

Elimination of Toxic Heavy Metals from Aqueous Systems Using Potential Biosorbents: A Review



S. Rangabhashiyam, R. Jayabalan, M. Asok Rajkumar
and P. Balasubramanian

1 Introduction

The growing concern of environmental pollutions and their associated toxicity effects is major problem faced by the today's world. The emerging pollutants impose serious health issue and environmental damages. The contamination of water bodies due to the higher presence of inorganic pollutants in the form of heavy metal is one of the important challenges for the researchers [1, 2]. Heavy metals ions mostly have a density of greater than 5 g/cm^3 and atomic weights in the range of 63.5–200.6 [3]. Heavy metal ions reported as the precedence pollutants than the other water pollutants since heavy metal ions are highly mobile in the water ecosystems and not biodegradable, resultant in continual occurrence in the environment [4]. The generalized categories of the Heavy metals [5] are mentioned in Fig. 1.

The reasons for the heavy metals pollution in water streams are due to heavy metals in earth's crust that undergoes solubilization in groundwater, which occurs through natural phenomena and soil pH. Besides natural process, the anthropogenic

S. Rangabhashiyam (✉) · P. Balasubramanian (✉)
Department of Biotechnology & Medical Engineering, NIT Rourkela, Odisha, India
e-mail: rambhashiyam@gmail.com

P. Balasubramanian
e-mail: biobala@nitrkl.ac.in

R. Jayabalan
Department of Life Science, NIT Rourkela, Odisha, India

M. Asok Rajkumar
Dean—R&D, Gnanamani College of Technology, Namakkal, Tamil Nadu, India

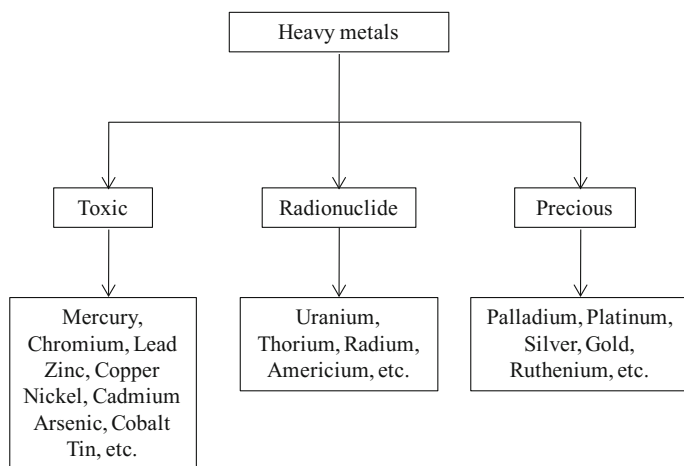


Fig. 1 Outline classification of heavy metals

activities resultants such as sewage, leachate sourced from mine tailings and landfill, liquid wastes clearance deep well, industrial lagoons wastes seepage, spills, leaks from industry and untreated or partially treated industrial effluents [6, 7]. The discharge of untreated industrial effluent acts as the most important cause for the pollution of water bodies. The wastewater is generated due the various industrial operations at different stages. The industrial sectors associated with the activities of fabrication, mining, paper and pulp, electroplating, textile, metal finishing, painting and printing, fertilizer production and batteries contribute in the metal augmented effluent streams [8, 9].

Disaster tragedy because of the toxic heavy metals pollution in water bodies is reported with Minamata disease, a neurological syndrome caused due to severe methyl mercury poisoning in Japan and Itai-Itai disease due to cadmium pollution in the river of Jintsu in Japan [10, 11]. The potential hazardous health effects due to the different toxic heavy metals in human systems [12] are presented in Fig. 2. Every toxic heavy metal exposure is linked with the property of harmful effects even at its low concentration. Therefore, various regulatory bodies prescribed the maximum allowable limit for the toxic heavy metal discharge from treated effluent into the environment. Table 1 represents the maximum permissible levels for some of the toxic heavy metals according to the World Health Organization (WHO), US Environmental Protection Agency (USEPA) and European Environment Agency (EEA) [13–15].

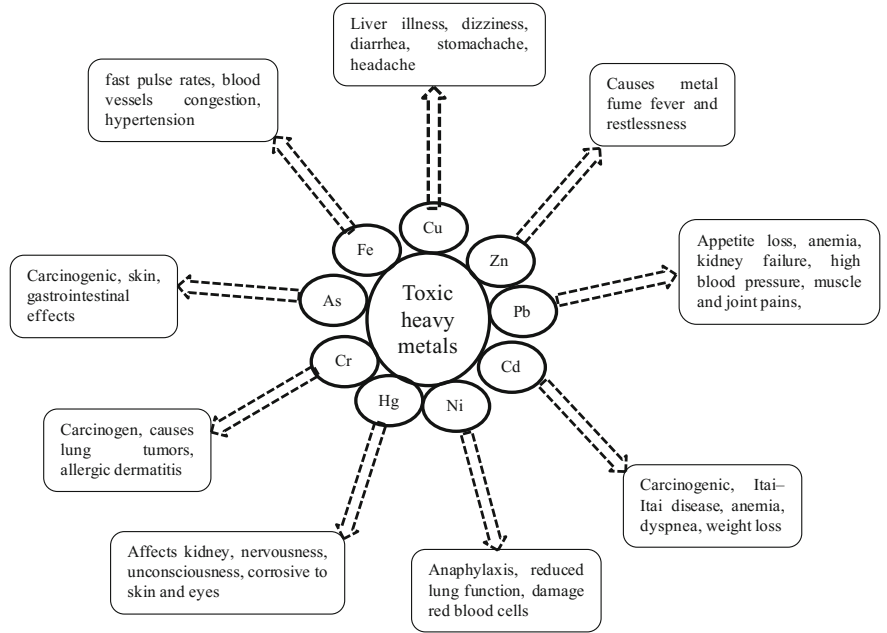


Fig. 2 Potential health effects due to toxic heavy metals

Table 1 Maximum permissible limit of some toxic heavy metals in drinking water

Toxic heavy metal	Maximum permissible limit (mg/L)		
	WHO	USEPA	EEA
Arsenic	0.01	0.01	0.01
Cadmium	0.005	0.005	0.005
Copper	1.0	1.3	–
Chromium	0.05	0.1	0.05
Lead	0.005	0.015	0.1
Mercury	0.001	0.002	0.001
Nickel	–	0.04	–
Zinc	5.0	5.0	–

2 Conventional Treatment Technologies and Biosorption

Considering the toxicity effects of heavy metals in the industrial effluents, in the recent years, there received lots of attention by researchers for the heavy metal sequestrations. The commonly used conventional methods for the removal of heavy metal ions are extraction, ion-exchange, filtration, flocculation, photocatalysis, precipitation, electrochemical treatments, etc. [16–18]. Each method is unique with their own merits and demerits (Table 2). Mostly, the conventional methods are

Table 2 Comparison of treatment technologies for the removal of heavy metals from aqueous streams

Technology	Advantages	Disadvantages
Coagulation and flocculation	Sludge production with good settling and dewatering characteristics	High cost investments for chemicals usage and higher sludge volume generation
Chemical precipitation	Simple process and requires only low capital cost investment	High maintenance costs for disposal of sludge, unsuccessful for removal of effluent with lower concentration of heavy metals
Membrane filtration	Requires less chemicals, operates at low pressure, occupies smaller space and high selective process	High cost investment needed for operation as well as for maintenance, causes membrane fouling and complex process
Flotation	Higher removal efficiency, low detention periods and more selective towards the metal removal	Requires high maintenance and operation cost
Photocatalysis	The process suitable for the simultaneous removal of metal, organic pollutant and associated with the formation of less by-products only	Limited applications and requires longer duration time
Ion-exchange	Highly selective for metal removal, large treatment capacity, more removal efficiency and fast kinetics	Higher cost of synthetic resins and limited pH tolerance
Electrochemical treatment	Free from the chemical requirements, metal selective and more efficient for metal removal	Need high initial cost investment and requires high electrical supply
Adsorption using activated carbon	Higher removal capacity, fast kinetics, higher removal efficiency and simple operation	Higher cost of activated carbon

costly, require chemicals, ineffective at low concentrations, waste sludge generation, etc. Recently, more consideration paid on working with non-conventional methods for the treatment of heavy metals.

3 Biosorption Technology

The process of biosorption is performed using biomass, which is inactive or even dead. The sources of biosorbents are from the dead biomass of bacteria, algae, fungi or in the form of waste biomass from industrial operations, the lignocellulosic biomass residues, etc. The biosorption technology has gained significant credibility in the recent years. The use of dead biomass offers the advantages of its usage even at the higher toxic metal concentrations can be subjected to adverse process conditions, free from the growth media requirements and possibilities of biomass

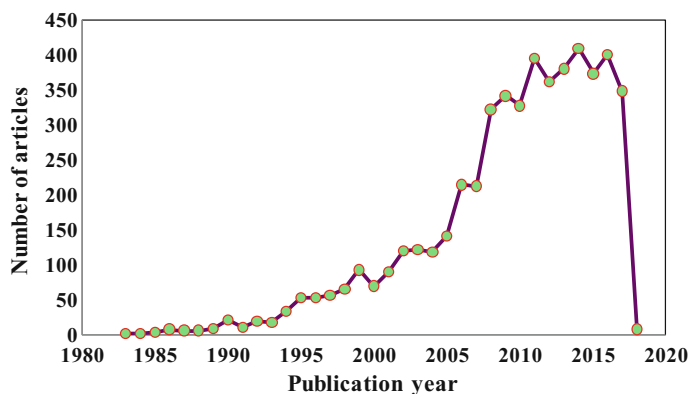


Fig. 3 Number of publications in the research area of metal biosorption

regenerations [19, 20]. The process of the heavy metal removal by the biosorbent from the aqueous solutions will be influenced by different physical and chemical factors, which will control the biosorption capacity and removal efficiency. In this regard, assessments of the biosorption parameters on the metal removal process are very essential. The batch operation of the biosorption process for the sequestration of heavy metals needs to consider the significant parameters such as initial pH, initial metal ions concentration, biosorbent dosage, size of the biosorbent, agitation speed, temperature and presence of coexisting ions (binary, ternary or multi-component system) [21]. In the present review, the biosorbents prepared from the dead microbial and lignocellulosic source are considered for the discussion. The articles published details extracted from the Scopus search using the key words metal biosorption which are illustrated in Fig. 3. Most of the articles reported on the toxic heavy metal removal using the microbial and lignocellulosic biomass residues.

4 Isotherm and Kinetic Models of Biosorption

The model expressions of the biosorption isotherm are used to understand the interactive behaviour between biosorbent and metal at constant temperature and equilibrium solute concentration. The isotherm models are significant to analyse the biosorption mechanism. The isotherm models optimize the biosorbent use through the estimation of biosorbent amount required to uptake determined concentration of metal from the aqueous solution. Moreover, it is useful in the prediction of distribution of biosorption sites and metal ions biosorbed on the biomass surface. Different equilibrium biosorption isotherm models have been employed for the biosorption investigation of heavy metals. Based on the parameters in the isotherm

Table 3 Nonlinear forms of the biosorption isotherm models

Biosorption isotherm models	Equations
Langmuir	$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e}$
Freundlich	$q_e = K_f C_e^{\frac{1}{n}}$
Temkin	$q_e = \frac{RT}{B} \ln(A_T C_e)$
Jovanovic	$q_e = q_{mj} \left(1 - e^{-(K_j C_e)} \right)$
Fowler–Guggenheim	$K_{FG} C_e = \frac{\theta_{FG}}{1 - \theta_{FG}} \exp \left(\frac{2 \theta_{FG} W}{RT} \right)$
Kiselev	$k_{1K} C_e = \frac{\theta_K}{(1 - \theta_K)(1 + k_n \theta_K)}$
Halsey	$q_e = \exp \left(\frac{\ln K_H - \ln C_e}{n_H} \right)$
Harkin–Jura	$q_e = \left(\frac{A_H}{B_2 - \log C_e} \right)^{1/2}$
Redlich–Peterson	$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^p}$
Khan	$q_e = \frac{q_s b_K C_e}{(1 + b_K C_e)^{1/K}}$
Koble–Corrigan	$q_e = \frac{A_{KC} C_e^m}{1 + B_{KC} C_e^n}$
Sips	$q_e = \frac{q_m K_S C_e^{m/s}}{1 + K_S C_e^{m/s}}$

Table 4 Kinetic models for the metal biosorption studies

Biosorption kinetic models	Equations
Pseudo-first-order	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$
Pseudo-second-order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$
Elovich	$q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t$
Ritchie’s	$\frac{1}{q_t} = \frac{1}{k_R q_e t} + \frac{1}{q_e}$
Intra-particle diffusion	$q_t = k_{id} \sqrt{t} + I$

expression, the models are classified into two, three, four and five, respectively [22]. The nonlinear equations of biosorption isotherm models are represented in Table 3.

The biosorption kinetic models are significant in determining the rate-controlling steps of the metal removal process such as metal transport and physicochemical interactions. The investigation of the biosorption kinetic models is significant for heavy metal removal studies, since it provides vital information’s on the dynamics of the biosorption process, reaction pathways and associated mechanisms. The findings of heavy metal biosorption rate are important to calculate the biosorbent residence time in the aqueous solution and important in the design of suitable biosorption process conditions. In a biosorption process, the transfer of heavy metal ions is characterized by either boundary layer diffusion or intra-particle diffusion, otherwise both. The different kinetic models [23, 24] used in the biosorption study are presented in Table 4.

5 Dead Microbial Biomass for Heavy Metal Biosorption

The biosorbents from the non-living microbial source tend to interact with the heavy metals by binding and concentrate them even at a very low concentration of the metal solution. The microbial dead biomass from algae, fungi and bacteria is widely used for the removal of heavy metals from the aqueous solutions as well as from the industrial effluent containing toxic heavy metals. The biosorption capacity of the different dead microbial towards the removal of toxic heavy metals from the aqueous solutions is summarized in Table 5.

Table 5 Biosorbents for the removal of heavy metals from aqueous solutions

Biosorbent	Heavy metal	Biosorption capacity (mg/g)	References
Microalgae			
<i>Fucus spiralis</i>	Cd(II)	64	[63]
<i>Desmodesmus pleiomorphus</i>	Cd(II)	47.1	[64]
<i>Spirulina platensis</i>	Zn(II)	30.96	[65]
<i>Isochrysis galbana</i>	Cr(III)	335.27	[66]
<i>Chlorella vulgaris</i>	Cr(VI)	161.41	[67]
<i>Scenedesmus obliquus</i>	Zn(II)	330	[68]
<i>Chlorella vulgaris</i>	Pb(II)	169	[69]
Bacteria			
<i>Bacillus megaterium</i>	Cr(VI)	30.7	[70]
<i>Bacillus firmus</i>	Cu(II)	381	[71]
<i>Paenibacillus polymyxa</i>	Cu(II)	112	[72]
<i>Bacillus circulans</i>	Cd(II)	26.5	[73]
<i>Pseudomonas fluorescens</i>	Hg(II)	72.3	[74]
<i>Alcaligenes</i> sp.	Pb(II)	66.7	[75]
<i>Pseudomonas aeruginosa</i>	Pb(II)	110	[76]
Fungi			
<i>Rhodotorula glutinis</i>	Pb(II)	75.5	[77]
<i>Aspergillus foetidus</i>	Cr(VI)	2.0	[78]
<i>Polyporus versicolor</i>	Pb(II)	57.5	[79]
<i>Aspergillus flavus</i>	Cu(II)	20.75	[80]
<i>Rhizopus oryzae</i>	Co(II)	13.56	[81]
<i>Candida utilis</i>	Zn(II)	181.7	[82]
<i>Rhizopus oligosporus</i>	Ni(II)	116	[83]
Plant biomass residue			
Grape stalk	Ni(II)	18.1	[84]
<i>Posidonia oceanica</i>	Cu(II)	76.92	[85]
<i>Ananas comosus</i> peel	Cd(II)	18.21	[86]
<i>Anna Witek-Krowiak</i>	Cu(II)	30.22	[87]
Cocoa pod husk	Zn(II)	14.07	[88]
Tobacco dust	Pb(II)	39.6	[89]
<i>Hydrilla verticillata</i>	Cr(VI)	29.43	[90]

5.1 Algae

The biomass of *Microcystisnovacekii* is tested for the removal of Pb(II) ions from aqueous solutions. The equilibrium data of the biosorption experiments are better described by the Langmuir model compared to the Freundlich isotherm. The analysis of the Potentiometric titrations indicated the presence of negative surface charge with two acidic groups. The FT-IR characterization of the lead loaded biosorbent suggested the functional groups, amide and carboxyl involved in the lead biosorption [25]. The methylated biomass of *Spirulina platensis* is utilized for the removal for Cr(VI) and compared with the native biomass. The pretreated biomass presented higher performance with more than 80% removal efficiency. The methylation of *Spirulina platensis* biomass favored methyl esters formation, decreased the carboxylate functional group and favored the adsorption of chromate ions [26]. The biosorption investigation of *Spirulina platensis* and *Chlorella vulgaris* towards the removal of Ni(II), Zn(II) and Pb(II) was reported. The biosorption process is significantly influenced by the parameter of initial metal ions concentration. The biomass of *C. vulgaris* showed better biosorption towards the heavy metals than the *Spirulina platensis*. The pseudo-second-order kinetic model best fitted the experimental data. The analysis of FT-IR results showed carboxylate functional groups contributed in coordination/ionic exchange of bivalent ions, hydroxyl, amino and amide group involvement. The values of pH_{zpc} for the biosorbent *Spirulina platensis* and *C. vulgaris* are calculated as 4.0 and 3.4 [27]. Metal biosorption in binary and ternary systems was examined for the metal ions Ni(II), Zn(II) and Pb(II) using *Spirulina platensis* and *C. vulgaris*. The results of the separation factor represent that both the biosorbents have affinity towards the metal in the order of $\text{Pb(II)} > \text{Zn(II)} > \text{Ni(II)}$. *C. vulgaris* behaved as better biosorbent because of higher equilibrium sorption capacities (q_{eq}) and removal efficiencies (Y_{R}). The biosorption capacity of the biosorbents showed decreased effect in the binary and ternary systems compared to the single-metal biosorption system [28].

To mechanistic removal of Cr(VI) from aqueous solution studied using *C. vulgaris*, the biosorption of Cr(VI) is mainly due to the amino and carboxyl functional groups; moreover, the removal performance increased with the increases of biomass protein content. The Cr(VI) reduced because of the presence of secondary alcohol groups on the biomass and Cr(III) binding with biomass by means of ion-exchange mechanism [29]. The biosorption capacity of *Scenedesmus obliquus* and *Desmodesmus pleiomorphus* towards the removal of Zn(II) and Cd(II) in single and binary systems was examined. The two microalgae are isolated from a heavy metal contaminated site in Northern Portugal. The simultaneous biosorptive uptake of Zn(II) and Cd(II) by *Scenedesmus obliquus* and *Desmodesmus pleiomorphus* was found lesser than the single-metal biosorption system. The native biosorbents are efficient for simultaneous removal of mixtures of Zn(II) and Cd(II) up to the initial concentration of 300 mg/L [30]. The biomass of *Chlorella sorokiniana* is immobilized using alginate and tested for the removal of Cu(II), Ni(II) and Cd(II) ions from drinking water. The maximum removal efficiency attained for the removal of Cu(II),

Ni(II) and Cd(II) was 97.10, 50.94 and 64.61%, respectively. The characterization of the metal-loaded biosorbent performed through EDS analysis confirmed the bonding of metal ions to the biosorbent. Apart from the single biosorption system, study performed on binary and multi-metal systems of Cu(II), Ni(II) and Cd(II). The removal of both Cd(II) and Ni(II) showed decreased affect in the presence of Cu(II) ions [31]. The strain of microalgae, *Micractiniumreisseri* KGE33, is immobilized using silica by means of sol–gel reaction. The de-oiled biomass residue from *M. reisseri* KGE33 is used as the source of biomass. Based on the use of algal dosage, the biosorbents are denoted as IMS 14, 70, and 100, respectively. The biosorbents were assessed for the removal of Cu(II) from the aqueous solutions. The value of the point of zero charge value for IMS100 is determined as 4.5. At the initial solution pH of 5.0, the biosorbent IMS 100 showed higher Cu(II) removal efficiency of 87.1%. The thermodynamic analysis revealed spontaneous and exothermic nature of biosorption process [32]. The application of biosorbent prepared using the dry biomass of *Scenedesmusquadricauda* is used towards the removal of Cd(II) and Pb (II) from simulated and real effluents. The metal removal from synthetic solutions attained equilibrium within 60 min. The regeneration of Cd(II), Pb(II)-loaded biosorbent is analysed using HNO₃. The biosorption efficiency of 65 and 69% is achieved for Cd(II) and Pb(II) removal from industrial effluent wastewater [33].

5.2 Bacteria

The bacterial strains of *Bacillus cereus* and *Bacillus pumilus* are assessed for the biosorption of Pb(II) in the batch system. The experimental data are best fitted with pseudo-second-order kinetics and Langmuir isotherm model. The maximum biosorption capacity of the biosorbents towards Pb(II) removal from aqueous solution occurred at the initial solution pH of 6.0 [34]. Biosorption of Cr(VI) is reported using four bacterial strains. The experimental conditions of initial Cr(VI) concentration range (350–450 mg/L) and 2.0 pH showed higher removal efficiency. The tested biosorbents, *Burkholderiacepacia* AL96Co, *Corynebacteriumkutscheri* FL108Hg, *Pseudomonas aeruginosa* CA207Ni and *Rhodococcus* sp. AL03Ni showed as suitable biosorbents for removal of Cr(VI) containing industrial wastewater [35]. The biosorbents from *Staphylococcus xylosus* and *Pseudomonas* sp. are used for the removal of Cd(II) and Cr(VI). The biosorption mechanisms are controlled by the factors of biosorbent surface functional groups and surface charge distribution on the biomass. The higher removal efficiency of greater than 88% denoted *Staphylococcus xylosus* and *Pseudomonas* sp. as potential biosorbents [36]. The Cd(II) removal using the biosorbent is prepared from *Exiguobacterium* sp. isolated near the mines of Okdong (Korea). The biosorption efficiency of greater than 95% Cd(II) removal was observed. The dead biomass for Cd(II) removal performance was similar to that of the living biomass [37]. The bacteria biomass of

Comamonastestosteroni, *Enterobacterludwigii* and *Zoogloearamigerai*s is studied for the removal of Cu(II), Pb(II) using fixed and suspended biomass [38].

Biosorbent prepared from the chromium-resistant bacteria *B. cereus* is isolated from the samples collected from sewage treatment plant. The removal process of Cr(VI) is found highly pH dependent, and the optimum pH is determined as 2.0. The rate-controlling step for the Cr(VI) biosorption is found due to the external mass transfer. The bioremediation of Cr(VI) involves biosorption mechanism in addition to the bio-oxidation and bio-reduction [39]. The northeast regions of China containing wastewater are associated with the problem of lead contamination. The lead-tolerant *Pseudomonas* sp. I3 is isolated from Mohe wetland and examined for the lead removal potentials. The lead biosorption by the biosorbent is confirmed through TEM-EDS analyses. The characterization results of FT-IR showed the participation of different functional groups in the Pb(II) biosorption [40]. A mutation done by ultraviolet irradiation on *Bacillus subtilis* is employed for the biosorption of heavy metals in single and multi-component systems. Fast removal of the metal ions occurred at the initial period of the biosorption process, and kinetics of the process is better described by the pseudo-first-order kinetic model. The biosorption of Hg(II), Cd(II) and Pb(II) in the binary and ternary metal system showed decreased biosorption due to the presence of other metal ions, but the biosorption sites are distinct for every metal considered. The experiments represented higher biosorption capacity in the single-metal systems [41]. The biosorption properties of polysaccharide producing *Ochrobactrumanthropi* are isolated from activated sludge examined towards the removal of cadmium, copper and chromium from aqueous solution. The maximum removal is observed at the initial solution pH values of 2.0 (Cr(VI)), 8.0 (Cd(II)) and 3.0 (Cu(II)), respectively. The biosorption parameter, initial metal concentration influenced on the uptake of metal by the biomass. The fit of equilibrium data to the biosorption isotherm models is better explained by both Langmuir and Freundlich models [42].

5.3 Fungi

The biomass of filamentous fungus, *Cephalosporiumaphidicola* IMI 68689, is tested for the removal of Pb(II) from aqueous solution. The results of the initial solution pH showed the significant influence in the uptake capacity for Pb(II) removal using *Cephalosporiumaphidicola*. The reuse examinations performed up to the cycles of five biosorption–desorption and found only 5% loss of efficiency [43]. Fungi isolates such as *Aspergillus* and *Rhizopus* are evaluated for the biosorption of Cr and Cd(II) ions. The maximum removal of Cr and Cd(II) ions is observed at the initial metal concentration of 6 mM [44]. Biosorption potential of *Trichoderma* sp. BSCR02 is evaluated for the removal of chromium from aqueous solutions. The optimal biosorbent dosage of 1.4 mg/mL was used for the biosorption of 200 mg/L initial chromium concentration and 5.0 initial solution pH. The biosorbent is reused up to five cycles without any significant decrease in removal efficiency of

biosorbent [45]. Biosorbents prepared by growing fungal isolates *Aspergillusniger* and *Aspergillusterreus* on luffa sponge, and the biosorbents are used for the removal of Pb(II) from aqueous solutions. The FT-IR analysis of the biosorbents indicated the presence of -OH , -NH , and -CH_3 functional groups and their involvement in the Pb(II) removal process. The SEM characterization of the biosorbents showed the homogeneous occurrence of fungal biomass on the structure of luffa sponge, which provides more contact sites for interaction with the metal ions. The Pb(II) interacted biosorbent presented muddy deposits of Pb(II) ions, confirmed the biosorption of metal ions. The biosorbents from the *Aspergillusniger* and *Aspergillusterreus* showed removal efficiency of about 51% of Pb(II) from 250 mM lead solution [46]. Batch biosorption experiments are conducted using the biosorbent from jelly fungus *Auriculariapolytricha* and are studied for the removal of Cd(II), Cu(II) and Pb(II) from aqueous solutions. The higher desorption efficiency is attained using the eluting agents of 0.05 mol/L HNO_3 and regenerated biosorbent reused up to six cycles of biosorption studies. The biosorption equilibrium data better fitted with the isotherm of Freundlich and Dubinin–Radushkevich, revealed the biosorbent surface as heterogeneous and favored the chemisorption mechanism of the metal removal process. The functional groups in the biosorbent such as hydroxyl, amino, carboxyl, and phosphoryl are mainly contributed in the metal biosorption process. The removals of metal ions are associated with the predominant mechanisms of synergistic ion exchange and surface complexation [47].

The fungus *Rhizopus* sp. is immobilized onto the various textile materials and tested for the removal of Cu(II) ions. The immobilized biosorbents presented better removal efficiency by reducing the Cu(II) ions concentration from 20 to 3.1–5.6 mg/L within the contact time of 150 min. The biosorption system has the merit of usage as real product, since the biomass attached with the textile media is separable, feasible to roll up, foldable, etc., and moreover offers the replacement of exhausted biosorbents after sufficient contact time [48]. The potential of two strains *Yarrowialipolytica* NCIM 3589 and *Yarrowialipolytica* NCIM 3590 is evaluated for the removal of Ni(II) from aqueous solution. The optimal conditions established for the maximum Ni(II) biosorption are initial solution pH 7.5, initial Ni(II) concentration 1000 mg/L and temperature 35 °C, respectively. The better fit of the Dubinin–Radushkevich isotherm model indicated that the biosorption of Ni(II) was due to the ion-exchange mechanism. The FT-IR analysis results showed that functional groups such as hydroxyl, carboxyl, amino and carbonyl are involved in the Ni(II) biosorption. The biosorption of Ni(II) onto the biosorbents is confirmed through the analysis of SEM–EDS characterization [49]. Biosorbent prepared from the *Penicilliumjanthinellum* isolates from mine location in Balya (Turkey) and employed for the removal of Pb(II) and Ni(II) from aqueous solutions. The biosorption factors include initial solution pH, initial Pb(II), Ni(II) concentration, biosorbent dosage and contact time. In order to understand the interaction between the parameters, optimization is conducted using Box–Behnken design. The higher removal efficiency of 76 and 47% for both Pb(II) and Ni(II) was attained at the optimal conditions of pH 4.5 (for both metals), initial metal concentrations of

123 mg/L (Pb(II)), 33 mg/L (Ni(II)), contact times of 65 min (Pb(II)), 89 min (Ni(II)) and biosorbent dosage of 0.2 g/L (Pb(II)), 1.6 g/L (Ni(II)), respectively [50]. The optimization technique of central composite face-centred design is subjected for the Pb(II) biosorption using biosorbent prepared from *Aspergillus terreus*. The parameters of agitation speed, initial solution pH, biosorbent dosage and temperature were considered for the optimization investigations. The results of the optimization study showed that the removal efficiency of Pb(II) is affected by individual parameter of initial solution pH, biosorbent dosage, and interactive parameters between initial solution pH and biosorbent dosage, initial solution pH and agitation speed, initial solution pH and temperature. The response surface of the optimization study is adequately described by the hierarchical quadratic model [51].

6 Lignocellulosic Biomass Residue for Heavy Metal Biosorption

The agro biomass residues such as almond shell, coconut shell, ground nut shell, *Tamarindus indica* seed and walnut shell are evaluated for the biosorption of Cr(VI) from aqueous solutions. In comparison of all the five biosorbents, the biosorbent prepared using the seed of *Tamarindus indica* showed higher performance towards the removal of Cr(VI). The biosorption of Cr(VI) using *Tamarindus indica* seed is decreased at the higher initial solution pH and is better at the higher temperature considered in the study. The biosorption of Cr(VI) is associated with the chemisorption mechanism [52]. The biomass of olive stones from the processing of olive oil industry is studied for the biosorption of Fe(II) from the industrial effluent. The characterisation of the biosorbent is done using mercuric porosimetry. The uptake capacity of the biosorbent was higher at the lower sorption capacity was higher at the lower biosorbent particle size. The removal efficiency of biosorbent attained 70% at the biosorbent dosage of 125 g/L [53]. The adsorptive removal of Pb(II) and Cd(II) is carried out using banana peel biomass. Compared to Pb(II) removal, the biosorbent presented more removal capacity towards Cd(II). The results of the Langmuir isotherm model revealed that 1.0 g of biosorbent is able to biosorb 5.71 mg of Cd(II) and 2.18 mg of Pb(II) in a separate batch biosorption system [54]. The waste biomass of *Citrus reticulata* is generated after juice extraction subjected for the different physical and chemical pretreatment. The prepared adsorbents potential is evaluated for the removal of Cr(III) and Cr(VI) removal from aqueous solution. The uptake capacity of the adsorbents depends on the structural changes of the biomass due to pretreatment and chromium oxidation state in the biosorption system. The maximum biosorption capacity of Cr(III) by H₂S modified biomass was 57.31 mg/g and Cr(VI) biosorption capacity of 51.68 mg/g by PEI + glutaraldehyde pretreated biomass [55].

Cadmium biosorption is carried out by using leaves and stem biomass portions of *Portulacaoleracea* without any pre-treatment. The maximum removal efficiency

of 72% is attained. Higher removal of Cd(II) is noticed up to 45 min and then gradually attained towards equilibrium around 100 min. The equilibrium biosorption data are better fitted with the isotherm models of both the Langmuir and Freundlich model equations [56]. The potential of *Barbulalambarenensis* biomass is evaluated for the biosorption of Pb(II) from aqueous solution. The optimum biosorption condition is established as 5.0 pH, contact time 60 min and temperature of 298 K. The FT-IR characterization results identified the presence of functional groups hydroxyl, carboxyl, carbonyl and amides involved in the Pb(II) biosorption [57]. The Cr(VI) removal is tested in a batch adsorption system using native and acids modified *Swieteniamahagoni* shells. The initial solution pH of the biosorption is mainly influenced on the Cr(VI) percentage removal. The thermodynamic analysis of the experiments represented spontaneous and endothermic nature of the Cr(VI) removal process. The coexisting ions has nil effect on the Cr(VI) adsorption process [58]. The biosorption of Pb(II) from synthetic and real effluent is reported using raw and immobilized biomass of *Mangifera indica*. The native biomass of *Mangifera indica* showed better Pb(II) removal efficiency compared to the compared to immobilized *Mangifera indica* biomass [59]. The biomass of *Sterculiaguttata* shell in native and ZnCl₂ activated employed for Cr(VI) adsorption from aqueous solution. The ZnCl₂ modified biomass presented higher surface area. The values of the Langmuir separation factor indicated the favorability of Cr(VI) adsorption by both native and modified adsorbents. The regeneration of biosorbent and its effective reuse is favored using the desorbing agent of 2.0 M NaOH concentration [60]. Direct burning of rice husk is associated with the problem of air pollution in Cairo and Nile Delta region (Egypt). To combat the problem experiments conducted for the use of plentifully available agro-industrial waste rice husk for biosorption of Cu(II) from water. The results showed rice husk as the potential precursor offering technical, societal, economical and ecological advantages for subjecting the rice husk towards the treatment of industrial effluents containing copper [61]. Peanut hull biomass employed as biosorbent in the native form Cu(II) removal from aqueous solution. The optimum biosorption operating conditions of the batch systems were pH 4.0, 150 rpm agitation speed, 60 min contact time, 1.0 g biosorbent dosage, 150 mg/L initial Cu(II) concentration and biosorbent particle size of particle size <0.250 mm. The experimental data are better fitted with the pseudo-second-order and intra-particle diffusion kinetic models, revealing the Cu (II) removal mechanism associated with physical and chemical adsorption process [62].

7 Biosorbent Regenerations

In order to reuse the biosorbent for good number of recycles and for the safe disposal of the exhausted biosorbent, the process of biosorbent regeneration after the biosorption process is essential. The regeneration of the biosorbent could be possible using the desorption process with the employment of suitable eluting

agents. The selection criteria of eluents for the desorption process depend on the biosorbent mechanical stability, biosorptive mechanism between the metal ions and the biomass [91]. The regeneration of the biosorbent, recycle number and desorbing agents of the metal removal process is summarized in Table 6. The biosorbent from *Lepiotahystrich* is used for the removal of Cu(II) and Pb(II) from aqueous solutions. The desorption study is performed in a batch system using 20 mL of desorbing agents of 0.1 M EDTA and 0.1 M HCl, for the contact time of 60 min. The results of the metal ions desorption showed HCl with better removal than EDTA. Moreover, the involvement of ion-exchange mechanism might affect the process of desorption for complete metal ions removal [92]. After the biosorption of Zn(II) using *Chlorella pyrenoidosa*, the metal loaded biomass is subjected for regeneration using the desorbing eluents of EDTA, HCl, and HNO₃. The desorption analysis showed that 0.1 M of HNO₃ presented better desorption process of Zn(II) from the biosorbent with the desorption efficiency of 95% [93].

Table 6 Biosorbents regeneration using desorption method

Biosorbent	Heavy metal	Number of recycles	Desorbing agents	References
Microalgae				
<i>Synechococcus</i> sp.	Cd(II)	5	HCl	[97]
<i>Chlorella miniata</i>	Cr(III)	–	NaOH, HNO ₃ , H ₂ SO ₄ , EDTA, Deionized H ₂ O	[98]
Bacteria				
<i>Tetraselmischuii</i>	Cd(II)	–	EDTA	[99]
<i>Bacillus laterosporus</i>	Ni(II), Cd(II)	3	HCl, HNO ₃ and H ₂ SO ₄	[100]
<i>Bacillus</i> sp.	Cu(II)	5	HNO ₃	[101]
<i>Arthrobacter</i> sp.	Pb(II)	–	EDTANa ₂ , NH ₄ NO ₃ and H ₂ O	[102]
Fungi				
<i>Pleurotusostreatus</i>	Cu(II), Ni(II), Zn(II) and Cr (VI)	–	HCl	[103]
<i>Aspergillusniger</i>	Ni(II), Zn(II), Cr(VI)	–	HCl	[104]
<i>Mucorracemosus</i>	Cr(VI)	–	HCl, NaOH	[105]
Plant biomass residue				
<i>Myriophyllumspicatum</i>	Pb(II), Cu(II), Cd(II), Ni(II), Zn(II)	3	HNO ₃	[106]
Sugarcane bagasse	Co(II), Cu(II), Ni(II)	–	HNO ₃	[107]
Garden grass	Cu(II)	5	H ₂ SO ₄	[108]

The biosorption experiments of Cu(II), Cd(II), Ni(II), Pb(II) and Zn(II) removal are performed using the NaOH-treated stem biomass of *Arundodonax*. Then, the metal-loaded biosorbent is subjected to desorption using 50 mL of 0.1 M HCl. The recycles of biosorption and desorption are performed up to 3 times. The desorption efficiency of greater than 88% is attained for the elution of Cu(II), Cd(II), Ni(II), Pb(II) and Zn(II) using 0.1 M HCl [94]. The biomass of the cashew nut shell is tested for the biosorption of Cd(II), Pb(II) and Cr(III) from contaminated water. The results of biosorbent regeneration showed that higher desorption efficiency is observed for Cd(II), Pb(II), whereas lower desorption efficiency with Cr(III) removal [95]. In order to check the reuse of *Saccharomyces cerevisiae* for As(III) biosorption, the metal-loaded biosorbent is treated with eluent of 0.5 M NaOH. The desorption efficiency of more than 75% is achieved. During each cycle of biosorption and desorption process, the uptake capacity of the biosorbent is changed by 20–25% and showed that prepared biosorbent could be employed for recycles up to three to four times without significant loss compared to original biosorption capacities [96].

8 Conclusion

The biosorption plays an important role in the separation technology for heavy metal removal from aqueous systems. The present review reported the potential sources of biosorbents from the dead microbial and plant biomass residues in the application of heavy metal sequestration. The utilization of such biosorbents is recommended for heavy metal removal due to their merits of low or no cost, wide distribution, renewable source, eco-friendly and property of more affinity for heavy metal biosorption. The potential biosorbent employment in the biosorption technology is investigated as an alternate approach for the existing conventional treatment methods. The process parametric influences on the removal of heavy metals removal by different biosorbents were discussed. The explanations of the mechanisms associated with the biosorption of heavy metals are illustrated using the isotherm and kinetic models. The aspects of biosorbent regenerations using the different desorbing agents and possibilities of biosorbent recycle for successive biosorption study were also reviewed. Even though a large number of publications are available in heavy metal biosorption, the research publications are found inadequate in view of industrial scale applications.

Acknowledgements Financial support for this work was provided by the Science and Engineering Research Board, Department of Science and Technology, India (PDF/2016/000284). The authors are thankful to the National Institute of Technology Rourkela for research facility support.

References

1. Rangabhashiyam, S., Sujata, L., Balasubramanian, P.: Biosorption characteristics of methylene blue and malachite green from simulated wastewater onto *Carica papaya* wood biosorbent. *Surfaces and Interfaces*. <https://doi.org/10.1016/j.surfin> (2017)
2. Nabil, A.F., Bnar, M.I.: The use of new chemically modified cellulose for heavy metal ion adsorption. *J. Hazard. Mater.* **343**, 324–331 (2018)
3. Fu, F., Wang, Q.: Removal of heavy metal ions from wastewaters: a review. *J. Environ. Manage.* **92**, 407–418 (2011)
4. Rangabhashiyam, S., Anu, N., Selvaraju, N.: Biosorption of heavy metals using low cost agricultural by products. *Res. J. Chem. Environ.* **17**, 112–123 (2013)
5. Bishop, P.L.: Pollution prevention: fundamentals and practice (2000)
6. Evanko, C.R., Dzombak, D.A.: Remediation of metals-contaminated soils and groundwater. Technology Evaluation Report, TE-97-01. Ground-Water Remediation Technologies Analysis Center, Pittsburg, PA (1997)
7. Rangabhashiyam, S., Anu, N., Selvaraju, N.: Equilibrium and kinetic modeling of chromium (VI) removal from aqueous solution by a novel biosorbent. *Res. J. Chem. Environ.* **18**(4), 30–36 (2014)
8. Srivastava, N.K., Majumder, C.B.: Novel biofiltration methods for the treatment of heavy metals from industrial wastewater. *J. Hazard. Mater.*, 1–8 (2008)
9. Celik, A., Demirbas, A.: Removal of heavy metal ions from aqueous solutions via adsorption onto modified lignin from pulping wastes. *Energy Sources* **27**, 1167–1177 (2005)
10. Friberg, L., Elinder, C.G.: Encyclopedia of Occupational Health. International Labor Organization, Geneva (1985)
11. Kjellstrom, T., Shiroishi, K., Erwin, P.E.: Urinary beta₂-microglobulin excretion among people exposed to cadmium in the general environment. *Environ. Res.* **13**, 318–344 (1977)
12. Ahmaruzzaman, M.: Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. *Adv. Coll. Interface. Sci.* **166**, 36–59 (2011)
13. World Health Organization (WHO). Guidelines for Drinking-Water Quality, 4th edn. 1–541 (2011)
14. Eroglu, M.S., Toprak, S., Urgan, O., Ozge, M.E., Onur, M., Arzu, D., Haldun, M., Akoglu, M., Cigdem, O., Ebru, M.A.: Parameters of water quality: interpretation and standards. *Saudi Med. J.* **33**, 3–8 (2012)
15. Mohod, C.V., Dhote, J.: Review of heavy metals in drinking water and their effect on human health. *Int. J. Innovative Res. Sci. Eng. Technol.* **2**, 2992–2996 (2013)
16. Sabolc, P., Tatjana, S.K., Jelena, R., Snezana, M., Sasa, M.L., Maja, T.S.: Utilization of fruit processing industry waste as green activated carbon for the treatment of heavy metals and chlorophenols contaminated water. *J. Clean. Prod.* **162**, 958–972 (2017)
17. Li, F., Liang, L., Zan, Q., Haomiao, X., Jianfang, X., Naiqiang, Y.: A novel method for the sequential removal and separation of multiple heavy metals from wastewater. *J. Hazard. Mater.* **342**, 617–624 (2018)
18. Nguyen, T.A.H., Ngo, H.H., Guo, W.S., Zhang, J., Liang, S., Yue, Q.Y., Li, Q., Nguyen, T. V.: Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater. *Biores. Technol.* **148**, 574–585 (2013)
19. Gadd, G.M.: Biosorption: critical review of scientific rationale, environmental importance and significance for pollution treatment. *J. Chem. Technol. Biotechnol.* **84**, 13–28 (2009)
20. Kshama, A.S., Varsha, K.V.: Kinetics and equilibrium studies on biosorption of nickel from aqueous solution by dead fungal biomass of *Mucorhiemalis*. *Chem. Eng. J.* **171**, 1234–1245 (2011)
21. Rangabhashiyam, S., Selvaraju, N.: Evaluation of the biosorption potential of a novel *Caryotaurens* inflorescence waste biomass for the removal of hexavalent chromium, from aqueous solutions. *J. Taiwan Inst. Chem. Eng.* **47**, 59–70 (2015)

22. Rangabhashiyam, S., Anu, N., Giri, N.M.S., Selvaraju, N.: Relevance of isotherm models in biosorption of pollutants by agricultural byproducts. *J. Environ. Chem. Eng.* **2**, 398–414 (2014)
23. Ayushi, V., Shashi, K., Surendra, K.: Biosorption of lead ions from the aqueous solution by *Sargassumfilipendula*: equilibrium and kinetic studies. *J. Environ. Chem. Eng.* **4**, 4587–4599 (2016)
24. Susmita, S.G., Krishna, G.B.: Kinetics of adsorption of metal ions on inorganic materials: a review. *Adv. Coll. Interface. Sci.* **162**, 39–58 (2011)
25. Rita, F.L.R., Sérgio, M.S.M., Francisco, A.R.B., Clésia, C.N., Iara, C.C., Débora, C.M.: Evaluation of the potential of microalgae *Microcystisnovacekii* in the removal of Pb^{2+} from an aqueous medium. *J. Hazard. Mater.* **179**, 947–953 (2010)
26. Elisabetta, F., Alessandra, L., Carlo, S., Attilio, C.: Chromium (VI) removal by methylated biomass of *Spirulinaplatisensis*: the effect of methylation process. *Chem. Eng. J.* **156**, 264–269 (2010)
27. Livia, S.F., Mayla, S.R., Joao, C.M.C., Alessandra, L., Elisabetta, F., Patrizia, P., Attilio, C.: Adsorption of Ni^{2+} , Zn^{2+} and Pb^{2+} onto dry biomass of *Arthrospira (Spirulina) platensis* and *Chlorella vulgaris*. I. Single metal systems. *Chem. Eng. J.* **173**, 326–333 (2011)
28. Mayla, S.R., Livia, S.F., João, C.M.C., Alessandra, L., Elisabetta, F., Attilio, C.: Metal biosorption onto dry biomass of *Arthrospira(Spirulina) platensis* and *Chlorella vulgaris*: multi-metal systems. *J. Hazard. Mater.* **217–218**, 246–255 (2012)
29. Qiao, H.S., Tian, T.Z., Li-Hua, C., Xin, H.X., Huan, L.C.: Hexavalent chromium detoxification by nonliving *Chlorella vulgaris* cultivated under tuned conditions. *Chem. Eng. J.* **228**, 993–1002 (2013)
30. Cristina, M.M., Paula, M.L.C., Xavier, F.M.: Capacity of simultaneous removal of zinc and cadmium from contaminated media, by two microalgae isolated from a polluted site. *Environ. Chem. Lett.* **9**, 511–517 (2011)
31. Petrovič, A., Simonič, M.: Removal of heavy metal ions from drinking water by alginate-immobilised *Chlorella sorokiniana*. *Int. J. Environ. Sci. Technol.* **13**, 1761–1780 (2016)
32. Hongkyun, L., Eunjung, S., Hyun, S.Y., Young, T.P., Dohyeong, K., Min, K.J., Chi, K.K., Won, S.S., Jaeyoung, C.: Biosorption of Cu(II) by immobilized microalgae using silica: kinetic, equilibrium, and thermodynamic study. *Environ. Sci. Pollut. Res.* **23**, 1025–1034 (2013)
33. Nourollah, M., Ehsan, M., Omidvar, F.: Biosorption of Cd and Pb ions from aqueous solutions by biomass of the green microalga *Scenedesmusquadricauda*. *J. Appl. Phycol.* **27**, 311–320 (2015)
34. Ferdag, C., Necip, A., Demet, Y., Asim, O.: Biosorption of lead from aqueous solutions by *Bacillus* strains possessing heavy-metal resistance. *Chem. Eng. J.* **73**, 422–428 (2011)
35. Ganiyu, O.O., Matthew, O.I., Oluwafemi, S.O., Olukayode, O.A.: Chromium (VI) biosorption properties of multiple resistant bacteria isolated from industrial sewerage. *Environ. Monit. Assess.* **185**, 6809–6818 (2013)
36. Ziagova, M., Dimitriadis, G., Aslanidou, D., Papaioannou, X., Tzannetaki, E.L., Liakopoulou, K.M.: Comparative study of Cd(II) and Cr(VI) biosorption on *Staphylococcus xylosus* and *Pseudomonas* sp. in single and binary mixtures. *Biores. Technol.* **98**, 2859–2865 (2007)
37. Jin, H.P., Hyo, T.C.: Characterization of cadmium biosorption by *Exiguobacterium* sp. isolated from farmland soil near Cu–Pb–Zn mine. *Environ. Sci. Pollut. Res.* **23**, 11814–11822 (2016)
38. Ryan, B., Majid, S., Abdolmajid, M., Hazim, A.M.Q.: Biosorption of IIPb and Cu using fixed and suspended bacteria. *J. Environ. Chem. Eng.* **2**, 1663–1671 (2014)
39. Paul, F.N., Zejiao, L., Jingjing, L.: The biosorption of Cr(VI) ions by dried biomass obtained from a chromium-resistant bacterium. *Front. Chem. Sci. Eng.* **8**, 454–464 (2014)

40. Dandan, L., Xingjian, X., Hongwen, Y., Xuerong, H.: Characterization of Pb^{2+} biosorption by psychrotrophic strain *Pseudomonas* sp. I3 isolated from permafrost soil of Mohe wetland in Northeast China. *J. Environ. Manage.* **196**, 8–15 (2017)
41. Ting, W., Hongwen, S.: Biosorption of heavy metals from aqueous solution by UV-mutant *Bacillus subtilis*. *Environ. Sci. Pollut. Res.* **20**, 7450–7463 (2013)
42. Ozdemir, G., Ozturk, T., Ceyhan, N., Isler, R., Cosar, T.: Heavy metal biosorption by biomass of *Ochrobactrum anthropi* producing exopolysaccharide in activated sludge. *Biores. Technol.* **90**, 71–74 (2003)
43. Tunalı, S., Akar, T., Ozcan, A.S., Kiran, I., Ozcan, A.: Equilibrium and kinetics of biosorption of lead(II) from aqueous solutions by *Cephalosporium aphidicola*. *Sep. Purif. Technol.* **47**, 105–112 (2006)
44. Shaheen, Z., Farrukh, A., Iqbal, A.: Tolerance and biosorption potential of filamentous fungi isolated from metal contaminated agricultural soil. *Biores. Technol.* **98**, 2557–2561 (2007)
45. John, R.M., Benila, S., Pasumalai, A.S.: Optimization of Chromium Biosorption by Fungal Adsorbent, *Trichoderma* sp. BSCR02 and its Desorption Studies. HAYATI. *J. Biosci.* **24**, 65–71 (2017)
46. Sriharsha, D.V., Lokesh, K.R., Savitha, J.: Immobilized fungi on *Luffacylindrica*: an effective biosorbent for the removal of lead. *J. Taiwan Inst. Chem. Eng.* **80**, 589–595 (2017)
47. Haiwei, H., Lixiang, C., Yuxuan, W., Renduo, Z., Wenfeng, W.: Biosorption behavior and mechanism of heavy metals by the fruiting body of jelly fungus (*Auriculariapolytricha*) from aqueous solutions. *Appl. Microbiol. Biotechnol.* **96**, 829–840 (2012)
48. Pedro, F.G., Patrik, R.L., Nils, K.P., Mohammad, J.T.: Heavy metal biosorption by *Rhizopus* Sp. Biomass Immobilized on Textiles. *Water Air Soil Pollut.* **225**, 1834 (2014)
49. Nikhil, R.S., Ashok, V.B., Ameeta, R.K., Smita, S.Z.: Removal of Ni (II) ions from aqueous solutions by biosorption onto two strains of *Yarrowialipolytica*. *J. Environ. Manage.* **102**, 115–124 (2012)
50. Aytar, P., Gedikli, S., Buruk, Y., Cabuk, A., Burnak, N.: Lead and nickel biosorption with a fungal biomass isolated from metal mine drainage: Box-Behnken experimental design. *Int. J. Environ. Sci. Technol.* **11**, 1631–1640 (2014)
51. Cerino, C.F.J., García, L.A.M., García, R.R.B., Garza, G.M.T., Soto, R.E., Sánchez, G.M.N., Quezada, L.I.: Response surface methodology for lead biosorption on *Aspergillusterreus*. *Int. J. Environ. Sci. Technol.* **8**, 695–704 (2011)
52. Agarwal, G.S., Bhuptawat, H.K., Chaudhari, S.: Biosorption of aqueous chromium(VI) by tamarindusindica seeds. *Biores. Technol.* **97**, 949–956 (2006)
53. Leopoldo, M.N., Saloua, B.D.A., Gassan, H., Catherine, F., Salvador, R., José, A.G., Javier, O.: Adsorption of iron on crude olive stones. *Ind. Crops Prod.* **32**, 467–471 (2010)
54. Jamil, A., Umer, S., Waheed, Z., Muhammad, S., Amara, D., Shafique, A.: Removal of Pb (II) and Cd(II) from water by adsorption on peels of banana. *Biores. Technol.* **101**, 1752–1755 (2010)
55. Ammara, Z., Haq, N.B., Muhammad, A.H., Faiza, S.: Kinetic and equilibrium modeling for Cr(III) and Cr(VI) removal from aqueous solutions by *Citrus reticulata* waste biomass. *Water Air Soil Pollut.* **191**, 305–318 (2008)
56. Dubey, A., Mishra, A., Singhal, S.: Application of dried plant biomass as novel low-cost adsorbent for removal of cadmium from aqueous solution. *Int. J. Environ. Sci. Technol.* **11**, 1043–1050 (2014)
57. Olu-Owolabi, B.I., Paul, N.D., William, C.E.: Mechanism of Pb^{2+} removal from aqueous solution using a nonliving moss biomass. *Chem. Eng. J.* **195**, 270–275 (2012)
58. Rangabhashiyam, S., Selvaraju, N.: Efficacy of unmodified and chemically modified *Swieteniamahagoni* shells for the removal of hexavalent chromium from simulated wastewater. *J. Mol. Liq.* **209**, 487–497 (2015)
59. Raziya, N., Qaisar, M., Munawar, I., Jan, N.: Biosorption of Pb(II) onto immobilized and native *Mangiferaindica* waste biomass. *J. Ind. Eng. Chem.* **35**, 185–194 (2016)

60. Rangabhashiyam, S., Selvaraju, N.: Adsorptive remediation of hexavalent chromium from synthetic wastewater by a natural and ZnCl₂ activated *Sterculiaguttata* shell. *J. Mol. Liq.* **207**, 39–49 (2015)
61. Abdelhafez, S.E., Hamad, H.A., Zaatout, A.A., Malash, G.F.: Management of agricultural waste for removal of heavy metals from aqueous solution: adsorption behaviors, adsorption mechanisms, environmental protection, and techno-economic analysis. *Environ. Sci. Pollut. Res.* **24**, 1397–1415 (2017)
62. Rehab, M.A., Hesham, A.H., Mohamed, M.H., Gihan, F.M.: Potential of using green adsorbent of heavy metal removal from aqueous solutions: Adsorption kinetics, isotherm, thermodynamic, mechanism and economic analysis. *Ecol. Eng.* **91**, 317–332 (2016)
63. Cordeo, B., Lodeiro, P., Herrero, R., Sastre De Vicente, M.E.: Biosorption of cadmium by *Fucus spiralis*. *Environ. Chem.* **1**, 180–187 (2004)
64. Cristina, M., Monteiro, P.M.L., Castro, F., Xavier, M.: Cadmium removal by two strains of *Desmodesmus pleiomorphus* Cells. *Water Air Soil Pollut.* **208**, 17–27 (2010)
65. Huijuan, M., Yunfeng, X., Hong, C.: Bioremediation of surface water co-contaminated with zinc (II) and linear alkylbenzenesulfonates by *Spirulinaplatisensis*. *Phys. Chem. Earth, Parts A/B/C* **47–48**, 152–155 (2012)
66. Kishore, K.K., Krishna, P.M., Sarada, B., VenkataR.M.: Challa: entrapment of marine microalga, *Isochrysis galbana*, for biosorption of Cr(III) from aqueous solution: isotherms and spectroscopic characterization. *Appl. Water Sci.* **3**, 85–92 (2013)
67. Sibi, G.: Biosorption of chromium from electroplating and galvanizing industrial effluents under extreme conditions using *Chlorella vulgaris*. *Green Energy Environ.* **1**, 172–177 (2016)
68. Cristina, M.M., Paula, M.L., Castro, F., Xavier, M.: Biosorption of zinc ions from aqueous solution by the microalga *Scenedesmus obliquus*. *Environ. Chem. Lett.* **9**, 169–176 (2011)
69. El-Naas, M.H., AbuAl-Rub, F., Ashour, I., Al Marzouqi, M.: Effect of competitive interference on the biosorption of lead(II) by *Chlorella vulgaris*. *Chem. Eng. Process.* **46**, 1391–1399 (2007)
70. Srinath, T., Verma, T., Ramteke, P.W., Garg, S.K.: Chromium(VI) biosorption and bioaccumulation by chromate resistant bacteria. *Chemosphere* **48**, 427–435 (2002)
71. Salehizadeh, H., Shojasodati, S.A.: Removal of metal ions from aqueous solution by polysaccharide produced from *Bacillus firmus*. *Water Res.* **17**, 4231–4235 (2003)
72. Acosta, M.P., Valdman, E., Leite, S.G.F., Battaglini, F., Ruzal, S.M.: Biosorption of copper by *Paenibacillus polymyxa* cells and their Exopolysaccharide. *World J. Microbiol. Biotechnol.* **21**, 1157–1163 (2005)
73. InceYilmaz, E., Ensari, N.Y.: Cadmium biosorption by *Bacillus circulans* strain EB1. *World J. Microbiol. Biotechnol.* **21**, 777–779 (2005)
74. Sheikh, S.Z., Mun, H.C., Jung, H.S., Hyunju, P., Ju, X., Ki-Whan, C., Sung, C.Y.: Enhanced biosorption of mercury(II) and cadmium(II) by cold-induced hydrophobic exobiopolymer secreted from the psychrotroph *Pseudomonas fluorescens* BM07. *Appl. Microbiol. Biotechnol.* **80**, 531–544 (2008)
75. Yu, J., Sumei, Y., Chunying, T., Tao, S., Liying, D., Jinsong, L., Xin, B., Xiuhong, X., Juanjuan, Q.: Biosorption characteristic of *Alcaligenes* sp. BAPb.1 for removal of lead(II) from aqueous solution. *Biotech* **7**, 123 (2017)
76. Sen, S.K., Raut, S., Dora, T.K., Mohapatra, P.K.D.: Contribution of hot spring bacterial consortium in cadmium and lead bioremediation through quadratic programming model. *J. Hazard. Mater.* **265**, 47–60 (2014)
77. Cho, D.H., Kim, E.Y.: Characterization of Pb²⁺ biosorption from aqueous solution by *Rhodotorulaglutinis*. *Bioprocess Biosyst. Eng.* **25**, 271–277 (2003)
78. Prasanjit, B., Sumathi, S.: Uptake of chromium by *Aspergillus foetidus*. *J. Mater. Cycles Waste Manage.* **7**, 88–92 (2005)
79. Ülkü, Y., Gülay, Ö., Filiz, B.D., Neslihan, E., Alev, E., Ayla, D.: Heavy metal biosorption by white-rot fungi. *Water Sci. Technol.* **38**, 323–330 (1998)

80. Shazia, I., Rabia, S., Hunnia, Z., Mehwish, J.: Biosorption and bioaccumulation of copper and lead by heavy metal-resistant fungal isolates. *Arab. J. Sci. Eng.* **40**, 1867–1873 (2015)
81. Mohammed, M.G., Al-Fakih, A.A., Mohamed, I.A.: Biosorption of Pb(II) and Co(II) ions from aqueous solutions using pretreated *Rhizopusoryzae* (Bread Mold). *Arab. J. Sci. Eng.* **39**, 2435–2446 (2014)
82. Muhammad, F., Ahmad, S., Haydar, T., Ahmad, Q.: Enhancement of biosorption of zinc ions from aqueous solution by immobilized *Candida utilis* and *Candida tropicalis* cells. *Int. Biodeterior. Biodegradation* **83**, 119–128 (2013)
83. Duygu, H.O., Van Leeuwen, J.: Fungal Biosorption of Ni(II) ions. *Sustain. Bioenergy Bioprod.*, 45–58 (2011)
84. Villaescusa, I., Fiol, N., Martinez, M., Miralles, N., Poch, J., Serarols, J.: Removal of copper and nickel ions from aqueous solutions by grape stalks wastes. *Water Res.* **38**, 992–1002 (2004)
85. Yasser, H., Amina, R., Taoufik, B.: Biosorption potential of the mediterranean plant (*Posidoniaoceanica*) for the removal of Cu^{2+} ions from aqueous media: equilibrium, kinetic, thermodynamic and mechanism analysis. *Korean J. Chem. Eng.* **31**, 1211–1218 (2014)
86. Foo, L.P.Y., Tee, C.Z., Raimy, N.R., Hassell, D.G., Lee, L.Y.: Potential Malaysia agricultural waste materials for the biosorption of cadmium(II) from aqueous solution. *Clean Technol. Environ. Policy* **14**, 273–280 (2012)
87. Witek-Krowiak, A.: Application of beech sawdust for removal of heavy metals from water: biosorption and desorption studies. *Eur. J. Wood Wood Prod.* **71**, 227–236 (2013)
88. Njoku, V.O.: Biosorption potential of cocoa pod husk for the removal of Zn(II) from aqueous phase. *J. Environ. Chem. Prod. Eng.* **2**, 881–887 (2014)
89. Qi, B.C., Aldrich, C.: Biosorption of heavy metals from aqueous solutions with tobacco dust. *Biores. Technol.* **99**, 5595–5601 (2008)
90. Ashutosh, M., Brahma, D.T., Ashwani, K.R.: Biosorption of Cr(VI) and Ni(II) onto *Hydrillaverticillata* dried biomass. *Ecol. Eng.* **73**, 713–723 (2014)
91. Vijayaraghavan, K., Balasubramanian, R.: Is Biosorption suitable for decontamination of metal-bearing wastewaters? A critical review on the state-of-the-art of biosorption processes and future directions. *J. Environ. Manage.* **160**, 283–296 (2015)
92. Zacharia, K., Jackson, K., Douglas, O.: Biosorption studies of lead and copper using rogers mushroom biomass *Lepiotahystris*. *S. Afr. J. Chem. Eng.* **23**, 62–70 (2017)
93. Hassan, R., Satish, D.K., Praveen, G.S.: Study of physical chemistry on biosorption of Zinc by using *Chlorella pyrenoidosa*. *Russ. J. Phys. Chem. A* **86**, 1332–1339 (2012)
94. Hai-Liang, S., Lu, L., Ke-Yun, Y.: Removal of several metal ions from aqueous solution using powdered stem of *Arundodonax* L. as a new biosorbent. *Chem. Eng. Res. Des.* **92**, 1915–1922 (2014)
95. Gustavo, F.C., Affonso, C.G. Jr., César, R.T.T., Juliana, C., Herbert, N., Marcio, A.F.: Removal of metal ions Cd (II), Pb (II), and Cr (III) from water by the cashew nut shell *Anacardiumoccidentale* L. *Ecol. Eng.* **73**, 514–525 (2014)
96. Yunhai, W., Yajun, W., Jianxin, Z., Qi, D.Y.W.: The characteristics of waste *Saccharomyces cerevisiae* biosorption of Arsenic(III). *Environ. Sci. Pollut. Res.* **19**, 3371–3379 (2012)
97. Asma, S., Muhammad, I.: Immobilization of blue green microalgae on loofa sponge to biosorb cadmium in repeated shake flask batch and continuous flow fixed bed column reactor system. *World J. Microbiol. Biotechnol.* **22**, 775–782 (2006)
98. Xu, H., Yuk, S.W., Nora, F.Y.T.: Surface complexation mechanism and modeling in Cr(III) biosorption by a microalgal isolate, *Chlorella miniata*. *J. Colloid Interface Sci.* **303**, 365–371 (2006)
99. Antonio, C.A.C., Francisca, P.F.: The behaviour of the microalgae *Tetraselmischuii* in cadmium-contaminated solutions. *Aquacult. Int.* **6**, 57–66 (1998)
100. Rajeswari, M.K., Vidya, S.K., Srinikethan, G.: Cadmium (II) and Nickel (II) biosorption by *Bacillus laterosporus* (MTCC 1628). *J. Taiwan Inst. Chem. Eng.* **45**, 1628–1635 (2014)

101. Waihung, L., Lau, M.N., Hong, C., Peter, H.F.Y., Shirley, N.S., Po-Keung, W.: Biosorption and desorption of copper (II) ions by *Bacillus* sp. Appl. Biochem. Biotechnol. **107**, 581–591 (2003)
102. Tianqi, W., Jun, Y., Zhimin, Y., Yue, Z., Fei, W., Huilun, C.: Isolation of lead-resistant *Arthrobacter* strain GQ-9 and its biosorption mechanism. Environ. Sci. Pollut. Res. (2017). <https://doi.org/10.1007/s11356-017-0694-7>
103. Amna, J., Rukhsan, B., Umer, S., Jamil, A.: Removal of heavy metals by adsorption on *Pleurotostreatus*. Biomass Bioenerg. **35**, 1675–1682 (2011)
104. Rajender, K., Divya, B., Rajesh, S., Narsi, R.B.: Metal tolerance and sequestration of Ni(II), Zn(II) and Cr(VI) ions from simulated and electroplating wastewater in batch process: Kinetics and equilibrium study. Int. Biodeterior. Biodegradation **66**, 82–90 (2012)
105. Ting, L., Huidong, L., Zhao, L., Xiao, X., Lingli, C., Le, D.: Removal of hexavalent chromium by fungal biomass of *Mucor racemosus*: influencing factors and removal mechanism. World J. Microbiol. Biotechnol. **23**, 1685–1693 (2007)
106. Jelena, V.M., Mirjana, D.S.M.L., Mihajlović, Z.R., Lopičić, M.S.P., Tatjana, D.Š., Mirjana, Đ.R.: Compost of aquatic weed *Myriophyllum spicatum* as low-cost biosorbent for selected heavy metal ions. Water Air Soil Pollut. **225**, 1927 (2014)
107. Stela, N.C.R., Amália, L.P.X., Filipe, S.T., Megg, M.C.E., Fernanda, J.G., Laurent, F.G., Rossimiriam, P.F., Leandro, V.A.G.: Modeling mono- and multi-component adsorption of cobalt(II), copper(II), and nickel(II) metal ions from aqueous solution onto a new carboxylated sugarcane bagasse. Part I: Batch adsorption study. Ind. Crops Prod. **74**, 357–371 (2015)
108. Hossain, M.A., Ngo, H.H., Guo, W.S., Setiadi, T.: Adsorption and desorption of copper(II) ions onto garden grass. Biores. Technol. **121**, 386–395 (2012)