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REVIEWS

Biosorption of heavy metals from aqueous solutions using indigenous and modified lignocellulosic materials

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Abstract This critical review emphasizes on the potential applications of low-cost lignocellulosic material in the field of heavy metal pollution remediation. It contains the information related to binding mechanism, relative uptake capacities, effect of modification on increment in uptake capacities, equilibrium, kinetic and thermodynamic modeling involved. This effort offers a good understanding about the role of functional groups in biosorption process. However, there exists a large barrier which inhibits the industry to switch on the biosorption process in place of conventional technologies. Future investigations on (1) assessment of low-cost lignocellulosic materials on multi-metal samples and real world samples, (2) low-cost methods of modification, (3) development of multifunctional lignocellulosic materials can help to decrease this barrier.

Keywords Lignocellulosic materials · Modification methods · Biosorption mechanism · Kinetic · Thermodynamics

1 Introduction

Heavy metals are highly toxic, show bioaccumulation and persistency against biodegradation (Anwar et al. 2009; Kumar et al. 2012). These enter the aquatic system via various industrial activities like electroplating, battery manufacturing, leather tanning, etc. (Nguyen et al. 2013). A list of 13 toxic heavy metals (antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc) has been generated by USEPA in 1978 (Ramos et al. 2002). Sources and toxicity of some common heavy metals are enlisted in Table 1.

Safe disposal of wastewater (especially considering the heavy metal content) is the critical environmental challenge for the industry. Numerous methodologies have been developed in this regard as tabulated in Table 2. The materials used in these methods are generally highly expensive rendering these uneconomical for developing countries. Moreover, some of these methods generate the concentrated sludge during the wastewater treatment process which poses another disposal problem. In addition, some of these methods become ineffective or too much costly at low metal ions concentrations i.e. 100 mg/L or below (Ceribasi and Yetis 2001; Marin-Rangel et al. 2012; Mishra et al. 2012). For this reason, there is a constant need to search for a best possible technology for heavy metal removal while considering its cost and efficiency.

2 Biosorption: an effective solution

Biosorption is a broad term utilized for the removal of materials (metal ions, organic compounds etc.) due to

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Table 1 Sources and toxicity of some common heavy metals (adapted from (Farooq et al. 2010b))

Metals	Sources	Toxicity to humans
Lead	Electroplating, batteries manufacturing, Pigments	Brain damage, malaise, loss of appetite, anaemia
Cadmium	Electroplating, smelting, alloy formation, pigments, plastics, mining	Carcinogenic, renal disturbance, lung insufficiency, bone lesions, weight loss
Mercury	Forest fires, fossil fuel burning, chloralkali industries	Neurological and renal disturbances, impairment of pulmonary function, corrosive, to skin, eyes, kidney damage
Chromium	Electroplating, tanneries, textile, metallurgy, paints, Steel manufacturing	Carcinogenic, mutagenic, teratogenic, vomiting, severe diarrhea, lung tumors
Arsenic	Smelting, mining, fossil fuels, rock sediments	Gastrointestinal symptoms, disturbances of cardiovascular and nervous system functions, bone marrow depression, haemolysis, liver tumors
Copper	Circuit board manufacturing, electronics plating, drawing of wires, copper polish, paints	Reproductive damages, neurotoxicity, dizziness, diarrhea
Nickel	Non-ferrous metal, mineral processing, paint manufacturing, electroplating, steam electric power plants	Chronic bronchitis, lung cancer

Table 2 Common methods to remove heavy metals from wastewater

Methods	Advantages	Disadvantages
Chemical Precipitation	Easy operation, cost-effective	Large amount of sludge, extra operational cost for sludge disposal
Chemical Coagulation	Sludge settling, dewatering	Costly, high consumption of chemicals
Ion-exchange	Selective for metal ions, regeneration of materials	Costly, available for less number of metal ions
Electrochemical methods	Selectivity for metal ions, no chemical consumption, Most of the metals can be removed	High capital and running cost, current density
Adsorption using activated carbon	High efficiency (>99 %)	Costly, No regeneration, performance depends on adsorbent
Membrane Filtration	Low space requirement, low pressure, high separation selectivity	High operation cost
Electro-dialysis	High selectivity	High operation cost due to membrane fouling and energy consumption
Photo-catalysis	Removal of metals and organic pollutant simultaneously, less harmful by-products	Long time duration, limited applications

Source: Nguyen et al. (2013)

the attractive forces between the substrate and biosorbent (material generated from biological origin). It offers a promising technique to metal contaminated waters even at low concentration, with advantages like (1) high efficiency (2) low cost (3) easy operation and (4) metal recovery etc. Both living as well as dead biomass have been utilized for the effective removal of metal ions. Using living biomass, the removal of metal ions from aqueous solution is also termed as bioaccumulation. Biosorption and bioaccumulation show various mechanisms for the metal removal (Chojnacka 2010; Chojnacka et al. 2005). Bioaccumulation is a slow process as compared to biosorption due to its nutrient dependence (Chojnacka 2010).

Biosorbents can be further classified into (1) from microbial origin and (2) from lignocellulosic materials. This paper includes the recent studies on the biosorption efficiency and capacity of lignocellulosic materials, their methods of chemical alteration, optimal working conditions and preference order of biosorbents.

3 Biosorption using biomass from microbial origin

Microbial biomasses contain several functional groups on their cell wall and can bind metal ions from dilute aqueous solutions. Several microbial biomasses including algae (Gupta and Rastogi 2008; Liping et al. 2007; Vogel et al. 2010), fungus (Arbanah et al. 2012; Tsekova et al. 2010; Yahaya et al. 2009), bacteria (Wang and Chen 2009), sea weeds (Elangovan et al. 2008; Murphy et al. 2008, 2009), have been used for metal recovery from aqueous solutions. Biosorption capacities of microbial biomasses for metal binding as reported by some researchers are enlisted in Table 3.

Use of microbial biomasses is attractive due to their high efficiency for dilute solutions of metal ions. The problems and the costs associated with the growth conditions, nutrient dependence, and place for growth at gross levels makes such a useless suitable for industrial adoption especially in developing countries. Moreover, the invariable weather conditions also affect their growth.

4 Biosorption using lignocellulosic materials

Lignocellulosic materials are generated due to agricultural activities and thus sometimes also termed as agricultural wastes or agricultural byproducts. These may be different parts of plant materials like stem, bark, leaves, roots, fruit peals, husk, hull, shell and bran etc. Cellulose, hemicelluloses and lignin are the main components of these materials. Lignocellulosic materials offer strong forces of attraction for the binding of metal ions due to presence of high content of hydroxyl group (Anwar et al. 2011; Okoro and Okoro 2011). Certain other functional groups including amino, amido, carboxyl, esters, alcohols, carbonyl, sulphur containing groups and acetamide are also present on the surface of lignocellulosic materials. These functional groups bind metal ions either by replacing them with hydrogen ions (ion exchange), adsorption or by donation of electron pairs (complex formation). Due to rich in functional groups, lignocellulosic materials could be a massive source as adsorbent materials for the detoxification of metal contaminated waters (Akar et al. 2012; Jiménez-Cedillo et al. 2013; Lee and Rowell 2004; Marin-Rangel et al. 2012).

There are numerous studies using lignocellulosic materials to replace the already operated instrumental/chemical methods for the removal of metal ions from wastewater. A number of reviews have been published in this regard (Demirbas 2008; Farooq et al. 2010b; Miretzky and Cirelli 2010; O'Connell et al. 2008; Sud et al. 2008). The adoption of this technique in place of conventional technologies is advantageous due to the high affinity and high selectivity of lignocellulosic materials towards heavy metal ions (Banerjee et al. 2012). Moreover, the low cost, agricultural origin and abundant availability provides the feasibility towards its applicability at large scale (Ali et al. 2011). In addition, the lignocellulosic materials can be processed, applied and recovered without potentially devastating the environment (Wan Ngah and Hanafiah 2008). The recyclability of these adsorbent materials for the purpose of heavy metal ions treatment is thought to reduce the wastes in an eco-friendly way, thus making lignocellulosic materials more superior. Hence, it agrees well with the perception of development of sustainable method of waste management.

5 Biosorbent selection criteria

The selection of best lignocellulosic materials is not very easy. Different researchers give different views about the selection of the biosorbent materials. Some researchers believe that low cost and easy availability is the best selection criteria (Ali et al. 2011; Anwar et al. 2010b). This criteria is most helpful for the developing countries where the industrial investment is comparatively less. While some argues that high adsorption capacity and selectivity should be the deciding factor in selection of biosorbent materials (Chojnacka 2010; Wang and Chen 2010). Most of the studies given in this regard revealed that a good biosorbent material should meet several requirements like, high adsorption capacity, high selectivity, low cost, easy desorption and regeneration, negligible leaching into aqueous systems.

6 Comparison of adsorption capacity of different lignocellulosic materials

A number of studies have been carried out to find out the adsorption capacity of biological materials

Table 3 Biosorption capacities of various microbial biomasses

Type	Name of specie	Metal	Biosorption capacity (mg/g)	Reference
Bacteria	*Bacillus megaterium*	Cr(VI)	30.7	Srinath et al. (2002)
	Pseudomonas putida	Zn(II)	17.7	Chen et al. (2005)
		Cu(II)	8.0	Pardo et al. (2003)
	Bacillus sp.	Cu(II)	16.3	Tunali et al. (2006)
	Halomonas sp.	Cu(II)	12.023	Manasi et al. (2014)
Yeast	Yeast	Ni(II)	46.3	Ozer and Ozer (2003)
		Cr(VI)	86.95	Lokeshwari and Joshi (2009)
		Cu(II)	144.9	Peng et al. (2010)
Algae	*Laminaria japonica*	Re(VII)	1.45 (at pH = 6)	Xiong et al. (2013)
	Azollafiliculoides	Pb(II)	124	Ganji et al. (2005)
		Cd(II)	58	Ganji et al. (2005)
		Cu(II)	33	Ganji et al. (2005)
		Zn(II)	34	Ganji et al. (2005)
	Chlorella vulgaris	Zn(II)	17	Melcáková and Ruzovic (2010)
	Spirogyra sp.	Pb(II)	140.84	Gupta and Rastogi (2008)
	Caulerpa lentillifera	Pb(II)	28.7	Pavasant et al. (2006)
	Gelidium algae	Pb(II)	64.0	Vilar et al. (2005)
	Chlamydomonas reinhardtii	Pb(II)	96.3	Tuzun et al. (2005)
Fungi	*Penicillium chrysogenum*	Ni(II)	55	Deng and Ting (2005)
		Cu(II)	92	Deng and Ting (2005)
	Mucor rouxii	Pb(II)	25.22	Yan and Viraraghavan (2003)
		Zn(II)	16.62	Yan and Viraraghavan (2003)
		Cd(II)	8.36	Yan and Viraraghavan (2003)
		Ni(II)	6.34	Yan and Viraraghavan (2003)
	Cunninghamella echinulata	Pb(II)	45	Morsy (2004)
		Cu(II)	20	Morsy (2004)
		Zn(II)	18.8	Morsy (2004)
	Rhizopus arrhizus	Ni(II)	29.52	Subudhi and Kar (2008)
		Cu(II)	17.58	Subudhi and Kar (2008)
	Polyporous versicolor	Ni(II)	57	Dilek et al. (2002)
	Pleurotus cornucopiae	Cu(II)	25	Danis (2010)
	Pleurotus ostreatus	Cr(III)	2.36	Javaid and Bajwa (2007)
		Cu(II)	8.06	Javaid et al. (2011)
		Ni(II)	20.40	Javaid et al. (2011)
		Zn(II)	3.22	Javaid et al. (2011)
		Cr(VI)	10.75	Javaid et al. (2011)
	Silica gel-immobilized L. *salmonicolor*	Ni(II)	114.44	Akar et al. (2013)
	Ganoder malucidum	Cr(III)	2.16	Shoaib (2012)

(Table 4). Some of these emphasize on the removal efficiency of biosorbents for metal ion, while others highlight the uptake capacity of biosorbent materials for heavy metal ions. Comparison on the basis of removal efficiency (removal percentage) is not preferable because it does not give clear idea about the binding of ions per unit mass of biosorbent material. For instance, (Anwar et al. 2010a) reported that 2

Table 4 Biosorption capacities of various lignocellulosic materials

Metal ion	Adsorbent	q_{max} (mg/g)	References
As(V)	Pine leaves	3.27	Shafique et al. (2012)
	Sorghum Biomass	2.765	Haquea et al. (2007)
	M. Oleifera	2.16	Sharma et al. (2006)
Cd(II)	Cortex banana waste	67.20	Kelly-Vargas et al. (2012)
	Neem Bark	27.57	Naiya et al. (2009)
	Sawdust	26.73	Naiya et al. (2009)
	T. aestivum	23.20	Ali et al. (2011)
	Cashew nut shell	22.11	Kumar et al. (2012)
	T. aestivum (straw)	14.56	Dang et al. (2009)
	T. aestivum (straw)	11.56	Tan and Xiao (2009)
	Sorghum biocolor L.	7.87	Salman et al. (2013b)
	Castor seed hull	6.98	Sen et al. (2010)
	Banana peels	5.71	Anwar et al. (2010a)
	A. hypogea shells	2.81	Mahajan and Sud (2013)
Pb(II)	*T. aestivum*	90.09	Ali et al. (2011)
	S. melongena	71.42	Yuvaraja et al. (2014)
	C. inophyllum seed husk	34.51	Lawal et al. (2010)
	Pine cone activated carbon	27.53	Momčilović et al. (2011)
	Solid waste of olive oil	23.69	Blázquez et al. (2010)
	Pigeon pea hulls powder	23.64	Ramana et al. (2012)
	P. dioica	22.37	Cruz-Olivares et al. (2011)
	Pine cone powder	16.34	Ofomaja and Naidoo (2010)
	T. resupinatum	10.38	Athar et al. (2013)
	N. sativa seeds	8.08	Bingöl et al. (2012)
	Sorghum biocolor L.	6.289	Salman et al. (2013b)
	S. bengalense	4.431	Din et al. (2014)
	A. nilotica leaves	2.51	Waseem et al. (2012)
	Banana peels	2.18	Anwar et al. (2010a)
	A. sisalana (sisal fiber)	1.34 (23 °C)	dos Santos et al. (2011)
Cr(III)	Yellow passion-fruit shells	85.1	Jacques et al. (2007)
	Agave bagasse	11.44	Bernardo et al. (2009)
	Agave lechuguilla	11.31	Romero-Gonzalez et al. (2006)
	Sorghum bicolor L.	7.03	Salman et al. (2013a)
	Olive stone	4.08	Calero et al. (2009)
	Pea waste	3.56	Anwar et al. (2010b)
	P. longifolia	1.87	Anwar et al. (2011)
Cr(VI)	Wheat bran	310.58	Singh et al. (2009)
	Pistachio hull waste	116.3	Moussavi and Barikbin (2010)
	Rice bran	58.9	Wang et al. (2008)
	Rice husk	52.1	Krishnani et al. (2008)
	Sawdust	41.52	Gupta and Babu (2009)
	Wheat bran	40.8	Wang et al. (2008)
	Eichhornia crassipes root activated carbon	36.34	Giri et al. (2012)
	F. religiosa	26.25	Qaiser et al. (2007)
	Rice straw	3.15	Gao et al. (2008)

Table 4 continued

Metal ion	Adsorbent	q_{max} (mg/g)	References
	A. scholaris	1.45	Rehman et al. (2012)
Cu(II)	*T. indica* seed powder	133.24	Chowdhury and Saha (2011)
	Rose petals waste	124.21	Manzoor et al. (2013)
	Watermelon shell	111.10	Banerjee et al. (2012)
	Cortex lemon waste	70.40	Kelly-Vargas et al. (2012)
	Cortex orange waste	67.20	Kelly-Vargas et al. (2012)
	Cortex banana waste	36.00	Kelly-Vargas et al. (2012)
	T. aestivum	21.01	Ali et al. (2011)
	O. Sativa	12.36	Athar et al. (2014)
	Sorghum biocolor L.	4.34	Salman et al. (2013b)
	Olive solid waste	3.81	Chouchene et al. (2013)
	P. longifolia leaf powder	1.74	Rehman et al. (2013)
Ni(II)	Orange peels	62.30	Gonen and Serin (2012)
	Cassava peels	57.00	Kurniawan et al. (2011)
	Moringa oleifera bark	30.38	Reddy et al. (2011)
	Pigeon pea hulls powder	23.63	Ramana et al. (2012)
	S. bengalense	15.79	Din and Mirza (2013)
	Water bamboo husk	8.40	Asberry et al. (2014)
	Banana peels	5.133	Kakalanga et al. (2012)
	P. longifolia leaf powder	4.08	Rehman et al. (2013)
	Egg plant peels	3.205	Kakalanga et al. (2012)
	A. hypogea shells	2.82	Mahajan and Sud (2013)
	Sugarcane baggase	2.23	Alomá et al. (2012)
	Olive solid waste	2.16	Chouchene et al. (2013)
	Sweet potato peels	0.509	Kakalanga et al. (2012)
Zn(II)	Cedrusdeodara sawdust	97.39	Mishra et al. (2012)
	Orange waste	43.16	Marin et al. (2010)
	Carrot residues	29.61	Eslamzadeh et al. (2004)
	Sugar beet pulp	17.78	Pehlivan et al. (2005)
	Sawdust	14.10	Naiya et al. (2009)
	Neem bark	13.29	Naiya et al. (2009)
Co(II)	*S. bengalense*	14.7	Din et al. (2013b)
	P. longifolia leaf powder	3.99	Rehman et al. (2013)
Fe(III)	Water bamboo husk	4.7	Asberry et al. (2014)
Hg(I)	Sugarcane bagasse	35.71	Khoramzadeh et al. (2013)
Hg(II)	Bacillus subtilis biomass	68.5	Wang et al. (2010)
	Eucalyptus bark	34.60	Ghodbane and Hamdaoui (2008)
	Allium sativum L.	0.6497	Eom et al. (2011)

grams of powdered banana peels can remove 89.2 % lead ions from its 50 mL aqueous solution of 50 mg/L concentration after shaking it for 20 min. However, the reported maximum adsorption capacity (2.18 mg/g) was significantly low. Similar trend have been reported by other researchers (Aman et al. 2008; Rehman et al. 2012; Saka et al. 2012).

A variety of literature is available in this regard. Classifying the reported studies, the loading capacities of lignocellulosic materials may be compared in two

categories (1) untreated lignocellulosic materials and (2) pretreated/modified lignocellulosic materials.

7 Untreated lignocellulosic materials

Table 4 illustrates the adsorption capacitates of various untreated lignocellulosic materials for heavy metal uptake. There is a large variation in the adsorption capacities of different lignocellulosic materials for heavy metals. The influencing factors are origin of biomass, nature of adsorbent, surface morphology of adsorbent, metal variation, uptake mechanism and nature of binding forces. As can be seen from Table 4, some of the biosorbent material shows extremely large biosorption capacities for heavy metal without any pretreatment. One gram of rose petal waste adsorbed 124.1 mg of copper from aqueous solution (Manzoor et al. 2013), 310.58 mg of Cr(VI) by one gram of wheat bran (Singh et al. 2009), 111.10 mg copper by one gram of powdered watermelon shells (Banerjee et al. 2012) etc. This can be attributed to the availability of large number active sites for metal binding. A study conducted by (Anwar et al. 2010a) released that banana peels show relatively high biosorption capacity for cadmium (5.71 mg/g) than for lead (2.18 mg/g). Some lignocellulosic materials tended to prefer heavy metals compared to other biosorbents. Copper uptake by lemon waste (70.4 mg/g) was greater than banana (36 mg/g) and orange (67.20 mg/g) waste (Kelly-Vargas et al. 2012). Similar effect has been noted by (Kakalanga et al. 2012) for nickel removal from aqueous solution. They introduced an order banana peels > egg plant peels > sweet potato peels for nickel adsorption based on their loading capacities.

It has also been observed that same biosorbent material showed different biosorption capacity for same metal ion. *T. aestivum* showed different adsorption capacities for binding cadmium ions; 11.56, 14.56 and 23.20 mg/g (Ali et al. 2011; Dang et al. 2009; Tan and Xiao 2009). Similar effect has been reported for wheat bran for Cr(VI) uptake; 310.58 and 40.8 mg/g (Singh et al. 2009; Wang et al. 2008). This variation can be due to the variation in cellulose content, growth conditions, processing/handling conditions etc.

The variation in the biosorption capacities of lignocellulosic materials in the literature is very diverse and it becomes very hard to choose best lignocellulosic materials for heavy metal binding. However, an overview of the literature suggests that various lignocellulosic materials are potential candidates for metal removal from aqueous solutions on industrial scale due to their low cost and high effectiveness regarding metal binding.

8 Pretreated/modified lignocellulosic materials

Several studies have been conducted using untreated lignocellulosic materials to eliminate heavy metal ions from aqueous solutions (Table 4). Though, significant drawback are also accompanies their usage such as low adsorption capacity in many cases, release of soluble organic matter/lignin into the solution. This leached organic load cause increase in chemical oxygen demand (COD), biochemical oxygen demand (BOD) and total organic carbon (TOC) eventually depleting the dissolved oxygen content in treated water samples. Modification of raw lignocellulosic materials eliminates such type of drawbacks. There is an emerging trend to modify the lignocellulosic materials to enhance the binding capacity, minimize leaching of soluble organic compounds and colored substances (Farooq et al. 2011; Wan Ngah and Hanafiah 2008).

Several methods of modifying the biosorbent materials have been reported in the literature including physical modification, chemical modification, cell modification etc. (Figure 1). Physical modification is the simplest one but less effective. In contrary, chemical modifications are highly effective (Park et al. 2010). Several chemical modifying agents have been reported in literature. These agents can be classified as bases, acids and organic compounds etc. Some other methods also have been reported to cause an increase in number of functional groups and graft polymerization. It was claimed that pretreatment of biological material significantly increase the biosorption capacity of the material (Rehman et al. 2012; Wang and Chen 2010). It can be attributed to better ion-exchange, increment in number and types of functional groups, metal holding capacity of already present groups that favors the better metal uptake. The latest findings of some researchers regarding effect of modification are summarized in Table 5.

The effect of mineral acids on the adsorption capacity of biosorbent materials have been reported by (Lasheen et al. 2012). Their study revealed that treatment of orange peels with nitric acid (HNO_3,

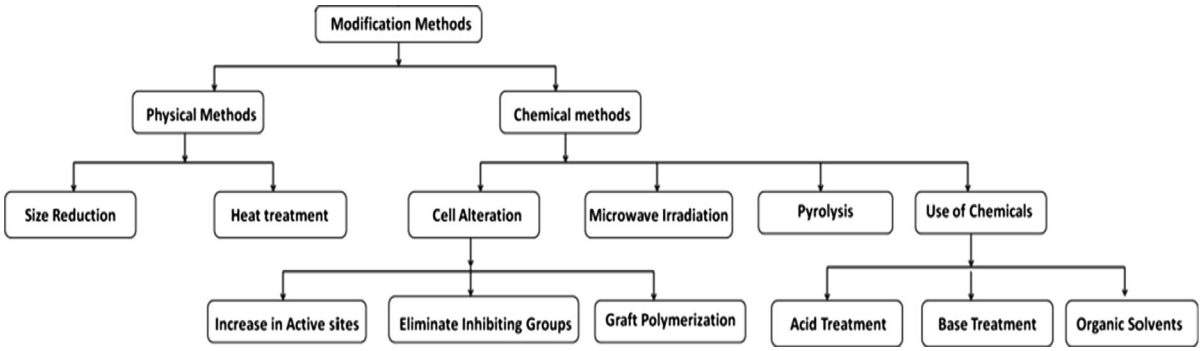

Fig. 1 Classification of pretreatment methods

0.1 M) removed potassium and calcium ions, thus making the uptake of cadmium ions more attractive. Similar findings have been reported by (Osman et al. 2010). (Rehman et al. 2012) reported that pretreatment with hydrochloric acid (HCl, 0.1 M) significantly increased the Cr(VI) removal efficiency (87.33 %) of the biological material as compared to the raw biomass (47.38 %). (Boota et al. 2009) in their study has revealed that modification of biomass with sulfuric acid increased the negative sites on the biomass surface with an increment in surface area, thus increasing the biosorption capacity of the biomass significantly for metal cations.

Inorganic bases have also been used as modifying agents. (Rehman et al. 2012) found that use of Sodium hydroxide (NaOH, 0.001 M) increasd the adsorption capacity of *A. scholarlis* to 163.4 % than its raw form. In another study conducted by the same group, they reported a decrease in the adsorption capacity of biological material (*P. longifolia*) pretreated with 0.01 M NaOH (Rehman et al. 2011). The reason may attribute the change in surface morphology is different for different materials. (Ofomaja and Naidoo 2010) investigated the effect of concentration of NaOH on the pine cone powder regarding its metal uptake capacity. They found that increase in concentration of NaOH (0.01–0.05 M) increases the Pb(II) uptake capacity of modified pine cone powder (39.41–51.47 %) as compared to raw pinecone powder. They claimed that bond formed between Pb(II) ions and the active sites on the said biomass were stronger for the pretreated adsorbent. The results obtained were in good agreement with a previous study conducted by (Kumar and Bandyopadhyay 2006).

Modification of non-living biological materials with organic compounds has also been reported in recent literature. The literature in this regard reveals that adsorption capacity of lignocellulosic materials is directly related with number of functional groups on the biomaterial surface (Goyal and Srivastava 2009; Panda et al. 2008). (García-Mendieta et al. 2012) has reported that treatment of green tomato husk with formaldehyde (0.2 %) slightly increases its uptake capacity for Mn(II) and Fe(III). (Hu et al. 2011) found that modification of pineapple peel fibers with succinic anhydride increased its biosorption capacity significantly. The reason attributed to the increase in metal binding sites due to modification of dead biomass. A relatively new modification method has been proposed by (Farooq et al. 2011). They claimed that modification of wheat straw with urea in solid state under microwave irradiation increases the Pb(II) uptake capacity to significantly high levels (822.8 %). They stated that modification under these conditions increases the nitrogen content in the studied biomass, which was in turn confirmed by FTIR-spectra (Fourier Transform Infrared) and elemental analysis. This along with increase in surface area resulted in producing an effective biosorbent for metal removal from aqueous solutions. Similar finding have been recently reported for Cr(III) removal by urea modified sorghum biomass (Salman et al. 2013a). Modification of functional groups present on the surface of orange peels by graft polymerization has been investigated by (Feng et al. 2011). They revealed that this modification improves the ion exchange and chelation capacity of the raw orange peels.

Literature revealed that chemical pretreatment of lignocellulosic materials causes significantly increase in the adsorption capacity. However, this may contain some drawbacks. The cost of treatment may rise, creating difficulty for industrial adoption. In addition,

Table 5 Effect of modification on biosorption capacities of lignocellulosic maerials

Biosorbent	Modifying agent	Metal ions	q_m (mg/g)	Change in q_m (%)	References
T. aestivum	Urea	Cd(II)	39.22	(+)822.8	Farooq et al. (2011)
S. bengalense	Urea	Pb(II)	12.65	(+)167.4	Din et al. (2013a)
Sorghum bicolor L.	Urea	Cr(III)	16.36	(+)132.7	Salman et al. (2013a)
O. sativa	Urea	Cu(II)	19.19	(+)55.2	Athar et al. (2014)
Sorghum bicolor L.	Thiourea	Pb(II)	17.82	(+)183.4	Salman et al. (2014)
Orange peels	The grafted polymerization	Ni(II)	162.6	(+)1,555.8	Feng et al. (2011)
Orange peels	The grafted polymerization	Cd(II)	293.3	(+)362.9	Feng et al. (2011)
Orange peels	The grafted polymerization	Pb(II)	476.1	(+)319.5	Feng et al. (2011)
Green Tomato husk	Formaldehyde (0.2 %)	Mn(II)	15.22	(+)10.89	García-Mendieta et al. (2012)
Green Tomato husk	Formaldehyde (0.2 %)	Fe(III)	19.83	(+)5.09	García-Mendieta et al. (2012)
P. longifolia	NaOH(0.01 M)	Cr(VI)	0.165	−96.5	Rehman et al. (2011)
Pine cone powder	NaOH(0.01 M)	Pb(II)	22.78	(+)39.41	Ofomaja and Naidoo (2010)
Pine cone powder	NaOH(0.01 M)	Pb(II)	24.75	(+)51.47	Ofomaja and Naidoo (2010)
A. scholaris	NaOH(0.001M)	Cr(VI)	3.82	(+)163.4	Rehman et al. (2012)
Orange peels	NaOH and $CaCl_2$	Cu(II)	70.73	(+)59.73	Feng and Guo (2012)
Orange peels	NaOH and $CaCl_2$	Pb(II)	209.8	(+)84.84	Feng and Guo (2012)
Orange peels	NaOH and $CaCl_2$	Zn(II)	56.18	(+)164.38	Feng and Guo (2012)
Sawdust	NaOH (1.0 M)	Cd(II)	73.62	(+) ~ 280	Memon et al. (2007)
Orange peels	NaOH	Cu(II)	50.25	(+)41.3	Feng et al. (2010)
Rice husk	NaOH	Cd(II)	20.24	(+)135.90	(Kumar and Bandyopadhyay (2006)
Rice husk	$NaHCO_3$	Cd(II)	16.18	(+)88.58	Kumar and Bandyopadhyay (2006)
Sugar cane bagasse	Hydrous ferric hydroxide	As(V)	22.1	–	Pehlivan et al. (2013)
Orange peels	HNO_3 (0.1 M)	Cd(II)	13.7	(+)229.3	Lasheen et al. (2012)
Orange peels	HNO_3 (0.1 M)	Cu(II)	15.27	(+)378.6	Lasheen et al. (2012)
Orange peels	HNO_3 (0.1 M)	Pb(II)	73.53	(+)544.4	Lasheen et al. (2012)
A. scholaris	HCl(0.1 M)	Cr(VI)	6.88	(+)374.5	Rehman et al. (2012)
P. longifolia	HCl(0.1 M)	Cr(VI)	5.128	(+)8.21	Rehman et al. (2011)
C. reticulata	H_2SO_4 and EDTA	Cu(II)	87.14	–	Boota et al. (2009)
C. reticulata	H_2SO_4 and EDTA	Zn(II)	86.40	–	Boota et al. (2009)
Wheat residue	Epichlorohydrin, DMF, EDTA, TEA	Cr(VI)	322.58	–	Chen et al. (2010)
Rice husk	Epichlohydrin	Cd(II)	11.12	(+)29.60	Kumar and Bandyopadhyay (2006)

treatment may cause weight loss as found by (García-Mendieta et al. 2012). They reported 26.7 % weight loss during modification of green tomato husk with formaldehyde (0.2 %). This loss might be due to the dissolution of lignin in the formaldehyde solution. Weight loss hinders the use of lignocellulosic materials for long term use. Conversely, (Lasheen et al. 2012) reported that there is no appreciable weight loss during modification of orange peels with HNO_3 (0.1 M). Moreover, the use of vast chemicals as modifying agents may cause the leaching of organic compounds which are unexpected. For this reason, there is still a need of investigating the methods for modification which increase the metal uptake capacity while considering the mentioned challenges.

9 Governing mechanisms of biosorption

Being an alternate method of metal removal from aqueous solution, it is important to look into the mechanism involved in binding of metal ions with

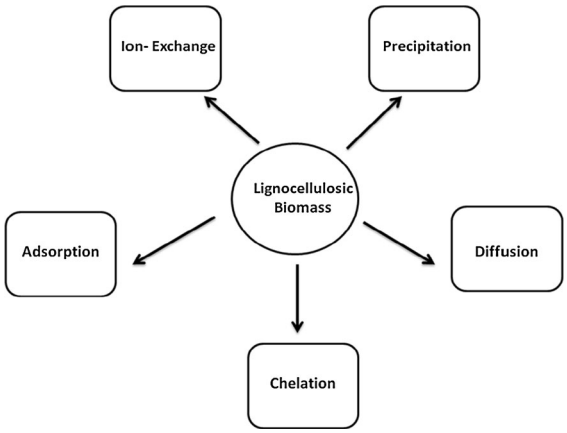

Fig. 2 Mechanism of Biosorption

lignocellulosic materials. The actual mechanism of biosorption is not fully understood yet because it is found to be affected by various factors including (1) types of lignocellulosic material, (2) Chemistry of metal solution, (3) environmental conditions, etc. Although several mechanisms have been proposed for binding of heavy metal ions onto biosorbent surface (Fig. 2).

(Feng and Guo 2012) examined the mechanism of Cu(II), Zn(II) and Pb(II) ions removal using orange peels and found that ion-exchange predominantly governed the process. The replacement of the heavy metal ions was with Ca(II) ions as confirmed by X-ray fluorescence experiment. (Farooq et al. 2007) in their previous study also reported that Pb(II) removal from aqueous solution using *Triticum aestivum* followed adsorption as well as ion-exchange mechanism. They confirmed thorough pH measurement that decrease in pH of the solution during the process resulted by the exchange of Pb(II) ions from solution with H^+ ions from biomass. Similar results were found by (Taha et al. 2011) using potato peel for Pb(II), Cd(II) and Zn(II) adsorption. They also claimed the exchange of hydrogen ions with these ions as confirmed from pH decrease of solutions while processing. These findings were in good agreement with another previous study conducted by (Panda et al. 2008).

Studies revealed that more than one mechanism can govern the retention of heavy metal onto biosorbent at the same time. (Netzahuatl-Muñoz et al. 2012) found that ion-exchange and electrostatic attraction were the governing mechanisms involved in Cr(III) retention on *Cupressus lusitanica* bark. They also found that change in oxidation state of chromium affected the mechanism. Cr(IV) was found to be removed by four step mechanism by the same specie: (1) Cr(VI) complexes formation, (2) change in oxidation state from Cr(VI) to Cr(III), (3) carboxyl groups formation and (4) formation of Cr(III)-carboxylate complexes.

Using the modern technologies like FTIR, SEM (Scanning Electron Microscope, TEM (Transmission Electron Microscope), EDX (Energy dispersive X-ray) along with basic titration, scientists are able to discover that ion-exchange, surface precipitation, metal chelation by active functional groups like carboxyl and hydroxyl groups dominantly governs the biosorption mechanism (Ofomaja and Naidoo 2010; Witek-Krowaik et al. 2013). (Salman et al. 2014) in their recent study revealed that carboxyl and hydroxyl functional groups present on the surface of sorghum biomass were mainly responsible for Pb(II) elimination from aqueous solution along with adsorption as confirmed by FTIR. They also confirmed the effect of function groups by altering/modifying the sorghum surface using thiourea. The adsorption capacity of the adsorbent was found to be increased by many times due to newly inducted functional groups which confirmed the metal chelation on biosorbent surface. This may attribute to the better chelation offered by sulfur containing groups compared to nitrogen and oxygen already present on the biosorbent surface. Their finding were in good agreement with the previous study conducted by (Haquea et al. 2007). Employing potentiometric titration and FTIR it was found that carboxyl and hydroxyl groups were mainly responsible for arsenic ions chelation onto the surface of *sorghum bicolor* L. Various other studies affirmed the effective interaction of carboxyl and hydroxyl groups towards heavy metal ions (Athar et al. 2013; Feng et al. 2011; Kumar et al. 2012; Lasheen et al. 2012).

Revealing the literature, it is apparent the functional groups like carboxyl, hydroxyl, amino and thio, etc. on the lignocellulosic materials play important role in removal of metal ions from aqueous solution. However, it does not guarantee the effective removal of metal ions in varying conditions. The reason behind is that the process of biosorption is influenced the various condition. For example, the number of binding sites, their accessibility, chemical state of binding sites and affinity between the sites and metal ions (Park et al. 2010).

Table 6 Adsorption equilibrium models: description and nomenclature

Model	Non-linear form	Nomenclature	References
Langmuir	$q_e = \frac{b \cdot q_m \cdot C_e}{1+b \cdot C_e}$	q_e (mg/g) = adsorption capacity at equilibrium; C_e (mg/L) = metal concentration at equilibrium; q_m (mg/g) = monolayer adsorption capacity of adsorbent; b (L/mg) = Langmuir constant related to the free energy of adsorption	Langmuir (1916)
Freundlich	$q_e = K_F \cdot C_e^{1/n}$	q_e (mg/g) = adsorption capacity at equilibrium; C_e (mg/L) = metal concentration at equilibrium; K_F (L/g) and n are indicative of the extent of adsorption and the degree of non-linearity, respectively	Freundlich (1906)
Tempkin	$q_e = B_T \cdot \ln K_T \cdot C_e$	B_T (kJ/mol) = heat of adsorption; K_T (L mol/kJ g) = adsorption potential; q_e (mg/g) = adsorption capacity at equilibrium; C_e (mg/L) = metal concentration at equilibrium	Tempkin and Pyzhev (1940)
Dubinin–Radushkevich	$q_e = q_m \cdot \exp(-\beta\varepsilon^2)$	q_e (mg/g) = adsorption capacity at equilibrium; qm (mg/g) theoretical saturation constant; β (mol^2/J^2) = constant connected with the mean free energy of adsorption; ε (J/mol) = Polanyi potential	Dubinin and Radushkevich (1947)
	Polanyi potential $\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right)$	R (J/K mol) = universal constant; T (K) = working temperature; C_e (mg/L) = metal concentration at equilibrium	
	Mean free energy of adsorption $E = \frac{1}{\sqrt{2\beta}}$	Physical and chemical adsorption can be predicatable from the magnitude of mean free energy of adsorption E = 1–8 kJ/mol (Physical adsorption) E > 8 kJ/mol (Chemical adsorption)	
Redlich-Peterson	$q_e = \frac{K_R \cdot C_e}{1+\alpha_R \cdot C_e^{\beta}}$	K_R = Redlich-Peterson constant (L/g); α_R = constant having unit (L/mg); C_e (mg/L) = metal concentration at equilibrium; β = exponent that lies between 0–1	Redlich and Peterson (1959)
Toth	$q_e = \frac{K_T \cdot C_e}{(q_T + C_e)^{\frac{1}{t}}}$	q_e (mg/g) = adsorption capacity at equilibrium; C_e (mg/L) = metal concentration at equilibrium; q_T (mg/g) = Toth maximum adsorption capacity; K_T = the Toth constant; t = the Toth model exponent	Toth (1971)
Sips	$q_e = \frac{q_{m_s} K_s \cdot C_e^{\beta_s}}{1+K_s C_e^{\beta_s}}$	q_e (mg/g) = adsorption capacity at equilibrium; C_e (mg/L) = metal concentration at equilibrium; K_s (L/mg) = Sips equilibrium constant; q_{ms} (mg/g) = Sips adsorption capacity; β_s = Sips model exponent	Sips (1948)

Studies also revealed that surface adsorption (monolayer or multilayer) can also be the possible route of metal ion elimination from aqueous media. Different mathematical models (equilibrium models) have been presented to investigate the distribution of metal ions between the solution and biological materials. The famous equilibrium models along with their mathematical equation are enlisted in Table 6. Literature shows that most of the studied biosorption systems followed Langmuir equilibrium model which indicated that monolayer adsorption was the possible mechanism of metal ions retention on the biomass surface. Adsorption capacities calculated form Langmuir equation of the recently reported studies has already been mentioned in Table 4. The agreement of Freundlich equilibrium model to experimental data showed the adsorption on heterogeneous surface in a multilayer fashion. Some studies claimed that the adsorption of metal ions follows Freundlich model more as compared to others (dos Santos et al. 2011; Farooq et al. 2007; Wang et al. 2008). Mean free energy calculated from Dubinin–Radushkevich model can predict the nature of adsorption. (Din and Mirza 2013) reported that the nature of Ni(II) adsorption onto *S. bengalense* is physical. This attributes to the physical attractive forces offered by the electronegative functional groups present onto the surface of biological materials. In contrast, the adsorption of arsenic onto pine leaves had shown chemical nature of adsorption process (Shafique et al. 2012). (Uluozlu et al. 2008) reported similar results suggesting that biosorption processes of Pb(II) and Cr(III) ions onto *P. tiliaceae* was carried out by chemical ion-exchange instead of physical attraction.

10 Biosorption κinetics

Kinetic studies have been reported to evaluate the reaction rate and its order involved. The simplest model initially applied in this regard is the Elovich model shown as

$$q_t = \frac{\ln(a \times b)}{b} + \frac{\ln(t)}{b} \quad (1)$$

where, 'q_t' represents the amount of adsorbate adsorbed at a given instant of time, 'a' and 'b' are constants, 'a' gives an idea about rate constant and 'b' shown the rate of adsorption at zero coverage.

As an alternative, pseudo first order and pseudo second order kinetic model have appeared in the literature and numerous studies have been evaluated using these models. Pseudo first order is based on the fact that rate of reaction is proportional to number of free accessible binding sites present on the biosorbent material. It is can be expressed as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

where q_e (mg/g) is the amount of adsorbing specie at equilibrium, q_t (mg/g) is the amount of adsorbing specie at a given time t, k_1 is the rate constant for first order reaction. The linear form of pseudo first order model is expressed as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

Taking '$\ln(q_e - q_t)$' on y-axis and 't' on y-axis, linear plot is generated having the slope '$-k_1$' and intercept 'ln q_e'. From value of intercept 'q_e' can b calculated and compared to the experimental value. The precision between the calculated and experimental 'q_e' values gives an idea about the possible order of the biosorption process.

Pseudo second order model is based on the fact that rate of biosorption is proportional to the square of number of active binding sites on the surface of biosorbent. It is represented as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

where 'k_2' is rate constant for second order reaction. Its linear form is shown as (Ho 2006);

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

A plot between (t/q_t) and (t) should generate a straight line having slope of ($1/q_e$) and intercept ($1/k_2q_e^2$). The calculated q_e value compared with that of experimental value. Another important factor which determines the applicability of specific model to the experimental kinetic data i.e. coefficient of determination R^2. Its value close to 1 ($R^2 > 0.98$) shows the fitness of experimental data to kinetic model (Al-Garni 2005).

(Salman et al. 2014) and (Athar et al. 2013) in their recent studies has suggested a demonstrative reaction between divalent metal cation and active sites on biomass.

$$M + 2B \rightarrow B_2M \quad (6)$$

where, 'M' represents the divalent metal ion and 'B' represents the active site on the biomass surface. According to their suggestion the biosorption rate would be directly proportional to square of number of accessible binding sites present onto the biosorbent surface. This statement corresponds to the term $(q_e - q_t)^2$ in the pseudo second order model. The best fit of the pseudo second order model indicates that one divalent metal binds to two monovalent binding sites (Lasheen et al. 2012). Numerous other studies in the literature have reported the best fit of pseudo second order model to biosorption kinetic data (Ali et al. 2011; Athar et al. 2014; Farooq et al. 2011; Feng et al. 2011; Ibrahim et al. 2012; Nameni et al. 2008; Ramana et al. 2012; Salman et al. 2013a, b).

As per theoretical concept, the biosorption process takes place in three stages (1) mass transfer of sorbents from the aqueous phase onto the solid surface, (2) sorption of solute onto the surface sites and (3) Internal diffusion of solute via either a pore diffusion model (intra-particle diffusion) or homogeneous solid phase diffusion (boundary layer diffusion). The sorption of solute onto the surface sites is rapid enough as compared to other steps so it is unlikely to be rate determining step. McKay et al. (1981) introduced a mathematical model to study the mass transfer as a rate determining step.

$$\ln\left(\frac{C_e}{C_o} - \frac{1}{1 + m_d K}\right) = \ln\left(\frac{m_d K}{1 + m_d K}\right) - \left(\frac{1 + m_d K}{m_d K}\right) \cdot \beta_1 \cdot S_s \cdot t \quad (7)$$

where 'm_d' is the mass of the biosorbent per unit volume, 'K' is the constant obtained from Langmuir

constants, 'β_1' is the mass transfer coefficient, and 'S_s' is the outer specific surface of the biosorbent particles per unit volume of particle free slurry. The value of 'm_d' and 'S_s' can be calculated by using the following expressions

$$m_d = \frac{W}{v} \tag{8}$$

$$S_s = \frac{6m_d}{d_p \delta_\rho (1 - \varepsilon_p)} \tag{9}$$

where 'W' is the amount of the biosorbent used, 'v' is the volume of praticel-free slurry solution, 'd_p' represents diameter of particle, 'δ_ρ' is the density of particles and 'ε_p' is the porosity of the biosorbent particles. If the plot between $\ln(C_e/C_o - 1/(1 + m_dK))$ and time (t) comes out as a straight line then mass transfer would be considered as rate determining step, otherwise internal diffusion (boundary layer diffusion or intra-particle diffusion) will be the rate determining step.

A mathematical expression (Eq. 10) termed as intra-particle diffusion model (IPD) has been appeared in the literature in order to investigate that which type of diffusion could govern the reaction rate (Mohan and Singh 2002).

$$q_t = k_{id} t^{1/2} \tag{10}$$

where, k_{id} is the intra-particle diffusion constant. If the plot between 'q_t' and '$t^{1/2}$' (the straight line) passes through origin then rate determining step is the intra-particle diffusion, otherwise boundary layer diffusion could be considered as the rate determining step. Most of the reported cases indicated the a combination of intra-particle and boundary layer diffusion governed the process (Ali et al. 2011; Argun et al. 2007; Din et al. 2013a; Farooq et al. 2011, 2010a; Ozacar et al. 2008).

11 Thermodynamic parameters

Temperature change has a significant influence on the sorption of metal ions. Temperature change is directly related with the kinetic energy of metal ions. Increase in temperature accounts for the increased diffusion process. As the lignocellulosic materials are porous substances, therefore, so diffusion possibility along with adsorption cannot be neglected as a mechanism of metal retention onto its surface.

$\Delta G°$ (Gibbs free energy), $\Delta H°$ (Enthalpy) and $\Delta S°$ (Entropy) are the important thermodynamic parameters related with the temperature change of biosorption system.

$$\Delta G^\circ = -RT \ln K_D \tag{11}$$

where R (8.314 $Jmol^{-1}$ K^{-1}) is universal gas constant, T is temperature in Kevin scale and K_D ($C_o - C_e/C_e$) is the distribution coefficient. $\Delta H°$ and $\Delta S°$ can be calculated from the linear of $\ln K_D$ and 1/T obtained from the linear Eq. 12.

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{12}$$

Another linear expression (Eq. 14) can be used to calculate the values of ΔH^o and ΔS^o obtained from the rearrangement of the Eq. 12 in which the plot of $\Delta G°$ versus T yields a straight line.

$$-RT \ln K_D = \Delta H^\circ - T\Delta S^\circ \tag{13}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{14}$$

These parameters give important information about the biosorption process. ΔG^o is an indicative of the feasibility of biosorption process. Its negative value shows that the biosorption process is feasible in the working conditions. The increment in its magnitude with negative sign with increase in temperature shows that the feasibility of the process increases with increase in temperature. ΔH^o indicates the energy change in the biosorption system. Its positive value shows that the biosorption process is endothermic and has negative value for exothermic process.

Various studies use these parameters to evaluate the thermodynamic relation of the biosorption process.

(Feng et al. 2011) reported that biosorption of Pb(II), Cd(II) and Ni(II) using orange peels was a spontaneous process as the calculated free energy value appears with negative sign. Cd(II) biosorption onto urea modified wheat straw was also found to be spontaneous and endothermic (Farooq et al. 2011). Several other studies in the recent and previous year shows similar findings for heavy metal sorption using lignocellulosic materials (Argun et al. 2007; Din et al. 2013a; Din and Mirza 2013; Salman et al. 2014). In contrast, some studies reported that the biosorption process for metal ions removal using lignocellulosic biomass is exothermic. (Uluozlu et al. 2008) found positive values of free energy

and negative value of enthalpy for the biosorption of Pb(II) and Cr(III) using *P. tiliaceae* biomass. This indicates the decrease in feasibility of metal sorption with increase in temperature and its exothermic nature. (Singh et al. 2009) also found that the removal of Cd(II) using wheat bran was an exothermic process.

12 Conclusion

The use of lignocellulosic materials as low cost biosorbent for heavy metal removal has been reviewed. Chemical modifications rather expensive but appreciably increase the biosorption capacity of these materials. The modified materials give better information about the reaction mechanism and functional groups responsible for binding. These materials can be used to successfully remove the heavy metal ions from the aqueous media. The modification procedures being used, at present, need exploration based upon the cost of effectively removing a specific metal ion, or a mixture, from a multi-metal system. This requires a further deep insight into the mechanism of effective modification, biosorption capacity, recycling ability of the biosorbent material (with or without modification) and the cost and engineering of the whole process for the scale-u and design-perfection purposes.

The information about the behavior of simple and modified lignocellulosic materials for the biosorption of multi-metal ions is inadequate at present. A multi-metal system may show a completely different chemical behavior towards the biosorbent than a single metal system; even it is prepared synthetically having common anions. In addition, a real sample of waste-water may bear a variety of cations, anions and other neutral species, which may hinder the biosorption of a particular metal ion specifically. Hence, a modeling of multi-metal system (as close to the real sample as possible) may be an additive advantage to the field of biosorption. Once studied, biosorption may serve the environment with better friendly materials and help science and technology in returning the natural environment to the people of planet earth. In addition, recycling of the metal adsorbed biosorbents should be studied in order to make them economically and ecologically favorable.

References

Akar ST, Arslan S, Alp T, Arslan D, Akar T (2012) Biosorption potential of the waste biomaterial obtained from *Cucumis melo* for the removal of Pb^{2+} ions from aqueous media: equilibrium, kinetic, thermodynamic and mechanism analysis. Chem Eng J 185–186:82–90

Akar T, Celik G, Ari AG, Akar ST (2013) Nickel removal characteristics of an immobilized macro fungus: equilibrium, kinetic and mechanism analysis of the biosorption. J Chem Technol Biotechnol 88:680–689

Al-Garni SM (2005) Biosorption of lead br gram −ve cap[sulated and non-capsulated bacteria. Water SA 31:345–350

Ali SZ, Athar M, Salman M, Din MI (2011) Simultaneous removal of Pb(II), Cd(II) and Cu(II) from aqueous solutions by adsorption on *Triticum aestivum*—a green approach. Hydrol Current Res 2:118. doi:10.4172/2157-7587.1000118

Alomá I, Martín-Lara MA, Rodríguez IL, Blázquez G, Calero M (2012) Removal of nickel(II) ions from aqueous solutions by biosorption on sugarcane bagasse. J Taiwan Inst Chem Eng 43:275–281

Aman T, Kazi AA, Sabri MU, Bano Q (2008) Potato peels as solid waste for the removal of heavy metal copper(II) from waste water/industrial effluent. Colloid Surf B 63:116–121

Anwar J, Shafique U, Salman M, Waheed-uz-Zaman A, Anwar S, Anzano JM (2009) Removal of Chromium(III) by using coal as adsorbent. J Hazard Mater 171:797–801

Anwar J, Shafique U, Waheed-uz-Zaman A, Salman M, Dar A, Anwar S (2010a) Removal of Pb(II) and Cd(II) from water nby adsorption on peels of banana. Bioresour Technol 101:1752–1755

Anwar J et al (2010b) Removal of chromium from water using pea waste—a green approach. Green Chem Lett Rev 3:239–243

Anwar J et al (2011) Removal of chromium on *Polyalthia longifolia* leaves biomass. Int J Phytoremed 13:410–420

Arbanah M, Najwa MRM, Ku Halim HM (2012) Biosorption of Cr(III), Fe(II), Cu(II), Zn(II) ions from liquid laboratory chemical waste by *Pleurotus ostreatus*. Int J Biotechnol Wellness Ind 1:152–162

Argun ME, Dursun S, Ozdemir C, Karatas M (2007) Heavy metal adsorption by modified oak sawdust: thermodynamics and kinetics. J Hazard Mater 141:77–85

Asberry HB, Kuo C, Gung C, Conte ED, Suenc S (2014) Characterization of water bamboo husk biosorbents and their application in heavy metal ion trapping. Microchem J 113:59–63

Athar M, Farooq U, Aslam M, Salman M (2013) Adsorption of Pb(II) ions onto biomass from *Trifolium resupinatum*: equilibrium and kinetic studies. Appl Water Sci 3: 665–672. doi:10.1007/s13201-013-0115-0

Athar M, Farooq U, Ali SZ, Salman M (2014) Insight into the binding of copper(II) by non-toxic biodegradable material (*Oryza sativa*): effect of modification and interfering ions. Clean Technol Environ Policy 16:579–590

Banerjee K, Ramesh ST, Nidheesh PV, Bharathi KS (2012) A novel agricultural waste adsorbent, watermelon shell for the removal of copper from aqueous solutions. Iran J Energy Environ 3:143–156

Bernardo GR, Rene RJ, Catalina ADM (2009) Chromium(III) uptake by agro-waste biosorbents: chemical characterization, sorption–desorption studies, and mechanism. J Hazard Mater 170:845–854

Bingöl D, Hercan M, Elevli S, Kılıç E (2012) Comparison of the results of response surface methodology and artificial neural network for the biosorption of lead using black cumin. Bioresour Technol 112:111–115

Blázquez G, Calero M, Hernáinz F, Tenorio G, Martín-Lara MA (2010) Equilibrium biosorption of lead(II) from aqueous solutions by solid waste from olive-oil production. Chem Eng J 160:615–622

Boota R, Bhatti HN, Hanif MA (2009) Removal of Cu(II) and Zn(II) using lignocellulosic fiber derived from *Citrus reticulata* (Kinnow) waste biomass. Sep Purif Technol 44:4000–4022

Calero M, Hernainz F, Blázquez G, Martín-Lara MA, Tenorio G (2009) Biosorption kinetics of Cd(II), Cr(III) and Pb(II) in aqueous solutions by olive stone. Braz J Chem Eng 26:265–273

Ceribasi HI, Yetis U (2001) Biosorption of Ni(II) and Pb(II) by *Phanerochaete chrysoporium* from a binary metal system—kinetics. Water SA 27:15–20

Chen XC, Wang YP, Lin Q, Shi JY, Wu WX, Chen YX (2005) Biosorption of copper(II) and zinc(II) from aqueous solution by *Pseudomonas putida* CZ1. Colloid Surf 46B:101–107

Chen S, Yue Q, Gao B, Xu X (2010) Equilibrium and kinetic adsorption study of the adsorptive removal of Cr(VI) using modified wheat residue. J Colloid Inter Sci 39:256–264

Chojnacka K (2010) Biosorption and bioaccumulation—the prospects for practical appliactions. Environ Int 36:299–307

Chojnacka K, Chojnacki A, Górecka H (2005) Biosorption of Cr^{3+}, Cd^{2+} and Cu^{2+} ions by blue-green algae *spirulina sp.*: kinetics, equilibrium and the mechanism of the process. Chemosphere 59:75–84

Chouchene A, Jeguirim M, Trouvé G (2013) Biosorption performance, combustion behavior, and leaching characteristics of olive solid waste during the removal of copper and nickel from aqueous solutions. DOI, Clean Technol Environ Policy. doi:10.1007/s10098-10013-10680-10099

Chowdhury S, Saha PD (2011) Biosorption kinetics, thermodynamics and isosteric heat os sorption of Cu(II) on to *Tamarindus indica* seed powder. Colloid Surf B Biointerfaces 88:697–705

Cruz-Olivares J, Pérez-Alonso C, Barrera-Díaz C, Natividad R, Chaparro-Mercado MC (2011) Thermodynamical and analytical evidence of lead ions chemiosorption onto *Pimenta dioica*. Chem Eng J 166:814–821

Dang VBH, Doan HD, Dang-Vu T, Lohi A (2009) Equilibrium and kinetics of biosorption of cadmium(II) and copper(II) ions by wheat straw. Bioresour Technol 100:211–219

Danis U (2010) Biosorption of copper(II) from aqueous solutions by *Pleurotus cornucopiae*. Paper no. 2010-252. Ohrid, Republic of Macedonia: Balwois Conference

Demirbas A (2008) Heavy metal adsorption onto agro-based waste materials: a review. J Hazard Mater 157:220–229

Deng SB, Ting YP (2005) Characterization of PEI-modified biomass and biosorption of Cu(II), Pb(II) and Ni(II). Water Res 39:2167–2177

Dilek FB, Erbay A, Yetis U (2002) Ni(II) biosorption by *Polyporous versicolor*. Process Biochem 32:723–726

Din MI, Mirza ML (2013) Biosorption potentials of a novel green biosorbent *Saccharum bengalense* containing cellulose as carbohydrate polymer for removal of Ni(II) ions from aqueous solutions. Int J Bio Macromol 54:99–108

Din MI, Farooq U, Athar M, Mirza ML (2013a) Environmentally benevolent urea modified *Saccharum bengalense* as a high capacity biosorbent for removal of Pb(II) ions: metal uptake modeling and adsorption efficiency. Desalin Water Treat. doi:10.1080/19443994.19442013.19808584

Din MI, Mirza ML, Ata S, Athar M, Mohsin I (2013) Thermodynamics of biosorption for removal of Co(II) Ions by an efficient and ecofriendly biosorbent (*Saccharum bengalense*): kinetics and isotherm modeling. J Chem: Article ID 528542. doi:10.1155/2013/528542

Din MI, Hussain Z, Mirza ML, Shah AT, Athar MM (2014) Adsorption optimization of lead (II) using *Saccharum bengalense* as a non-conventional low-cost biosorbent: isotherm and thermodynamic modeling. Int J Phytoremed 16:889–908

dos Santos WNL, Cavalcante DD, Da Silva EGP, das Virgens CF, Dias FS (2011) Biosorption of Pb(II) and Cd(II) ions by *Agave sisalana* (sisal fiber). Microchem J 97:269–273

Dubinin MM, Radushkevich LV (1947) The equation of the characteristic curve of the activated charcoal. Proc Acad Sci USSR Phys Chem Sect 55:331–337

Elangovan R, Philip L, Chandraraj K (2008) Biosorption of chromium species by aquatic weeds: kinetics and mechanism studies. J Hazard Mater 152:100–112

Eom Y, Won JH, Ryu JY, Lee TG (2011) Biosorption of mercury (II) ions from aqueous solution by garlic (*Allium sativum* L.) powder. Korean J Chem Eng 28:1439–1443

Eslamzadeh T, Nasernejad B, Pour BB, Zamani A, Bygi ME (2004) Removal of heavy metals from aqueous solution by carrot residues. Iran J Sci Technol Trans A28A1:161–167

Farooq U, Khan MA, Athar M (2007) *Triticum aestivum*: a novel biosorbent for lead(II) ions. Agrochimica L1:309–318

Farooq U, Khan MA, Athar M, Sakina M, Ahmad M (2010a) Environmentally benign urea-modified *Triticum aestivum* biomass for lead (II) elimination from aqueous solutions. Clean 38:49–56

Farooq U, Kozinski JA, Khan MA, Athar M (2010b) Biosorption of heavy metal ions using wheat based biosorbents—a review of the recent literature. Bioresour Technol 101:5043–5053

Farooq U, Khan MA, Athar M, Konzinski JA (2011) Effect of modification of environmentally friendly biosorbent wheat (*Triticum aestivum*) on the biosorptive removal of cadmium (II)ions from aqueous solution. Chem Eng J 171:400–410

Feng N, Guo X (2012) Characterization of adsorptive capacity and mechanisms on adsorption of copper, lead and zinc by modified orange peel. Trans Nonferrous Met Soc China 22:1224–1231

Feng N, Guo X, Liang S (2010) Enhanced Cu(II) adsorption by orange peels modified with sodium hydroxide. Trans Nonferrous Met Soc China 20:146–152

Feng N, Guo X, Liang S, Zhu Y, Liu J (2011) Biosorption of heavy metals from aqueous solutions by chemically modified orange peel. J Hazard Mater 185:49–54

Freundlich HMF (1906) Over the adsorption in solution. J Phys Chem 57:385–471

Ganji T, Khosravi M, Rakhshaee R (2005) Biosorption of Pb, Cd, Cu and Zn from the wastewater by treated *Azolla filiculoides* with H_2O_2/$MgCl_2$. Int J Environ Sci Technol 1:265–271

Gao H, Liu Y, Zeng G, Xu W, Li T, Xia W (2008) Characterization of Cr(VI) removal from aqueous solutions by a surplus agricultural waste—rice straw. J Hazard Mater 31:446–452

García-Mendieta A, Olguín MT, Solache-Ríos M (2012) Biosorption properties of green tomato husk (*Physalis philadelphica* Lam) for iron, manganese and iron–manganese from aqueous systems. Desalination 284:167–174

Ghodbane I, Hamdaoui O (2008) Removal of mercury(II) from aqueous media using eucalyptus bark: kinetic and equilibrium studies. J Hazard Mater 160:301–309

Giri AK, Patel R, Mandal S (2012) Removal of Cr(VI) from aqueous solution by *Eichhornia crassipes* root biomass-derived activated carbon. Chem Eng J 186:71–81

Gonen F, Serin DS (2012) Adsorption study of orange peels: removal of Ni(II) ions from aqueous solution. Afr J Biotechnol 11:1250–1258

Goyal P, Srivastava S (2009) Characterization of novel *Zea mays* based biomaterial designed for toxic metals biosorption. J Hazard Mater 172:1206–1211

Gupta S, Babu BV (2009) Removal of toxic metal Cr(VI) from aqueous solutions using sawdust as adsorbent: equilibrium, kinetics and regeneration studies. Chem Eng J 150: 352–365

Gupta VK, Rastogi A (2008) Biosorption of lead from aqueous solutions by green algae *Spirogyra* species: kinetic and equilibrium studies. J Hazard Mater 152:407–414

Haquea MN, Morrison GM, Perrusquía G, Gutierŕez M, Aguilera AF, Cano-Aguilera I, Gardea-Torresdey JL (2007) Characteristics of arsenic adsorption to sorghum biomass. J Hazard Mater 145:30–35

Ho YS (2006) Review of pseudo second-order models for adsorption systems. J Hazard Mater B136:681–689

Hu X, Zhao M, Song G, Huang H (2011) Modification of pineapple peel fiber with succinic anhydride for Cu(II), Cd(II) and Pb(II) removal from aqueous solutions. Environ Technol 32:739–746

Ibrahim HS, Ammar NS, Soylak M, Ibrahim M (2012) Removal of Cd(II) and Pb(II) from aqueous solution using dried water hyacinth as a biosorbent. Spectrochim Acta Part A Mol Biomol Spectrosc 96:413–420

Jacques RA, Lima EC, Dias SLP, Mazzocato AC, Pavan FA (2007) Yellow passion-fruit shell as biosorbent to remove Cr(III) and Pb(II) from aqueous solution. Sep Purif Technol 57:193–198

Javaid A, Bajwa R (2007) Biosorption of Cr(III) ions from tannery wastewater by *Pleurotus ostreatus*. Mycopathologia 5:71–79

Javaid A, Bajwa R, Shafique U, Anwar J (2011) Removal of heavy metals by adsorption on *Pleurotus ostreatus*. Biomass bioener 35:1675–1682

Jiménez-Cedillo MJ, Olguín MT, Fall C, Colin-Cruz A (2013) As(III) and As(V) sorption on iron-modified non-pyrolyzed and pyrolyzed biomass from *Petroselinum crispum* (parsley). J Environ Manag 117:242–252

Kakalanga SJ, Jabulani XB, Olutoyin OB, Utieyin OO (2012) Screening of agricultural waste for Ni(II) asorption: kinetics, equilibrium and thermodynamic studies. Int J Phys Sci 7:2525–2538

Kelly-Vargas K, Cerro-Lopez M, Reyna-Tellez S, Bandala ER, Sanchez-Salas JL (2012) Biosorption of heavy metals in polluted water, using different waste fruit cortex. Phys Chem Earth 37–39:26–29

Khoramzadeh E, Nasernejad B, Halladj R (2013) Mercury biosorption from aqueous solutions by sugarcane bagasse. J Taiwan Inst Chem Eng 44:266–269

Krishnani KK, Meng X, Christodoulatos C, Boddu VM (2008) Biosorption mechnasim of nine different heavy metals onto biomatrix from rice husk. J Hazard Mater 153:1222–1234

Kumar U, Bandyopadhyay M (2006) Sorption of cadmium from aqueous solution using pretreated rice husk. Bioresour Technol 97:104–109

Kumar PS, Ramalingam S, Sathyaselvabala V, Kirupha SD, Murugesan A, Sivanesan S (2012) Removal of Cd(II) from aqueous solution by agricultural waste cashew nut shell. Korean J Chem Eng 29:756–768

Kurniawan A, Kosasih AN, Febriano J, Ju YH, Sunarso J, Indraswati N (2011) Evaluation of cassava peel waste as low-cost biosorbent for Ni sorption: equilibrium, kinetics, thermodynamics and mechanisms. Chem Eng J 172:158–166

Langmuir I (1916) The constitution and fundamental properties of solids and liquids. J Am Chem Soc 38:2221–2295

Lasheen MR, Ammar NS, Ibrahim HS (2012) Adsorption/desorption of Cd(II), Cu(II) and Pb(II) using chemically modified orange peel: equilibrium and kinetic studies. Solid State Sci 14:202–210

Lawal OS, Sanni AR, Ajayi IA, Rabiu OO (2010) Equilibrium, thermodynamic and kinetic studies for the biosorption of aqueous lead(II) ions onto the seed husk of *Calophyllum inophyllum*. J Hazard Mater 177:829–835

Lee B, Rowell RM (2004) Removal of heavy metal ions from aqueous solutions using lignocellulosic fibers. J Natural Fibers 1:97–108

Liping D, Yingying S, Hua S, Xinting W, Xiaobin Z (2007) Sorption ans desorption of lead (II) from wastewater by green algae *Cladophora fascicularis*. J Hazard Mater 143:220–225

Lokeshwari N, Joshi K (2009) Biosorption of heavy metal (chromium) using biomass. Glob J Environ Res 3:29–35

Mahajan G, Sud D (2013) Application of ligno-cellulosic waste material for material for heavy metal ions removal from aqueous solution. J Environ Chem Eng 1:1020–1027

Manasi Rajesh V, Kumar ASK, Rajesh N (2014) Biosorption of cadmium using a novel bacterium isolated from an electronic industry effluent. Chem Eng J 235:176–185

Manzoor Q, Nadeem R, Iqbal M, Saeed R, Ansari TM (2013) Organic acids pretreatment effect on *Rosa bourbonia* phyto-biomass for removal of Pb(II) and Cu(II) from aqueous media. Bioresour Technol 132:446–452

Marin ABP, Aguilar MI, Ortuno JF, Meseguer VF, Saez J, Florenz M (2010) Biosorption of Zn(II) by orange waste in batch and packed bed systems. J Chem Technol Biotechnol 85:1310–1318

Marin-Rangel VM, Cortes-Martines R, Villanueva RAC, Garnica-Romo MG, Martinez-Flores HE (2012) As(V) biosorption in an aqueous solution using chemically treated lemon (*Citrus aurantifolia swingle*) residues. J Food Sci 71:10–14

McKay G, Otterburn MS, Sweeny AG (1981) Surface mass transfer process during colour removal from effluents using silica. Water Res 15:321–331

Melcáková I, Ruzovic T (2010) Biosorption of zinc from aqueous solution using algae and biomass. Nova Biotechnol 10:33–43

Memon SQ, Memon N, Shah SW, Khuhawar MY, Bhanger MI (2007) Sawdust—a green and economical sorbent for the removal of cadmium(II) ions. J Hazard Mater B139: 116–121

Miretzky P, Cirelli AF (2010) Cr(VI) and Cr(III) removal from aqueous solution by raw and modified lignocellulosic materials: a review. J Hazard Mater 180:1–19

Mishra V, Balomajumder C, Agarwal VK (2012) Kinetics, mechanistic and thermodynamics of Zn(II) ion sorption: a modeling approach. Clean Soil Air Water 40:718–727

Mohan D, Singh KP (2002) Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse—an agricultural waste. Water Res 36:2304–2318

Momčilović M, Purenović M, Bojić A, Zarubica A, Ranđelović M (2011) Removal of lead(II) ions from aqueous solutions by adsorption onto pine cone activated carbon. Desalination 276:53–59

Morsy E (2004) *Cunninghamella echinulataa* new biosorbent of metal ions from polluted water in Egypt. Mycologia 96:1183–1189

Moussavi G, Barikbin B (2010) Biosorption of chromium(VI) from industrial wastewater onto pistachio hull biomass. Chem Eng J 162:893–900

Murphy V, Hughes H, McLoughlin P (2008) Comparitive study of chromium biosorption by red, green and brown seeweed biomass. Chemosphere 70:1128–1134

Murphy V, Tofail SAM, Hughes H, McLoughlin P (2009) A novel study of hexavalent chromium detoxification by selected seaweed species using SEM-EDX and XPS analysis. Chem Eng J 148:425–433

Naiya TK, Chowdhury P, Bhattacharya K, Das SK (2009) Sawdust and neem bark as low-cost natural biosorbent for adsorptive removal of Zn(II) and Cd(II) ions from aqueous solutions. Chem Eng J 148:68–79

Nameni M, Moghadam MRA, Aram M (2008) Adsorption os hexavalent chromium aqueous solutions by wheat bran. Int J Environ Sci Technol 5:161–168

Netzahuatl-Muñoz AR, Guillén-Jiménez FDM, Chávez-Gómez B, Villegas-Garrido TL, Cristiani-Urbina E (2012) Kinetic study of the effect of pH on hexavalent and trivalent chromium removal from aqueous solution by *Cupressus lusitanica* bark. Water Air Soil Pollut 223:625–641

Nguyen TAH et al (2013) Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater. Bioresour Technol 148:574–585

O'Connell DW, Birkinshaw C, O'Dwyer TF (2008) Heavy metal adsorbents prepared from the modification of cellulose: a review. Bioresour Technol 99:6709–6724

Ofomaja AE, Naidoo EB (2010) Biosorption of lead(II) onto pine cone powder: studies on biosorption performance and process design to minimize biosorbent mass. Carbohydr Polym 82:1031–1042

Okoro IA, Okoro SO (2011) Agricultural byproducts as green chemistry adsorbents for the removal and recovery of metal ions from watewater environment. Cont J Water Air Soil Pollut 2:15–22

Osman HE, Badwy RK, Ahmad HF (2010) Usage of some agricultural byproducts in the removal of some heavy metals from industrial wastewater. J Phytol 2:51–62

Ozacar M, Sengil IA, Turkmenler H (2008) Equilibrium and kinetic data, and adsorption mechanism for adsorption of lead onto valonia tannin resin. Chem Eng J 143:32–42

Ozer A, Ozer D (2003) Comparative study of the biosorption of Pb(II), Ni(II) and Cr(VI) ions onto *S. cerevisiae*: determination of biosorption heats. J Hazard Mater 100:219–229

Panda GC, Das SK, Guha AK (2008) Biosorption of cadmium and nickel by functionalized husk of *Lathyrus sativus*. Colloid Surf B 62:173–179

Pardo R, Herguedas M, Barrado E, Vega M (2003) Biosorption of cadmium, copper, lead and zinc by inactive biomass of *Pseudomonas putida*. Anal Bioanal Chem 376:26–32

Park D, Yun Y, Park JM (2010) The past, present, and future trends of biosorption. Biotechnol Bioprocess Eng 15:86–102

Pavasant P, Apitatikul R, Sungkhum V, Suthiparinyanont P, Wattanachira S, Marhaba TF (2006) Biosorption of Cu^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} using dried marine green macroalga *Caulerpa lentillifera*. Bioresour Technol 97:2321–2329

Pehlivan E, Cetin S, Yanik BH (2005) Equilibrium studies for the sorption of zinc and copper from aqueous solutions using sugar beat pulp and fly ash. J Hazard Mater 135:193–199

Pehlivan E, Tran HT, Ouédraogo WKI, Schmidt C, Zachmann D, Bahadir M (2013) Sugarcane bagasse treated with hydrous ferric oxide as a potential adsorbent for the removal of As(V) from aqueous solutions. Food Chem 138:133–138

Peng Q, Liu Y, Zeng G, Xu W, Yang C, Zhang J (2010) Biosorption of copper(II) by immobilizing *Saccharomyces cerevisiae* on the surface of chitosan-coated magnetic nanoparticles from aqueous solution. J Hazard Mater 177:676–682

Qaiser S, Saleemi AR, Ahmad MM (2007) Heavy metal uptake by agro based waste materials. Electron J Biotechnol 10:409–416

Ramana DKV, Reddy DHK, Yu JS, Seshaiah K (2012) Pigeon peas hulls waste as potential adsorbent for removal of Pb(II) and Ni(II) from water. Chem Eng J 197:24–33

Ramos R, Jacome L, Barron J, Rubio L, Coronado R (2002) Adsorption of zinc(II) from an aqueous solution onto activated carbon. J Hazard Mater B90:27–38

Reddy DHK, Ramana DKV, Seshaiah K, Reddy AVR (2011) Biosorption of Ni(II) from aqueous phase by *Moringa oleifera* bark, a low cost biosorbent. Desalination 268:150–157

Redlich O, Peterson DL (1959) A useful adsorption isotherm. J Phys Chem 63:1024–1026

Rehman R, Anwar J, Tariq M, Salman M, Saleem M (2011) Evaluation of batch biosorption of chromium(VI) from aqueous solution by chemically modified *Polyalthia longifolia* leaves. J Chem Soc Pak 33:846–852

Rehman R, Anwar J, Mahmud T, Salman M, Mahboob S (2012) Optimization of operational conditions for batchwise biosorption of chromium (VI) using chemically treated *Alstonia scholaris* leaves as biosorbent. J Chem Soc Pak 34:292–298

Rehman R, Shafique U, Anwar J, Ghafoor S (2013) Kinetic and isothermal biosorption studies of Co(II), Cu(II) and Ni(II)

using *Polyalthia longifolia* leaf powder. Asian J Chem 25:8285–8288
Romero-Gonzalez J, Peralta-Videa JR, Rodriguez E, Delgado M, Gardea-Torresdey JL (2006) Potential of *Agave lechuguilla* biomass for Cr(III) removal from aqueous solutions: thermodynamic studies. Bioresour Technol 97:178–182
Saka C, Sahin O, Kucuk MM (2012) Applications on agricultural and forest waste adsorbents for the removal of lead (II) from contaminated waters. Int J Environ Sci Technol 9:379–394
Salman M, Athar M, Farooq U, Nazir H, Noor A, Nazir S (2013a) Microwave-assisted urea-modified sorghum biomass for Cr(III) elimination form aqueous solutions. Korean J Chem Eng 30:1257–1264
Salman M, Athar M, Farooq U, Nazir S, Nazir H (2013b) Insight to rapid removal of Pb(II), Cd(II), and Cu(II) from aqueous solution using an agro-based adsorbent *Sorghum bicolor* L. biomass. Desalin Water Treat 51:4390–4401
Salman M, Athar M, Farooq U, Rauf S, Habiba U (2014) A new approach to modification of an agro-based raw material for Pb(II) adsorption. Korean J Chem Eng 31:467–474
Sen TK, Mohammod M, Maitra S, Dutta BK (2010) Removal of cadmium from aqueous solution using castor seed hull: a kinetic and equilibrium study. Clean Soil Air Water 38:850–858
Shafique U, Ijaz A, Salman M, Waheed-uz-Zaman A, Jamil N, Rehman R, Javaid A (2012) Removal of arsenic from water using pine leaves. J Taiwan Inst Chem Eng 43:256–263
Sharma P, Kumari P, Srivastava S, Sirvastava MM (2006) Biosorption studies on shelled *Moringa oleifera* Lamarck seed powder: removal and recovery of arsenic from aqueous system. Int J Miner Process 78:131–139
Shoaib A (2012) Removal of Cr(III) ions from tannery wastewater through fungi. Online J Sci Technol 2:74–78
Singh KK, Hasan SH, Talat M, Singh VK, Gangwar SK (2009) Removal of Cr(VI) from aqueous solutions using wheat bran. Chem Eng J 151:113–121
Sips R (1948) Combined form of Langmuir and Freundlich equations. J Chem Phys 16:490–495
Srinath T, Verma T, Ramteke PW, Garg SK (2002) Chromium (VI) biosorption and bioaccumulation by chromate resistant bacteria. Chemosphere 48:427–435
Subudhi E, Kar NR (2008) *Rhizopus arrhizusean* efficient biosorbent for copper effluent treatment. Int J Integr Biol 2:166–171
Sud D, Mahajan G, Kaur MP (2008) Agricultural waste material as potential adsorbent for sequestrating heavy metal ions from aqueous solutions—a review. Bioresour Technol 99:6017–6027
Taha GM, Arifen AE, El-Nahas S (2011) Removal efficiency of potato peels as a new biosorbent material for uptake of Pb(II), Cd(II) and Zn(II) from the aqueous solutions. J Solid Waste Technol Manag 37:128–140
Tan G, Xiao D (2009) Adsorption of cadmium ion from aqueous solution by ground wheat stems. J Hazard Mater 164: 1359–1363
Tempkin MI, Pyzhev V (1940) Kinetics of ammonia synthesis on promoted iron catalyst. Acta Phys Chim USSR 12:327–356
Toth J (1971) State equations of the solid gas interface layer. Acta Chem Acad Hung 69:311–317
Tsekova T, Todopova D, Ganeva S (2010) Removal of heavy metals from industrial wastewater by free and immobilized cells of *Aspergillus* niger. Int Biodeterior Biodegerad 64:447–451
Tunali S, Cabuk A, Akar T (2006) Removal of lead and copper ions from aqueous solutions by bacterial strain isolated from soil. Chem Eng J 115:203–211
Tuzun I, Bayramoglu G, Alcin YE, Basaran G, Celik G, Arica MY (2005) Equilibrium and kinetic studies on biosorption of Hg(II), Cd(II) and Pb(II) ions onto microalgae *Chlamydomonas reinhardtii*. J Environ Manag 77:85–92
Uluozlu OD, Sari A, Tuzen M, Soylak M (2008) Biosorption of Pb(II) and Cr(III) from aqueous solution by lichen (*Parmelina tiliaceae*) biomass. Bioresour Technol 99:2972–2980
Vilar VJP, Botelho CMS, Boaventura RAR (2005) Influence of pH, ionic strength and temperature on lead biosorption by *Gelidium* and agar extraction algal waste. Process Biochem 40:3267–3275
Vogel M, Günther A, Rossberg A, Li B, Bernhard G, Raff J (2010) Biosorption of U(VI) by the green algae *Chorella vulgaris* in dependence of pH value and cell activity. Sci Total Environ 409:384–395
Wan Ngah WS, Hanafiah MAKM (2008) Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: a review. Bioresour Technol 99: 3935–3948
Wang J, Chen C (2009) Biosorbents for heavy metals removal and their future. Biotechnol Adv 27:195–226
Wang J, Chen C (2010) Research advances in heavy metal removal by biosorption. Acta Sci Circumst 30:673–701
Wang XS, Li ZZ, Sun C (2008) Removal of Cr(VI) from aqueous solutions by low-cost biosorbents: marine macroalgae and agricultural by products. J Hazard Mater 153:1176–1184
Wang XS, Li F, He YW, Miao HH (2010) Hg(II) removal from aqueous solutions by *Bacillus subtilis* biomass. Clean 38:44–48
Waseem S, Din MI, Nasir S, Rasool A (2012) Evaluation of Acacia nilotica as a non conventional low cost biosorbent for the elimination of Pb(II) and Cd(II) ions from aqueous solutions. Arab J Chem. doi:10.1016/j.arabjc.2012.1003.1020
Witek-Krowaik A, Harikishore K, Reddy D (2013) Removal of microelemental Cr(III) and Cu(II) by using soybean meal waste: unusual isotherms and insights of binding mechanism. Bioresour Technol 127:350–357
Xiong Y, Xu J, Shan W, Lou Z, Fang D, Zang S, Han G (2013) A new approach for rhenium(VII) recovery by using modified brown algae *Laminaria japonica* adsorbent. Bioresour Technol 127:464–472
Yahaya YA, Don MM, Bhatia S (2009) Biosorption of Copper(II) on to immobilized cells of *Pycnoporus sanguineus* from aqueous solution: equilibrium and kinetic studies. J Hazard Mater 161:189–195
Yan G, Viraraghavan T (2003) Heavy-metal removal from aqueous solution by fungus *Mucor rouxii*. Water Res 37:4486–4496
Yuvaraja G, Krishnaiah N, Subbaiah MV, Krishnaiah A (2014) Biosorption of Pb(II) from aqueous solution by *Solanum melongena* leaf powder as a low-cost biosorbent prepared from agricultural waste. Colloid Surf B: Biointerfaces 114:75–81