · Bioremediation

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8.1 Introduction

An ecosystem consists of all living beings in our environment, and due to anthropogenic activities in our environment such as industrialization, scientific advancement, and rapid urbanization, many changes occurred. Modifications are in the form of physical, chemical, and also in biological terms. Environmental contaminations will affect soil, water as well as the atmosphere in the due course of time. It is like a cycle where the pollutant compositions which are made by a human from the earth components whether knowingly or unknowingly affect the living beings and the consequences are seen to be worse when the time is prolonged.

Life on the earth is mainly seen above the soil and some in water. Water is essential for all living beings in earth, and it is not evenly distributed in our earth surface. Major amount of water are seen in ocean, and only 2.5% of freshwater are only available for food production, recreational use, drinking water supply which are seen in the form of lake, pond, river, and streams. The esthetic value of surface water is affected due to the intervention of toxic pollutants which includes pharmaceutical, industrial waste, fertilizers, radioactive waste. The emission of these types of waste affects the water quality, and the living organisms in the ecosystem are also disturbed. Due to continuous emission, the soil under the water gets affected. The basic food substances for the food chain are plants and the soil microbes, and it is also considered as an energy source for a higher level of organisms. The work of soil microbes is incredible as they get energy from dead and decomposed matter and provide energy in the form of nitrogen, carbon, oxygen, potassium, hydrogen, phosphorus to plants for their growth. Because of smaller in size by nature, they have lesser biomass but the impact of microbes in the nutrient cycle was found to be effective. Microbes in the terrestrial environment play major role in carbon and nitrogen cycles. Soil microbes are bonded with toxic substance due to exposure of toxic pollutants.

The intervention of toxic pollutants such as heavy metals, radioactive waste, pesticides, herbicides, weedicide, hazardous waste, waste from paint, dye, battery, metal plating, manufacturing industries to our environment leads to a lot of impacts on the ecosystem. Some of the toxic pollutants that affect soil microbes are pesticides, herbicides which are found to be seen in excessive during agricultural practices. Compounds such as azoxystrobin, maneb, sulfur, atrazine, mecoprop, paraquat, endosulfan, cypermethrin are used in large scale for agricultural practices. Leaching and accumulation on soil make constant threat to human health as well as to the environment. Atrazine is used as weedicide in the farms of sugarcane and corn to enhance the production when used in suggested amount. Due to its low price and availability, farmers use atrazine in large amount, as a result of this not only plants and animals get affected, the aquatic life also affected due to leaching and runoff. Around 5 kg of agrotoxins is consumed annually per person in Brazil (Andleeb et al. 2016; Zhang et al. 2014; Xie et al. 2013; Chrisman et al. 2009). Polycyclic aromatic hydrocarbons will be coming under organic pollutants. Benzene, toluene, ethylbenzene, xylene, Polychlorinated biphenyls (PCB), and the pharmaceutical components such as carbamazepine, caffeine, hormonal drugs are released from various sources like hospital municipal waste, human as well as animal excreta, wastage discharge from pharmaceutical manufacturing industries, and excess drug utilizing. Depends upon the intake and the individual human metabolisms, drugs are excreted from our body. The wastewater from households and from hospitals is treated with common effluent treatment plants, and these treatment plants are not specially designed for removing those drugs (Zhang et al. 2012; Hooper et al. 2009). Heavy metals such as lead, mercury, cadmium, chromium, arsenic, and beryllium are in terms of individual metals and metal compounds which affect people's health adversely. In mere amount, some of the metal compounds are necessary to lead our life and if it consumed in a large amount, they become toxic. Heavy metals are generally derived from industries like plastic manufacturing, electroplating, fertilizers, pigment, and mining.

Algae, bacteria, and some aquatic plants are best-known indicators in terms of species count and in densities; it also acts as biological monitoring system in assessment of water quality. Some of the indications on the top of water bodies such as eutrophication and algal blooming prove that the water is affected by toxic pollutants. As a result of it, the life of the species inside as well as on the surface of the water is interrupted from their routine life. Due to prolonged emission of toxic pollutants, photosynthesis does not occur, and in due course of time, living organisms never exist in water bodies. In addition, when these toxic pollutants mixed with water found on the terrestrial level, the differences in characteristics such as pH, COD, BOD, electrical conductivity, turbidity, odor, the taste of water are affected, and the changes depend upon the pollutants in which the water interacts. The soil which is beneath the water gets affected in the due course of time and during the runoff; water acts as a natural carrier and settles the toxic pollutants in various zones of the environment. Finally, the soil gets affected and the microbes in the soil are accumulated with toxicity; this process may lead to biomagnification, defined as an increase in the composition of a particular substance in living organisms at successively higher levels in the food chain and finally affect human's health.

As they come under the classification of toxic substance, they require special handling and special disposal sites. Municipal wastewater is not designed for the removal of heavy metals and for toxic pollutants. Pretreatment has to be done at the source itself, and the treatment provided should be cheaper because it often deals with a lot of effluents.

Many treatment technologies from conventional to modern such as activated sludge, coagulation-cum-flocculation, sedimentation, filtration, membrane process, and advanced oxidation process (Table 8.1) were used to minimize the consequences. In every treatment, the pollutants may be separated from the mainstream whether in the solid or liquid phase and further degradation or decomposition of that segregated pollutants was considered to be a tedious step; the cost involved in this process was found to be high and all the above processes are designed to target single pollutant. Treatment processes such as anaerobic/aerobic digestion, incineration, composting, landfill for last-stage treating are not 100% efficient in set

Table 8.1 Data on the biosorption of dye, heavy metal, phenol, and radioactive element by various biosorbents

S. no.	Treatments	Merits	Demerits
1	Activated sludge treatment	Biological pollutants are removed using this method	Short circuits occur in due course of time
			Maintenance problem
2	Coagulation-cum-flocculation	Lightweight particles are bonded up for removal in the combination of fast and slow mixing	The chemicals added are added up to the sludge
3	Sedimentation	Not suitable for heavy metal and hazardous pollutant removal	Cleaning and biomass accumulation are time-consuming
			Not suitable for targeted pollutants
4	Filtration	Clarifies liquid are efficiently removed by this method	Less dense pollutants are removed using this method
			Live or dead biomass are accumulated in this method
5	Membrane process	Pure effluents	Membrane fouling and cleaning are tedious
			The retentate formed consists of enormous toxic substance
6	Adsorption	Conventional sorbents	Not efficient for the removal of heavy metals
7	Advanced oxidation process	Used with the combinations of conventional treatments	Targeted pollutants are only removed
			Very costly

backing the components which are taken from our earth, i.e., not converted to its primary form which is considered to be harmless. For example, trivalent chromium (Cr(III)) in trace amount is needed for optimal health and found to be biologically active in food. It enhances the insulin. It is a hormone used for storage for carbohydrate, fat, and proteins whereas hexavalent chromium (Cr(VI)) is considered as pollutants due to the discharge into the environment from industries, mainly from leather industries.

Bioremediation is a technique by which microorganisms are used for cleaning up of contaminants from our environment, and the addition of nutrients and electron acceptors increases the removal efficiency, generally, oxygen or nitrogen will be used as electron acceptor. The microorganisms use contaminants as a food source and convert the contaminants into biomass and harmless by-products such as CO_2 and other inorganic salts. The combination of bioremediation with different techniques increases the efficiency in removal. Biosorption is a process in which biomolecules are used to bind the ions, especially non-degradable contaminants. Bacteria, fungi, algae, industrial, and agricultural waste are generally used as biosorbents. Biosorption techniques have good potential to replace all other conventional technologies where no secondary pollutants were accumulated.

8.2 Potential of Biosorption

The mechanism for biosorption is difficult to predict because several factors such as the biosorbent used, the substance to be sorbed, and the environmental conditions are to be included. In laboratory level, we can determine the above factors when coming to a real end except for biosorbent dosage nothing cannot be predicted because day by day, the pollutants will be accumulated and the environmental condition changes time to time. Bio refers to the biological activity of dead or living organisms, and sorption refers to absorption and adsorption especially. The metabolic inactive materials are passively bonded to the biomass. Fast-growing biomass and also dead cell biomass do not leave toxicity effects after treatment. The same biomass used can be used for many adsorption cycles (Volesky 2003; Norton and Baskaran 2004). The toxicants are taken up by live or dead biomaterials passively. Figure 8.1 gives detailed explanation regarding the biosorption process. Two types of phases are seen in biosorption; solid phase, generally refers to biosorbent and a liquid phase, refers to solvent. It is considered as a potential mechanism for removal of metal ions and the various functional groups on the cell wall offer certain attraction forces and provide high removal efficiency. The adsorbate is attracted and bonded over the adsorbent due to higher affinity, and this process is continued until equilibrium is reached. The distribution between solid and liquid phases determines the adsorbent affinity. It is known as a physicochemical process which includes absorption, adsorption, ion exchange, precipitation, and surface complexation, and biosorption is carried out using microbial systems such as bacteria, fungi, algae, toxic metals, and radionuclides (Macek and Makova 2011). Detoxification and transformation of organic as well as inorganic pollutants are the major properties of microorganisms. Biosorption is widely used in the removal of metal ions. The removal of metal ions mostly depends on the (1) type and availability of biomass, (2) composition of the wastewater, and (3) type of biomass preparation. When compared to ion exchange process, biosorption is considered as 1/10 times cheaper. Biosorption has number of advantages, they are:

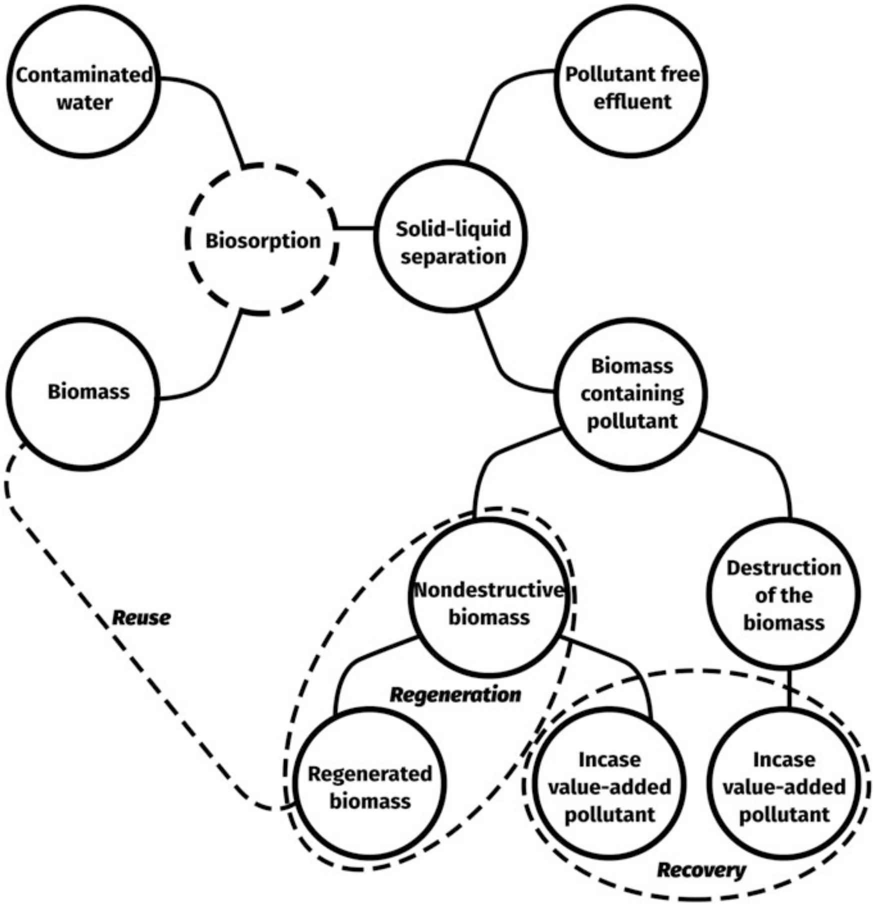

Fig. 8.1 Flowchart explaining about biosorption process

Cost efficiency: Biosorbents are used from waste materials which are abundant in our environment.

Process selective: Depends on the nature and quantity of pollutant, specific biomass is selected for removal of particular pollutants.

Regeneration: Used biosorbents can be used for a number of times, and the efficiencies are decreased after many numbers of times.

Formation of sludge: Secondary pollutants are not formed in sludge, and there are no chemical pollutants present in the sludge.

Recovery of metals: After the removal of pollutants using biomass, the pollutants are taken back to original form as there is no any chemical intervention.

Proficiency in performance: Biosorption is considered as an efficient technique than other techniques. Ion exchange was considered as equal and efficient technique to biosorption but it is costly.

No additional nutrient requirement: Other than biomass, other compounds are not added so additional nutrients are not added for their growth as it utilizes from the pollutants.

Efficiency: A large volume of wastewater can be treated at a time.

Operational conditions: Consideration of pH, temperature, and other physio-chemical parameters are found to be in wide range. Biosorption used to treat water which especially contains mixed wastes and heavy metals.

The drawback of biosorption process are as follows (Rao and Prabhakar 2011),

- So far all studies are carried out in laboratory-/small scale due to difficulties in scale-up
- The major problem associated with disposal of used adsorbent
- When dealing with wastewater, the mechanism involved in the biosorption process is difficult to predict
- Several parameters should be optimized in order to achieve higher removal efficiency
  - temperature has to be maintained in the range of 20–35 °C throughout the process and
  - pH influences the affinity of the functional groups in the biomass and the competition of metallic ions
  - biomass concentration, for low concentrations the specific uptake will be higher
- Biosorption is mainly used in treating wastewater where varieties of contaminants are already present. The removal of one contaminant may be influenced by the other contaminant.

8.3 Biosorption and the Pollutants

Dye, heavy metal, phenols, and radioactive waste are considered as major toxic pollutants in our environment, and their biosorbent capacities are listed in Table 8.2. Their occurrence due to human activities and the importance of biosorption techniques are highlighted below.

8.3.1 Biosorption and Heavy Metal

Heavy metal contamination may result from natural activities such as forest fire, volcanic eruption, and anthropogenic activities such as mining and industrial manufacturing companies. Cadmium and zinc contamination are found in paddy field (Simmons et al. 2003). The industrialization leads to a sudden increase of

Table 8.2 Data on the biosorption of dye, heavy metal, phenol, and radioactive element by various biosorbents

Compounds	Biosorbents	Compound removal	Biosorption capacity (mg/g)	Reference
Dye	*Stoechospermum marginatum*	Acid blue 25	42.0	Daneshvar et al. (2012a, b)
		Acid orange 7	36.7	
		Acid black 1	23.8	
	Chitosan film	Acid Red 18	194.6	Dotto et al. (2013a)
		FD & C blue no. 2	154.8	
	NaOH treated husk	Brilliant green dye	58.5	Mane and Babu (2011)
	Posidonia oceanica	Astrazon dye	68.97	Cengiz (2012)
	Lignocellulosic waste	Reactive red 2	23.6	Akar et al. (2013)
	Pyracantha coccinea	Orange G	128	Ari et al. (2013)
	Jackfruit leaf powder	Amido black 10B dye	3.7	Ojha and Bulasara (2014)
	White rice husk ash	Brilliant green dye	85.56	Tavliveva et al. (2013,
	Tannery solid waste	Yellow 194, red 357, black 210	300	Piccin et al. (2012)
	Sargassum glaucescens	Acid black 1	30.9	Daneshvar et al. (2012a, b)
	Pumpkin seed hull	Methylene blue	141.1	Hameed and El-Khaiary (2008)
	Coal fly ash	Reactive black	54.3	Pengthamkeerati et al. (2008)
Heavy metal	*Sargassum sinicola*	Copper	3.44	Prado et al. (2010)
	Staphylococcus xylosus	Cadmium(II)	250	Zigova et al. (2007)
		Chomium(VI)	278	
	Pseudomonas sp	Cadmium(II)	143	Zigova et al. (2007)
		Chomium(VI)	95	
	Fucus spiralis	Cadmium	114.5	Romera et al. (2007)
	Pseudomonas Putida	Lead	50.9	Pardo et al. (2003)
		Copper	32.5	
		Cadmium	46.2	
	Enterobacter sp.	Lead	50.9	Lu et al. (2006)
		Copper	32.5	
		Cadmium	46.2	
	Myriophyllum spicatum	Lead(II)	55.12	Yan et al. (2010)

(continued)

Table 8.2 (continued)

Compounds	Biosorbents	Compound removal	Biosorption capacity (mg/g)	Reference
	Nostoc linckia	Chromium(VI)	42.6	Mona et al. (2011)
	Candida sp.	Chromium(VI)	44.38	Jimenez et al. (2009)
	Streptomyces rimosus	Cadmium	63.3	Seletnia et al. (2004)
	Gelatinous colonies	Copper(II)	27.78	Tran et al. (2016)
		Cadmium(II)	28.57	
		Lead(II)	76.92	
	Sargassum oligocystum	Mercury(II)	60.25	Delshab et al. (2016)
		Cadmium(II)	153.85	
		Copper(II)	45.25	
	Saccharomyces cerevisiae	Copper(II)	29.9	Amirnia et al. (2015)
		Lead(II)	72.5	
	Lepiota hystrix	Copper(II)	74.8	Kariuki et al. (2017)
		Lead(II)	62.52	
	Nizamuddin zanardini	Lead(II)	50.41	Montazer et al. (2011)
		Cadmium(II)	19.42	
		Nickel(II)	10.06	
	Sargassum ilicifolium	Lead(II)	195	Tabaraki et al. (2014)
	Chlamydomonas reinhardtii	Mercury(II)	2.2 ± 0.67	Tuzun et al. (2005)
		Cadmium(II)	42.6 ± 0.54	
		Lead(II)	96.3 ± 0.86	
	Laminaria hyperborea *Bifurcaria bifurcata* *Sargassum muticum*	Cadmium(II)	23.9 − 39.5	Vilar et al. (2005)
		Zinc(II)	18.6 − 32.0	
	Fucus spiralis	Lead(II)	32.3 − 50.4	
		Lead(II)	64	
	Cystoseira baccata	Cadmium(II)	101	Lodeiro et al. (2006)
		Lead(II)	186	
	Cystoseira crinitophylla	Copper(II)	160	Christoforidis et al. (2015)
Phenol	Date-pit activated carbon	Phenol	262.3	Naas et al. (2010)
	Activated carbon	Phenol	278	Wu and Yu (2006)
	Chitosan calcium alginate blended beads	Phenol, O-chlorophenol	108.69	Siva Kumar Nadavala et al. (2009)
	Organobentonite	Phenol	193.0	Perez et al. (2011)

(continued)

Table 8.2 (continued)

Compounds	Biosorbents	Compound removal	Biosorption capacity (mg/g)	Reference
	Activated carbon (tea industry waste)	Phenol	142.9	Gundogdu et al. (2012)
	Funalia trogii pellets	2-chlorophenol	147.0	Bayramoglu et al. (2009)
	Fungal mycelia	Chlorophenol	5.0	
	Phanerochaete chrysosporium	Phenol	13.5	Farkas et al. (2013)
	Spirulina sp. LEB18	Phenol	159.33	Dotto et al. (2013a)
Radioactive element	Biocomposite	Uranium	50.3	Sule et al. (2011)
	Dictyopteris polypodioides	Uranium	62.5	Bampaiti et al. (2015)
	Saccharomyces cerevisiae	Uranium	113.5	Faghihian and Peyvandi (2012)
	Trichoderma harzianum	Uranium	612	Akhtar et al. (2007)
	RD256	Uranium	354	Akhtar et al. (2007)
	RD257		408	
	Cladophora hutchinsiae	Uranium	152	Bagdaa et al. (2017)
	Rhizopus arrhizus	Americium-241	88.6	Jalali et al. (2004)
	Chitosan-Polyvinyl alcohol	Cobalt(II)	14.39	Zhu et al. (2014)
	Crab shell	Selenium(II)	144.9	Vijayaraghavan and Balasubramanian (2010)
		Europium(II)	49.5	

metal in the soil as well as in the aquatic environment. Plating, battery, dye, tannery, pharmaceutical, nuclear power industries discharge heavy metal such as nickel, chromium, cadmium, mercury, lead, zirconium, uranium, thorium. Cadmium is a lustrous metal, comes from various sources like battery manufacturing, metal plating, mineral processing, fertilizers. Cadmium health risk was first detected in Japan in the time of 1950s when the municipal sewage sludge was used as fertilizer for crops. Cadmium metal causes cancer and produces serious health hazards, and it is mobile in soil and accumulates to the roots, leaves, and stems of the plants (Chakravarty et al. 2010; Vullo et al. 2009; Cruz et al. 2004). Mercury, arsenic, and lead are found naturally on earth; when they react with the earth components, they create health hazards to the living things. When mercury mixes with water, the bacteria convert mercury to methylmercury and it is accumulated into the fish, and it reaches to the higher level of organisms with the help of food chain. Mercury is found in fluorescent lamps, thermostat switches, and medical equipment. Arsenic are found in some pesticides, and lead are found along with PVC pipes; lead affects the brain in children and also damages the kidney, central nervous system, and liver. Severe exposure leads to abortion and sterility. In industrial concentrations, the outcome of lead is in the range of 200–500 mg/l which is very high when compared to WHO standards (Kwon and jeon 2013; Masoudzadeha et al. 2011; Prado et al. 2010). Properties like the interaction with intramolecular proteins and nucleic acid, high solubility in water, permeability through biological membranes make chromium (VI) more toxic than chromium (III). Due to its toxicity, the discharge standard fixed by pollution control board is 0.05 mg/l (Congeevaram et al. 2007). Chromium is generally used in industries like chrome plating, tanning, paper and wood pulp, and textile. In the Gulf of California due to human activities, pollutants are increased in coastal areas. A research work was done on the shores of sea which is located at Santa Rosalia and in La Paz provides an evidence for the bioaccumulation of copper and phosphorite deposition along the sea shore due to mining activities (Figueroa et al. 2008; Méndez et al. 2006). Many technologies namely precipitation, filtration, ion exchange, electrochemical treatment are found to be ineffective when dealing with the factors like volume, concentration of metals, salinity, temperature of the waste water. Many of these technologies are ineffective when the concentrations are less than 100 mg/l (Ahluwalia et al. 2007; Mulligan et al. 2001).

In recent times, biosorption has been used as alternative technology because of its low cost, biosorbent recovery, minimization in chemical sludge, and biosorption has particular techniques such as acting like a chemical substance in the removal of metal and reusability of biosorbents may be reused and metals are recovered (Özdemir et al. 2009; Vijayaraghavan and Yun 2008; Volesky 2007; Pagnanelli et al. 2000). Extracellular polysaccharides present in the cell wall are responsible for metal adsorption, but it depends upon the species and the growth condition. Cell composition is the most influencing factor in deciding the biological properties of biomass. In gram-positive bacteria, anionic functional groups such as peptidoglycan and teichoic acids and in gram-negative bacteria phospholipids and lipopolysaccharides are the anionic characters which are responsible for the metal binding nature of bacteria (Pagnanelli et al. 2010). The choice of biomass is based on origin, type, and the targeted composition of the solution. This type of biomass consists of different functional groups such as carboxylic, amino, sulfates which are responsible for the binding of metals to the cell wall. The modification of biomass is done using simple pretreatment techniques and modification techniques. Some of the agricultural waste such as peat, coconut shell, coffee leaf, nutshell and industrial waste from various industries are also used as biosorbents (Chuber et al. 2004).

8.3.2 Biosorption and Dyes

Dyes are synthetic organic colorants with complex aromatic structures, having applications in the various industrial fields. More than 9,000 types of dyes have been incorporated in color index. 7 × 105 tonnes of dyes are produced worldwide among them two-thirds have been used by textile industries. Textile industries are ranked one in the usage of dyes for fibers and other industries like pharmaceutical, food, agro industries (Preetha et al. 2015). The textile industries contribute 10–15% used dyes to the effluents. The effluents from dye consuming and manufacturing industries have high biological and chemical demand, without preliminary treatment discharged to the streams, and the esthetic values as well as the characteristics of the water get disturbed. The color hindrances the passage of sunlight to the water bodies; as a result, photosynthesis is affected and the plants and aquatic organisms get affected. In due course of time, the biomass in the water bodies will be increased due to the dead and decay of living substances; as a result, the aquatic ecosystem gets affected. Recently, pollution control board of Delhi sets minimum control standards for dye effluents including decolorization of effluents before emission (Bekc et al. 2008; Garg et al. 2004; Mohan et al. 2002). Among all the dyes water soluble, reactive dyes and bright-colored acid are found to be dangerous and it was not disturbed when treated with conventional treatment systems.

Dyes generally have a complex aromatic structure which makes them difficult to degrade. Dyes are classified as anionic-direct, acid and reactive dyes, cationic-basic dyes, non-ionic disperse dyes (Fu et al. 2001). The anionic- and ionic-based chromophores consist of azo groups. Toxic amines are formed due to the reductive cleavage of amine groups. Reactive dyes are a combination of azo groups and different reactive groups like difluorochloropyremidine, vinyl sulfane, chlorotriazine; they are mostly used in textile industries for its simple applications and low energy consumption. Acid dyes tend to be problematic because they pass through the conventional treatments unaffected. Basic dyes are very bright in low concentrations (O'Mahony et al. 2002; Robinson T et al. 2001). Dye effluents are generally treated with physical or chemical treatment process. This include chemical coagulation, flocculation, sedimentation, filtration, membrane process, ion exchange, oxidation, precipitation, adsorption; these technologies show effective color reduction, but there are some constraints like cost for the plant treatment and maintenance, accumulation of sludge with disposal problems, addition of unwanted chemicals during the process, sensitive to unwanted compounds present in the wastewater. In recent years, a number of studies were focused on microorganisms and the dyes. A wide variety of microorganisms like bacteria, fungi, algae are used in aerobic, anaerobic, and sequential anaerobic–aerobic process (Manu and choudri 2001; Robinson et al. 2001). Many researches show that degradation of biological pollutants mainly depends on the parameter conditions such as aeration, temperature, redox potential, pH to obtain the maximum dye reduction. The efficiency in removal of particular microorganisms on concern dye has to be investigated before treatment as the composition of dye wastewater consists of salts, inorganics, nutrients, and organic compounds (Donmez 2002; Aksu 2003). Another biological treatment is known as bioaccumulation in which living biomass is used for degrading the dyes, and it has limitations such as energy has to be provided externally, and there is inhibition in cell growth during higher concentrations of cell growth.

Biosorption was found to be a potential treatment for removal of dye. It can be defined as sequestering of organic pollutants using dead biomass which may be bacteria, fungi, yeast, seaweeds; it is considered as low-cost treatment when comparing to other ones. So it can be used as removal techniques for non-biodegradable pollutants such as dyes (Vijayaraghavan and Yun et al. 2008; Khataee and Dehgha 2011; Khataeea and Kasi 2010). Low-cost adsorbents such as barley husk, rice husk, and citrus biomass are employed for the removal of dyes like methylene blue and red BA (Bhatti et al. 2012; Sun et al. 2007; Haq et al. 2011). Due to large surface area, algae also used a biosorbent. The presence of functional group such as amino, phosphate, carboxylic, hydroxyl in the cell wall contributes to a major part in the degradation of dyes (Daneshwar et al. 2007; Tien 2002; Srinivasan and Viraraghavan 2010).

8.3.3 Biosorption and Phenol

Phenol is an organic pollutant and considered as a priority pollutant by US Environmental Protection Agency (USEPA) with a considerable limit of 0.1 mg/l, and World Health Organization permissible limit is 1 μg/l. It is a combustible substance with a pungent smell, and they are considered as protoplasmic toxins. It is soluble in oil, water, and many organic solvents (Yousef et al. 2011; Busca et al. 2008; Ahmaruzzaman 2008). The occurrence of phenols to the environment is due to paint, pesticide, petroleum, and petrochemical industries. Chlorophenols are used in manufacturing process of fungicide, herbicide, pharmaceuticals, etc. (Rubin and Rodiguez 2006; Wu and Yu. 2006). The intrusion of phenol to human body impulses tissue erosion, paralysis in the nervous system, and protein degeneration. Phenol can be removed using physical, chemical, and biological treatments. Treatments like solvent extraction, electrochemical methods, and chemical oxidation are widely used for the removal of phenol compounds. High cost, toxic, and secondary products are some of the drawbacks found in these types of treatments. Because of low cost and wide availability, biosorption is found to be efficient technique.

The use of microorganisms like algae, bacteria, fungi, and agricultural and industrial wastes is used for the removal of phenolic compounds (Bayramoglu and Arica 2009; Navarro et al. 2008). Sargassum multicum algae have been used for the removal of phenol and 2-chlorophenol, and 2, 4-chlorophenol is removed using non-living fungal pellets of Phanerochaete chrysosporium (Sampedro et al. 2007; Aranda et al. 2006). Compounds like Caulerpa scalpelliformis, Funalia trogii, Pleurotus sajor caju, Bacillus subtilis, Phanerochaete chrysosporium, Ca-alginate beads are tried for the removal of phenols, and their adsorption capacity was found to be efficient.

8.3.4 Biosorption and Radioactive Waste

Uranium, Thorium, Selenium, and cobalt are some of the radioactive components. The derivatives are found in various forms in our environment. Uranium is in different isotopes such as U-238, U-235, and U-235. The sources of uranium are from mining and nuclear power generation (Kahouli 2011). Rare earth elements such as lanthanides, scandium, and the elements coming under the group17 in chemical element table and the source of outcome are from wind turbines, batteries in the car, magnets used in a computer. The element cerium plays a role in polishing glass and in the manufacturing of glass and magnets. Americum-234 and Cobalt-60 are also used as radio element in the nuclear industry along with uranium and thorium. Cobalt (II) component is used in paint and pigment, electronic manufacturing, and nuclear power plants (Baun and Christensen 2004). Strontium-90 is seen in the fission products of Fukushima nuclear accident happened on 2011; it is considered as a hazardous substance to our environment and to the living organisms (Nagaoka et al. 2014; Nagaoka et al. 2015). Rare earth elements, as well as radioactive elements, enter the food chain, and bioaccumulation occurs in living organisms (Tai et al. 2010). The potential applications of biosorption using microorganisms attracted researchers in the removal of radioactive elements. The size of the biosorbents may be smaller, but it has high adsorption capacity. Different species such as Pinus brutia, Platanus orientalis, Turbinaria conoides, Agrobacterium sp. HN1 are used in the removal of rare earth metals.

8.4 Factors Consideration in Biosorption Process

8.4.1 Cost of Biosorbents

In biosorption process major amount of investments are done on the processing of biosorbents in order to improve its sorption efficiency. The preprocessing and drying of real biomass will increase its sorption efficiency. This stage includes a collection of industrial biomass as well as natural biomass from various environments, for example, marine algae are collected from high seas or offshore areas. It is a well-known fact that different biomaterial compounds are made ready to use as biosorbents using different technologies and treatment. The overall treatment depends upon the cost of the prepared biosorbent. The cost of biosorbents should be lower than that of ion exchange, membrane process, electrochemical treatment, advanced oxidation process, etc. Harvesting and drying of algal biomass seem to be of high value. The cost constraint makes the preparation of biomass in laboratory level and converting into real time if it gives beneficiary results. Type and source of a biomass play major role in determining the cost of biosorbents. Manufacturers will take into account of both production and maintenance of biomass if the biomass has to be cultivated. Choosing naturally available biosorbents decreases the

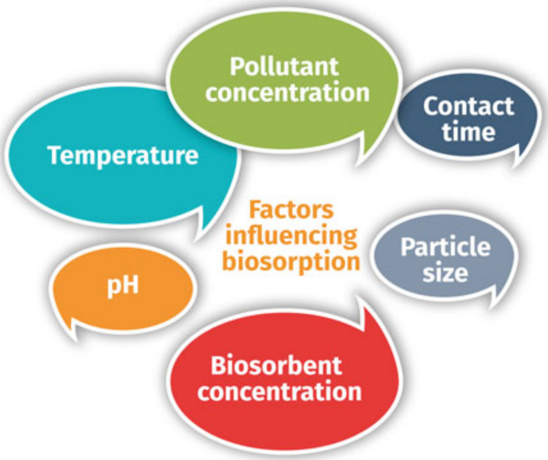

Fig. 8.2 Some of the factors influencing the adsorption process

production cost. The waste from industries such as food, leather, pharmaceutical, and enzyme are free of cost because of disposal problems faced by these industries. The only cost spent are in the places of transportation and further treatment (Volesky and Naja 2007; Bagdaa et al. 2017; Tran et al. 2016) (Fig. 8.2).

8.4.2 Biosorbent Regeneration

Regeneration of biosorbents is an important step due to the investments in preparation and generation of biosorbents. The recovery options are to be cheap so that the used biomass can be utilized for multiple cycles. Depending upon the type and the mechanism of biosorbents, eluents are chosen. The following requirements are necessary for choosing the eluants, they are (1) it should not affect the biomass, (2) eco-friendly, (3) cost-efficient (Vijayaraghavan and Yun 2008; Zhu et al. 2014). Both acids and base medium were used for desorption process. The eluents like $CaCl_2$ with HCl, EDTA, NaOH are reported.

8.4.3 Biosorbent Immobilization

The biosorbents which are formed from microorganisms are of small in size; densities, mechanical strength, and rigidity are found to be low. Even though they have many advantages like low process cost, rapid equilibrium attainment, high adsorption capacity, improving biomass–liquid separation, mechanical strength, stability, efficiency in the removal of metal ions, increase in lifetime of adsorbent (Shashirekha et al. 2008; Wang and Chen 2009), the main drawback in using biomass as it includes solid–liquid separation problems, swelling of biomass (Vijayaraghavan and Yun 2007a, b). Among many techniques, immobilization technique was found to be practical.

Three processes such as biochemical reaction, adsorption, and mass transfer occur simultaneously as well as within the adsorbent. Packed or fluidized bed reactors and usage of polymeric matrix make immobilization more efficient. The benefits like biomass regeneration, particle size control, liquid–solid separation, and minimal clogging. The polymeric matrix used in biosorbents includes sodium alginate, polysulfone polyacrylamide, and polyurethane (Vijayaraghavan et al. 2007). The polymeric matrix plays a key role in immobilization, and it determines the mechanical and chemical strength of the biosorbent. However, there are some limitations like mass transfer and additional processing cost, i.e., the amount invested on immobilization process. Mass transfer is a key factor in determining the equilibrium attainment of biosorbent.

Two types of immobilization were found normally; they are entrapment and attachment. Natural polymers (alginate, rubber, cellulose derivatives) and synthetic polymers (nylon, teflon, polyester, polyethylene) which are derived from petroleum and oil coming under the category of entrapment are also used. Alginate is used in major extent for cell entrapment because of its non-toxicity in nature (Couto 2009; Dalel et al. 2013). Bark, leaf, flower, and stem of trees have large surface area and cavities that are due to the biostructural matrix of plant materials, for example, papaya wood, loofa sponge from the dried fruit of Luffa cylindrica, activated carbon (Podder and majumder 2016; Saeed et al. 2009; Iqbal and Saeed 2007) are used. In some cases, volcanic rock matrix is used for immobilization technique. Bacteria are immobilized using volcanic rock matrix, and it consists of the compounds such as SiO_2, Al_2O_3, Fe_2O_3, CaO, Na_2O, MgO, K_2O, FeO, and TiO_2. The volcanic rock matrix is grounded and sieved according to the need (Ni et al. 2012). The active sites in silica gel are found to be high, and it is also used as immobilization matrix (Akar et al. 2009). Immobilization of microorganisms in natural or synthetic polymeric matrix increases its mechanical strength, porosity, size, and resistance. Entrapment is the most commonly used technique for immobilization of organisms. While using the microorganisms in reactors, immobilized biosorbents are found to be more efficient in avoiding clogging and solid–liquid separation, regeneration of biomass are made easy etc., (Li et al. 2007; Wu and Yu 2007).

8.4.4 Charge of Biomass

The cell wall of the biomass plays a major role in sorption. The binding sites within the cell wall are to be induced in order to improve the biosorption capacity. The positive charge pollutant has to be attracted to negative charged binding sites. Phosphonate, sulfonate, hydroxyl, amine are some of the functional groups available for binding the dyes. When the binding site strength is low, the biomass exhibits low adsorption capacity. To overcome this, the functional groups which are less important are to be converted to active binding sites. Many chemicals, as well as thermal treatments, are available (Won et al. 2008). Sludge which has high negative charge exhibits high biosorption. Proteins, carbohydrates, nucleic acid, and lipids are responsible for the negative charge. The net charge of the biomass has to be examined in order to provide the binding sites, and the binding sites also depend on specific applications (Farkas et al. 2013; Dotto et al. 2013a, b).

8.4.5 Biosorption Process Design

Three types of design are followed while using biosorption experiments. They are packed bed, fluidized bed, and continuous stirred bed reactors. From the earlier studies, it is well known that packed bed columns are suitable for biosorption process. Liquid–solid separation is found to be good in this type, and the effluent quality was good (Chu 2004; Aksu and Gonen 2004). Scaling was found to be minimal. The efficiency will be increased if immobilized biosorbents are used in packed bed and clogging will be eliminated when biosorbents are used in pelletized form. Regeneration of biomass was found to be easy. Occasionally, fluidized and continuous stirred bed reactors are used. Biomass should be in powdered form while using stirred bed reactors, and the cost, operation, and maintenance are found to be high. Fluidized bed requires high flow rate. There are some difficulties in achieving high flow rate when using fluidized bed (Aksu 2005; Vijayaraghavan and Yun 2008).

8.5 Biomass Types

Availability has to be taken into account when choosing the type of biomass. Biosorbents can be obtained either by nature such as fungi (molds, mushrooms, yeast), bacteria (gram-positive bacteria, gram-negative bacteria, *Cyanobacteria,* etc.,), algae (micro-algae, macro-algae, seaweed), industrial wastes (activated sludge, food industries, fermentation industries, etc.,), agricultural wastes (bark, leaves, stem of trees, fruit/vegetable waste, rice and wheat straws, and husk). Table 8.3 represents different species and their adsorption capacity for different pollutants. Many types of research are conducted under metal and dye treatments using biosorbents. Some biosorbents are seemed to be metal-specific and some bind over a wide range of metals without priority (Volesky and Holan 1995; Vieira 2000). The origin of biomass is from various sources such as (i) organisms which grow quickly, (ii) organisms which are available in a large amount, (iii) industrial and agricultural waste which are available at low cost. Generally, biosorbents are found naturally, mainly from algae, fungi, and bacteria. They are modified using acids, base, or thermal treatments. Figure 20.1 refers to the classification and processing steps in preparing biosorbent (Fig. 8.3).

Table 8.3 Data on the various types of biosorbents used for the treatment purpose

Biosorbent types	Biosorbents	Compound removal	Biosorption capacity (mg/g)	Reference
Algae	*Spirulina*	Yellow 12	714	Marzballi et al. (2017)
	Chlorella vulgaris	Cd (II)	85.6	Aksu (2001)
	Spirogyra	Copper	38.2	Lee and Chang (2011)
	Ceramium virgatum	Chromium	26.5	Sari and Tuzen (2008)
	Cladophora hutchinsiae	Selenium	74.9	Tuzen and Sari (2010)
	Spirogyra condensate, Rhizoclinium hieroglyphicum	Chromium	14.82 11.81	Onyancha et al. (2008)
	Spirogyra neglecta	Lead(II)	116.1	Singh et al. (2007)
		Copper(II)	115.3	
	Tricho viride	Lead(II)	1825.2	Singh et al. (2010)
		Cadmium(II)	1597.92	
		Copper(II)	1215.84	
	Ulva fasciata, Sargassum sp.	Copper(II)	73.5 72.5	Karthikeyan et al. (2007)
	Chlorella vulgaris	Uranium(VI)	26.6	Vogel et al. (2010)
	Scenedesmus obliquus	Zinc	209.6	Monteiro et al.2009)
	Cladophora fascicularis	Lead(II)	198.5	Deng et al. (2006)
	Anabaena spharica	Cadmium(II)	111.1	Abdel et al. (2013)
		Lead(II)	121.95	
	Chlorella vulgaris	Cadmium	68.5	
		Nickel	28.3	
	Chlamydomonas reinhardtii	Lead(II)	96.3	
Bacteria	*Rhodococcus opacus*	Nickel(II)	7.63	Cayllahua et al. (2009)
	Enterobacter sp.	Copper	32.5	Lu et al. (2006)
		Cadmium	46.2	
	Pseudomonus putida	Lead(II)	271.7	Ulsu and Tanyol. (2006)
		Copper(II)	46.8	
	Arthrobacter sp.	Copper(II)	175.87	Hasan and Srivastava. (2009)

(continued)

Table 8.3 (continued)

Biosorbent types	Biosorbents	Compound removal	Biosorption capacity (mg/g)	Reference
	Bacillus sp.	Copper(II)	89.62	Zheng et al. (2008)
	Geobacillus toebii	Cadmium(II)	9.2	Ozdemir et al. (2009)
		Copper(II)	48.5	
		Nickel(II)	21	
		Zinc(II)	21.1	
		Manganese(II)	13.9	
	Geobacillus thermoleovorans	Cadmium(II)	38.8	Ozdemir et al. (2009)
		Copper(II)	41.5	
		Nickel(II)	42	
		Zinc(II)	29	
	Bacillus sp. FM1	Chromium(VI)	64.102	Masood and Malik (2011)
		Copper(II)	78.125	
	Sphaerotilus natans	–	5.4	Beolchini et al. (2006)
Fungi	*Pleurotus eryngii*	Flouride	66.6	Amin et al. (2015)
	Saccharomyces cerevisiae	Fluoride	12.227	Qiu and Feng (2017)
	Fomes fomentarius	Methylene blue	204.38–232.73	Maurya et al. (2006)
	Phellinus igniarius		25.12–36.82	
	Paecilomyces lilacinus	Cadmium	41.99	Zeng et al. (2013)
	Schizophyllum commune	Phenolic	120	Kumar et al. (2011)
		2-chlorophenol	178	
		4-chlorophenol	244	
	Lactarius scrobiculatus	Lead(II)	56.2	Anayurt et al. (2009)
		Cadmium(II)	53.1	
	Coriolus versicolor	Zirconium	71.0	Sana et al. (2013)
	Aspergillus flavus	Lead(II)	20.75–93.65	Iram and Abrar (2015)
	Aspergillus niger		3.25–172.25	
	Saccharomyces cerevisiae	Manganese(II)	41.3	Fadel et al. (2017)
Industrial waste	Spent grain	Copper	10.47	Lu and Gibbs (2008)
	Activated sludge	Mercury(II)	31.6	Kilic et al. (2008)

(continued)

Table 8.3 (continued)

Biosorbent types	Biosorbents	Compound removal	Biosorption capacity (mg/g)	Reference
	Chlorella sorokiniana	Chromium(III)	9.26 ± 1.28	Nasreen et al. (2008)
			58.80 ± 1.76	
	Egg shell	Methylene blue	94.9	Abdel et al. (2017)
		Congo red	49.5	
Agricultural waste	Sawdust	Malachite green dye	52.610	Deniz et al. (2017)
	Pinus roxburghii	Arsenic	3.27	Shafique et al. (2012)
	Saccharum bengalense	Congo red	125	Din et al. (2013)
	Sorghum straw (SS)	Chromium(III)	6.96	Bernardo et al. (2009)
	Oats straw (OS)		12.97	
	Agave bagasse (AB)		11.44	
	Sugarcane bagasse	Zirconium(IV)	107.4	Kausar et al. (2016)
	Rice husk	Tetracycline	8.37	Chen et al. (2016)
	S clerocarya birrea	Lead(II)	14.02	Moyo et al. (2015a, b)
		Copper(II)	7.22	
	Phytolacca americana L.	Lead(II)	2.66	Moyo et al. (2015a, b)
	Musa paradisiaca	Cadmium	67.2	Vargas et al. (2012)
	Citrus limonum	Copper	12	
	Citrus sinensis	Lead	28.8	
	Peanut shells	Lead(II)	39	Tasar et al. (2014)
	Kappaphycus alvarezii	Chromium(III)	0.86	Kang et al. (2011)
	hanerochaete chrysosporium	Lead(II)	76.33	Xu et al. (2012)
	Eucalyptus citriodora	Uranium	7.75	Bhatti and Hamid (2014a, b)
	Sugarcane bagasse	Mercury	35.71	Bhatti and Hamid (2014a, b)
	Solanum lycopersicum	Copper(II)	46.04	Yargic et al. (2014)

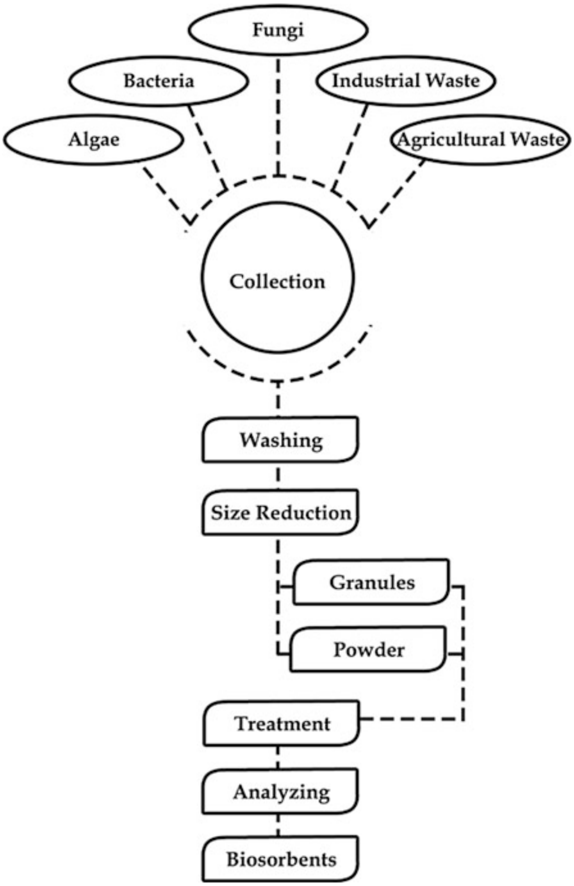

Fig. 8.3 Various types of biomass and its processing steps

8.5.1 Biosorption Using Algae

The cell wall of micro-algae includes several macromolecules such as polysaccharides which have charged groups, which are responsible for the binding of pollutants. The amphoteric properties of the cell wall are due to the anionic and cationic sites. However, the use of micro-algae for wastewater has been limited due to the separation of algae from treated water. Generally, centrifugation and industrial filtration are used for harvesting micro-algae but they are not cost-effective. Immobilization of algae using a polymeric matrix such as silica gel, carrageenan, and alginate increases the efficiency. The immobilized algae can be used for several cycles. Several mechanisms like surface adsorption, biosorption, adsorption on extracellular biopolymers, and adsorption on extracellular biominerals are studied. The functional groups like hydroxyl, carboxyl, carbonyl, and amino groups are available in the algal cell wall (Chojnacka et al. 2005).

The use of algae is economically viable because of its wide availability, economic and eco-friendly, less chemical or biological sludge, high volume-to-surface area ratio, regeneration capacity. The chemical structure such as porosity, swelling effects, flexibility, rigidity, and the chemical composition refers to the chemical groups that are generally known as active sites for the binding of metals. The electrostatic attraction and the complexation on the cell wall of algae play an important role. Alginic acid or alginate is embedded in Phaeophyta with sulfated polysaccharide in a smaller amount and the Rhodophyta consist of sulfated galactan and amorphous embedded polysaccharides matrix. These properties make algal groups excellent biosorbents (Davis et al. 2003; Plazacazon et al. 2014). They are eukaryotic organisms produce their food by means of photosynthesis, and they are known as primary producers and it determines the hydrophobic organic compounds in an aquatic system. They are generally known as thallophytes, and thallophytes are responsible for photosynthesis in autotrophic organisms (Torres et al. 2008).

From many research it was concluded that, algae was used as a biosorption substance inorder to remove mainly heavy metals and it has many advantages like high removal efficiency, efficiency in cost and minimum sludge obtainment which is found to be non-toxic. Hydroxyl, carboxyl, amino, and sulfhydryl are the binding sites generally seen in algae (Gonzalez et al. 2011). Algae are the ancestor for nutrient organic matter (NOM), and NOM consists of rubbery and glass domain. Algae are known by its good low-cost sorbivity and mainly used for the production of biofuel (Carro et al. 2011; Singh et al. 2011). Due to the presence of cellulose and protein on the cell wall with a lot of proteins bounded on green algae, these are helpful for binding of metals. The polysaccharides consist of amino, carboxyl, sulfate, and hydroxyl groups, which are helpful in biosorption process. Brown algae consist of three components in its cell wall; they are cellulose, sulfated polysaccharides, and alginic acid. Due to its aligate content, brown algae show higher uptake to different metal ions (Bulgariu and Bulgariu 2012; Karthikeyan et al. 2007; Lee and Chang 2011; Romera et al. 2007).

Different reactions such as coordination, chelation of metal, ion exchange, adsorption, and microprecipitation on the cell wall are responsible for metal removal. Two types of uptake are possible, active and passive. During active uptake, ion transports across the cell membrane and it is metabolism-dependent and in passive uptake metabolism where metal ions absorb onto the cell surface. In some cases, metal ion transportation occurs due to passive diffusion. The factors such as metal concentration, biomass, pH, temperature, and metabolism are considered when using algae. Studies are made using living as well as non-living biomass, and the attraction has shifted toward non-living algae because inactive biomass has the greater metal binding capacity, low cost, abundantly available; they do not require nutrient to grow. Before proceeding with biosorption, in order to improve the adsorption capacity as well as binding ability of biomass prior treatment should be provided. $CaCl_2$, HCL, NaOH, NaCl, ethanol.

8.5.2 Biosorption Using Bacteria

In recent times, cyanobacteria have been used for the removal of Cr(VI) heavy metal. Around 80% of Cr(VI) are removed (Kiran et al. 2007). The properties of bacteria such a nutrition in autotrophic mode, smaller size are able to grow in controlled conditions uses bacteria in the wider range of environmental conditions. Fast growth and non-toxic nature make bacteria favorable for the use of biosorbents. Instead of using biomass as a dry powder, immobilized form gives better results in adsorption. The recovery of biomass was made easy if the biomass is in rigid form and it also avoids biomass-liquid density. Biomass is converted into a polymeric matrix or in the form of gel or beads to increase its mechanical strength, which increases the removal efficiency as compared to the free cell biomass (Garido et al. 2005). A lot of *cyanobacteria* are dumped after using it as biosorbent. Many types of researches are done in order to extract hydrogen from this biomass but the biomass after the extraction of hydrogen is again a serious issue (Dutta et al. 2005; Yan and Vijayaraghavan 2003). *Rhodococcus opacus* is a gram-positive bacteria which consist of polysaccharides, mycolic acid, lipid groups, and carboxylic groups on the surface, and the behavior of these compounds impacts on cell wall (Botero et al. 2007).

Different shapes of bacteria are seen; they include cocci, rods, spiral, and filamentous. Eubacteria do not have cell nuclei but have a cell wall. The strength of bacterial cell wall depends upon peptidoglycan, and the cell shape depends on peptidoglycan. All cell walls of the bacteria are not the same. The cell wall is the important component that differentiates the species. Two types of bacteria exist in common; gram negative and gram positive. Gram positive consist of thick peptidoglycan layer which is connected by amino acid bridges and consist of 90% of peptidoglycan. The substance teichoic acid gives overall negative charge, that is due to the phosphodiester bonds between the teichoic acid monomers and another type is known as gram-negative bacteria which consists of 10–20% peptidoglycan, and the cell wall additionally consists of phospholipids and lipopolysaccharides. Chemical modification and genetically modified bacteria are generally used as biosorbents (Vijayaraghavan and Yun 2008). Depending on binding mechanisms, a number of surface binding sites in bacteria are selected for pollutant removal. Due to its small size and capability to grow under certain conditions and its adaptability over a wide range of environmental conditions, bacteria are used as biosorbents (Eman. 2012; Kinoshita et al. 2013).

8.5.3 Biosorption Using Fungi

Fungi are non-pathogenic and robust for humans and animals, and it can be easily produced using fermentation process or from the industrial waste. Cell walls are responsible for the sequestration of heavy metal, and cell wall alone does not contribute to the removal of pollutants. Various components such as polysaccharides contribute to 90% constituents to the cell wall. The ultrasonic studies reveal that the outer layer consists of glucan, mannans, and the inner layer made up of parallel arrangements of chitin chain, cellulose chain, the yeast of non-cellulosic glucan, and there will be a continuous transition between two layers.

Many studies showed that fungi as a good biosorbent for the removal of metals because of its efficiency when compared to conventional adsorbents like activated carbons, brown algae, polymers. Many fungal biosorbents are found in abundant, and they have less nutrient requirement. The separation of biomass from the treated medium requires a simple operation. Modification of biomass is possible using physical and chemical treatments. Fungi is a eukaryotic, non-photosynthetic organism, macromolecular structures consist of glucans, mannans, proteins, and chitins, and other substances such as polysaccharides, pigments, and lipids are responsible for binding efficiency. It depends on organic substance as their whole source for their growth and metabolic activity. Molds are known as filamentous fungi and mycelial structures are seen on molds. The sexual pore available on mold provides resistance against heat, freezing, drying, etc. Rhizopus arrhizus is a type of mold. The size of mold varies from 5 to 20 μm. Molds are generally formed as pellets, and the size of pellet varies from 50 μm to 1 mm; it depends on the type of mold and growth conditions. Fungi are classified into four categories such as phycomycetes, ascomycetes, basidiomycetes, and deutromycetes. In many research, the phenolic compounds have been removed using the fungal biomass namely, *bacillus subtilis*, *fungal trogil*, *Trametes versicolor*, *Emericella nidulans* and *Penicillium miczynskii*. Phanerochaete chrysosporium (Wu and Yu 2006; Bayramoglu et al. 2009; Kumar et al. 2009; Matinari et al. 2007).

Fungi easily grow in a faster manner, and they can be modified genetically as well as morphologically. The fungi groups are mostly robust than bacteria. Bioremediation occurs in the tropical forest than in temperate because of climatic conditions (Gadd 2001). Aspergillus efficiently removes nickel and chromium. Recent research provides information regarding the fungi species involved in treating the sludges (Lacina et al. 2003). The inter- and intracellular enzymes are useful for the absorption of pollutants. These enzymes are helpful in degradation of dye. *Pleurotus eryngii* are edible species seen in the oyster of the mushroom genus which utilize dyes as a carbon source and use it for growth. If the carbon or nitrogen source is not available, fungi will secrete an enzyme which degrades the complex molecules to simple molecules (Hadibarata et al. 2011; Gao and Liu 2010). White rot fungi secretes lignin peroxidase, manganese peroxidase, and laccase which are known as ligninolytic enzymes, these enzymes have the ability to degrade the pollutants (Hadibarat and Kristanti 2012). The white rot fungi species such as *coriolopsis sp, Penicillium simplicissimum,* and *pleurotus* show degradation of dye. Many disadvantages like long growth phase, enzyme unreliable production, and large reactor size are seen. Usage of fungi alone has a disadvantage, i.e., the system is no stable and after 20–30 days, bacteria will grow and dominate the system (Anastasi et al. 2011; Gadd 2009; Quan et al. 2004).

8.5.4 Biosorbents from Agricultural Waste

Recent studies reveal that biosorbents from agricultural waste such as bark of trees, hazelnut shell, rice bran, wheat husk, rice husk, wheat bran, sawdust (sawdust was naturally available abundant biomass in forest as well as in agriculture), tea leaves, maize corn cob, sugarcane bagasse, apple, banana, orange peels, sugar beet pulp, soybean hulls, grapes stalks, sunflower stalks have been tried (Cimino et al. 2000). Agricultural adsorbents consist of cellulose and hemicellulose and lignin which are responsible for hydroxyl groups. Cellulose is pure organic polymer consist of anhydroglucose bound together in a large straight-chain molecule. By means of b-(1, 4) glycosidic linkages, anhydroglucose are held together, due to these linkages, cellobiose forms unit of cellulose chains. The intramolecular and intermolecular hydrogen bonds are formed in between OH groups; microfibril is formed from the bundles of linear cellulose which are the base for cell wall (Demirbas 2000; Hashem et al. 2007). Apart from hydroxyl groups, it has a variety of other functional groups such as carboxyl, phenolic, polysaccharides, amido, amino, alcohol, acetamido. These functional groups donate an electron pair to form complexes with a metal ion or substitute hydrogen ions instead of metal ions. Agricultural waste has abundant binding groups (Cedillo et al. 2013; Marin-Rangel et al. 2011; Zafar et al. 2007).

Many studies reported the biosorption of metal ion using agricultural waste. Strong affinity and high selectivity toward heavy metal are the reason for the usage of agricultural waste (Banerjee et al. 2012). As agricultural wastes usually are low of cost because of abundantly available agricultural originating materials and more over agricultural waste can be processed, used for treatment and recovered without any harmful effects on the environment. It is known as an effective adsorbent for the removal of metal and metal ions and the recycling of agricultural waste and their by-products for heavy metals and also believed to be economically friendly (Ngah et al. 2008; Okoro and Okoro. 2011). Choosing a good agricultural biosorbent is not an easy task for researchers. Many attempts were made in this area. Abundant availability and cheapness are the main key factors in selecting the biosorbents and some other factors like desorption rate, regeneration capacity, and the negligible release of unexpected compound (Park et al. 2010). The adsorption capacities of heavy metals depend on the type of agricultural waste and the pretreatment process provided. In a study, it is released that the removal of heavy metal decreases from cotton stalks, maize stalk, and rice straw. The removal efficiency of the cotton stalk is high; this is due to the presence of cellulose, hemicellulose, and lignin (Mosa et al. 2011). In another research, zinc, cadmium, and iron were investigated with the biosorbents such as rice hull, sawdust, sugarcane bagasse, and wheat straw, and the higher adsorption was found in rice hull; this is because of silanol group presence (Osmon et al. 2010).

Zerovalent iron particles are an environmentally friendly agent used for removing the pollutants present in the environment. Zerovalent iron particles generally have large surface area and high reactivity. This property makes them unstable in an aqueous environment. In order to stabilize, zerovalent iron particles are blended with biochar as it increases the efficiency of removal. Rice husk consists of floristic fiber, protein, and dome functional groups such as hydroxyl, amidogen, and carboxyl (Han et al. 2004), and additionally, rice husk is found abundant as a by-product from agriculture. Agricultural waste can be easily obtained because of its low cost. (i) Commercial value is low and it is readily available in nature. (ii) They are coming under the category of renewable sources. (iii) They are high affinity toward removal of metals (Santos et al. 2013; Chatterje et al. 2010).

8.5.5 Biosorption from Industrial Waste

The contamination of heavy metal in water bodies is a major issue, and it is harmful to the living things. The discharge from industries like battery manufacturing, automotive, metal plating, tanneries, welding, paper, and pulp industries releases a different concentration of metals and other pollutants in a large amount (He and Chen. 2014). The trace amount of this substance also produces harmful effects to the environment. Among many processes, biosorption was found to be efficient technique due to its regenerative property, efficiency in removal (Vijayaraghavan and Yun 2008). It is found to be a suitable technique for our environment. Drawbacks such as pH of biomass and slow removal rate are to be rectified. The use of natural biosorbents is generally specific to particular ion removal, in order to remove multi-metal ion different biosorbent need to be applied. The industrial waste from whiskey, brewery, leather, wastewater treatment plants, poultry is used as biosorbents after treatment. As it is a sludge, it consists of active as well as dead biomass, and at the cell wall of biomass, different types of chemical compositions are seen which helps in fast removal of metal ion when comparing to microorganism biomass. In some cases, the microbial organisms are separated from activated sludge or from contaminated soil and used as biosorbents due to its high efficiency in removal (Abdel et al. 2017; Ramrakhiani et al. 2017; Nasreen et al. 2008).

8.6 Application of Biosorbents

Many natural biosorbents are used with little modification in the preparation. In recent times, industrial waste is also used as biosorbents after treatment. Biosorption is known as cost-effective and potential technique, and it treats a large amount of wastewater including heavy metals. Two trends are followed; one is using hybrid technologies and another one using commercial biosorbents just like ion-exchange resin (Volesky 2007). The difficulties in using biosorption induce people to use other technologies such as bioreduction and bioprecipitation. The research on living cells is also under process instead of dead cells. For large-scale treatments, the combination of the biological process as well as the process like chemical precipitation, membrane technology, and electrochemical process is also done. High-value pharmaceutical is purified using biosorption process, compounds such as proteins, pharmaceuticals, and drugs are recovered using biosorption. The advantages of biosorptions are (1) cost-efficient, (2) more versatile and flexible, (3) metal concentration reduction level is efficient, (4) regeneration capacity, and (5) biosorption capacity. In developing countries, biosorption is used as most efficient technology due to following reasons such as (1) large availability of biomaterials, (2) shortage of advanced water treatment systems, (3) biosorption was considered as efficient and cheaper method when comparing to other advanced technologies. Biosorption was compared with the ion-exchange resins in the market. Ion exchange is selective and gives anticipated removal efficiencies. In the case of biosorption, many functional groups are available so there is no problem in selectivity and the efficiencies are achieved. Instead of using biosorbents in powdered form, granulated forms are used. It avoids clogging, and there is a good separation between liquid and solid (Bhatti and Hamid 2014a, b; Xu et al. 2012).

8.7 Conclusion

Biosorption technique for the removal of toxic pollutants such as hazardous waste, radioactive waste, fertilizers, pharmaceutical was found to be efficient when comparing to conventional techniques. The cost of the raw materials for the preparation of biosorbents is found to be low, and there is no huge capital investments required. As biosorbents have regeneration capacity, it can be utilized for several cycles without any compromise in efficiency. It was found that the combination of biosorption with other techniques like membrane technology, electrochemical treatment, photo catalysis, and ozonation increases the removal efficiency tremendously. To increase the mechanical strength, chemical strength and rigidity of biosorbents which are derived from living species such as fungi, bacteria, and algae and from agricultural and industrial waste are immobilized using synthetic and natural polymeric matrix. Immobilization is another higher end technique in biosorption which increases the resistance, surface area, and porosity of biosorbents. On the whole, biosorption was found to be suitable and a cheaper technique for all sorts of pollutants. The selectivity and specificity of suitable biosorbents for particular pollutant matters.

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