



Bioadsorbents for remediation of heavy metals: Current status and their future prospects

Vinod Kumar Gupta^{1,2,3†}, Arunima Nayak⁴, Shilpi Agarwal¹

¹Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, India

²Department of Applied Chemistry, University of Johannesburg, Johannesburg 2028, South Africa

³Center for Environment and Water, The Research Institute, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

⁴Department of Chemistry, Graphic Era Deemed University, Dehradun 248001, India

ABSTRACT

The biosorption process has been established as characteristics of dead biomasses of both cellulosic and microbial origin to bind metal ion pollutants from aqueous suspension. The high effectiveness of this process even at low metal concentration, similarity to ion exchange treatment process, but cheaper and greener alternative to conventional techniques have resulted in a mature biosorption technology. Yet its adoption to large scale industrial wastewaters treatment has still been a distant reality. The purpose of this review is to make in-depth analyses of the various aspects of the biosorption technology, starting from the various biosorbents used till date and the various factors affecting the process. The design of better biosorbents for improving their physico-chemical features as well as enhancing their biosorption characteristics has been discussed. Better economic value of the biosorption technology is related to the repeated reuse of the biosorbent with minimum loss of efficiency. In this context desorption of the metal pollutants as well as regeneration of the biosorbent has been discussed in detail. Various inhibitions including the multi mechanistic role of the biosorption technology has been identified which have played a contributory role to its non-commercialization.

Keywords: Algae, Bacteria, Biosorption, Fungi, Plant organic waste, Toxic metal

1. Introduction

Technological advances by humans have resulted in the contamination of water bodies resulting in the presence of toxic pollutants at concentrations well above the limits set by World Health Organization (WHO) and the Environmental protection agency (EPA) [1, 2]. The hazards imposed to humans and aquatic life associated with exposure to metals like chromium, lead, mercury, cadmium and arsenic have been well established in the literature [3-8]. The toxicity of such metal ions arise due to their non-biodegradable nature thereby accumulating in the living cells and impairing the normal functions of various organs of living beings. Technologies like chemical precipitation, electrochemical separation, membrane separation, reverse osmosis, ion exchange and adsorption resins though effective for metal remediation, yet are not competitive in industrial application [9-22]. Such methods involve either large capital or operational costs, and are not effective in removing metal ions present in ppm levels [12, 18]. Chemical precipitation involves large generation of harmful sludge which

requires further treatment thereby increasing the overall cost. Such disadvantages along with the requirement of more effective and economical methods for treatment of metal laden wastewater have resulted in the development of biosorption as an alternative technology. Biosorption is the property exhibited by inactive, non-living substances of biological origin to bind and to accumulate metal ions from aqueous solution [23, 24]. In other words the interaction between the biomass and the metal ions is physico-chemical, metabolism independent process with the underlying mechanism being absorption, adsorption, ion exchange, surface complexation and precipitation [24-26]. Bioaccumulation is another technology using living biomass for heavy metal removal. It is an active process depending on the metabolism of the living organism [27, 28]. But the toxicity of metal ions hinders metal uptake by living organisms and hence bioaccumulation has lower kinetics and lesser efficiency as compared to biosorption. The biosorption technique has enjoyed immense success in comparison to conventional techniques in sequestering metal ions from ppm to ppb levels in aqueous suspension [29-33]. Also, its metal removal



This is an Open Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

Copyright © 2015 Korean Society of Environmental Engineers

Received February 16, 2015 Accepted March 24, 2015

† Corresponding author

Email: vinodfcy@iitr.ernet.in

Tel: +91-1332-285801 Fax: +91-1332-273560

efficiency has been reported to be very high even in very dilute complex solutions having diverse types of pollutants. Its faster kinetics of metal removal has made it beneficial for treating large volume of wastewater. It has been found to be operative over a wide range of temperature, pH conditions along with the presence of other ions. Such advantages along with the lower cost of the biosorbents, potential for regeneration of the biosorbents, metal recovery and minimum generation of toxic sludge have made the biosorption process more competitive for industrial application. Compared to ion exchange and adsorption resins, the use of dead biomass as biosorbent is more environmental friendly because of its easy disposal [31]. The immense potential of this technology has thus led to its evolution from an alternative approach to a powerful technology for the treatment of industrial wastewater for metal removal and recovery [32, 33]. The metal uptake by biosorption is a surface phenomenon and is a function of the surface properties of the biosorbent. Since the ultimate efficiency of the biosorption process hinges on the performance of the biosorbent material, a critical study is required on the different materials of biological origin that have been successfully tested as biosorbents for metal ions. Table 1 and 2 summarizes the findings of an in-depth literature study carried out focusing on not only the different biosorbents used thus far but also on their capacities for metal uptake. Elaborate and detailed comparison of the biosorptive performance of various biomasses has been made by various researchers and scientists [150-170]. Researchers have summarized the role of various biomasses in heavy metal removal from aqueous solutions as can be evident from the review works. Vijayaraghavan and Yun [150] demonstrated the biosorption potential of bacterial biosorbents. Bishnoi and Garima [151], Sag [152] and Wang and Chen [153] made extensive studies on fungal biosorbents. McHale AP and McHale S [154] and later Gupta and Mohapatra [155] concluded that microbial biomass were an economical alternative for removal of heavy metals from waste water. The progress and prospects of using various algal species as metal biosorbents were assessed by Wilde and Benemann [156], Mehta and Gaur [157] and Romera et al. [158]. Among the plant based biomass, sawdust of various tree species has been established as an efficient biosorbents by Shukla et al. [159]. Crini [160], Gerente et al. [161] and Suhas and Carrott [162] demonstrated chitosan, polysaccharide and lignin based materials as economical biosorbents. Individual biosorption performances of rice husk and wheat straw/bran were extensively reviewed by Foo and Hameed [163] and Farooq et al. [164] for the removal of metal ions from waters. Various agricultural waste biomasses were compared on the basis of their biosorption performance for the removal of heavy metals as evident from various reviews [165-168]. Ngah and Hanafiah [169] reviewed studies on chemically treated plant waste based biosorbents and concluded that the treated biosorbents were better in the removal of metal ions like Cd, Cu, Pb, Zn and Ni from various aqueous streams. Similar conclusion was drawn on modified biosorbents by O'Connell et al. [170]. From such reviews, it is clearly evident that the biosorbents studied till data fall under two major classes; the plant based biomass and microbial based biomass. Secondly the discussion in such reviews is restricted to a particular type of biomass for metal ion remediation from aqueous phase. Infact few researchers have attempted to compile

and compare data related to various biomasses a broad range of biomass [171-173]. Overall it can be seen that the biosorption performance of a particular biosorbent for specific metal ions has been found to vary widely as can be evident from the compiled literature data as presented in the Tables. This may be because of different process parameters selected by the researchers in their search for optimum biosorbent. Some used biomass in their native form and others used their modified forms so as to improve their metal uptake performance. In spite of the limitations of comparative analyses, overall a major conclusion can be made that micro-organisms like micro algae, macro algae, bacteria, fungi, yeast, agricultural wastes and certain industrial wastes have demonstrated good biosorption properties for metal ions.

The overall objective of the study is to make a critical in-depth study on each such class of biosorbents so as to evaluate the various factors affecting the biosorption process along with their underlying mechanism. The findings and analyses are henceforth presented in the present work in the following sections. Current research work on the biosorption is not only summarized but also future directions are suggested. The future prospects pertaining to the establishment of the biosorption technology as a solid foundation for heavy metal remediation from industrial waste streams are discussed.

2. Biosorbent Materials

Economic consideration and efficiency of the biosorption technology hinges on the effectiveness of the biosorbents, the easy availability of their precursors and cost effectiveness of the entire process. The easy availability of the biological sources *viz.* micro-organisms like algae, fungi, weeds, bacteria, yeasts agricultural waste products along with their cost effective processing to biosorbents have resulted in the establishment of a mature and wide spread prevalence of the biosorption technology. The biosorbents have been categorized under microorganism like bacteria, fungi, yeast, algae, agricultural by-products like rice husk, bran of rice, wheat, sugarcane bagasse, fruit wastes, weeds etc. and other polysaccharide materials. The biosorbents, irrespective of their source have demonstrated good metal removal efficiencies. The microbial biosorbents have been either cultured or developed in the laboratory or have been procured from various food processing or pharmaceutical industries. Potential bacterial biosorbents showing good metal removal capacities have been identified as gram positive bacteria (*Bacillus*, *Corynebacterium*, *Streptomyces*, *Staphylococcus* sp., etc.), gram negative bacteria (*Pseudomonas*, *Enterobacter*, *Aeromonas* sp., etc.) and cyanobacterium (*Anabaena* sp., etc.) [105-121]. Fungal biosorbents which include yeast (*Penicillium*, *Saccharomyces*), molds (*Aspergillus*, *Rhizopus*) and mushrooms have shown the lowest biosorption potential [122-128]. Various species of red algae (*Gelidium*), blue-green algae (*Nostoc*, *Spirulina* sp., etc.), green (*Ulva*, *Oedogonium* sp., etc.) and brown algae (*Cystoseira*, *Sargassum* sp., etc.) [129-149] have also been used as efficient biosorbents. Weeds (*Parthenium*, *Spirodela*, *Fucusceranoides*) [133, 134] are another class of biosorbents which have shown good metal removal properties. Such microbial species have been widely used as efficient biosorbents because of their

Table 1. Biosorption Capacities of Various Biomass of Plant Origin for Removal of Toxic Metal Ions from Waste Water

Toxic metal ions	Biomass source	Biomass	Adsorption capacity (mg/g)	Reference
Cd(II)	Rice			
Cd(II)	Rice waste	Rice husk (phosphate treated)	2,000.00	[34]
Cd(II)	Rice waste	Rice husk (alkali treated)	125.94	[35]
Cd(II)	Rice Husk	Natural rice husk	73.96	[35]
Cd(II)	Rice waste	Rice husk (H ₃ PO ₄ treated)	102.00	[36]
Cd(II)	Rice waste	NaOH treated rice husk (NRH)	20.24	[37]
Cd(II)	Rice waste	NaHCO ₃ treated rice husk (NCRH)	16.18	[37]
Cd(II)	Rice	Epichlorohydrin treated rice husk (ERH)	11.12	[37]
Cd(II)	Rice waste	Rice husk (sulfuric acid treatment)	40.92	[38]
Cd(II)	Rice waste	Rice husk ash	39.87	[39]
Cd(II)	Wheat waste	Wheat bran (ultrasonic treatment)	51.58	[40]
Cd(II)	Wheat waste	Wheat bran	22.78	[40]
Cd(II)	Wheat waste	Wheat straw	39.22	[41]
Cd(II)	Wheat	Wheat straw (urea treated)	4.25	[41]
Cd(II)	Wheat waste	Wheat straw	21.00	[42]
Cd(II)	Wheat waste	Wheat bran	21.00	[43]
Cd(II)	Wheat waste	Wheat bran	15.82	[43]
Cd(II)	Wheat waste	Wheat straw	14.56	[44]
Cd(II)	Wheat waste	Wheat straw	11.60	[45]
Cd(II)	Coconut waste	Puresorbe	285.70	[46]
Cd(II)	Coconut waste	Coir pith	93.40	[47]
Cd(II)	Coconut	Copra meal	4.99	[48]
Cd(II)	Peels	Orange peel (chem mod)	136.05	[49]
Cd(II)	Peel	Orange peel	47.60	[49]
Cd(II)	Peel	Mango peel	68.92	[50]
Cd(II)	Peels	Banana peel	35.52	[51]
Cd(II)	Peel	Banana peel	5.71	[52]
Cd(II)	Peel	Pomelo peel	21.83	[53]
Cd(II)	Seeds	Raw date pit	35.90	[54]
Cd(II)	Coffee waste	Raw coffee powder	15.65	[55]
Cd(II)	Tea	Tea waste	11.29	[56]
Cd(II)	Bark	Pinus roxburghii bark	3.01	[57]
Cr(VI)	Wheat	Wheat straw (chem mod)	322.58	[58]
Cr(VI)	Wheat	Wheat bran (chem mod)	93.00	[59]
Cr(VI)	Wheat	Wheat bran	310.58	[60]
Cr(VI)	Wheat	Wheat straw	21.34	[61]
Cr(VI)	Peel	Banana peel	131.56	[62]
Cr(VI)	Seed	Sapotaceae seed (chitosan+acid)	84.31	[54]
Cr(VI)	Seed	Sapotaceae seed (chitosan coated)	76.23	[54]
Cr(VI)	Seed	Sapotaceae seed (acid coated)	59.63	[54]
Cr(VI)	Coconuts	CSC (chitosan+HNO ₃)	10.88	[63]
Cr(VI)	Coconut	CSC (chitosan+H ₂ SO ₄)	4.05	[63]
Cr(VI)	Coconut	CSCCC (chitosan)	3.65	[63]
Cr(VI)	Fruit	Bael fruit	17.27	[64]
Cr(VI)	Husk	Groundnut husk (Ag coated)	11.40	[65]
Cr(VI)	Husk	Groundnut husk	7.00	[65]
Cr(VI)	Shell	Almond shell	3.40	[66]
Cr(VI)	Shells	Hazelnut shell	8.28	[66]

Toxic metal ions	Biomass source	Biomass	Adsorption capacity (mg/g)	Reference
Cr(VI)	Shells	Walnut shell	8.01	[66]
Cr(VI)	Bark	Pinus roxburghii bark	4.15	[67]
Cu(II)	Wheat	Wheat bran	8.34	[68]
Cu(II)	Wheat	Wheat bran	6.85	[69]
Cu(II)	Wheat	Wheat straw	11.43	[44]
Cu(II)	Wheat	Wheat bran	12.70	[70]
Cu(II)	Wheat	Wheat bran	17.42	[71]
Cu(II)	Wheat	Wheat bran (dehydrated)	51.50	[72]
Cu(II)	Sago	Sago husk ash	12.40	[73]
Cu(II)	Rice	Rice husk (acid treated)	29.00	[74]
Cu(II)	Peel	Potato peel (ZnCl ₂ treatment)	74.00	[75]
Cu(II)	Peel	Orange peel (chem mod)	70.67	[49]
Cu(II)	Peel	Orange peel	50.94	[49]
Cu(II)	Peel	Mango peel	46.09	[76]
Cu(II)	Hull	Peanut hull	21.25	[77]
Cu(II)	Hull	Peanut hull pellet	12.00	[78]
Cu(II)	Hull	Peanut hull	9.00	[78]
Cu(II)	Seed	Cicerarientinum	18.00	[79]
Cu(II)	Shell	Chestnut shell	12.56	[80]
Cu(II)	Shell	Chestnut shell (acid treated)	5.48	[81]
Cu(II)	Bark	Casuarina equisetifolia bark	16.58	[82]
Cu(II)	Bark	Rhizophoraapiculata tannin	8.78	[83]
Cu(II)	Bark	Pinus roxburghii bark	3.81	[67]
Cu(II)	Tea	Tea waste	8.64	[56]
Cu(II)	Tea	Tea waste	48.00	[84]
Co(II)	Coconut	Coir pith	12.82	[85]
Co(II)	Peel	Lemon peel	22.00	[86]
Hg(II)	Rice	Rice husk (sulphuric acid treatment)	384.62	[87]
Hg(II)	Shell	Walnut shell (ZnCl ₂ mod)	151.50	[88]
Hg(II)	Wheat	Wheat bran (chem mod)	70.00	[59]
Hg(II)	Coconut	Chem mod coir pith (PGCP-COOH)	13.73	[89]
Pb(II)	Rice	Rice husk (acid treated)	108.00	[74]
Pb(II)	Rice	Rice husk ash	91.74	[90]
Pb(II)	Rice	Rice husk ash	39.74	[73]
Pb(II)	Wheat	Wheat bran	87.00	[91]
Pb(II)	Wheat	Wheat bran (chem mod)	62.00	[59]
Pb(II)	Coconut	Coir pith waste	263.00	[92]
Pb(II)	Tea	Spent black tea	129.90	[93]
Pb(II)	Tea	Spent green tea	90.10	[93]
Pb(II)	Tea	Tea waste	65.00	[84]
Pb(II)	Coffee	Coffee (ZnCl ₂ mod)	63.00	[95]
Pb(II)	Peel	Mango peel	99.05	[50]
Pb(II)	Peel	Banana peel	2.18	[52]
Pb(II)	Bark	Moringa oleifera bark	34.60	[95]
Pb(II)	Bark	Rhizophoraapiculata tannin	31.32	[83]
Pb(II)	Shell	Shell carbon	30.00	[96]
Pb(II)	Shel	Hazelnut shell	28.18	[97]
Pb(II)	Seed	Cicerarientinum	20.00	[79]
Pb(II)	Shell	Chestnut shell (acid treated)	8.50	[81]

Toxic metal ions	Biomass source	Biomass	Adsorption capacity (mg/g)	Reference
Pb(II)	Shell	Almond shell	8.08	[97]
Ni(II)	Bark	Pinus roxburghii bark	3.53	[67]
Ni(II)	Bark	Acacia leucocephala bark	294.10	[98]
Ni(II)	Peel	Orange peel	158.00	[99]
Ni(II)	Peel	Pomegranate peel	52.00	[100]
Ni(II)	Peel	Mango peel	39.75	[76]
Ni(II)	Seed	Guava seed (chem mod)	32.05	[101]
Ni(II)	Seed	Guava seed	18.05	[101]
Ni(II)	Coconut	Coir pith	15.95	[85]
Ni(II)	Tea	Tea waste	73.00	[102]
Zn(II)	Shell	Shell carbon (H ₃ PO ₄ +chitosan)	60.41	[103]
Zn(II)	Shell	Shell carbon (chitosan mod)	50.93	[103]
Zn(II)	Shell	Chestnut shell (acid treated)	2.41	[81]
Zn(II)	Seed	Cicerarientinum	20.00	[79]
Zn(II)	Rice	Rice husk ash	39.17	[73]
Zn(II)	Rice	Rice husk (sulphuric acid treatment)	19.38	[87]
Zn(II)	Wheat	Wheat bran	16.40	[70]
Zn(II)	Tea	Tea waste	8.90	[104]
Zn(II)	Peel	Mango peel	28.21	[76]
Se(IV)	Rice	Rice husk (sulphuric acid treatment)	41.15	[38]

widespread prevalence in nature and can be grown in large mass at minimal cost. Also various fungal and bacterial species are generated as wastes from different food/pharmaceutical industries. Agricultural wastes like rice/wheat husk, bran, fruit or vegetable, soybean hulls, saw dust of bark of various trees etc. have also shown good metal biosorption properties. The biosorption capacities of the biomass were determined from equilibrium studies by various researchers and such have been tabulated in Table 1, 2. Biosorbents as can be seen in the table show promising biosorption potential for metal removal and have different affinity to different heavy metals. Also some biosorbents can bind onto a wide range of heavy metals with no specific priority, whereas others are specific for certain types of metals [30, 172, 173]. Due to the enormous difference in the nature of the biosorbents used and the differences in the experimental conditions, it is difficult to make a comparison on the efficiency of the biosorbents for the removal of metal ions. Irrespective of such differences, statistics reveals an increased biosorption capacity for the biomass from microbial origin. Data presented in Table 1, 2 shows that the biomass derived from bacteria showed an average metal ion adsorption capacity of 132.2 mg/g ranging from 12.23 to 567.7 mg/g. Biosorption capacity greater than 100 mg/g is demonstrated by the gram positive bacterial species of *Bacillus*, *Corynebacterium*, *Streptomyces* and *Staphylococcus* sp. [105, 107, 109, 110, 116]. Fungal biomass showed a very low average biosorption capacity of 42.99 mg/g ranging from 6.34 to 204 mg/g. Algal biomass on the other hand had an average metal removal capacity of 113.5mg/g ranging from 10.60 to 357 mg/g. Irrespective of the metal ions, among all species of algal biomass, the brown algae for example *Cystoseira baccata*, *Sargassum* sp. have exhibited the highest biosorption capacity [130, 134, 138-142, 148]. Cellulosic material showed 69.38 mg/g

average metal ion adsorption capacity with a range from 2.18 to 2,000 mg/g. Irrespective of the metal ions, the incidences of biosorbents from microbial and cellulosic origin reporting a biosorption capacity greater than 100 mg/g are 25 (32%) and 15 (12.9%) respectively. But the incidences of the same in the range less than 100 mg/g are 53 (67%) and 116 (87%) Thus biosorbents like the algae and bacteria showed very high adsorption capacity thereby could be used in industrial applications. In fact to qualify a biosorbent for industrial application requires it to have not only high adsorption capacity, but also should have characteristics like wide spread availability, economical viability and capacity to be regenerated [26, 172]. But the fungal biosorbents and certain agricultural residues showed very less biosorption capacity. Various researchers have carried out modification of the biosorbents either by physical or chemical methods with a view to improve its metal removal capacity.

A critical analysis of these two major classes of biomass as biosorbent for metal ions reveals that their chemical and physical characteristics have a contributory role.

2.1. Cellulosic Materials as Metal Biosorbents

Agricultural and plant based by-products have showed good biosorption potential for heavy metal ions like Cd(II), Cu(II), Cr(III), Cr(VI), Pb(II), Hg(II), Zn(II), etc. as is evident from the biosorption capacities in Table 1. Various researchers have demonstrated good biosorption potential in biomass like rice bran, rice husk, wheat bran and husk, saw dust, bark, groundnut shells, coconut shells, hazelnut shells, walnut shells, cotton seed hulls, waste tea leaves, maize corn cob, apple, banana, orange peels, soybean hulls, grapes stalks, water hyacinth, sugar beet pulp, sunflower stalks, coffee beans, cotton stalks, etc. Irrespective of the metal ions, rice and

Table 2. Biosorption Capacities of Various Biomass of Microbial Origin for Removal of Toxic Metal Ions from Waste Water

Metal ions	Biomass source	Maximum capacity (mg/g)	Reference
Biomass type : Bacteria			
Pb(II)	<i>Corynebacterium glutamicum</i>	567.7	[105]
Pb(II)	<i>Enterobacter</i> sp.	50.9	[106]
Pb(II)	<i>Pseudomonas putida</i>	270.4	[107]
Pb(II)	<i>Streptomyces rimosus</i>	135	[108]
Pb(II)	<i>Thiobacillus ferrodoxins</i>	443.00	[109]
Zn(II)	<i>Thiobacillus ferrooxidans</i>	172.4	[110]
Zn(II)	<i>Cyanobacterium</i>	71.42	[111]
Cu(II)	<i>Enterobacter</i> sp.	32.5	[106]
Cu(II)	<i>Pseudomonas putida</i>	96.9	[107]
Cu(II)	<i>Streptomyces coelicolor</i>	66.7	[112]
Cu(II)	<i>Thiobacillus ferrooxidans</i>	39.8	[110]
Cu(II)	<i>Pseudomonas</i> p.	89.60	[113]
Cu(II)	<i>Sphigomonas</i> p.	50.10	[114]
Cd(II)	<i>Aeromonas caviae</i>	155.3	[115]
Cd(II)	<i>Enterobacter</i> sp.	46.2	[106]
Cd(II)	<i>Pseudomonas</i> sp.	278.0	[116]
Cd(II)	<i>Staphylococcus xylosus</i>	250.0	[116]
Cd(II)	<i>Streptomyces rimosus</i>	64.9	[108]
Cd(II)	<i>Pseudomonas</i> f.	66.25	[117]
Cr(IV)	<i>Aeromonas caviae</i>	284.4	[115]
Cr(IV)	<i>Bacillus thuringiensis</i>	83.3	[118]
Cr(IV)	<i>Pseudomonas</i> sp.	95.0	[116]
Cr(IV)	<i>Staphylococcus xylosus</i>	143.0	[116]
Cr(VI)	<i>Actinomyccete</i> sp.	32.63	[119]
Cr(VI)	<i>Chrococcus</i>	21.36	[120]
Cr(VI)	<i>N. calicola</i>	12.23	[120]
Ni(II)	<i>Bacillus thuringiensis</i>	45.9	[121]
Ni(II)	<i>Actinomyccete</i> sp.	36.55	[119]
Biomass : Fungi			
Hg(II)	<i>Tolypocladium</i> sp. (residue from fermentation industry)	161.1	[122]
Cd(II)	<i>Saccharomyces cerevisiae</i> (waste brewer's yeast)	15.4	[123]
Cd(II)	<i>Baker's yeast</i> (lab cultured)	11.63	[124]
Cd(II)	<i>Phomopsis</i> sp. (lab cultured)	29	[125]
Pb(II)	<i>Saccharomyces cerevisiae</i> (waste brewer's yeast)	85.6	[123]
Pb(II)	<i>Penicillium chrysogenum</i> (lab cultured)	204	[126]
Pb(II)	<i>Penicillium oxalicum</i> (residue from fermentation industry)	47.4	[122]
Ni(II)	<i>Saccharomyces cerevisiae</i> (waste brewer's yeast)	6.34	[123]
Ni(II)	<i>Penicillium chrysogenum</i> (lab cultured)	55	[126]
Ni(II)	<i>Penicillium chrysogenum</i> (raw)	13.2	[127]
Ni(II)	<i>Penicillium chrysogenum</i> (alkaline pre-treatment)	19.2	[127]
Cr(VI)	<i>Mucor hiemalis</i>	53.5	[128]
Cu(II)	<i>Aspergillus niger</i>	26.0	[129]
Cr(III)	<i>Penicillium chrysogenum</i> (raw)	18.6	[127]
Cr(III)	<i>Penicillium chrysogenum</i> (alkaline pre-treatment)	27.2	[127]
Cr(III)	<i>Saccharomyces cerevisiae</i> (waste brewer's yeast)	12.8	[123]
Zn(II)	<i>Phomopsis</i> sp. (lab cultured)	10.3	[125]
Zn(II)	<i>Penicillium chrysogenum</i> (raw)	6.8	[127]
Zn(II)	<i>Penicillium chrysogenum</i> (alkaline pre-treatment)	25.5	[127]

Metal ions	Biomass source	Maximum capacity (mg/g)	Reference
Biomass : Algae			
Hg(II)	<i>Cystoseira baccata</i>	329	[130]
Cd(II)	<i>Ulva onoi</i>	61.9	[131]
Cd(II)	<i>Ulva onoi</i> (NaOH pre-treatment)	90.7	[131]
Cd(II)	<i>Gelidium sesquipedale</i>	18.0	[132]
Cd(II)	<i>Parthenium hysterophorous</i>	27	[133]
Cd(II)	<i>Spirodela polyrhiza</i> (L.) <i>Schleiden</i> biomass	36	[134]
Cd(II)	<i>Spirulina</i>	357	[135]
Cd(II)	<i>Fucusceranoides</i>	90	[136]
Cd(II)	<i>Oedogonium</i> h.	88.90	[137]
Pb(II)	<i>Sargassum</i> sp.	303	[138]
Pb(II)	<i>Sargassum</i> sp.	266	[139]
Pb(II)	<i>Spirodela polyrhiza</i> (L.) <i>Schleiden</i> biomass	137	[134]
Pb(II)	<i>Oedogonium</i> h.	145.00	[140]
Pb(II)	<i>Spirogyra</i>	140.00	[141]
Pb(II)	<i>Nostoc</i>	93.50	[140]
Zn(II)	<i>Ulva onoi</i>	74.6	[131]
Cu(II)	<i>Sargassum</i> sp.	87.1	[138]
Cu(II)	<i>Spirogyra</i>	133.30	[142]
Cr(VI)	<i>U. lactuca</i> (dry)	10.61	[143]
Cr(VI)	<i>U. lactuca</i> (activated)	112.36	[143]
Cr(VI)	<i>Oedogonium</i> h. (raw)	31	[144]
Cr(VI)	<i>Oedogonium</i> h. (acid activated)	35.2	[144]
Cr(VI)	<i>Nostoc</i>	22.92	[145]
Cr(VI)	<i>Spirogyra</i>	14.70	[146]
Ni(II)	<i>Sargassum</i> sp.	71.6	[147]
Ni(II)	<i>Sargassum</i> (acid treated)	250.00	[148]
Ni(II)	<i>Sargassum</i> (raw)	181.00	[148]
Ni(II)	<i>Oedogonium</i> h. (acid treated)	44.20	[149]
Ni(II)	<i>Oedogonium</i> h. (raw)	40.90	[149]

wheat based biomass have demonstrated high biosorption capacity as is seen in Table 1. Research studies have demonstrated high carbon, low ash content and reasonable hardness in such biosorbents. Researchers have also identified the presence of different components and features in such biomass which have been contributory to the uptake of heavy metal ions from aqueous solutions [27, 30, 31]. Cellulose, hemicelluloses and lignin were found to be the major components in rice and wheat based products but the proportion of such components was found to vary in each [163, 164, 165]. Rice based biomass showed a proportion of 32.24% cellulose, 21.34% hemicelluloses, 21.44% lignin whereas wheat based biomass revealed 39% cellulose, 35% hemicelluloses and 14% lignin [173-175]. Basso et al and Qaiser et al have proved that cellulose has good metal uptake properties [176, 177]. The presence of cellulose and hemicelluloses in agricultural and plant biomass has thus improved their biosorption potential. Other agricultural precursors like tea, coffee, shells, nuts and seeds of various fruits, etc. were found to have cellulose, hemicelluloses and lignin [177, 178]. Researchers have made elaborate studies via techniques like Fourier transform infrared (FT-IR) and Raman spectroscopy,

electron dispersive spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), electron microscopy (scanning and/or transmission), nuclear magnetic resonance (NMR), X-ray diffraction analysis (XRD) on various biosorbents like *moringaoleifera* bark [95], *rhizophora apiculata* tannin [83], rice husk ash [90], raw coffee powder [55], hazel nut shell [97], peanut hull pellet [78], mango peel [50], etc. in order to elucidate the mechanism of metal binding onto such biosorbents. Different functional groups like carbonyl (ketone), carboxyl, sulfhydryl (thiol), sulfonate, thioether, amine, alcohols, esters, etc. were identified. Such functional groups were able to bind with metal ions through replacement of hydrogen ions with metal ions in solution or by donation of an electron pair from these groups to form complexes with metal ions in solution. The mechanism identified were thus chemisorption, complexation, ion exchange, chelation, physical adsorption [177, 178]. Sawdust of various tree species in its virgin form revealed a cellulose-lignin polymeric structure as illustrated by Shukla et al. [159]. The analysis of surface properties showed that the metal binding sites were mainly composed of phenolic and alcohol hydroxyl.

2.2. Microbial Materials as Metal Biosorbents

The efficiency and the mechanism of the uptake of metal ions onto the microbes depend on the cellular surface of the microbes [23]. This is because the biosorption is a surface phenomenon. The mechanism of metal binding as documented by various reviews involves the interaction and exchange of metal ions followed by complex formation with the metal ions on the reactive chemical sites on the surface of the microbial cell followed by ion [29-31, 171, 172]. This is finally followed by precipitation of excess metal ions on the cell surface. The components of the cell wall are known to vary among the different microbes. Keeping in view the role of microbial cell wall in the biosorption of metal ions, a critical analysis on the cell wall components of different microorganisms would help in assessing and explaining the different metal uptake capacity as observed in different microbial community [172]. All species of bacteria have a cell wall composed of a linear polymer called the peptidoglycan. It accounts for 40-90% of the bacterial cell wall [150]. The core of the peptidoglycan is multilayered containing a peptide cross bridge while the adjacent glycan units are cross linked via amino acids like D-glutamic acid, D-alanine, and meso-di-aminopimelic acid. Cross-bridging between the peptide chains is a common feature of the bacterial cell wall. The frequency of cross bridging is close to 100% as in *Staphylococcus aureus* whereas it is 30% in a gram negative bacteria like *E-Coli*. The cross bridging is nearly absent in many gram negative bacteria. The peptidoglycan in gram positive bacteria also contains large amounts of teichoic acids, polymers of glycerol or ribitol joined by phosphate groups. Whereas the peptidoglycan cell wall in gram negative bacteria is composed of phospholipids, lipopolysaccharides, enzymes, glycoproteins and lipoproteins. Such components of the bacterial cell wall were found to be actively involved as metal binding sites [179]. The glycoproteins and lipoproteins were found to play a contributory role in Cd^{2+} ion uptake of both gram negative and gram positive bacteria [116]. Some of the other potential metal binding sites on the cell wall were found to be lipoproteins, teichoic acid, teichouronic acid, peptidoglycan, amino, carboxylate, phosphoryl groups of phospholipids, etc. Extensive studies as reviewed [150] have demonstrated the role of such groups on the bacterial cell in the binding sites of metal cations [150]. Fungal cell wall is rigid and is composed of approximately 80-90% chitin which is a nitrogen containing polysaccharide [151, 152]. Proteins, lipids, polyphosphates and inorganic ions are also constituents of the fungal cell wall [180]. Cellulose is the principal component of all classes of algae [156, 157, 179]. Sulphated polysaccharides are present in the cell wall of both brown and red algae but is absent in green algae. A higher proportion of proteins are bonded to the polysaccharides in the cell wall of green algae. The cell wall of brown algae contains alginic acid and the corresponding salts of sodium, potassium, magnesium and calcium [179]. Thus the potential metal binding sites on the bacterial cell wall are the peptidoglycan, teichoic acids and lipoteichoic acids. Whereas chitin, proteins and phosphates are the principal active sites on the fungal cell wall, cellulose, alginate and glycan in algal cell wall proved to play a very important role in metal binding [179].

3. Biosorption Mechanism

Due to the complex nature of the cell wall of the microbial biomass, the mechanism of the biosorption process is not well understood. The process can take place via many mechanisms depending on the speciation of the metal ion, the source of biomass and its processing to biosorbent [29-31, 171, 172]. Various reviews have highlighted that metal binding to the microbial cell wall follows complex mechanisms like the ion exchange, chelation and adsorption. This can be followed by the deposition of metal ion in the inter- and intra-fibrillar capillaries and spaces of the structural polysaccharide or peptidoglycan network as a result of the concentration gradient and diffusion through cell walls and membranes. With the help of sophisticated techniques like the Fourier transform infrared (FT-IR) and the Raman spectroscopy, nuclear magnetic resonance spectroscopy (NMR), electron spin resonance (ESR) spectroscopy, and X-ray absorption spectroscopy (XAS), which includes X-ray absorption near-edge (XANES) and extended X-ray fine structure (EXAFS) spectroscopy, and X-ray reflectivity, researchers have identified the key functional groups present in the biomass cell surface in the biosorption process [50, 51]. These are the hydroxyl groups of polysaccharides, sulphated polysaccharides, uronic acids and the amino acids, the ketone group in peptide bonds, carboxyl groups in uronic acid and amino acid, sulphhydryl (thiol) group in sulphated polysaccharides, thioethers and amines in amino acids, imine and imidazole in amino acids, phosphonate in phospholipids, and phosphordiester in teichoic acid and lipopolysaccharides [30, 179-181]. A review of the acidity constants of such functional groups reveals that the biomass surface charge is predominantly negative at pH 3-10. This has been verified by Volesky and Holan [30]. Over this entire pH range, the ligands of each such group identified as the O, S, N and P were known to easily bind with the cationic metals ions facilitating electrostatic interactions. The biosorbent behavior for metallic ions is thus a function of the chemical make-up of the microbial cells of which it consists as verified by the works of Volesky and Holan [30]. But the presence of favourable functional groups on the microbial cell wall does not guarantee the binding of metal ions because steric, conformational and other external factors could be operative. The pH of the aqueous medium is known to affect the biosorption process and the operative underlying mechanisms; thereby affecting the capacity of the biomass for metal uptake [158]. The metal adsorbates undergo ionization as well as there is a change in solubility as a result of the pH of the aqueous medium. The functional groups on the biomass surface too undergo protonation and deprotonation as a result of the increased acidity or basicity of the aqueous medium. Thus at higher solution pH, the solubility of metal ions decreases leading to precipitation and complication of the biosorption process. Also, as a result of the protonation of the functional groups on the biomass surface, more protons are released resulting in lowering of pH in aqueous medium. Excess protons too results in increased competition with the metal cations and subsequent lesser biosorption. It is thus essential to maintain a constant pH during the biosorption process as maximum and faster uptake takes place in the initial phases. An exhaustive review of literature reveals that irrespective of the biomass type and source, the pH at which

maximum biosorption occurs depends on the speciation of metal ion at that pH. Ni(II), Cd(II), Pb(II) and Zn(II) are known to exist in their bivalent form at pH values of ≤ 6.5 , 8, 7 and 8 respectively. Perusal of literature revealed that maximum biosorption of such metal ions occurred for Ni(II), Cd(II), Pb(II) and Zn(II) at pH values of 5-7, 6-7, 5-7 and 4-8 respectively [182]. Optimum pH for Cr(VI) occurred at pH 1-5, due to the strong electrostatic interaction with the HCrO_4^- species.

4. Design of Better Biosorbents

The biosorption process is typically a surface phenomenon in which the cell wall components of the biomass have a direct involvement, as discussed earlier. The use of biosorbents in their native form has demonstrated various shortfalls on account of their low biosorption capacity as well as variable physical stability [169, 170, 183]. Various researchers have focused on modifying the biomass surface via chemicals so as to achieve both structural durability as well as efficient biosorption capacity for heavy metal ions. Results with respect to the maximum biosorption capacity have been promising not only with the plant based biomass but also with microbial biomass. This is revealed from data presented in Table 1 [34-38, 49, 50, 54, 58, 59, 63, 74, 75, 87, 88, 92, 93, 98] and Table 2 [131, 143, 144, 148, 149]. Analyses and reviews have revealed that surface modification of biomass have brought about significant changes in their hydrophobicity, water sorbency, ion exchange capability, resistance to microbiological attack and thermal resistance. Methods employed for modification of cell surface are the physical pre-treatments which include heating/boiling, freezing/thawing, drying, autoclaving and lyophilization. The chemical treatments used for surface modification by various workers have been identified as washing with detergents, alkaline solutions (sodium hydroxide, calcium hydroxide, sodium carbonate) mineral and organic acid solutions (hydrochloric acid, nitric acid, sulphuric acid, tartaric acid, citric acid, thioglycolic acid), organic compounds (ethylenediamine, formaldehyde, epichlorohydrin, methanol), oxidizing agent (hydrogen peroxide), etc. Such pre-treatments helped in modifying the surface functional groups either by removing or masking the groups or by exposing more metal binding sites. Amination of hydroxyl and carboxyl group, carboxylation and phosphorylation of hydroxyl group, carboxylation of amine group, saponification of ester group, sulfonation, xanthanation, thiolation, halogenation, oxidation, etc. have resulted in enhancement of biosorptive efficiency. This has been corroborated by earlier works of Vieira and Volesky [184]. Various biomasses irrespective of their source like pine bark, Spirogyra, rose petals, rubber leaves, walnut shell and sawdust showed promising biosorption capacities with alkaline pre-treatment. [185-190]. Calcium oxide pre-treatment provided strong basic sites on the surface of date pit (*Phoenix dactylifera*) causing higher biosorption for positively charged Cu(II) and Ni(II) from aqueous suspension [191]. Another factor responsible for higher biosorption capacity of the pretreated biosorbents was its greater mesoporous surface area of $645.5 \text{ cm}^2/\text{g}$. KOH proved to be the most promising alkaline activating agent in producing efficient biosorbents for Ni(II) and Zn(II) from bamboo as investigated by Lalhrualtuang et al. [192].

KOH pre-treatment have resulted in the incorporation of favourable functional groups but also have helped in the increase in micropore volume and increase in surface area. In yet another example, alkali modified rice husk showed faster kinetics as well as higher biosorption for Cd(II) than the virgin rice husk [35]. The higher biosorption of modified rice husk (125.94 mg/g) was attributed to the surface structural changes of the biosorbent. Acid treatment too has resulted in the better biosorption behaviors of the biosorbents. For example, rice husk was modified by various organic acids like citric acid, salicylic acid, tartaric acid, oxalic acid, mandelic acid, maleic and nitrilotriacetic acid and were tested for biosorption of lead and copper. Tartaric acid modified rice husk demonstrated highest binding capacity but when the same biosorbent was esterified, it resulted in lesser biosorption for the same metal ions. The maximum adsorption capacities for Pb(II) and Cu(II) were reported to be 108.0 and 29.0 mg/g, respectively [74]. But some researchers have observed a change in surface texture due to acid pre-treatment which in turn has helped in improving the biosorption performance. H_2SO_4 treated wheat bran [72] showed better biosorption for Cu(II) (51.5 mg/g at pH 5 and contact time 30 mins) due to increase in its surface area. It was postulated that there was a significant conversion of macropores to micropores resulting in higher surface area as a result of the acid treatment. In yet another example, acid pre-treatment resulted in oxidation of existing functional groups on corncob based biosorbent resulting in decrease of surface area and surface volume [193]. Improved biosorption performance due to acid pre-treatment is also observed due to incorporation of acidic functional groups [189, 194]. Irrespective of the behavior to metal ions, various biomasses have shown better biosorption tendency as a result of chemical modification. Sha et al. [49] demonstrated that under identical conditions of pH and contact time, chemically modified orange peel was a better biosorbent showing a capacity of 70.67 mg/g and 136.05 mg/g for Cu(II) and Cd(II) removals than its unmodified counterpart. Sawdust of *Pinus sylvestris* pre-treated with formaldehyde showed enhanced biosorption for the removal of Cd(II) and Pb(II) from aqueous solutions [195]. HCl treated sawdust of Mulberry showed a maximum biosorption capacity of 403.73 mg/g for Cd(II) ions at pH of 6 after a 30 min shaking [196]. Different complexing groups like the aminoalkyl [197], 2,2-diaminoethyl, and amidoxime [198], or an ionic moiety such asphosphate [199], thiolate [200], carboxy [201], and carboxymethyl [202, 203] were also used for modification of various biomass so as to enhance their biosorption for heavy metal ion. Observations of improved biosorption capacity are seen in the case of chemically treated algal species of *Ulva onoi* [131], *U. lactuca* [143], *Oedogonium h.* [144] and *Sargassum* [148]. Fungal species have shown better metal uptake capacity by alkali treatment whereas acid treatment of the same biomass almost had no influence on metal biosorption [183, 203]. Biomass of yeast treated with ethanol recorded highest biosorption for Cd(II) and Pb(II) as compared to that treated with NaOH [204]. Similarly, calcium chloride treated biomass of brown alga *F. vesiculosus* demonstrated highest biosorption for the removal of copper, cadmium, lead and nickel [205]. Thus it can be concluded that the functional groups present on the biomass have favoured the formation of hydrophilic and polar surface thereby facilitated the uptake or binding of the cationic metal ions.

Besides the direct chemical modification, literature reveals the grafting of various monomeric units like acrylic acid, acrylamide, acrylonitrile, ethylenediamine, hydroxylamine, glycidyl monomers, urea, etc. followed by functionalization of the biomass surface so as to develop a better biosorbent [206-209]. Graft co-polymerization is a process in which an additional polymer is introduced into the backbone of the main polymeric chain. Literature reveals that the long polymeric chain of the biomass has been activated via high energy radiation, photochemical or by chemical so as to initiate the process of polymerization or grafting. Various studies have already been carried out in this direction. Details on the preparation of efficient grafted biosorbents and their effects on the metal binding capacity are outlined by O'Connell *et al.* [170]. In a typical example, Grey *et al.* [210] developed an efficient biosorbent via succinic anhydride grafted wood pulp which showed a biosorption capacity of 169 mg/g for Cd(II). Wood sawdust was grafted via acrylonitrile and hydroxylamine and the resulting biosorbents brought about a binding capacity of 246 mg/g for Cu(II) and 188 mg/g for Ni(II) respectively [211]. Acrylamide, ethylenediamine and succinic anhydride used as grafting agents helped in designing a better biosorbent from banana stalk by Shibi and Anirudhan [212] for removal of Hg(II) from waste streams. Grafting of acrylic acid was also done on the surface of ozone pretreated *P. chrysogenum*. The developed biosorbent showed significant increase in the binding of for copper and cadmium. It was postulated that the higher biosorption was due to the presence of a large number of carboxyl groups present on the biomass surface and such groups were converted to carboxylate ions using NaOH [213].

Metal biosorption has also been enhanced by heat or chemical sterilization or by crushing. The use of such processes have helped in increasing the available surface area, thereby resulting in greater exposure of the biomass surface and more surface binding sites [214]. The use of microwave assisted chemical activation of various agricultural biomasses like orange peel, sunflower seed etc. [215] has resulted in development of refined porous properties and better

surface chemistry [216]. Such biosorbents showed significantly higher biosorption for metal ions [217, 218].

5. Regeneration of the Biosorbent

The recycling and reuse of the biosorbent for subsequent removal of metal ions from aqueous medium contributes to the economic viability of the biosorption process. A desirable factor is that the desorbing medium used for regeneration of the biomass should not damage the biosorbent. Besides, the loaded metals onto the surface of the biomass after biosorption are recovered. Literature reveals that chemicals like acids like HCl, bases like NaOH and chelating agents like EDTA have been used for desorption of metal ions along with simultaneous regeneration of the loaded biosorbent (Table 3). HCl is widely used as a desorbing chemical bringing about greater than 90% recovery of metal ions, yet various researches has proved that it brings about simultaneous hydrolysis of the functional groups present on the biomass. This would result in loss of biosorption efficiency of the regenerated biosorbent [220]. A detailed observation of Table 3 also highlights the fact that metal ions like Cd(II), Pb(II), Cu(II) Hg(II) can be eluted via acidic medium thereby proving beyond doubt that a basic medium would enhance the biosorption potential of the biomass. This corroborates our earlier conclusion about the effect of pH on the biosorption potential. Cr(VI) and Ni(II), on the other hand could be desorbed using a basic medium as evident from the Table 3 thereby indicating the requirement of an acidic pH for maximizing biosorption. Table 3 thus highlights the fact that the desorbing medium required for maximum recovery of metals is dependent on the metal ions to be recovered but is independent of the biosorbent type and its source. From such observations, it can be concluded that the mechanism underlying the biosorption of metal ions is same irrespective of the nature, type and source of biosorbent. An ion exchange mechanism is operative during the metal uptake process

Table 3. Desorption of Metal Ions and Regeneration of the Biosorbents

Metal ions	Desorption medium	Biosorbent	Source of biomass	Cycle	Metal recovery (%)	Reference
Cd(II)	0.1 M HCl	Rice husk	Cellulose based	1	98.6	[35]
Cd(II)	0.1 M HCl	Baker's yeast	Microbial based	6	95.0	[125]
Cd(II)	0.1 M HCl	<i>Oedogonium Sp.</i>	Microbial based	5	84.8	[137]
Hg(II)	0.2 M HCl	Coir pith	Cellulose based	4	98.3	[48]
Hg(II)	0.2 M HCl	Coconut button	Cellulose based	3	96.5	[222]
Ni(II)	0.1 M NaOH	<i>Oedogonium Sp.</i>	Microbial based	4	70.0	[148]
Cr(VI)	0.1 M NaOH	<i>Oedogonium Sp.</i>	Microbial based	4	75.0	[144]
Cr(VI)	0.1 M NaOH	<i>Mucor hiemalis</i>	Microbial based			[128]
Cr(VI)	NaOH	Wheat bran	Cellulose based	1	100	[60]
Cr(VI)	0.1 M EDTA	<i>Nostoc muscorum</i>	Microbial based	5	90.0	[145]
Pb(II)	0.1 mol/L HCl	Nostoc	Microbial based	5	90.0	[140]
Pb(II)	0.1 mol/L HCl	<i>Oedogonium</i>	Microbial based	5	90.0	[140]
Pb(II)	0.1 M HCl	Baker's yeast	Microbial based	6	95.0	[125]
Pb(II)	Na ₂ EDTA	<i>Sargassum</i>	Microbial based	-	95.0	[139]
Pb(II)	0.2 mol/L HCl	Coconut button	Cellulose based	3	94.3	[219]
Cu(II)	0.2 mol/L HCl	Coconut button	Cellulose based	3	97.4	[219]

as has been discussed in our earlier work [182]. More than 70% recovery of metal ions along with the use of biosorbent for a continuous sorption/desorption for removal of metal ions from waste streams as evident from Table 3 highlights the economy of the biosorption process. But although desorption via chemicals results in regeneration of the biosorbent along with recovery of the metal ions, yet it results in higher investment cost.

6. Future Prospects

Biosorption of metal ions has been extensively studied as evident from innumerable research papers. The performance of the several biosorbents were reviewed and summarized; the major features are high versatility for wide-range of operational conditions, high selectivity for metal and not influenced by alkaline earth and common light metals, independent of concentration (for ≤ 10 ppm or ≥ 100 ppm), high tolerance to organics, and effective regeneration. According to Wang and Chen [179], biosorption is a cost-effective technology for the treatment of complex industrial wastewater containing high volume and low-concentration heavy metals. Many natural biosorbents both from cellulosic based and microbial origin having efficient biosorption characteristics have been identified. But many of such biosorbents have shown poor performance. Surface modifications carried out on such biosorbents helped improve their metal binding properties as evident from vast studies carried out but the modifications increase the overall cost of the process bringing it closer to the price of commercial ion-exchange resins. Also, there are instances, when the incorporation of functional groups as a result of chemical modification does not result in enhanced biosorption which might be due to steric, conformational or other effects. In spite of such short comings, both native as well as modified biosorbents have demonstrated their compatibility when tested with real industrial effluents. Faster kinetics and better performance under both laboratory as well as real effluent conditions as compared to commercial ion exchange resins and adsorbents are the major advantages of the biosorbents for removal of heavy metals, but the application of such biosorbents for industrial scale has not yet become a reality. It is well known that the biosorption process does not have competition with any of the other metal removal technologies like ion exchange, reverse osmosis, precipitation, etc. [30, 221]. Also, a huge market exists for cheap and efficient biosorbents due to the continuous discharge of complex metal effluents from industrial activities and simultaneous ever increasing environmental regulations. Earlier works have indicated the development of some commercial biosorbents by immobilization techniques. For example, AlgaSORB™ was developed by immobilization of *C. vulgaris* in silica and polyacrylamide gels [222] AMT-BIOCLAIM™ similarly comprised of *Bacillus subtilis* immobilized onto polyethyleneimine and glutaraldehyde. The biosorbent Bio-fix was made up of a variety of biomass including Sphagnum peat moss, algae, yeast, bacteria, and/or aquatic flora and immobilized onto high density polysulphone. Similarly a series of biosorbents were produced based on different types of biomaterial, including the algae *S. natans*, *A. nodosum*, *Halimeda opuntia*, *Palmyra pamata*, *Chondrus crispus* and *C. vulgaris*. The preparation of such commer-

cial biosorbents and their performance has been adequately reviewed by eminent researchers [31, 171, 222]. Such biosorbents showed effective metal removal over a wide pH range and solution conditions and could remove a wide range of metal ions. The biosorption process was not affected by the presence of calcium, magnesium and organics. Moreover the biosorbents resembled ion exchange resins. Very high biosorption capacity was demonstrated by such commercial biosorbents [222]. Although extensive efforts were made for the commercialization of the biosorption technology, yet it did not attract widespread industrial adoption. Certain factors inhibiting the widespread industrial application of the biosorption technology as identified by various researchers [30, 31, 150, 171, 179, 220, 222] working in this field include:

- a. difficulty in obtaining a reliable supply of inexpensive raw biomass
- b. Lower robustness of the biosorbents
- c. Non specificity and non selectivity of the biosorbents to the metal mixture solutions
- d. difficulty in regeneration and reuse of the biomass
- e. negative effects of co-existing ions on biosorptive capacity

Thus the following features need to be assessed prior to industrial application:

1) Effluent characteristics :

Biosorption of metal ions is strongly affected by the properties of the water to be treated, such as pH, ionic strength, coexisting ions, and suspended solids. An optimal pH of 7 is required for biosorption of metal cations. The biosorption decreases on lowering the pH, as acidic media tend to cause protonation of negatively charged sites on the biosorbents. pH of the aqueous media play a definite role in affecting the biosorption behavior to metal cations as the hydrogen ion itself is a tough competitor [223]. Industrial wastewater contains more than one type of metal ions and the competition between such metal ions for the limited binding sites on biosorbents tends to decrease the biosorption. The presence of Ca, Mg in hard water and Al, Fe in industrial effluents too may retard biosorption of the target heavy metal pollutants [220]. Also, the industrial waste water tends to have many organic moieties which may hinder the biosorption process. Thus, the performance of the biosorbents needs to be assessed in not only a single-metal solution system but also multi-metal and multi-pollutant solution systems prior to their industrial applications [30]. This evaluation would clarify at the same time the selectivity of the biosorbents in metal binding.

2) Biosorbent characteristics (like availability, overall manufacturing cost, regenerability and reusability, pollutant specificity, biosorptive capacity and rate, mechanical stability, etc.) :

The large scale availability of the biosorbent at one particular location, collection, development and finally transportation to the wastewater treatment site are some of the important criteria for economical viability and usability. Agricultural waste by-products like rice husk etc have shown good metal biosorption capacity. But their usage as biosorbent in industries would warrant not only their availability in tones per day but also their continuous

supply. Food processing industries could be a possible alternative for production of agricultural waste by-products. Although microbial biomass like algae, fungi and bacterial strains showing modest biosorption capacity are naturally available but their large scale production is expensive. Continuous supply of filamentous fungi and yeast for industrial application as biosorbent can be made possible from large-scale fermentation industries. Irrespective of their origin, the biosorbents require some modifications before their application into the real wastewater treatment systems. Modification of the virgin biosorbent materials not only helps to impart mechanical strength and resistance to chemical and microbial degradation but also improves biosorption capacity and selectivity for target metal pollutants. Physical or chemical modifications, grafting techniques as well as immobilization techniques as demonstrated by various research groups have been successful in enhancing the physico-chemical characteristics of the biosorbents. But such techniques will obviously increase operational costs making it unrealistic for industrial applications. Regeneration and reuse of the biosorbents for further biosorption of metal ions will definitely make the process more cost effective on an industrial scale. Dilute acid and alkaline solutions, salt solutions, and chelating agents such as ethylene-diammine-tetraacetic acid (EDTA) solution are reported to be effective in eluting metals from the metal-laden biosorbents.

Keeping in focus the inhibitions of the biosorption technology for its adoption in large scale wastewater treatment, the future prospects look promising on account of two considerations. Firstly, hybrid technologies comprising various processes like biosorption, bioreduction, bioprecipitation, electrochemical processes, membrane technology etc may be helpful for treating complex industrial wastewater in a large-scale and also for simultaneous removal of organic substances and heavy metal ions in solution. Novel biosorbents having increased robustness and increased specificity need to be developed. This could be achieved by immobilization technique and by optimization of process parameters. Various researchers have also suggested the development of a better biosorbent from various biomasses [220, 223]. More efforts should be made in the direction of reuse and recycling of the biosorbent.

7. Conclusions

Biosorption process is thus identified as basically an exchange of ions where the metal species in aqueous medium is exchanged for a counter ion attached to the biomass. The promising potential of the biosorption technology undoubtedly relies on the efficiency of the various microbial and plant based biomass. Various biomasses which are available in plenty and exhibiting good metal binding characteristics have been identified. A detailed study of literature has revealed the contributory role of active binding sites on the peptidoglycan and polysaccharides components of the cell wall of the biomasses. Besides, the higher metal uptake, the technology has numerous other advantages like faster kinetics, high metal binding over a broad range of pH, temperature and low capital and operation cost. Various publications have amply proposed it as a cost effective, green and effective technology which can be used complementarily with other traditional metal removal tech-

nologies like chemical precipitation, reverse osmosis, membrane technologies etc. Despite the market requirement for cheaper and greener treatment technologies and despite the major advantages of the biosorption technology, it has extremely limited industrial adoption even when used in conjunction with other conventional treatment approaches. The presence of multi functional groups on the biomass surface is responsible for its non selectivity to a particular metal ion. This non selective, non specific nature of the biosorbent and lower robustness of the technology is a major hindrance to its commercialization. Although immobilization and granulation has helped in increasing the robustness and further problems related to separation, yet the non-specific nature of the biosorbent is not yet been addressed. Future research directions of the biosorption technology relies on the identification and designing of better and more selective biosorbents, more development of biosorption models and identification of biosorption mechanisms, and further assessments of the costs of development.

Acknowledgement

Authors are thankful to the Department of Science and Technology, New Delhi, India, for the financial support under project grant DST/INT/South Africa/P-03/2014.

References

1. Celik A, Demirbas A. Removal of heavy metal ions from aqueous solutions via adsorption onto modified lignin from pulping wastes. *Energ. Source*. 2005;27:1167-1177.
2. International occupational safety and health information centre. Metals. In: Basics of chemical safety, Chapter 7. Geneva: International labour organization (ILO); 1999.
3. Gonzalez AR, Ndung'u K, Flegal AR. Natural occurrence of hexavalent chromium in the Aromas red sands aquifer, California. *Environ. Sci. Technol*. 2005;39:5505-5511.
4. Boening DW. Ecological effects, transport, and fate of mercury: a general review. *Chemosphere* 2000;40:1335-1351.
5. Hetherington LE, Brown TJ, Benham AJ, Lusty PAJ, Idoine NE. World mineral production 2001-2005. Nottingham: Nottingham British Geological Survey; 2007.
6. Forray FL, Hallbauer DK. A study of the pollution of the Aries River (Romania) using capillary electrophoresis as analytical technique. *Environ. Geol*. 2000;39:1372-1384.
7. Kotas J, Stasicka Z. Chromium occurrence in the environment and methods of its speciation. *Environ. Pollut*. 2000;107:263-283.
8. World health organization (WHO). Copper in Drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality. 2004.
9. Juttner K, Galla U, Schmieder H, Electrochemical approaches to environmental problems in the process industry. *Electrochim. Acta* 2000;45:2575-2594.
10. Yang XJ, Fane AG, McNaughton S. Removal and recovery of heavy metals from wastewater by supported liquid membranes. *Water Sci. Technol*. 2001;43:341-348.
11. Bose P, Bose MA, Kumar S. Critical evaluation of treatment

- strategies involving adsorption and chelation for wastewater containing copper, zinc, and cyanide. *Adv. Environ. Res.* 2002;7:179-195.
12. Wingenfelder U, Hansen C, Furrer G, Schulin R. Removal of heavy metals from mine water by natural zeolites. *Environ. Sci. Technol.* 2005;39:4606-4613.
 13. Dobrevsky I, Todorova-Dimova M, Panayotova T. Electroplating rinse wastewater treatment by ion exchange. *Desalination* 1997;108:277-280.
 14. Korngold E, Belayev N, Aronov L. Removal of chromates from drinking water by anion exchangers. *Sep. Purif. Technol.* 2003;33:179-187.
 15. Ahmed S, Chughtai S, Keane MA. The removal of cadmium and lead from aqueous solution by ion exchange with Na-Y zeolite. *Sep. Purif. Technol.* 1998;13:57-64.
 16. Cheng RC, Liang S, Wang HC, Beuhler MD. Enhanced coagulation for arsenic removal. *J. Am. Water Works Assoc.* 1994;86:79-90.
 17. Edwards M. Chemistry of arsenic removal during coagulation and Fe-Mn oxidation. *J. Am. Water Works Assoc.* 1994;86:64-78.
 18. Wang LK, Fahey EM, Wu ZC. Dissolved air flotation. In: Wang LK, Hung YT, Shammass NK, eds. *Physicochemical treatment processes*. New Jersey: Humana Press; 2004. p. 431-500.
 19. Matis KA, Zouboulis AI, Gallios GP, Erwe T, Blöcher C. Application of flotation for the separation of metal-loaded zeolite *Chemosphere* 2004;55:65-72.
 20. Chakravarti AK, Chowdhury SB, Chakrabarty S, Chakrabarty T, Mukherjee DC. Liquid membrane multiple emulsion process of chromium(VI) separation from wastewaters. *Colloids Surf. A Physicochem. Eng. Aspects.* 1995;103:59-71.
 21. Kongsricharoen N, Polprasert C. Chromium removal by a bipolar electrochemical precipitation process. *Water Sci. Technol.* 1996;34:109-116.
 22. Dabrowski A. Adsorption – from theory to practice. *Adv. Colloid Int. Sci.* 2001;93:135-224.
 23. Volesky B. Detoxification of metal-bearing effluents: biosorption for the next century. *Hydrometallurgy* 2001;59:203-216.
 24. Aksu Z. Application of biosorption for the removal of organic pollutants: a review. *Process Biochem.* 2005;40:997-1026.
 25. Stasinakis AS, Thomaidis NS. Fate and biotransformation of metal and metalloid species in biological wastewater treatment processes. *Crit. Rev. Environ. Sci. Technol.* 2010;40:307-364.
 26. Tsezos M. Biosorption of metals. The experience accumulated and the outlook for technology development. *Hydrometallurgy* 2001;59:241-243.
 27. Ahluwalia SS, Goyal D. Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresour. Technol.* 2007;98:2243-2257.
 28. Ahemad M, Malik A. Bioaccumulation of heavy metals by zinc resistant bacteria isolated from agricultural soils irrigated with wastewater. *Bacteriology J.* 2011;2:12-21.
 29. Volesky, B. Biosorption and me. *Water Res.* 2007;41:4017-4029.
 30. Volesky B, Holan ZR. Biosorption of heavy metals. *Biotechnol. Prog.* 1995;11:235-250.
 31. Volesky B. Introduction. In: Volesky B, eds. *Biosorption of heavy metals*. Boca Raton: CRC press; 1990. p. 3-5.
 32. Volesky B. Removal and recovery of heavy metals by biosorption. In: Volesky B, eds. *Biosorption of heavy metals*. Boca Raton: CRC press; 1990. p. 8-43.
 33. Volesky B. Advances in biosorption of metals: selection of biomass types. *FEMS Microbiol. Rev.* 1994;14:291-302.
 34. Ajmal M, Rao RAK, Anwar S, Ahamad J, Ahmad R. Adsorption studies on rice husk: removal and recovery of Cd(II) from wastewater. *Bioresour. Technol.* 2003;86:147-149.
 35. Akhtar M, Iqbal S, Kausar A, Bhangar MI, Shaheen MA. An economically viable method for the removal of selected divalent metal ions from aqueous solutions using activated rice husk. *Colloids Surf. B Biointerfaces* 2010;75:149-155.
 36. Ye H, Zhu Q, Du D. Adsorptive removal of Cd(II) from aqueous solution using natural and modified rice husk. *Bioresour. Technol.* 2010;101:5175-5179.
 37. Kumar U, Bandyopadhyay M. Sorption of cadmium from aqueous solution using pretreated rice husk. *Bioresour. Technol.* 2006;97:104-109.
 38. El-Shafey EI. Sorption of Cd(II) and Se(IV) from aqueous solution using modified rice husk. *J. Hazard. Mater.* 2007;147:546-555.
 39. Zulkali MMD, Ahmad AL, Norulakmal NH. Oryza sativa L. husk as heavy metal adsorbent: optimization with lead as model solution. *Bioresour. Technol.* 2006;97:21-25.
 40. Nouri L, Hamdaoui O. Ultrasonication-assisted sorption of cadmium from aqueous phase by wheat bran. *J. Phys. Chem. A* 2007;111:8456-8463.
 41. Farooq U, Khan MA, Athar M, Kozinski JA. Effect of modification of environmentally friendly biosorbent wheat (*Triticum aestivum*) on the biosorptive removal of cadmium (II) ions from aqueous solution. *Chem. Eng. J.* 2011;171:400-410.
 42. Verma B, Shukla NP. Removal of nickel (II) from electroplating industry by agrowaste carbons. *Indian J. Environ. Health* 2000;42:145-150.
 43. Nouri L, Ghodbane I, Hamdaoui O, Chiha M. Batch sorption dynamics and equilibrium for the removal of cadmium ions from aqueous phase using wheat bran. *J. Hazard. Mater.* 2007;149:115-125.
 44. Dang VBH, Doan HD, Dang-Vu T, Lohi A. Equilibrium and kinetics of biosorption of cadmium (II) and copper (II) ions by wheat straw. *Bioresour. Technol.* 2009;100:211-219.
 45. Tan G, Xiao D. Adsorption of cadmium ion from aqueous solution by ground wheat stems. *J. Hazard. Mater.* 2009;164:1359-1363.
 46. Pino GH, Mesquita LMS, Torem ML, Pinto GASP. Biosorption of cadmium by green coconut shell powder. *Miner. Eng.* 2006;19:380-387.
 47. Kadirvelu K, Namasivayam C. Activated carbon from coconut coirpith as metal adsorbent: Adsorption of Cd(II) from aqueous solution. *Adv. Environ. Res.* 2003;7:471-478.
 48. Ho YS, Ofomaja AE. Biosorption thermodynamics of cadmium on coconut copra meal as biosorbent. *Biochem. Eng. J.* 2006;30:117-123.
 49. Sha L, Xueyi G, Ningchuan F, Qinghua T. Adsorption of Cu²⁺ and Cd²⁺ from aqueous solution by mercapto-acetic acid modified orange peel. *Colloids Surf. B Biointerfaces* 2009;73:10-14.
 50. Iqbal M, Saeed A, Zafar SI. FTIR spectrophotometry, kinetics

- and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd^{2+} and Pb^{2+} removal by mango peel waste. *J. Hazard. Mater.* 2009;164:161-171.
51. Memon JR, Memon SQ, Bhangar MI, Zuhra Memon G, El-Turki A, Allen GC. Characterization of banana peel by scanning electron microscopy and FT-IR spectroscopy and its use for cadmium removal. *Colloids Surf. B Biointerfaces* 2008;66:260-265.
 52. Anwar J, Shafique U, Waheed-uz-Zaman, Salman M, Dar A, Anwar S. Removal of $\text{Pb}(\text{II})$ and $\text{Cd}(\text{II})$ from water by adsorption on peels of banana. *Bioresour. Technol.* 2010;101:1752-1755.
 53. Saikaew W, Kaewsarn P, Saikaew W. Pomelo peel: agricultural waste for biosorption of cadmium ions from aqueous solutions. *World Acad. Sci. Eng. Technol.* 2009;56:287-291.
 54. Kahraman S, Dogan N, Erdemoglu S. Use of various agricultural wastes for the removal of heavy metal ions. *Inter. J. Environ. Pollut.* 2008;34:275-284.
 55. Azouaou N, Sadaoui Z, Djaafri A, Mokaddem H. Adsorption of cadmium from aqueous solution onto untreated coffee grounds: Equilibrium, kinetics and thermodynamics. *J. Hazard. Mater.* 2010;184:126-134.
 56. Cay S, Uyanik A, Öz as A. Single and binary component adsorption of copper (II) and cadmium(II) from aqueous solutions using tea-industry waste. *Sep. Purif. Technol.* 2004;38:273-280.
 57. Padmini E, Sridhar S. Effect of pH and contact time on the uptake of heavy metals from industrial effluents by *Pongamia pinnata* Bark. *Asian J. Microbiol. Biotechnol. Environ. Sci.* 2007;9:187-190.
 58. Chen S, Yue Q, Gao B, Xu X. Equilibrium and kinetic adsorption study of the adsorptive removal of $\text{Cr}(\text{VI})$ using modified wheat residue. *J. Coll. Interf. Sci.* 2010;349:256-264.
 59. Farajzadeh MA, Monji AB. Adsorption characteristic of wheat bran towards heavy metal cations. *Separ. Pur. Tech.* 2004;38:197-207.
 60. Singh KK, Hasan HS, Talat M, Singh VK, Gangwar SK. Removal of $\text{Cr}(\text{VI})$ from aqueous solutions using wheat bran. *Chem. Eng. J.* 2009;151:113-121.
 61. Wang XS, Chen LF, Li FY, Chen KL, Wan WY, Tang YJ. Removal of $\text{Cr}(\text{VI})$ with wheat-residue derived black carbon: Reaction mechanism and adsorption performance. *J. Hazard. Mater.* 2010;175:816-822.
 62. Memon JR, Memon SQ, Bhangar MI, El-Turki, A, Hallam KR, Allen GC. Banana peel: a green and economical sorbent for the selective removal of $\text{Cr}(\text{VI})$ from industrial wastewater. *Colloids Surf. B Biointerfaces* 2009;70:232-237.
 63. Babel S, Kurniawan TA. $\text{Cr}(\text{VI})$ removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere* 2004;54:951-967.
 64. Anandkumar J, Mandal B. Removal of $\text{Cr}(\text{VI})$ from aqueous solution using Bael fruit (*Aegle marmelos correa*) shell as an adsorbent. *J. Hazard. Mater.* 2009;168:633-640.
 65. Dubey SP, Gopal K. Adsorption of chromium (VI) on low cost adsorbents derived from agricultural waste material: a comparative study. *J. Hazard. Mater.* 2007;145:465-470.
 66. Pehlivan E, Altun T. Biosorption of chromium (VI) ion from aqueous solutions using walnut, hazelnut and almond shell. *J. Hazard. Mater.* 2008;155:378-384.
 67. Sarin V, Pant KK. Removal of chromium from industrial waste by using eucalyptus bark. *Bioresour. Technol.* 2006;97:15-20.
 68. Basci N, Kocadagistan E, Kocadagistan B. Biosorption of copper (II) from aqueous solutions by wheat shell. *Desalination* 2004;164:135-140.
 69. Wang XS, Li ZZ, Sun C. A comparative study of removal of $\text{Cu}(\text{II})$ from aqueous solutions by locally low-cost materials: marine macroalgae and agricultural by-products. *Desalination* 2009;235:146-159.
 70. Dupont L, Bouanda J, Dumonceau J, Aplingcourt M. Biosorption of $\text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$ onto a lignocellulosic substrate extracted from wheat bran. *Environ. Chem. Lett.* 2005;2:165-168.
 71. Aydın H, Bulut Y, Yerlikaya C. Removal of copper (II) from aqueous solution by adsorption onto low-cost adsorbents. *J. Environ. Manag.* 2008;87:37-45.
 72. Ozer A, Ozer D, Ozer A. The adsorption of copper (II) ions on to dehydrate wheat bran (DWB): determination of the equilibrium and thermodynamic parameters. *Process Biochem.* 2004;39:2183-2191.
 73. Quek SY, Wase DAJ, Forster CF. The use of sago waste for the sorption of lead and copper. *Water Sa.* 1998;24:251-256.
 74. Wong KK, Lee CK, Low KS, Haron MJ. Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions. *Chemosphere* 2003;50:23-28.
 75. Moreno-Piraján JC, Giraldo L. Activated carbon obtained by pyrolysis of potato peel for the removal of heavy metal copper (II) from aqueous solutions. *J. Anal. Appl. Pyrolysis.* 2011;90:42-47.
 76. Iqbal M, Saeed A, Kalim I. Characterization of adsorptive capacity and investigation of mechanism of Cu^{2+} , Ni^{2+} and Zn^{2+} adsorption on mango peel waste from constituted metal solution and genuine electroplating effluent. *Sep. Sci. Technol.* 2009;44:3770-3791.
 77. Zhu CS, Wang LP, Chen W. Removal of $\text{Cu}(\text{II})$ from aqueous solution by agricultural by-product: peanut hull. *J. Hazard. Mater.* 2009;168:739-746.
 78. Johnson PD, Watson MA, Brown J, Jefcoat IA. Peanut hull pellets as a single use sorbent for the capture of $\text{Cu}(\text{II})$ from wastewater. *Waste Manag.* 2002;22:471-480.
 79. Mohammad M, Maitra S, Ahmad N, Bustam A, Sen TK, Dutta BK. Metal ion removal from aqueous solution using physic seed hull. *J. Hazard. Mater.* 2010;179:363-372.
 80. Yao ZY, Qi JH, Wang LH. Equilibrium, kinetic and thermodynamic studies on the biosorption of $\text{Cu}(\text{II})$ onto chestnut shell. *J. Hazard. Mater.* 2010;174:137-143.
 81. Vázquez G, Calvo M, Freire MS, González-Alvarez J, Antorrena G. Chestnut shell as heavy metal adsorbent: optimization study of lead, copper and zinc cations removal. *J. Hazard. Mater.* 2009;172:1402-1414.
 82. Mohan S, Sumitha K. Removal of $\text{Cu}(\text{II})$ by Adsorption Using *Casuarina Equisetifolia* Bark. *Environ. Eng. Sci.* 2008;25:497-506.
 83. Oo CW, Kassim MJ, Pizzi A. Characterization and performance of *Rhizophora apiculata* mangrove polyflavonoid tannins in the adsorption of copper(II) and lead(II). *Ind. Crops Prod.* 2009;30:152-161.

84. Amarasinghe BMWPK, Williams RA. Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. *Chem. Eng. J.* 2007;132:299-309.
85. Parab H, Joshi S, Shenoy N, Lali A, Sarma US, Sudersanan M. Determination of kinetic and equilibrium parameters of the batch adsorption of Co(II), Cr(III) and Ni(II) onto coir pith. *Process Biochem.* 2006;41:609-615.
86. Bhatnagar A, Minocha AK, Sillanpää M. Adsorptive removal of cobalt from aqueous solution by utilizing lemon peel as biosorbent. *Biochem. Eng. J.* 2010;48:181-186.
87. El-Shafey EI. Removal of Zn(II) and Hg(II) from aqueous solution on a carbonaceous sorbent chemically prepared from rice husk. *J. Hazard. Mater.* 2010;175:319-327.
88. Zabihi M, Ahmadpour A, Asl AH. Removal of mercury from water by carbonaceous sorbents derived from walnut shell. *J. Hazard. Mater.* 2009;167:230-236.
89. Anirudhan TS, Divya L, Ramachandran M. Mercury (II) removal from aqueous solutions and wastewaters using a novel cation exchanger derived from coconut coir pith and its recovery. *J. Hazard. Mater.* 2008;157:620-626.
90. Naiya TK, Bhattacharya AK, Mandal S, DasSK. The sorption of lead(II) ions on rice husk ash. *J. Hazard. Mater.* 2009;163:1254-1264.
91. Bulut Y, Baysal Z. Removal of Pb(II) from wastewater using wheat bran. *J. Environ. Manage.* 2006;78:107-113.
92. Kadirvelu K, Namasivayam C. Agricultural by-product as metal adsorbent: Sorption of lead(II) from aqueous solution onto coirpith carbon. *Environ. Technol.* 2000;21:1091-1097.
93. Zuorro A, Lavecchia R. Adsorption of Pb(II) on spent leaves of green and black tea. *Am. J. Appl. Sci.* 2010;7:153-159.
94. Boudrahem F, Aissani-Benissad F, Ait-Amar H. Batch sorption dynamics and equilibrium for the removal of lead ions from aqueous phase using activated carbon developed from coffee residue activated with zinc chloride. *J. Environ. Manage.* 2009;90:3031-3039.
95. Reddy DHK, Seshaiha K, Reddy AVR., Rao MM, Wang MC. Biosorption of Pb²⁺ from aqueous solutions by *Moringa oleifera* bark: equilibrium and kinetic studies. *J. Hazard. Mater.* 2010;174:831-838.
96. Sekhar MC. Removal of lead from aqueous effluents by adsorption on coconut shell carbon. *J. Environ. Sci. Eng.* 2008;50:137-140.
97. Pehlivan E, Altun T, Cetin S, Bhangar MI. Lead sorption by waste biomass of hazelnut and almond shell. *J. Hazard. Mater.* 2009;167:1203-1208.
98. Subbaiah MV, Vijaya Y, Kumar NS, Reddy AS, Krishnaiah A. Biosorption of nickel from aqueous solutions by *Acacia leucocephala* bark: Kinetics and equilibrium studies. *Colloids and Surf. B Biointerfaces* 2009;74:260-265.
99. Ajmal M, Rao RAK, Ahmad R, Ahmad J. Adsorption studies on Citrus reticulata (fruit peel of orange): removal and recovery of Ni(II) from electroplating wastewater. *J. Hazard. Mater.* 2000;79:117-131.
100. Bhatnagar A, Minocha AK. Biosorption optimization of nickel removal from water using Punica granatum peels waste. *Colloids and Surf. B Biointerfaces* 2010;76:544-548.
101. Ramana DKV, Jamuna K, Satyanarayana B, Venkateswarlu B, Rao MM, Seshaiha K. Removal of heavy metals from aqueous solutions using activated carbon prepared from *Cicer arietinum*. *Toxicol. Environ. Chem.* 2010;92:1447-1460.
102. Ahluwalia SS, Goyal D. Removal of heavy metals by waste tea leaves from aqueous solution. *Eng. Life Sci.* 2005;5:158-162.
103. Amuda OS, Giwa AA, Bello IA. Removal of heavy metal from industrial wastewater using modified activated coconut shell carbon. *Biochem. Eng. J.* 2007;36:174-181.
104. Wasewar KL, Atif M, Prasad B, Mishra IM. Batch adsorption of zinc on tea factory waste. *Desalination* 2009;244:66-71.
105. Choi SB, Yun YS. Lead biosorption by waste biomass of *Corynebacterium glutamicum* generated from lysine fermentation process. *Biotechnol. Lett.* 2004;26:331-336.
106. Lu WB, Shi JJ, Wang CH, Chang JS. Biosorption of lead, copper and cadmium by an indigenous isolate *Enterobacter* sp. J1 possessing high heavy-metal resistance. *J. Hazard. Mater.* 2006;134:80-86.
107. Uslu G, Tanyol M. Equilibrium and thermodynamic parameters of single and binary mixture biosorption of lead(II) and copper(II) ions onto *Pseudomonas putida*: effect of temperature. *J. Hazard. Mater.* 2006;135:87-93.
108. Selatnia A, Bakhti MZ, Madani A, Kertous L, Mansouri Y. Biosorption of Cd²⁺ from aqueous solution by a NaOH-treated bacterial dead *Streptomyces rimosus* biomass. *Hydrometallurgy* 2004;75:11-24.
109. Rodelo G, Gómez A, Ruiz-Manríquez A. Biosorption of Pb(II) by *Thiobacillus ferrooxidans*. *Rev. Int. Contam. Ambient.* 2002;18:33-37.
110. Liu HL, Chen BY, Lan YW, Cheng YC. Biosorption of Zn(II) and Cu(II) by the indigenous *Thiobacillus thiooxidans*. *Chem. Eng. J.* 2004;97:195-201.
111. Gaur N, Dhankhar R. Removal of Zn²⁺ ions from aqueous solution using *Anabaena variabilis*: Equilibrium and kinetic studies. *Int. J. Environ. Res.* 2009;3:605-616.
112. Ozturk A, Artan T, Ayar A. Biosorption of nickel(II) and copper(II) ions from aqueous solution by *Streptomyces coelicolor* A3(2). *Colloid Surf. B Biointerfaces* 2004;34:105-111.
113. Zheng GH, Wang L, Zhou Q, Li FT. Optimisation of cell surface and structural components for improving adsorption capacity of *Pseudomonas putida* 5-x to Cu²⁺. *Inter. J. Environ. Pollut.* 2008;34:285-296.
114. Wang XS, Huang LP, Li Y, Chen J. Removal of copper(II) ions from aqueous solution using *Sphingomonas paucimobolis* biomass. *Adsorption Sci. Tech.* 2010;28:137-147.
115. LoukidouMX, Karapantsios TD, Zouboulis AI, MatisKA. Diffusion kinetic study of cadmium(II) biosorption by *Aeromonas caviae*. *J. Chem. Technol. Biotechnol.* 2004;79:711-719.
116. Ziagova M, Dimitriadis G, Aslanidou D, Papaioannou X, Tzannetaki EL, Liakopoulou-Kyriakides M. Comparative study of Cd(II) and Cr(VI) biosorption on *Staphylococcus xylosum* and *Pseudomonas* sp. in single and binary mixtures. *Bioresour. Technol.* 2007;98:2859-2965.
117. Yu CL, Lu ZP, Ge FZ, Zhao EL. Biosorption of cadmium onto *Pseudomonas fluorescens*: Application of isotherm and kinetic models. *Adv. Mat. Res.* 2011;171-172:49-52.
118. Sahin Y, Ozturk A. Biosorption of chromium (VI) ions from aqueous solution by the bacterium *Bacillus thuringiensis*.

- Process Biochem.* 2005;40:1895-1901.
119. Congeevaram S, Dhanarani S, Park J, Dexilin M, Thamaraiselvi K. Biosorption of chromium and nickel by heavy metal resistant fungal and bacterial isolates. *J. Hazard. Mater.* 2007;146:270-277.
 120. Anjana K, Kaushik A, Kiran B, Nisha R. Biosorption of Cr(VI) by immobilized biomass of two indigenous strains of cyanobacteria isolated from metal contaminated soil. *J. Hazard. Mater.* 2007;148:383-386.
 121. Ozturk A. Removal of nickel from aqueous solution by the bacterium *Bacillus thuringiensis*. *J. Hazard. Mater.* 2007;147:518-523.
 122. Svecova L, Spanelova M, Kubal M, Guibal E. Cadmium, lead and mercury biosorption on waste fungal biomass issued from fermentation industry. I. Equilibrium studies. *Sep. Purif. Technol.* 2006;52:142-153.
 123. Chen C, Wang J. Influence of metal ionic characteristics on their biosorption capacity by *Saccharomyces cerevisiae*. *Appl. Microbiol. Biotechnol.* 2007;74:911-917.
 124. Yu J, Tong M, Sun X, Li B. Cystine-modified biomass for Cd(II) and Pb(II) biosorption. *J. Hazard. Mater.* 2007;143:277-284.
 125. Saiano F, Ciofalo M, Cacciola SO, Ramirez S. Metal ion adsorption by *Phomopsis* sp. biomaterial in laboratory experiments and real wastewater treatment. *Water Res.* 2005;39:2273-2280.
 126. Deng S, Ting YP. Characterization of PEI-modified biomass and biosorption of Cu(II), Pb(II) and Ni(II). *Water Res.* 2005;39:2167-2177.
 127. Tan TW, Cheng P. Biosorption of metal ions with *Penicillium chrysogenum*. *Appl. Biochem. Biotechnol.* 2003;104:119-128.
 128. Tewari N, Vasudevan P, Guha BK. Study on biosorption of Cr(VI) by *Mucor hiemalis*. *Biochem. Eng. J.* 2005;23:185-192.
 129. Mukhopadhyay M, Noronha SB, Suraiskumar GK. Kinetics modeling for the biosorption of copper by pretreated *Aspergillus niger* biomass. *Bioresour. Technol.* 2007;98:1781-1787.
 130. Herrero R, Lodeiro P, Rey-Castro C, Vilarino T, de Vicente MES. Removal of inorganic mercury from aqueous solutions by biomass of the marine macroalga *Cystoseira baccata*. *Water Res.* 2005;39:3199-3210.
 131. Suzuki Y, Kametani T, Maruyama T. Removal of heavy metals from aqueous solution by nonliving *Ulva* seaweed as biosorbent. *Water Res.* 2005;39:1803-1808.
 132. Vilar VJP, Botelho CMS, Boaventura RAR. Equilibrium and kinetic modeling of Cd(II) biosorption by algae *Gelidium* and agar extraction algal waste. *Water Res.* 2006;40:291-302.
 133. Ajmal M, Rao RAK, Ahmad R, Khan MA. Adsorption studies on *Parthenium hysterophorus* weed: removal and recovery of Cd(II) from wastewater. *J. Hazard. Mater.* 2006;135:242-248.
 134. Meitei MD, Prasad MNV. Lead (II) and cadmium (II) biosorption on *Spirodela polyrrhiza* (L.) *Schleiden* biomass. *J. Environ. Chem. Eng.* 2013;1:200-207.
 135. Solisio C, Lodi A, Soletto D, Converti A. Cadmium biosorption on *Spirulina platensis* biomass. *Bioresour. Technol.* 2008;99:5933-5937.
 136. Herrero R, Cordero B, Lodeiro P, Rey-Castro C, Sastre de Vicente ME. Interaction of cadmium (II) and protons with dead biomass of marine algae *Fucus* sp. *Marine Chemistry* 2006;99:106-116.
 137. Gupta VK, Rastogi A. Equilibrium and kinetic modeling of cadmium (II) biosorption by nonliving algal biomass *Oedogonium* sp. from aqueous phase. *J. Hazardous Materials* 2008;153:759-766.
 138. Chen JP, Yang L. Chemical modification of *Sargassum* sp. for prevention of organic leaching and enhancement of uptake during metal biosorption. *Ind. Eng. Chem. Res.* 2005;44:9931-9942.
 139. Martins BL, Cruz CCV, Luna AS, Henriques CA. Sorption and desorption of Pb²⁺ ions by dead *Sargassum* sp. biomass. *Biochem. Eng. J.* 2006;27:310-314.
 140. Gupta VK, Rastogi A. Biosorption of lead from aqueous solutions by nonliving algal biomass *Oedogonium* sp. and *Nostoc* sp. - a comparative study. *Coll. Surfaces B* 2008;64:170-178.
 141. Gupta VK, Rastogi A. Biosorption of lead from aqueous solutions by green algae *Spirogyra* species: Kinetics and equilibrium studies. *J. Hazard. Materials.* 2008;152:407-414.
 142. Gupta VK, Rastogi A, Saini VK, Jain N. Biosorption of copper (II) from aqueous solutions by algae *spirogyra* species. *J. Colloid Interface Sci.* 2006;296:59-63.
 143. El-Sikaily A, El Nemr A, Khaled A, Abdelwehab O. Removal of toxic chromium from wastewater using green alga *Ulva lactuca* and its activated carbon. *J. Hazard. Mater.* 2007;148:216-228.
 144. Gupta VK, Rastogi A. Biosorption of hexavalent chromium by raw and acid-treated green alga *Oedogonium hatei* from aqueous solutions. *J. Hazard. Mater.* 2009;163:396-402.
 145. Gupta VK, Rastogi A. Sorption and desorption studies of chromium (VI) from nonviable cyanobacterium *Nostoc muscorum* biomass. *J. Hazard. Mater.* 2008;154:347-354.
 146. Gupta VK, Srivastava AK, Jain N. Biosorption of chromium (VI) from aqueous solutions by green algae *Spirogyra* species. *Water Res.* 2001;35:4079-4085.
 147. Kalyani S, Srinivasa Rao P, Krishnaiah A. Removal of nickel (II) from aqueous solutions using marine macroalgae as the sorbing biomass. *Chemosphere* 2004;57:1225-1229.
 148. Gupta VK, Rastogi A, Nayak A. Biosorption of nickel onto treated alga (*Oedogonium hatei*): Application of isotherm and kinetic models. *J. Colloid Interface Sci.* 2010;342:533-539.
 149. Vijayaraghavan K, Padmesh TVN, Palanivelu K, Velan M. Biosorption of nickel(II) ions onto *Sargassum wightii*: Application of two-parameter and three-parameter isotherm models. *J. Hazard. Mater.* 2006;133:304-308.
 150. Vijayaraghavan K, Yun YS. Bacterial biosorbents and biosorption. *Biotechnol. Adv.* 2008;26:266-291.
 151. Bishnoi NR, Garima A. Fungus-an alternative for bioremediation of heavy metal containing wastewater: a review. *J. Sci. Ind. Res.* 2005;64:93-100.
 152. Sağ Y. Biosorption of heavy metals by fungal biomass and modeling of fungal biosorption: a review. *Separ. Purif. Reviews* 2001;30:1-48.
 153. Wang J, Chen C. Biosorption of heavy metals by *Saccharomyces cerevisiae*: a review. *Biotechnol. Adv.* 2006;24:427-451.
 154. McHale AP, McHale S. Microbial biosorption of metals: potential in the treatment of metal pollution. *Biotechnol. Adv.* 1994;12:647-652.
 155. Gupta R, Mohapatra H. Microbial biomass: an economical

- alternative for removal of heavy metals from waste water. *Indian J. Exp. Biol.* 2003;41:945-966.
156. Wilde EW, Benemann JR. Bioremoval of heavy metals by the use of microalgae. *Biotechnol. Adv.* 1993;11:781-812.
 157. Mehta SK, Gaur JP. Use of algae for removing heavy metal ions from wastewater: progress and prospects. *Crit. Rev. Biotechnol.* 2005;25:113-152.
 158. Romera E, González F, Ballester A, Blázquez ML, Muñoz JA. Biosorption with algae: a statistical review. *Cri. Rev. Biotechnol.* 2006;26:223-235.
 159. Shukla A, Zhang YH, Dubey P, Margrave JL, Shukla SS. The role of sawdust in the removal of unwanted materials from water. *J. Hazard. Mater.* 2002;95:137-152.
 160. Crini G. Non-conventional low-cost adsorbents for dye removal: a review. *Bioresour. Technol.* 2006;97:1061-1085.
 161. Gerente C, Lee VKC, Le Cloirec P, McKay G. Application of chitosan for the removal of metals from wastewaters by adsorption - mechanisms and models review. *Crit. Rev. Environ. Sci. Technol.* 2007;37:41-127.
 162. Suhas P, CarrottMR. Lignin-from natural adsorbent to activated carbon: a review. *Bioresour. Technol.* 2007;98:2301-2312.
 163. Foo KY, Hameed BH. Utilization of rice husk ash as novel adsorbent: A judicious recycling of the colloidal agricultural waste. *Adv. Coll. Inter. Sci.* 2009;152:39-47.
 164. Farooq U, Kozinski JA, Khan MA, Athar M. Biosorption of heavy metal ions using wheat based biosorbents – A review of the recent literature. *Bioresour. Technol.* 2010;101:5043-5053.
 165. Demirbas A. Heavy metal adsorption onto agrobased waste materials: a review. *J. Hazard. Mater.* 2008;157:220-229.
 166. Johnson TA, Jain N, Joshi HC, Prasad S. Agricultural and agro-processing wastes as low cost adsorbents for metal removal from wastewater: a review. *J. Sci. Ind. Res.* 2008;67: 647-658.
 167. Sud D, Mahajan G, Kaur MP. Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions-a review. *Bioresour. Technol.* 2008;99: 6017-6027.
 168. Ioannidou O, Zabaniotou A. Agricultural residues as precursors for activated carbon production-a review. *Renew. Sust. Energ. Rev.* 2007;11:1966-2005.
 169. Ngah WS Wan, Hanafiah MAKM. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. *Bioresour. Technol.* 2008;99:3935-3948.
 170. O'Connell DW, Birkinshaw C, O'Dwyer TF. Heavy metal adsorbents prepared from the modification of cellulose: a review. *Bioresour. Technol.* 2008;99:6709-6724.
 171. Veglio F, Beolchini F. Removal of metals by biosorption: a review. *Hydrometallurgy* 1997;44:301-316.
 172. Lesmana SO, Febriana N, Soetaredjo FE, Sunarso J, Ismadji S. Studies on potential applications of biomass for the separation of heavy metals. *Biochem. Eng. J.* 2009;44:19-41.
 173. Ahmedna M, Marshall WE, Rao RM. Production of granular activated carbons from select agricultural by-products and evaluation of their physical, chemical and adsorption properties. *Bioresour. Technol.* 2000;71:113-123.
 174. Rahman IA, Ismail J, Osman H. Effect of nitric acid digestion on organic materials and silica in rice husk. *J. Mater. Chem.* 1997;7:1505-1509.
 175. Lawther JM, Sun R, Banks WB. Extraction, fractionation and characterization of structural polysaccharides from wheat straw. *J. Agric. Food Chem.* 1995;43:667-675.
 176. Basso MC, Cerrella EG, Cukierman AL. Lignocellulosic materials as potential biosorbents of trace toxic metals from wastewater. *Chem. Res.* 2002;41:3580-3585.
 177. Kaiser S, Saleemi AR, Ahmad MM. Heavy metal uptake by agro based waste materials. *Electron. J. Biotechnol.* 2007;10: 409-416.
 178. Acemioglu B, Alma MH. Equilibrium studies on adsorption of Cu(II) from aqueous solution onto cellulose. *J. Colloid Interface Sci.* 2001;243:81-84.
 179. Wang J, Chen C. Biosorbents for heavy metals removal and their future. *Biotechnol. Adv.* 2009;27:195-226.
 180. Fourest E, Roux JC. Heavy metal biosorption by fungal mycelial by-product, mechanisms and influence of pH. *Appl. Microbiol. Biotechnol.* 1992;37:399-403.
 181. Davis TA, Volesky B, Mucci A. A review of the biochemistry of heavy metal biosorption by brown algae. *Water Res.* 2003;37:4311-4330.
 182. Gupta VK, Nayak A, Bhushan B, Agarwal S. A critical analysis on the efficiency of activated carbons from low-cost precursors for heavy metals remediation. *Crit. Rev. Environ. Sci. Tech.* 2015;45:613-668.
 183. Kapoor A, Viraraghavan T. Fungal biosorption - an alternative treatment option for heavy metal bearing wastewaters: a review. *Bioresour. Technol.* 1995;53:195-206.
 184. Vieira RHF, Volesky B. Biosorption: a solution to pollution? *Int. Microbiol.* 2000;3:17-24.
 185. Argun ME, Dursun S, Karatas M. Removal of Cd(II), Pb(II), Cu(II) and Ni(II) from water using modified pine bark. *Desalination* 2009;249:519-527.
 186. Afkhami A, Madrakian T, Karimi Z, Amini A. Effect of treatment of carbon cloth with sodium hydroxide solution on its adsorption capacity for the adsorption of some cations. *Colloids Surf. A* 2007;304:36-40.
 187. Nasir MH, Nadeem R, Akhtar K, Hanif MA, Khalid AM. Efficacy of modified distillation sludge of rose (*Rosa centifolia*) petals for lead(II) and zinc(II) removal from aqueous solutions. *J. Hazard. Mater.* 2007;147:1006-1014.
 188. Ngah WSW, Hanafiah MAKM. Biosorption of copper ions from dilute aqueous solutions on base treated rubber (*Hevea brasiliensis*) leaves powder: kinetics, isotherm, and biosorption mechanisms. *J. Environ. Sci.* 2008;20:1168-1176.
 189. Xie R, Wang H, Chen Y, Jiang W. Walnut shell-based activated carbon with excellent copper(II) adsorption and lower chromium(VI) removal prepared by acid-base modification. *Environ. Prog. Sustain. Energy* 2013;32:688-696.
 190. Memon SQ, Memon N, Shah SW, Khuhawar MY, Bhangar MI. Sawdust-A green and economical sorbent for the removal of cadmium(II) ions. *J. Hazard. Mater.* 2007;139:116-121.
 191. Danish M, Hashim R, Ibrahim MNM, et al. Sorption of copper(II) and nickel(II) ions from aqueous solutions using calcium oxide activated date (*Phoenix dactylifera*) stone carbon: equilibrium, kinetic, and thermodynamic studies. *J. Chem. Eng. Data* 2011;56:3607-3619.

192. Lalhruaitluanga H, Prasad MNV, Radha K. Potential of chemically activated and raw charcoals of *Melocanna baccifera* for removal of Ni(II) and Zn(II) from aqueous solutions. *Desalination* 2011;271:301-308.
193. El-Hendawy ANA. Influence of HNO₃ oxidation on the structure and adsorptive properties of corncob based activated carbon. *Carbon* 2003;41:713-722.
194. Shah J, Jan MR, Haq A, Sadia M. Biosorption of cadmium from aqueous solution using mulberry wood sawdust: equilibrium and kinetic studies. *Sep. Sci. Tech.* 2011;46:1631-1637.
195. Taty-Costodes VC, Fauduet H, Porte C, Delacroix A. Removal of Cd(II) and Pb(II) ions, from aqueous solutions, by adsorption onto sawdust of *Pinus sylvestris*. *J. Hazard. Mater.* 2003;105:121-142.
196. Chauhan GS, Jaswal SC, Verma M. Post functionalization of carboxymethylated starch and acrylonitrile based networks through amidoximation for use as ion sorbents. *Carbohydr. Polym.* 2006;66:435-443.
197. Saliba R, Gauthier H, Gauthier R, Petit-Ramel M. Adsorption of copper (II) and chromium (III) Ions onto amidoximated cellulose. *J. Appl. Polym. Sci.* 2000;75:1624-1631.
198. Oshima T, Kondo K, Ohto K, Inoue K, Baba Y. Preparation of phosphorylated bacterial cellulose as an adsorbent for metal ions. *React. Funct. Polym.* 2008;68:376-383.
199. Navarro R, Bierbrauer K, Giangos C, Goiti E, Reinecke H. Modification of poly (vinyl chloride) with new aromatic thiol compounds. Synthesis and characterization. *Polym. Degrad. Stab.* 2008;93:585-591.
200. Li FT, Yang H, Zhao Y, Xu R. Novel modified pectin for heavy metal adsorption. *Chin. Chem. Lett.* 2007;18:325-328.
201. Pushpamalar V, Langford SJ, Ahmad M, Lim YY. Optimization of reaction conditions for preparing carboxymethyl cellulose from sago waste. *Carbohydr. Polym.* 2006;64:312-318.
202. Chauhan GS, Chauhan K, Chauhan S, Kumar S, Kumari A. Functionalization of pine needles by carboxymethylation and network formation for use as supports in the adsorption of Cr⁶⁺. *Carbohydr. Polym.* 2007;70:415-421.
203. Wang J. Biosorption of copper(II) by chemically modified biomass of *Saccharomyces cerevisiae*. *Process Biochem.* 2002;37:847-850.
204. Goksungur Y, Uren S, Guvenc U. Biosorption of cadmium and lead ions by ethanol treated waste baker's yeast biomass. *Bioresour. Technol.* 2005;96:103-109.
205. Rincon J, Gonzalez F, Ballester A, Blazquez ML, Munoz JA. Biosorption of heavy metals by chemically-activated alga *Fucus vesiculosus*. *J. Chem. Technol. Biotechnol.* 2005;80:1403-1407.
206. Gupta VK, Agarwal S, Singh P, Pathania D. Acrylic acid grafted cellulosic Luffa cylindrical fiber for the removal of dye and metal ions. *Carbohydr. Polym.* 2013;98:1214-1221.
207. Anirudhan TS, Sreekumari SS, Jalajamony S. An investigation into the adsorption of thorium(IV) from aqueous solutions by a carboxylate-functionalised graft copolymer derived from titanium dioxide-densified cellulose. *J. Environ. Radioactivity* 2013;116:141-147.
208. Isobea N, Chen X, Kim U-Z, et al. TEMPO-oxidized cellulose hydrogel as a high-capacity and reusable heavy metal ion adsorbent. *J. Hazard. Mater.* 2013;260:195-201.
209. Shuaiyang W, Huiling L, Junli R, Chuanfu L, Feng P, Runcang S. Preparation of xylan citrate—A potential adsorbent for industrial wastewater treatment. *Carbohydr. Polym.* 2013;92:1960-1965.
210. Grey M, Marchetti V, Clement A, Loubinoux B, Gerardin P. Decontamination of synthetic solutions containing heavy metals using chemically modified sawdusts bearing polyacrylic acid chains. *J. Wood Sci.* 2000;46:331-333.
211. Saliba R, Gauthier H, Gauthier R. Adsorption of heavy metal ions on virgin and chemically-modified lignocellulosic materials. *Ads. Sci. Technol.* 2005;23:313-322.
212. Shibi IG, Anirudhan TS. Synthesis, characterisation, and application as a mercury(II) sorbent of banana stalk (*Musa paradisiaca*)-polyacrylamide grafted copolymer bearing carboxyl groups. *Ind. Eng. Chem. Res.* 2002;41:5341-5352.
213. Deng S, Ting YP. Fungal biomass with grafted poly(acrylic acid) for enhancement of Cu (II) and Cd(II) biosorption. *Langmuir* 2005;21:5940-5948.
214. Errasquin EL, Vazquez C. Tolerance and uptake of heavy metals by *Trichoderma atroviride* isolated from sludge. *Chemosphere* 2003;50:137-143.
215. Hesas RH, Daud WMAW, Sahu JN, Niya AA. The effects of a microwave heating method on the production of activated carbon from agricultural waste: A review. *J. Anal. App. Pyrolysis.* 2013;100:1-11.
216. Maldhure AV, Ekhe JD. Preparation and characterizations of microwave assisted activated carbons from industrial waste lignin for Cu(II) sorption. *Chem. Eng. J.* 2011;168:1103-1111.
217. Foo KY, Hameed BH. Preparation and characterization of activated carbon from sunflower seed oil residue via microwave assisted K₂CO₃ activation. *Bioresour. Technol.* 2011;102:9794-9799.
218. Foo KY, Hameed BH. Preparation, characterization and evaluation of adsorptive properties of orange peel based activated carbons via microwave assisted K₂CO₃ activation. *Bioresour. Technol.* 2012;104:679-686.
219. Anirudhan TS, Sreekumari SS. Adsorptive removal of heavy metal ions from industrial effluents using activated carbon derived from waste coconut buttons. *J. Environ. Sci.* 2011;23:1989-1998.
220. Gautam RK, Mudhoo A, Lofrano G, Chattopadhyay MC. Biomass-derived biosorbents for metal ions sequestration: Adsorbent modification and activation methods and adsorbent regeneration. *J. Environ. Chem. Eng.* 2014;2:239-259.
221. Volesky B, Naja G. Biosorption: application strategies. In: 16th International Biohydrometallurgy Symposium; 2005 Sep 25-29; Cape Town, South Africa.
222. Garnham GW. The use of algae as metal biosorbents. In: Wase J, Forster C, eds. *Biosorbents for metal ions*. London, UK: CRC Press; 1997. p. 11-37.
223. Park D, Yun YS, Park JM. The Past, Present, and Future Trends of Biosorption. *Bioprocess Eng.* 2010;15:86-102.