Chapter 14
Biomass-Based Absorbents for Heavy Metal Removal

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Contents

Abstract With the increasing industrialization, the heavy metal contamination has become a serious environmental issue. Different activities, such as fertilizer, pharmaceutical, chemical, automobile, petroleum, and textile units, discharge a large amount of heavy metals laden effluent that contaminates the water streams. Traditional processes such as precipitation, ion exchange, membrane technology, and advance oxidation have been utilized for the remediation of heavy metal contamination. These processes could not be attractive for commercial applications

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because of their poor removal rate, problem of disposal, and high operating cost. Biosorption is now becoming a good alternative and environmentally friendly option. Biosorption of heavy metals is a metal uptake process by using ion exchange, precipitation, surface complexation, etc.. Various sources of waste biomaterials are utilized for the treatment of metal-contaminated wastewater stream. As natural biosorbents are not giving higher efficiency, modifications are done by physical and chemical activation of the biomaterials. Scientific developments were done for improving the efficiency, but limited research was conducted for the regeneration or reuse of the biosorbents. In recent years, researchers are paying attention on the reuse of the spent biosorbents by using eluent solutions such as acids, bases, chelating agents, etc. and getting the potential results. This makes the biosorption process more efficient and economic than the other conventional methods for the treatment of metal-tainted effluent. This chapter highlights the toxic metals and the various sources of biomaterials which are utilized for heavy metal removal.

Keywords Biosorption · Heavy metal ions · Wastewater · Agricultural biosorbents · Bacterial biomass · Fungal biomass · Algal biomass · Regeneration

14.1 Introduction

Heavy metal contamination with the surface and groundwater becomes a serious problem nowadays. The toxic metals which have higher specific gravity (>5) are known as heavy metals. The metals such as Hg, Pb, Cu, Co, Cd, As, Fe, Se, V, Ni, Cr, and Zn make various toxic effects to the human health. The toxic metals coming out from various industries like mining operations, refining process, fertilizer processing, tanneries, battery manufacturing, paper mill, and pesticides are contaminating water bodies (Celik and Demirbas 2005; Kjellstrom et al. 1977; Pastircakova 2004). To avoid such problems, various national and international regulatory bodies have fixed some standard limit for heavy metals before discharging [Table 14.1].

Table 14.1 Permissible discharge limits of hazardous heavy metals

Metal contaminant	By Indian standards (mg/l)		By international organizations (μg/l)	
	Into inland surface waters Indian standards: 2490(1974)	Into public sewers Indian standards: 3306(1974)	WHO	USEPA
Arsenic	0.20	0.20	10	50
Mercury	0.01	0.01	01	02
Cadmium	2.00	1.00	03	05
Lead	0.10	1.00	10	05
Chromium	0.10	2.00	50	100
Nickel	3.0	3.0	–	–
Zinc	5.00	15.00	–	–
Copper	3.00	3.00	–	1300

Conventional methods for heavy metal elimination from water stream are precipitation, advance oxidation, ion- exchange process, membrane separation, biosorption, etc. Among these processes, biosorption is an effective process due to its economical operation, abundant availability of biomaterials, easy operating process, and high competence of metal eradication. This section focuses on the effect of toxic metals, the metal removal options available in literature, and the adsorbents which are utilized for metal removal.

14.2 Sources of Heavy Metals and Their Hazardous Effect

Heavy metals such as Cr, Pb, Cu, Co, Hg, Cd, As, Fe, Se, V, Ni, and Zn have great hazardous effects on living beings. The metals are mainly discharged from various industries like mining, fertilizer, pesticides, and chemical manufacturing which are responsible directly or indirectly for the contamination of surface and groundwater. Major sources of discharging various hazardous heavy metals and their health effects are presented in Table 14.2.

14.3 Conventional Methods for Hazardous Heavy Metal Eradication

14.3.1 Chemical Precipitation

It has simple operating procedure, higher efficiency, and low operating cost, so it is considered as the good process for metal removal (Ku and Jung 2001). The coagulant is added to the metal-contaminated wastewater, and then the metal gets precipitated which is separated by using sedimentation or filtration process. Coagulants have long-chained polymers consisting of cationic and anionic charge which react with metal ion and bind the molecules together. There are mainly two types of chemical precipitation processes where one is hydroxide precipitation and the other is sulfide precipitation. Various chemical precipitation processes found in the literature are illustrated in Table 14.3.

14.3.2 Ion-Exchange Process

An ion-exchange process is an important treatment process which has great removal capacity, and it is used commercially for large-scale treatment processes (Kang et al. 2004). Several types of resins are utilized in treatment processes. In metal

Table 14.2 Common sources and health problems due to hazardous heavy metals

Metal	Common source of contamination	Health hazards
Pb	Industries such as fertilizer, petrochemical, automobile industries, and oil refineries	Lead is responsible for damaging the liver, kidney, neuron, brain, etc.
Cu	Pesticides, electroplating, and paper industry are main source of copper discharge in the water stream	Though copper is useful for human, excessive amount of copper in living beings may cause serious health problems
Cr	Chromium ion comes in wastewater from electroplating, leather, paper, chromate preparation, manufacturing of dye, petrochemical, etc.	Chromium causes diseases like cancer, lung problem, irritation of skin, etc.
Hg	Main sources of the contamination of the water are thermal power plants, pharmaceutical waste, power plants, and electronics material	Mercury makes problem in the heart, kidneys, brain, and lungs
As	Arsenic discharging sources are mining, thermal power plants, fuel, electronic material, mining industries, metallurgy, and pharmaceuticals industries	Arsenic causes serious health problems such as skin disease, respiratory problem, gastrological, and nervous systems
Ni	Nickel contaminates the water stream from industries such as electroplating, textiles, thermal power plants, ceramics, battery, etc.	Nickel has the cacogenic effect in the human body. It causes neurological, cardio, and pulmonary problems
Cd	Cadmium contaminates the water from waste batteries, electronics wastes, and paints industries	Cadmium may create different health problems such as lung disease, chest pain, bone defects, and high blood pressure
Zn	Electroplating industries are the major sources of zinc contamination in wastewater	Due to zinc contamination, health diseases like vomiting and damages of the kidney and liver may arise

Table 14.3 Chemical precipitation process

Heavy metals	Metal concentration (mg/L)	pH	Precipitant	Percent removal	References
Zn^{2+}	32	9–10	Calcium oxide	99–99.3	Ghosh et al. (2011)
Pb^{2+}, Cu^{2+}, Cr^{3+}, Zn^{2+}	100	7–11	Calcium oxide	99.37–99.6	Chen et al. (2009)
$Pb^{2+}Cu^{2+}$, Zn^{2+},	2.3 0, 018, 1.34	3.0	Hydrogen sulfide	92–100	Alvarez et al. (2007)
Cr^{3+}	5363	8.0	Calcium oxide and magnesium oxide	>99	Guo et al. (2006)
Hg^{2+}	65.6, 188	4.7, 6.4	1,3-benzenediamidoethanethiolate	>99.9	Blue et al. (2008)

Table 14.4 Metal eradication by ion-exchange process

Species	Conc. (mg/L)	pH	Adsorption capacity (meq/g)	Removal (%)	References
Pb^{2+}	2072	4.0	0.21–1	–	Inglezakis and Grigoropoulou (2003)
Pb^{2+}	1036	4.0	NA	55	Inglezakis et al. (2007)
Ni^{2+}	2900	NA	0.5–1.77	–	Rodriguez-Iznaga et al. (2002)
Ni^{2+}	25	7.0	0.11	93.6	Argun (2008)
Zn^{2+}	65.4–654	5.0	2.237 ± 0.15	100	Athanasiadis and Helmreich (2005)
Pb^{2+}	162.65–400	4.0	1.361, 1.372	–	Berber-Mendoza et al. (2006)

removal process, exchange between the cation of the resin and metal ion is the reason of removal. In literature, various ion-exchange processes are reported as described in Table 14.4. In this process, synthetic resins get the preference for the large-scale application because of their higher efficiency (Alyuz and Veli 2009). Solution pH, temperature, and the concentration of the metal ion play an important role for the removal of metal ion (Gode and Pehlivan 2006). Another important factor that affects ion-exchange process is ionic charge. The effect of ionic charge was evaluated by some researchers (Abo-Farha et al. 2009). They utilized Ce^{4+}, Fe^{3+}, and Pb^{2+}, and the adsorption sequence was found as $Ce^{4+} > Fe^{3+} > Pb^{2+}$. Similar type of results was also observed by Kang and his group (Kang et al. 2004) where they utilized Co^{2+}, Ni^{2+}, and Cr^{3+}. Utilization of the zeolites was also reported in literature which gave the efficient results (Motsi et al. 2009). Many researchers used iron oxide with clinoptilolite to improve the process (Doula 2009).

14.3.3 Membrane Filtration

Though membrane filtration is a costly process, it is very efficient for the remotion of heavy metals. Ultrafiltration technique is operated at low pressure while removing the contaminants from wastewater. It is somewhere inefficient for removing small particle as the pore size is large. In order to improve the efficiency of this process, two types of techniques are used. The first one is micellar-enhanced ultrafiltration, and the second one is polymer-enhanced ultrafiltration. In this process, various complex agents were utilized as reported in literature which includes polyacrylic acid, poly (acrylic acid) sodium, polyethyleneimine, poly-ammonium acrylate, and humic acid. It is an efficient process and also requires low energy. Reverse osmosis process is another important membrane separation process where semipermeable membranes are utilized. The process is very efficient and capable to remove the dissolved specie from aqueous solution. Drinking water manufacturing companies are using the reverse osmosis techniques commercially. The system requires high power as pump is utilized for the operation which makes the process uneconomical for wastewater treatment.

Nanofiltration is considered as one of the most efficient processes among the membrane filtration processes. It was found as the efficient process for removal of Cr (VI) (Muthukrishnan and Guha 2008), Ni(II) (Murthy and Chaudhari 2008), and Cu(II) (Csefalvay et al. 2009; Ahmad and Ooi 2010). The literature review suggests it was utilized for rejection of smaller particles of arsenic also (Nguyen et al. 2009; Figoli et al. 2010). The nanofiltration is nowadays a very effective method because of its higher efficiency and low energy requirement (Erikson 1988). Researchers utilized NF90 and N30F resins in this process for the treatment of arsenic-loaded water (Figoli et al. 2010). Others (Murthy and Chaudhari 2008) used composite polyamide membrane, and 98% Ni(II) was removed. Other group of researchers (Murthy and Chaudhari 2009) utilized nanofiltration for binary mixture of cadmium and nickel at a concentration of 5 mg/L, and the removal percentages were 98.94% and 82.69%, respectively. Nanofiltration and reverse osmosis were also effective for copper removal (Csefalvay et al. 2009). Treatment of metal-contaminated effluent coming out from metallurgical industry was done using this method by Liu and his group (Feini et al. 2008). The literature study suggests that for the recovery of the precious metal like silver, nanofiltration or reverse osmosis was utilized (Koseoglu and Kitis 2009).

14.3.4 Coagulation and Flocculation

It is another useful choice for heavy metal remediation. In this process, various coagulants such as ferrous sulfate and aluminum sulfate are utilized. Researchers used poly-aluminum chloride to remove the toxic heavy metals (El Samrani et al. 2008). In this process, doses of coagulants are optimized on the basis of the concentration of the impurities. Chang and Wang utilized polyethyleneimine for this purpose (Chang and Wang 2007). In flocculation process, the impurities are separated by filtration or flotation process. The recent research trend utilizes polyacrylamide and polyferric sulfate in flocculation process. Various flocculants were reported in literature where these were utilized for the removal of metal ion.

14.3.5 Flotation

Flotation is an important treatment method and is widely used in large-scale application. In this process, the metal is removed through bubble which is floated over the solution. For the flotation, sometimes air is introduced to the solution, and sometimes precipitation and flotation are used. Here, metals are attached with the microbubbles, and due to lower density, it floats. The floating bubbles bearing metal ion are separated as sludge (Lundh et al. 2000). The researchers were using the flotation

Table 14.5 Electrochemical method

Method	Metal ions	pH	Removal efficiency (%)	References
Electrochemical	Mn^{2+}	7.0	78.2	Shafaei et al. (2010)
	Ni^{2+}, Zn^{2+}	6.0	100	Kabdasli et al. (2009)
	As(III), As(V)	8.30	>99	Parga et al. (2005)
	Cr(VI)	1.84	100	Olmez (2009)
	Zn^{2+}	7.0	96	Casqueira et al. (2006)
	Ni^{2+}, Cu^{2+}	6	98–99	Khelifa et al. (2005)

process for the long time, and efficient results were observed (Tassel et al. 1997, 1998). Yuan and his team (Yuan et al. 2008) utilized bio-surfactant for the separation of Cd, Pd, and Cu where the removal percentages were 71.17%, 89.95%, and 81.13%. Medina et al. tested the process for removal of trivalent chromium where 96.2% removal was observed (Medina et al. 2005). Though the process is good, the process alone is not capable to give the higher removal efficiency in many times.

14.3.6 Electrochemical Treatment

Electrochemical treatment is another efficient treatment process which is widely used in recent research. The method is very useful to maintain the discharge limit of the metal ions as instructed by the various regulatory bodies (Wang et al. 2007). As electrocoagulation is the part of the electrochemical treatment process, the researchers utilized aluminum or iron electrodes in this treatment process (Chen 2004). In this process, hydrogen gas is generated which helps the impurities to float. Researchers (Heidmann and Calmano 2008) applied this process by using aluminum electrodes to remove the zinc, copper, nickel, and chromium. Zn and Ni were removed by utilizing electrochemical treatment, and 100% removal was found (Kabdasli et al. 2009). Nanseu-Njiki et al. utilized the electrochemical process for the removal of mercury where 99.9% removal was observed (Nanseu-Njiki et al. 2009). The applications of the EC process for the removal of various metal ions are shown in Table 14.5.

14.4 Biosorption

From economical point of view, adsorption is now becoming a sustainable option for the treatment of wastewater. A large number of adsorbents were utilized for treatment of metal-contaminated wastewater as reported in literature. Biosorption is an important process where the efficiencies are good and regeneration processes are also easier. Nonliving plant biomass such as wheat shell, cork biomass, food waste, coconut shell, different leafs, rice husk, sago waste, wood sawdust, rice straw, rubber wood, papaya wood, and many more were used as biosorbents. Biomasses such as bacteria, algae, and fungi play a vital role for the treatment of tainted water. Different chitosan-based materials also show remarkable efficiency for heavy metal remediation. Different categories of the biosorbents are utilized for finding an efficient and economical option of the remediation of heavy metals in literature.

14.4.1 Agricultural Biosorbents

Various low-cost adsorbents were tested to know their metal adsorption capacity [Table 14.6]. Many reviews were done where agricultural adsorbents were utilized for elimination of hazardous heavy metals. Sud et al. reported employment of agricultural waste materials for the remediation of metal ions (Sud et al. 2008). Rice bran was tested for the treatment of copper, zinc, lead, and cadmium, and the removal percentages were above 80% (Montanher et al. 2005). Rubber wood sawdust was applied for removal of hexavalent chromium and found an efficient removal of 60–70% (Karthikeyan et al. 2005).

14.4.2 Carbonaceous Biosorbents

Activated carbon is commercially used for drinking water production. It has high surface area which makes the adsorbent efficient for the removal of the contaminants. Many researchers utilized the activated carbon for the removal of metal ions and got the promising results (Kang et al. 2008). Various activation processes are available in the literature where waste materials were utilized for the preparation of the carbonaceous biosorbents (Dias et al. 2007). It was found that eucalyptus bark was utilized to remove the Cu and Pb (Kongsuwan et al. 2009). Carbon nanotube was utilized for the removal of Pb by researchers (Wang et al. 2007; Kabbashi et al. 2009). Others removed the Cd and Cr by carbon nanotube (Kuo and Lin 2009; Pillay et al. 2009).It was also used for the removal of Cu as reported by Li et al. (2010). Various activated carbons which were utilized to remove the heavy metal ions are illustrated in Table 14.7.

14.4.3 Bacterial Biomass Biosorbents

Bacterial biomass is now becoming an effective biosorbents for treatment of heavy metal contamination. In case of bacterial biomass, researchers used *Bacillus cereus* and *Escherichia coli* for the treatment of metal-contaminated wastewater (Pan et al. 2007). Metal biosorption capacity of various bacterial biomasses is presented in Table 14.8. *Pseudomonas aeruginosa*, *Bacillus* sp., *Pseudomonas putida*, and *Corynebacterium glutamicum* have been tested for lead ions where they display good adsorption

Table 14.6 Remediation by agricultural biosorbents

Raw agricultural waste	Metal	Removal	References
Oat biomass	Chromium	>80%	Gardea-Torresdey et al. (2000)
Beech sawdust		100%	Acar and Malkoc (2004)
Bagasse fly ash		96–98%	Gupta and Ali (2004)
Wheat bran		>82%	Farajzadeh and Monji (2004)
Coconut shell fibers		>80%	Mohan et al. (2006)
Eucalyptus bark		Almost 100%	Sarin and Pant (2006)
Neem leaf powder		>96%	Venkateswarlu et al. (2007)
Rubber wood sawdust		60–70%	Karthikeyan et al. (2005)
Modified bagasse fly ash		67%	Gupta et al. (1999)
Sugarcane bagasse		Up to 97%	Garg et al. (2007)
Raw rice bran		40–50%	Oliveira et al. (2005)
Oryza sativa husk	Lead	98%	Zulkali et al. (2006)
Agricultural by product *Humulus lupulus*		75%	Gardea-Torresdey et al. (2002)
Agro waste of black gram husk		Up to93%	Saeed et al. (2005a, b)
Febrifuga bark		100%	Bankar and Dara (1985)
Rice bran		>80.0%	Montanher et al. (2005)
Sawdust of *Pinus sylvestris*		96%,	Taty-Costode et al. (2003)
Maple sawdust		80–90%	Yu et al. (2001)
Water hyacinth		70–80%	Kamble and Patil (2001)
Waste tea leaves		92%,	Ahluwalia and Goyal (2005)
Peels of peas, fig leaves	Cadmium	70–80%	Benaissa (2006)
Wheat bran		87.15%	Singh et al. (2005)
Three kinds treated rice husk		80–97%	Kumar and Bandyopadhyay (2006)
Rice polish		>90%	Singh et al. (2005)
Base-treated juniper fiber		–	Min et al. (2004)
Husk of black gram		99%	Saeed and Iqbal (2003)
Straw, sawdust, dates nut		>70%	
Dried parthenium powder		>99%	Ajmal et al. (2006)
Bagasse fly ash		65%	Srivastava et al. (2007)
Bagasse		90%	Mohan and Singh (2002)
Bagasse fly ash		90.0%	Gupta et al. (2003)
Rice bran		>80.0%	Montanher et al. (2005)
Papaya wood		98, 95, 67%	Saeed et al. (2005a, b)
Rice straw, soybean hulls		Pb > Cd	Johns et al. (1998)
Poplar wood sawdust		Cu > Cd	Sciban et al. (2007)
Powder of green coconut shell		98%	Pino et al. (2006)
Bark of *Abies sachalinensis* and *Picea glehnii*		Up to 63%	Seki et al. (1997)
Cassia fistula biomass	Nickel	100%	Hanif et al. (2007)
Maple sawdust		75%	Shukla and Pai (2005a, b)
Tea waste		86%	Malkoc and Nuhoglu (2005)
Waste tea leaves		92%, 84%, 73%	Ahluwalia and Goyal (2005)

Table 14.7 Removal of heavy metal ion by carbonaceous adsorbents

Activated carbons	Metal ion	Results	References
Coconut char-based activated carbon	Pb^{+2}	100%	Gajghate et al. (1991)
Activated carbon from coir pith	Hg^{+2}	100%	Kadirvelu et al. (2001)
Activated carbon of peanut shells	Cu^{+2}	Up to 75%	Wilson et al. (2006)
Activated sulfurized carbon (bagasse pith)	Cd^{+2}	98.8%	Krishnan and Anirudhan (2003)
Carbonized corn pith	Cu^{+2}	90%	Basci et al. (2003)
Carbon nanotubes	Cd^{+2}	25.7 mg/g	Vukovi et al. (2010)
Carbon nanotube immobilized	Cu^{+2}	67.9 mg/g	Li et al. (2010)
Carbon nanotube	Pb^{+2}	102.04	Kabbashi et al. (2009)

Table 14.8 Removal of metal ions by bacterial biomass

Bacteria species	Metal ions	Adsorption capacity (mg/g)	References
Pseudomonas aeruginosa	Pb	79.5	Chang et al. (1997)
Pseudomonas putida	Pb	270.4	Uslu and Tanyol (2006)
Bacillus sp.	Pb	92.3	Tunali et al. (2006)
Pseudomonas putida	Pb	56.2	Pardo et al. (2003)
Corynebacterium glutamicum	Pb	567.7	Choi and Yun (2004)
Streptomyces rimosus 30	Zn		Mameri et al. (1999)
Thiobacillus ferrooxidans	Zn	82.6	Celaya et al. (2000)
Pseudomonas putida	Zn	17.7	Chen et al. (2005)
Pseudomonas putida	Zn	6.9	Pardo et al. (2003)
Thiobacillus ferrooxidans	Zn	172.4	Liu et al. (2004)
Pseudomonas putida	Cu	96.9	Uslu and Tanyol (2006)
Pseudomonas aeruginosa	Cu	23.1	Chang et al. (1997)
Sphaerotilus natans	Cu	60	Beolchini et al. (2006)
Bacillus subtilis	Cu	20.8	Nakajima et al. (2001)
Pseudomonas putida	Cu	6.6	Pardo et al. (2003)
Pseudomonas putida	Cd	8.0	Pardo et al. (2003)
Aeromonas caviae	Cr(IV)	284.4	Loukidou et al. (2004)
Bacillus coagulans	Cr(IV)	39.9	Srinath et al. (2002)
Pseudomonas aeruginosa	Cd	42.4	Chang et al. (1997)
Streptomyces pimprina	Cd	30.4	Puranik and Paknikar (1997)
Pseudomonas sp.	Cr(IV)	95.0	Ziagova et al. (2007)
Bacillus megaterium	Cr(IV)	30.7	Srinath et al. (2002)
Bacillus thuringiensis	Ni	45.9	Ozturk (2007)
Streptomyces rimosus	Fe(III)	122.0	Selatnia et al. (2004)

capacity. Other species of the bacteria such as *Pseudomonas putida*, *Thiobacillus*, *Pseudomonas*, and *Aeromonas caviae* were also tested by other researchers. In case of low metal ion concentration, the bacterial biomasses show the higher efficiency.

14.4.4 Fungal Biomass Biosorption

Biosorption by using fungal biomass is a noble and economical process for the treatment of metal-contaminated water source. Various studies were reported in literature as summarized in Table 14.9 where fungal biomass shows the higher metal

Table 14.9 Removal of metal ions by fungal biomass

Fungal biomass	Metal ions	Adsorption capacity (mg/g)	References
Penicillium chrysogenum	Cd	11	Niu et al. (1993)
Penicillium chrysogenum	Cd	56	Holan and Volesky (1995)
Penicillium chrysogenum	Cr(VI)	–	Park et al. (2005)
Penicillium chrysogenum (modified)	Cd	210.2	Deng and Ting (2005)
Penicillium chrysogenum	Cd	39	Fourest et al. (1994)
Penicillium canescens	Pb	213.2	Say et al. (2003)
Penicillium chrysogenum	Pb	116	Kapoor and Viraraghavan (1995)
Penicillium purpurogenum	Cd	110.4	Say et al. (2003)
Penicillium digitatum	Cd	3.5	Veglio and Beolchini (1997)
Penicillium chrysogenum	Pb	96	Skowronski et al. (2001)
Penicillium notatum	Cd	5.0	Kapoor and Viraraghavan (1995)
Aspergillus niger (live)	Pb	2.25	Kapoor et al. (1999)
Penicillium chrysogenum	Pb	116	Niu et al. (1993)
Penicillium chrysogenum (raw)	Cr(III)	18.6	Tan and Cheng (2003)
Aspergillus flavus	U, Th		Hafez et al. (1997)
Aspergillus niger (growing)	Cu	15.6	Dursun et al. (2003)
Aspergillus carbonarius	Cu, Cr		Alasheh and Duvnjak (1995)
Aspergillus oryzae	Cu, Cd, Zn		Vianna et al. (2000)
Aspergillus awamori	Cu		Tsekova et al. (2000)
Aspergillus niger	Cu(II)	9.53	Dursun et al. (2003)
Aspergillus fumigatus	Au, Ag, Cu		Gomes and Linardi (1996)
Aspergillus terreus (immobilized in polyurethane foam)	Fe	164.5	Dias et al. (2002)
Aspergillus terreus	Cu	224	Gulati et al. (2002)
Aspergillus niger	Ag	–	Akthar et al. (1995)

adsorption capacity. In these studies, many species of fungal biomasses, such as *Penicillium chrysogenum*, *Penicillium* spp., *Aspergillus niger* (live), *Penicillium chrysogenum*, and *Aspergillus terreus* (immobilized in polyurethane foam) were tested. Various fungal biomasses such as *Aspergillus niger* (Dursun 2006) and *Saccharomyces cerevisiae* (Cojocaru et al. 2009) were used for the removal of metal ion. Metabolic activities of fungi depend on the presence of metal ion. There are many instances where fungal biomass shows the higher metal binding efficiencies.

14.4.5 Algal Biomass Biosorbents

Many algae show potential capacity of metal ion adsorption. As it is available in large quantities in nature, it has been used as an economical biosorbent. The researchers used dried marine green algae for the elimination of copper and zinc (Ajjabi and Chouba 2009). According to Brinza et al. 2007, brown algae show the higher metal adsorption capacity than the other forms (Brinza et al. 2007). Various studies from literature are reported in Table 14.10. Adsorption of lead by algal biomass was reported by Deng et al. (2007).

14.4.6 Chitosan Composite Biosorbents

Chitosan is basically a biopolymer and capable to remove the metal ions effectively from the wastewater. For the increasing of the adsorption capacity, various modifications of the chitosan were done and reported in literature. Various chitosan composites which are reported in literature are shown in Table 14.11. Some researchers utilized the chitosan for the treatment of copper, chromium, lead, and

Table 14.10 Removal of metal ions by algal biomass

Algal biomass	Metal ions	Adsorption capacity (mg/g)	References
Aphanothece halophytica	Zn	133	Incharoensakdi and Kitjaharn (2002)
Cladophora crispata	Cr	3	Nourbakhsh et al. (1994)
Ascophyllum nodosum	Ni, Pb	30, 270–360	Holan and Volesky (1995)
Ascophyllum nodosum	Cd	215	Holan et al. (1993)
Chlorella vulgaris	Cr	3.5	Nourbakhsh et al. (1994)
Sargassum fluitans	Cu	51	Kratochvil et al. (1997)
Pachymeniopis sp.	Cr(VI)	225	Lee et al. (2000)
Sargassum natans	Cd	135	Holan et al. (1993)
Sargassum sp.	Cd	120	Cruz et al. (2004)
Fucus spiralis	Cd	64	Cordeo et al. (2004)

Table 14.11 Removal of metal ions by chitosan composite biosorbents

Adsorbent	Metal ions	Adsorption capacity (mg/g)	References
Magnetic chitosan	Cr^{+6}	69.40	Huang et al. (2009)
Chitosan/cellulose	Cu^{+2}	26.50	Sun et al. (2009)
Chitosan/perlite	Cu^{+2}	196.07	Kalyani et al. (2005)
Chitosan/alginate	Cu^{+2}	67.66	Ngah and Fatinathan (2008)
Chitosan/calcium alginate	Ni^{+2}	222.2	Vijaya et al. (2008)
Chitosan/clinoptilolite	Cu^{+2}	574.49	Dragan et al. (2010)
Chitosan/clinoptilolite	Cu^{+2}	719.39	Dinu and Dragan (2010)
Chitosan/clinoptilolite	Co^{+2}	467.90	Dinu and Dragan (2010)
Chitosan/cotton fibers	Cu^{+2}	24.78	Zhang et al. (2008)

zinc (Sun et al. 2009). The utilization of the mixture of sand and chitosan was found for the removal of copper (Kalyani et al. 2005). As the surface areas of the chitosan composites are large, the adsorbents are capable to give higher adsorption capacity.

14.5 Chemical Modification of the Biosorbents

Many instances are reported in literature where biosorption capacities of natural biosorbents were increased by various chemical treatments. As reported in the literature, modification of the adsorbents was done by utilizing acids such as nitric acid, hydrochloric acid, sulfuric acid, citric acid, etc. Chemical modifications of the adsorbents were also made by using calcium hydroxide, sodium hydroxide, sodium carbonate, etc. Some organics such as formaldehyde, ethylenediamine, etc. were involved in the modification of the adsorbents. Hydrogen peroxide was also used for modification of the raw adsorbents. Chemically modified adsorbents which were utilized to remove the metal ions are presented in Table 14.12. Hydrochloric acid was utilized for the modification of oak tree sawdust (Argun et al. 2007). Peanut husk was modified by using sulfuric acid and utilized for the treatment of copper, chromium, and lead (Li et al. 2007). Some researchers modified banana pith by the treatment with nitric acid (Low et al. 1995).

14.6 Responsible Functional Groups

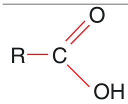
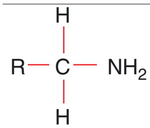
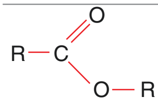
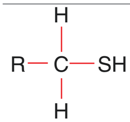
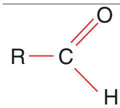
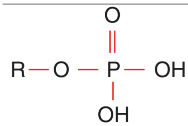
Biosorption of metal ion depends on the active groups. Various components such as cellulose, chitin, and glycol present in the biosorbents bind the metal ion. Some functional groups such as hydroxyl, amino, ester, sulfhydryl, carbonyl, and

Table 14.12 Removal of metal ions by chemically modified biosorbents

Adsorbent	Chemicals for modification	Metal ion	Adsorption capacity (mg/g)	References
Rice husk	Tartaric acid	Cu^{+2}	31.85	Wong et al. (2003)
Sawdust (cedrus deodar wood)	NaOH	Cd^{+2}	73.62	Memon et al. (2007)
Sawdust (poplar tree)	H_2SO_4	Cu^{+2}	13.95	Acar and Eren (2006)
Sawdust (oak tree)	HCl	Cu^{+2}	3.60	Argun et al. (2007)
Sawdust	Reactive Orange 13	Cu^{+2}	8.07	Shukla and Pai (2005a, b)
Sawdust (*Pinus sylvestris*)	Formaldehyde in sulfuric acid	Pb^{+2}	9.78	Taty-Costode et al. (2003)
Cassava tuber bark waste	Thioglycolic acid	Cd^{+2}	26.3	Horsfall Jr. et al. (2006)
Jute fibers	Reactive orange 13	Cu^{+2}	8.40	Shukla and Pai (2005a, b)
Banana pith	HNO_3	Cu^{+2}	13.46	Low et al. (1995)
Cork powder	$CaCl_2$	Cu^{+2}	15.6	Chubar et al. (2004)
Peanut husk	H_2SO_4	Pb^{+2}	29.14	Li et al. (2007)
Sugarbeet pulp	HCl	Cu^{+2}	0.15	Pehlivan et al. (2006)
Spent grain	HCl	Cd^{+2}	17.3	Low et al. (2000)
Bagasse fly ash	H_2O_2	Pb^{+2}	2.50	Gupta and Ali (2004)
Corncorb	HNO_3	Cd^{+2}	19.3	Leyva-Ramos et al. (2005)
Terminalia arjuna nuts	$ZnCl_2$	Cr^{+6}	28.43	Mohanty et al. (2005)
Sugarcane bagasse	$NaHCO_3$	Cu^{+2}	114	Junior et al. (2006)
Banana stem	Formaldehyde	Pb^{+2}	91.74	Noeline et al. (2005)
Alfalfa biomass	NaOH	Pb^{+2}	89.2	Tiemann et al. (2002)
Imperata cylindrica leaf powder	NaOH	Pb^{+2}	13.50	Hanafiah et al. (2006)

carboxyl group participate for the binding of metal ions as described in Table 14.13. For the determination of the metal uptake by the active sites of the biosorbent, various instruments such as Infrared spectroscopy, X-ray diffraction analysis, electron dispersive spectroscopy, nuclear magnetic resonance, etc. are utilized.

Table 14.13 Functional groups involved in biosorption (R stands for residue and others are elements)

Functional group	Name
	Hydroxyl
	Carboxyl
	Amino
	Ester
	Sulfhydryl
	Carbonyl, terminal end
	Phosphate

14.7 Regeneration of Biosorbents

Desorption of metal ions from adsorbent has an important significance for the reuse of the adsorbent. Regeneration study is required to check the economical feasibility of the biosorbent. Now, in recent trend, regeneration of the adsorbents is carried out by elution processes where acids, bases, and other chemicals are utilized. Elutent is an important factor in regeneration study, and the selection of the elutent is done based on its high efficiency, low cost, and environmentally friendly nature. Regeneration efficiencies of different biosorbents were investigated by various researchers as described in Table 14.14. Scientists (Bai and Abraham 2003) reported the regeneration of immobilized fungal biomass by using 0.01 N NaOH and Na_2CO_3 where 78% and 91.91 ± 3.9% regeneration were achieved. Others (Saeed et al. 2005a, b) utilized 0.1 N HCl for desorption of copper, cadmium, and zinc ions from the papaya wood and obtained the efficiency of 99.4%, 98.5%, and 99.3% after fifth cycle. Some researchers (Gupta and Nayak 2012) utilized nitric acid for the regeneration of orange peel powder with Fe_3O_4 and got the regeneration efficiency of 98.28% even after fifth cycle. Furthermore, it can be concluded that regeneration of the biosorbent makes bisorption process more effective and efficient.

Table 14.14 Regeneration efficiency of the different biosorbents

Adsorbent	Metal	Elutant	Regeneration efficiency	Number of cycles	References
Immobilized fungal biomass (*Rhizopus nigricans*)	Cr(VI)	0.01 N NaOH,	78%	25	Bai and Abraham (2003)
		Na_2CO_3	91.91 ± 3.9%		
Papaya wood	Cu(II)	0.1 N HCl	99.4%	5	Saeed et al. (2005a, b)
	Cd(II)		98.5%		
	Zn(II)		99.3%		
Coconut coir pith	As(V)	0.1 M HCl	(96.0%)	1	Anirudhan and Unnithan (2007)
			(95.7%)	2	
			(95.3%)	3	
			(93.8%)	4	
Marine algal biomass (*Cladophora fascicularis*)	Cd(II)	EDTA	83%		Deng et al. (2008)
Nonviable cyanobacterium (c) biomass	Cr(VI)	0.1 M HNO3 and EDTA	90%		Gupta and Rastogi (2008)
Orange peel powder with Fe3O4	Cd(II)	0.1 M HNO3	98.19%	1	Gupta and Nayak (2012)
			98.66%	2	
			98.58%	3	
			98.82%	4	
			98.28%	5	

14.8 Conclusion

To combat the environmental degradation in a sustainable way, many technologies have been developed. Among them, biosorption in considered as an efficient and economical process for its easy operation, local availability, and low cost. Some of the waste biomasses which are locally available in abundant quantities are utilized as biosorbents. Natural biosorbents such as activated carbon, wood sawdust, leaf powder, bacterial biomass, algal biomass, and fungal biomass were utilized for treatment of metal-tainted effluent. As most of the natural biosorbents have low adsorption capacity, researchers attempted to increase the adsorption capacity by a number of pretreatment techniques. These pretreatment includes physical and chemical activation where in physical treatment, the adsorbents are heated at high temperature with controlled rate of heating. In chemical treatment, various acids, bases, and other chemicals are utilized. Chemical modification increases the binding sites and modifies the functional groups of the adsorbent resulting enhancement of the adsorption capacity as well as their mechanical strength. Literature review suggests utilization of various biosorbents for the removal of heavy metals and their adsorption capacity were investigated at laboratory scale. The results are promising, but the real application of those bioadsorbent is very limited. So to increase the industrial applications of the biosorbents, more pilot-scale studies are required.

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