**REVIEW ARTICLE** 



# Removal of heavy metals from emerging cellulosic low-cost adsorbents: a review

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**Abstract** Heavy metal pollution is a major problems in the environment. The impact of toxic metal ions can be minimized by different technologies, viz., chemical precipitation, membrane filtration, oxidation, reverse osmosis, flotation and adsorption. But among them, adsorption was found to be very efficient and common due to the low concentration of metal uptake and economically feasible properties. Cellulosic materials are of low cost and widely used, and very promising for the future. These are available in abundant quantity, are cheap and have low or little economic value. Different forms of cellulosic materials are used as adsorbents such as fibers, leaves, roots, shells, barks, husks, stems and seed as well as other parts also. Natural and modified types of cellulosic materials are used in different metal detoxifications in water and wastewater. In this review paper, the most common and recent materials are reviewed as cellulosic low-cost adsorbents. The elemental properties of cellulosic materials are also discussed along with their cellulose, hemicelluloses and lignin contents.

**Keywords** Heavy metals · Cellulosic low-cost adsorbents · Wastewater treatment technologies · Adsorption

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# Introduction

Heavy metals are elements which have atomic density more than 5. Some toxic heavy metals, such as lead, cadmium, nickel, cobalt, chromium, arsenic, iron and zinc, cause metal toxicity in living organisms . The major metal polluting industries are tannery, electroplating, textile, fertilizer, pesticide and metal processing industries as well as mining sectors. These toxic metals are major pollutants of freshwater reserves (Babarinde et al. 2006). Most of the metals are non-biodegradable, highly toxic and carcinogenic in nature. Toxic heavy metals reach through various food chains and cause toxic effects on the ecosystem as well as humans and animals. Therefore, it is necessary to treat metal-contaminated wastewater before its discharge into the environment.

A number of technologies are available to treat heavy metal-laden wastewater. Among them, some popular techniques are chemical precipitation (Ku and Jung 2001), ion exchange (Alyüz and Veli 2009), adsorption (Park et al. 2007; Kongsuwan et al. 2009; Guo et al. 2010), ultrafiltration (Landaburu-Aguirre et al. 2009; Sampera et al. 2009), reverse osmosis (Shahalam et al. 2002; Mohsen-Nia et al. 2007), nanofiltration (Murthy and Chaudhari 2008; Muthukrishnan and Guha 2008; Nguyen et al. 2009; Figoli et al. 2010), electrodialysis (Sadrzadeha et al. 2009; Nataraj et al. 2007), coagulation (El Samrani et al. 2008; Chang and Wang 2007), flocculation (Chang et al. 2009; Duan et al. 2010; Bratskaya et al. 2009), flotation (Lundh et al. 2000; Polat and Erdogan 2007) and electrochemical process (Heidmann and Calmano 2008; Nanseu-Njiki et al. 2009). Comparatively, the adsorption process seems to be a significant technique due to its wide applications, such as ease of operation, economical feasibility, wide availability and simplicity of design (Faust and Aly 1987).



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For cellulosic low-cost biosorbents, agricultural waste or plant wastes are mostly used in heavy metal sequestration, due to their low economic value and widespread availability, and also the potential to treat wastewater at a large scale. The cellulosic plant materials used in heavy metal detoxification are rice husk (Sobhanardakani et al. 2013; Nakbanpote et al. 2000; Feng et al. 2006), wheat straw (Farooq et al. 2011, Dang et al. 2009; Dhir and Kumar 2010; Pehlivan et al. 2009a, b, c), banana peel (Memon et al. 2009; Sahu et al. 2013; Ajmal et al. 2000), grape bagasse (Farinella et al. 2007), corn stalk (Zheng et al. 2012), bel fruit shells (Anandkumar and Mandal 2009), coir pith (Parab et al. 2006), hemp fibers (Tofan et al. 2013) and corn cob (Buasri et al. 2012).

In the category of low-cost adsorbents, both non-cellulosic and cellulosic materials are used. In non-cellulosic materials, zeolites (Basaldella et al. 2007), clay (Adebowale et al. 2006), chitosan (Gamage and Shahidi 2007), red mud (Nadaroglu et al. 2010), dairy sludges (Sassi et al. 2010) and metal oxides (Mishra et al. 2004) are utilized as adsorbents. The use of cellulosic waste materials as adsorbent is considered as promising in the future. The main sources of cellulosic contents are agricultural waste material and industrial by-products. Non-agricultural wastes are also prominent, because these are also efficient in metal removal, as presented by many current studies.

In this review, cellulosic emerging modified or natural adsorbents has been characterized with the lignocellulosic and composite properties of widely used materials. The potential of cellulosic adsorbent materials for various heavy metal uptake capacities was also reported.

#### Techniques used in heavy metal removal

Many techniques are used at the present time for wastewater treatment. The present study will summarize the widely used technique for heavy metal removal from wastewater. For treatment of waste water, many methods are common, viz. precipitation, neutralization, membrane filtration, ion exchange, flotation and adsorption. Both, physical and chemical treatment technologies have been developed, such as the electrochemical process (Vlyssides and Israilides 1997), coagulation/flocculation (Song et al. 2006), oxidation (Szpyrkowicz et al. 2001), reverse osmosis (Hanra and Ramchandran 1996), membrane filtration (Sabry et al. 2007) and adsorption (Nagah and Hanafiah 2008) for treatment of different types of water. Among these, adsorption technology is the least expensive and effective separation technique for the removal of metal ions from industrial wastewater (Demirbas et al. 2008a, b).



# **Chemical precipitation**

It is a simple and very common technique to remove heavy metals due to its ease in operation and inexpensive nature (Ku and Jung 2001). Chemical precipitation technique is used for the treatment of metal-containing wastewater by forming an insoluble precipitate through the addition of chemicals (Karthikeyan et al. 1996). Some other chemical precipitation techniques are also used such as hydroxide precipitation, sulfide precipitation and heavy metal chelating precipitation. As precipitant agents, lime and limestones are most commonly used in chemical precipitation due to being a simple process, convenience and effectiveness in treating inorganic effluents at higher concentrations (Mirbagherp and Hosseini 2004; Aziz et al. 2008). Despite the advantages, it also has some disadvantages, such as requiring an excess amount of chemicals in the treatment. It has some other drawbacks such as generation of excessive sludge and the problem of sludge disposal into the environment.

#### Ion exchange

The ion exchange method is basically based on the capability to exchange cations with metals in the wastewater (Maranon et al. 1999; Kononova et al. 2000; Monteagudo and Ortiz 2000; Pagano et al. 2000). There are different types of materials used, which may be natural (alumina, carbon, silicates) or synthetic (zeolites and resins). Among them, zeolites are most abundantly used in the ion exchange process (Fernandez et al. 2005). The ion exchange process takes place by both cations and anions exchange in aqueous medium by ion exchange. The drawback of this method is that it is highly sensitive to the pH of the solution, and the ion exchange is non-selective in operation.

# Membrane process

The membrane filtration technique used different types of membranes and removal of various heavy metals in aqueous solution. This technique removes oils, suspended solids, heavy metals, and organic and inorganic materials (Barakat 2011; Fu and Wang 2011). Different forms of this technique are used based on the size of the particles, such as ultrafiltration (UF), nanofiltration (NF), reverse osmosis (OS) and electrodialysis (ED), depending on the type of wastewater.

#### Ultrafiltration

In this method, dissolved molecules, heavy metal ions and other contaminants are filtered using a membrane, according to their molecular size. Different types of membranes allow only the passage of low molecular solutes, and the remaining ones, such as larger molecules and heavy metals, do not pass through and are separated out. It has also been divided into subcategories, such as micellar enhanced ultrafiltration (Landaburu-Aguirre et al. 2012; Yurlova et al. 2002), complexation–ultrafiltration (Molinari et al. 2008) and chelating enhanced ultrafiltration (Kryvoruchko et al. 2002).

#### Nanofiltration

Nanofiltration is membrane separation technique that is used in heavy metal separation from aqueous solutions (Mohammad et al. 2004; Al-Rashdi et al. 2011). It is applied to the removal of different heavy metals such as copper (Cséfalvay et al. 2009; Ahmad and Ooi 2010), arsenic (Nguyen et al. 2009; Figoli et al. 2010), nickel (Murthy and Chaudhari 2008) and chromium (Muthukrishnan and Guha 2008). It is reliable, comparatively easy to operate and has low energy consumption than others (Erikson 1988).

#### Reverse osmosis

Reverse osmosis (RO) technique is used mainly for the separation and fractionation of organic and inorganic substances and heavy metals in aqueous and nonaqueous solutions. The RO technique can be used to treat different types of industrial effluents, viz., chemical, textile, petrochemical, electrochemical, food, paper and tannery industries (Mohsen-Nia et al. 2007). In combination with the pilot membrane reactor, this technique is efficient in metal removal at high level (Dialynas and Diamadopoulos 2009). It has some disadvantages also: it consumes high power for the pumping pressure and the restoration of the membrane.

# Electrodialysis

Electrodialysis (ED) is a separation process in which dissolved ions are removed from one solution to another solution across a charged membrane under an electric field (Sadrzadeh et al. 2008; Mohammadi et al. 2005). It is used in the treatment of wastewater as well as in the production of drinking water from seawater, separation and recovery of heavy metals ions and in salt production (Sadrzadeha et al. 2009). It is applied for heavy metal removal, such as chromium (Nataraj et al. 2007), copper and ferrous (Cifuentes et al. 2009), by various researchers.

# Flotation

Flotation has been widely applied for the removal of toxic metal ions from wastewater (Polat and Erdogan 2007;

Waters 1990; Tassel et al. 1997; Tessele et al. 1998). Other techniques of flotation are ion flotation, dissolved air flotation (DAF) and precipitate flotation. DAF is a more commonly used process than any other flotation techniques in the removal of heavy metals from aqueous solutions (Zabel 1984).

## **Chemical coagulation**

Coagulation technique is used to prepare colloids. Some coagulates are used, such as aluminum, ferrous sulfate and ferric chloride that neutralize impurities present in wastewater/water. It is an important method showed by various researchers (El Samrani et al. 2008; Chang and Wang 2007). Ferric chloride solution and polyaluminium chloride (PAC) coagulants are used in heavy metal removal (El Samrani et al. 2008).

# **Electrochemical method**

Electrochemical methods involves the redox reactions for metal removal under the influence of external direct current in the electrolyte solution. The coagulation process destabilizes colloidal particles by adding a coagulant and results in the sedimentation process (Shammas 2004). For increase in the rate of coagulation, the flocculation process takes place which enhances the change of unstable particles into bulky floccules (Semerjian and Ayoub 2003).

# Adsorption

Adsorption is a very significantly economic, convenient and easy operation technique. It shows high metal removal efficiency and is applied as a quick method for all types of wastewater treatments. It is becoming a popular technique, because in this process the adsorbent can be reused and metal recovery is possible (Barakat 2011; Fu and Wang 2011; Zamboulis et al. 2011).

# Activated carbon (AC)

At present, activated carbon (AC) is the mostly used adsorbent worldwide. AC is not only efficient in removal of heavy metals, but also for other contaminants present in water/wastewater. These can be used in both batch and column mode operation due to its high surface area, microporous structure and porosity properties. In the preparation of activated carbon, many agricultural waste biomasses are used such as bagasse (Onal et al. 2007), coconut shell, tea waste, peanut hull (Oliveira et al. 2009), apple waste (Maranon and Sastre 1991), sawdust (Ajmal et al. 1998), rice husk (Naiya et al. 2009), banana pith (Low et al. 1995), tree bark (Gundogdu et al. 2009) and activated



cotton fibers (Kang et al. 2008). The adsorption capacity of the lignocellulosic material can be increased by physical and chemical modification of adsorbents. It is costly in nature at the industrial level. So, researchers are focusing on the use of low-cost adsorbents for the treatment operation.

#### Low-cost adsorbents

With the availability and cheapness of various waste materials, industrial by-products, agricultural wastes and other natural waste materials, the low-cost technique has become popular nowadays. The focus on selecting low-cost adsorbent is because of the high cost of commercially activated carbon. Researchers are preparing industrial by-products as low cost adsorbents, such as pulp and paper waste (Stniannopkao and Sreesai 2009), fertilizer waste (Gupta et al. 1997), steel converter slag (Mendez et al. 2009), steel making slag (Kim et al. 2008), sugarcane bagasse (Soliman et al. 2011), bagasse fly ash (Gupta and Ali 2000; Rao et al. 2002; Gupta et al. 2010) that are very common. Household wastes such as fruit waste (Kelly-Vargas et al. 2012), marine origin adsorbent such as peat (Brown et al. 2000; Márquez-Reyes et al. 2013) and red mud (Sahu et al. 2013; Bertocchi et al. 2006; Gupta et al. 2001) are also used in the treatment. Nonagricultural adsorbents are also used as low-cost adsorbents such as lignin (Betancur et al. 2009; Reyes et al. 2009), diatomic (Sheng et al. 2009), clino-pyrrhotite (Lu et al. 2006), aragonite shells (Kohler et al. 2007), natural zeolites (Apiratikul and Pavasant 2008), clay (Al-Jlil and Alsewailem 2009), kaolinite (Gu and Evans 2008) and peat (Liu et al. 2008).

#### **Bioadsorbents**

Mostly agricultural and plant wastes were used as bioadsorbents for wastewater treatment; these are very efficient and promising in the biosorption technique. There are generally three types based on the sources:(1) non-living biomass such as bark, lignin, shrimp, krill, squid, crab shell, etc.; (2) algal biomass; (3) microbial biomass, e.g., algae, bacteria, fungi and yeast.

Agricultural wastes in the preparation of bioadsorbents are also promising such as potato peel (Aman et al. 2008), sawdust (Ajmal et al. 1998; Kaczala et al. 2009), citrus peels (Schiewer and Patil 2008), mango peel (Iqbal et al. 2009a, b), corn cob (Leyva-Ramos et al. 2005; Vaughan et al. 2001), rice husk (Chockalingam and Subramanian 2006), tree fern (Ho 2003), wheat bran (Ozer and Ozer 2004), grape bagasse (Farinella et al. 2007), coconut copra meal (Ho and Ofomaja 2006), orange waste (Dhakal et al. 2005), walnut, hazelnut, almond shell (Pehlivan and Altun 2008), tea waste (Malkoc and Nuhoglu 2005), dried parthenium powder (Ajmal et al.



2006), sugarcane bagasse (Khan et al. 2001; Mohan and Singh 2002), pine needles (Dakiky et al. 2002), peanut shell (Namasivayam and Periasamy 1993), tamarind seeds (Gupta and Babu, 2009), sunflower stalk (Sun and Xu 1997) and black gram husk (Saeed et al. 2005).

# Characterization of cellulosic waste material

Bioadsorbents are composed of mainly cellulose, hemicelluloses, lignin and extractives, and many other compounds such as lipid, starch, hydrocarbons, simple proteins and ash (Sud et al. 2008).

# Cellulose

Cellulose  $(C_5H_8O_4)_m$  is a long linear polysaccharide polymer consisting of  $\beta$ -(1,4) linked glucose units. It is an important constituent of plant cell wall. It is present in plant cell combined with hemicelluloses and lignin. It is generally insoluble in water. The material with high cellulose contents are plant fibers, woods, stalks, stems, shells, straw, grasses, etc. (Table 1; Fig. 1).

# Hemicelluloses

Hemiceluloses  $(C_5H_8O_4)_m$  are another important constituent of plants materials. Hemicellulose is a dietary fiber consisting of a heterogenous group of polysaccharide substances that contain a number of sugars including xylose, mannose, galactose, arabinose and glucuronic acids. These are generally insoluble in water, but some hemicelluloses containing acids are water soluble. The materials with high hemicellulosic contents are barks, leaves, grasses, corn cobs, husks and shells (Table 1).

# Lignin

Lignin  $[C_9H_{10}O_3(OCh_3) 0.9-1.7]_n$  is a highly branched polymer consisting of phenol units which include transconiferyl, trans-sinapyl and trans-p-coumaryl. It is also insoluble in water and has both characteristics of dietary and functional fibers. It is mostly present in the stems, seeds of vegetables and fruits and cereals. The materials with high lignin contents are cereal material husks, others shells, leaves, barks, grasses and fruit seeds (Table 1).

# Extractives

Extractives are organic materials and generally soluble in neutral solvents which includes resin, fats, alcohols, turpentine, tannins, fatty acids, waxes and flavonoids (Demirbas 2008a, b).

# Table 1 Lignocellulosic contents in plant material

Plant materials	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractive (%)	References
Husk					
Coconut husks	40.0	0.2	43.0	5.5	Reddy and Yang (2005)
Millet husks	44.9	36.2	18.9	12.7	Raveendran et al. (1995)
Olive husks	25.0	24.6	50.4	8.9	Kristensen (1996) and Demirbas (2004)
Rice husks	43.8	31.6	24.6	6.67	Raveendran et al. (1995), Kristensen (1996) and Nakbanpote et al. (2000)
Shell					
Almond shells	50.7	28.9	20.4	2.4	Demirbas (2004)
Almond shells	28.99	35.16	30.01	5.0	Pehlivan et al. (2009a, b, c)
Coconut shells	40.3	27.8	31.9	8.4	Raveendran et al. (1995)
Coconut shells	14.0	32.0	46.0	-	Cagnon et al. (2009)
Dende shells	24.9	27.0	45.4	1.1	Ouensanga et al. (2003)
Hazelnut shells	26.6	30.0	43.4	3.9	Demirbas (2004, 2009)
Hazelnut shells	18.24	28.90	48.57	4.83	Pehlivan et al. (2009a, b, c)
Peanut shells	42.2	22.1	35.7	10.9	Raveendran et al. (1995)
Walnut shells	28.1	26.6	45.3	2.7	Demirbas (2004) and Prasad et al. (2007)
Straws					
Barley straw	48.6	29.7	21.7	14.8	Sander (1997), Abbasi and Abbasi (2010), Naik et al. (2010) and Tamaki and Mazza (2010)
Legume straw	29.2	35.5	35.3	3.8	Demirbas (2009)
Rice straw	52.3	32.8	14.9	9.3	Raveendran et al. (1995), Kristensen (1996), Prasad et al. (2007), Demirbas (2009) and Abbasi and Abbasi (2010)
Rice straw	43.3	25.1	5.4	13.1	Wartelle and Marshall (2006)
Rye straw	49.9	29.6	20.5	11.0	Sander (1997) and Abbasi and Abbasi (2010)
Wheat straw	44.5	33.2	22.3	12.4	Raveendran et al. (1995), Kristensen (1996), Sander (1997), McKendry (2002), Demirbas (2004), Prasad et al. (2007), Abbasi and Abbasi (2010), Naik et al. (2010) and Tamaki and Mazza (2010)
Wheat straw	31.5	33.3	11.6		Chen et al. (2008)
Stems/woods					
Albizzia wood	59.5	6.7	33.8	1.9	Kataki and Konwer (2001)
Birch	50.2	32.8	17.0	3.0	Kristensen (1996), Tillman and Harding (2004) and Shen et al. (2009)
Eucalyptus	52.7	15.4	31.9	2.2	Huber et al. (2006)
Oak	58.4	31.4	10.2		Shen et al. (2009)
Pine	48.1	23.5	28.4	3.9	Kristensen (1996), Tillman and Harding (2004), Huber et al. (2006) and Shen et al. (2009)
Softwood	43.3	27.4	29.3		Kristensen (1996), McKendry (2002) and Demirbas (2009)
Spruce	43.6	27.4	29.0	1.8	Tillman and Harding (2004)
Leaves					
Albizzia leaves	25.3	44.6	30.1	3.0	Kataki and Konwer (2001)
Premna leaves		50.8	18.9	4.6	Kataki and Konwer (2001)
Pterospermum leaves	22.1	50.6	27.3	3.7	Kataki and Konwer (2001)
Syzygium leaves	28.1	42.9	29.0	3.3	Kataki and Konwer (2001)
Barks					
Albizzia bark	22.5	44.9	32.6	4.5	Kataki and Konwer (2001)
Premna bark	19.0	60.4	20.6	2.6	Kataki and Konwer (2001)
Pterospermum bark	20.7	53.2	26.1	3.1	Kataki and Konwer (2001)
Syzygium bark	22.6	46.4	31.0	3.0	Kataki and Konwer (2001)



Table 1 continued

Plant materials	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractive (%)	References
Grasess					
Bamboo	43.9	26.5	29.6	2.8	Scurlock et al. (2000) and Abbasi and Abbasi (2010)
Bermuda grass	37.3	53.2	9.5		Prasad et al. (2007)
Elephant grass	31.5	34.3	34.2		Abbasi and Abbasi (2010)
Orchard grass	41.7	52.2	6.1	23.3	Demirbas (2009) and Abbasi and Abbasi (2010)
Rye grass	49.1	41.4	9.5		Abbasi and Abbasi (2010)
Sweet sorghum grass	50.6	24.7	25.0		Huber et al. (2006)
Timothy grass	38.0	33.1	28.9		Naik et al. (2010)
Stalks					
Corn stalk	49.0	37.9	13.1	10.5	Raveendran et al. (1995), Kristensen (1996) and Yanik et al. (2007)
Cotton stalk	62.2	18.4	15.4		Yanik et al. (2007)
Sorghum stalk	27.0	25.0	11.0		Reddy and Yang (2005)
Sunflower stalk	58.8	23.8	17.4	13.1	Yanik et al. (2007), Pettersson et al. (2008)
Fibers					
Flax fiber	75.9	20.7	3.4	25.6	Williams and Reed (2006)
Jute bust fiber	53.3	21.2	25.5		Abbasi and Abbasi (2010)
Kenaf bast fiber	47.0	30.2	22.8		Abbasi and Abbasi (2010)
Pineapple leaf fiber	70–80	18.0	5-12	0.8	Reddy and Yang (2005)
Seeds/hulls					
Cotton seed hull	48.7	18.5	22.3	1.1	Wartelle and Marshall (2006)
Guava seeds	28.0	15.5	41.7	16.8	Ouensanga et al. (2003)
Jujube seeds	37.3	25.9	35.4	0.3	Ouensanga et al. (2003)
Pulps					
Apple pulp	16.0	16.0	21.0		Cagnon et al. (2009)
Plum pulp	6.5	14.5	39.0		Cagnon et al. (2009)
Bagasse					
Olive baggase	31.1	15.6	25.21	28.09	Demiral et al. (2011)
Others					
Corn cob	38.4	40.7	9.1	1.3	Feng et al. (2006)
Ectodermus of opuntia	28.2	14.4	14.5		Barrera et al. (2006)
Holm oak	37.9	25.9	27.8	4.8	López et al. (2013)
Newspaper	40–55	25–40	18–30		Chandra et al. (2012)
Pyrenean oak	33.9	25.5	31.2	5.2	López et al. (2013)
Stone pine	41.0	20.1	31.2	6.8	López et al. (2013)

# Properties of cellulosic low-cost adsorbents

# **Proximate properties**

Low-cost cellulosic biomass properties are generally proximate analysis, ultimate analysis and compositional properties. These properties show the variation of its constituents derived from different plant and agricultural waste. It generally shows the variation in fixed carbon, volatile matter, moisture and ash content in plant and agricultural materials (Table 2).



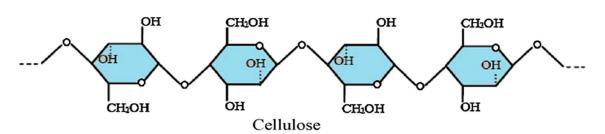


Fig. 1 Structure of cellulose (Chandra et al. 2012)

#### **Ultimate properties**

It gives the information about the elemental knowledge of a particular biomass followed by oxygen content, hydrogen content, nitrogen content and sulfur content (Table 3).

# **Compositional properties**

The compositional properties of cellulosic adsorbents are characterrized with parameters like cellulose content, hemicelluloses content and lignin content.

# Adsorption characteristics of cellulosic low-cost adsorbents

In the removal of metals from aqueous solution, different types of plant parts are used such as stems, stalks, leaves, husk, shells, roots, and barks and many others. These are freely and easily available, because India is rich in plant biomass. Agricultural plant materials are very common in

Table 2 Proximate analysis of cellulosic materials/biomass (%wt.)

the preparation of low-cost adsorbents. Most of the countries are rich in plant biodiversity and have large agricultural areas.

# Husks

Rice is a crop that is cultivated all over the world. The hard outer covering of the grains of rice is a waste material generated from the rice milling process. In the world, rice is the major source of food calorie and livelihood. It is grown worldwide in most of the countries such as China, India and Indonesia. There is the problem of utilization of rice husk in rice-growing countries. Lignocellulogic agricultural waste material contains approximately 35 % cellulose, 25 % hemicelluloses, 20 % lignin, 17 % silica (including ash) and 3 % crude protein. It has been used widely in heavy metal removal from aqueous solutions (Ajmal et al. 2003; Bishnoi et al. 2004; Dadhlich et al. 2004). Sobhanardakani et al. 2013 applied untreated rice husk for removal of Cr(III) and Cu(II) from synthetic wastewater. He achieved the maximum sorption capacity

Plant material	Fixed carbon	Ash	Volatile matter	Moisture	References
Cashew nut shell	22.21	2.75	65.25	9.83	Kumar et al. (2012a, b)
Holm oak	7.4	2.3	80.8	9.5	López et al. (2013)
Moringa oleifera bark	20.1	11.1		2.5	Reddy et al. (2011)
Mangifera indica sawdust	16.28	8.32	66.0	9.4	Kapur and mondal (2013)
Olive bagasse	21.6	4.4	67.2		Sensöz et al. (2006)
Peanut shell	23.17	3.12	68.69	5.02	AL-Othman et al. (2012)
Pyrenean oak	6.0	2.4	80.5	11.1	López et al. (2013)
Rice husk		17.1	59.5		Mahvi et al. (2004)
Silver fir	6.5	0.4	78.7	14.4	López et al. (2013)
Stone pine	7.4	0.7	82.2	9.8	López et al. (2013)
Sugarcane bagasse	7.0	22.1	70.9		Grover et al. (2002)
Sugarcane leaves	14.9	7.7	77.4		Grover et al. (2002)
Sunflower waste carbon		3.8		2.8	Jain et al. (2013)
Tea waste		4.8		5.4	Mondal (2010)
Wheat straw	11.7	7.7	77.4		Grover et al. (2002)



 Table 3 Ultimate analysis of cellulosic biomass/material (%wt.)

Plant material	С	Н	Ν	S	0	References
Almond shell	48.17	5.89			45.93	Pehlivan et al. (2009a, b, c)
Cashew nut shells	45.21	4.25	0.21		37.75	Kumar et al. (2011)
Hazelnut shell	48.92	5.65			45.42	Pehlivan et al. (2009a, b, c)
Holm oak	48.0	5.9	0.5	0.02	45.6	López et al. (2013)
Jacaranda mimosifolia	48.2	4.4	0.2		47.2	Trevino-Corderoa et al. (2013)
Maize straw	45.6	5.4	0.3	0.04	43.4	Taner et al. (2004)
Moringa oleifera bark	44.8	5.9	0.8	0.9	47.6	Reddy et al. (2011)
Olive bagasse	53.4	7.5	1.7		37.4	Sensöz et al. (2006)
Peanut shell	49.36	5.71	0.72		44.42	AL-Othman et al. (2012)
Prunus domestica	52.0	6.20	0.3		45.2	Trevino-Corderoa et al. (2013)
Pyrenean oak	48.5	5.9	0.5	0.01	45.1	López et al. (2013)
Silver fir	51.2	6.4	0.2		42.2	López et al. (2013)
Stone pine	50.4	6.0	0.3	0.01	43.3	López et al. (2013)
Sugarcane leaves	39.7	5.5		0.2	46.8	Grover et al. (2002)
Sunflower waste carbon	44.0	2.8	8.5		44.7	Jain et el. (2013)
Tea waste	57.6	8.25	0.42	0.52	33.1	Mondal (2012)
Wheat straw	46.7	6.3	0.4	0.1	41.2	Taner et al. (2004)

of 22.5 and 30 mg/g, respectively. The adsorption capacities of different husk materials are in listed in Table 4.

It was reported that peanut husk modified with Fe and formaldehyde gives improve result. It was found that Femodified formaldehyde husk shows six times higher adsorption capacity than formaldehyde-modified peanut husk (Olguin et al. 2013). Wong et al. (2003) used tartaric acid-modified rice husk in the removal of Cu(II) and Pb(II) ions from aqueous solutions. He reported that the maximum metal uptake were found to be 29 and 108 mg/g at 27 °C for Cu(II) and Pb(II) metal ions, respectively. Fixed bed column study was also performed by the phosphate-treated rice husk in the removal of Pb(II), Cu(II), Zn(II) and Mn(II) at different time intervals. Table 5 (Mohan and Sreelakshmi 2008) describes the operating conditions for column experiments.

It was investigated that the flow rate 20 ml/min is optimum for the 10 mg/l solution. The breakthrough time was find to increase from 1.3 to 3.5 h for Pb(II), 4.0 to 9.0 h for Cu(II), 12.5 to 25.4 h for Zn(II) and 3.0 to 11.3 h for Mn(II) for increasing bed height up to 10–30 cm.

#### Straw and bran

The adsorbents prepared from straw and bran are commonly wheat straw and barley straw. Wheat straws have high worldwide production in some countries such as China, India and Russia. In 2013/14, the world wheat



supplies increased from 5.3 million tons to 887.3 million tons (WASDE 2013). Wheat straw is commonly used mainly as cattle fodder. So it is needed to utilize wheat straw and bran for other applications also. The wheat straw is also lignocellulosic waste material that constitutes 34–40 % cellulose, 20–35 % hemicelluloses, 8–15 % lignin and sugars and other compounds (Keng et al. 2013). It was reported that wheat straw treated with microwave radiation gave significant results. It was found that the adsorption capacity was 39.22 mg/g (Farooq et al. 2011). The adsorption capacities of wheat straw and bran in heavy metal removal are given in Table 6.

Chojnacka (2006) investigated that ground straw removal of Cr(III) metal ions takes places when equilibrium is reached in less than 20 min. Farooq et al. (2011) found that wheat straw followed Langmuir model with maximum biosorption capacity ( $q_{max}$ ) mg/g. The maximum sorption occurred at pH 6 and the equilibrium time was 20 min. Barley husk showed the maximum sorption capacities of 69 and 88 % for Cu(II) and Pb(II), respectively (Pehlivan et al. 2009a, b, c). It was found that the favorable pH values for the removal of Cu(II) and Pb(II) were 6.0 and 6.6, respectively. The Langmuir isotherm model was fit with the sorption equilibrium results. The equilibrium sorption obtained after 2 h and the adsorption capacities for Cu(II) and Pb(II) were 4.64 mg/g and 23.20 mg/g, respectively (Pehlivan et al. 2009a, b, c).

Table 4 Adsorption capacities of husk materials for the removal of heavy metals from water/wastewater

Cellulosic materials	Type of adsorbent	Heavy metals	Adsorption capacity (mg/g)	References
Peanut husk	MB (FeCl <sub>3</sub> and formaldehyde)	Cr(VI)	33.1	Olguin et al. (2013)
Rice husk	NB	Cd(II)	8.58	Tan et al. (1993)
Rice husk	NB	Ni(II)	102	Feng et al. (2006)
Rice husk	NB	Cr(VI)	45.6	Scatchard (1949)
Rice husk	NB	Cr(III)	1.90	Marshall et al. (1993)
Rice husk	NB	Cu(II)	7.1	Nakbanpote et al. (2000)
Rice husk	NB	Cr(III)	22.5	Sobhanardakani et al. (2013)
Rice husk	NB	Cu(II)	30.0	Sobhanardakani et al. (2013)

NB natural or unmodified biosorbent

 Table 5 Operational parameter for column experiments

Column bed height	10-30 cm
Column diameter	2.5 cm
Weight of adsorbate uptake	36 g
Volume of wastewater uptake	501 ml
Initial conc.	10 mg/l
Flow rate	20 ml/min

# Fruit peel/pulp

The tropical as well as temperate countries produce different types of fruits depending on climatic variations. The peels of different types of fruits are considered as fruit waste material that can be used for biosorption of heavy metals in different wastewater (Table 7). The apple pulps constitute 16 % cellulose, 16 % hemicelluloses and 21 % lignin (Cagnon et al. 2009). As biosorbent, orange peel indicates high metal adsorption potential due to its high content of cellulose, pectin (galacturonic acid), hemicelluloses and lignin (Feng et al. 2011). The adsorption of Cr(VI) ions from an aqueous solution of mosambi (sweet lime) peel dust has also been reported by Saha et al. 2013) without any prior modification. The adsorption of Cr(VI) was studied at different parameters such as sorbate concentration, pH, contact time and temperature with the highest adsorption capacity of 250 mg/g (Table 7) at pH 2.0 and 40 °C. The adsorption data was fit with the Langmuir isotherm that confirmed monolayer adsorption of hexavalent chromium on mosambi (sweet lime) peel.

Huang and Zhu (2013) prepared chemically modified biosorbent from muskmelon by the saponification process with alkaline solution of Ca(OH)<sub>2</sub>. They reported that the optimum equilibrium pH range for 100 % adsorption 4–6.4. They also revealed the factor responsible for the uptake of metal ions was pectic acid present in muskmelon peel. The maximum adsorption capacities were found to be 0.81 mol/kg for Pb(II) ions at equilibrium time of up to 10 min. The use of sugar beet pulp for Cr(IV) removal was studied by Altundogan et al. (2007). The adsorbent was treated with sulfuric acid medium and sulfur dioxide gas reactant. The lower pH (2–3) was reported with the 24 mg/ g adsorption capacities at 25 °C.

# Bagasse

In the plant waste, bagasse is a very common waste material that was generated from the sugarcane industry as by-products (Table 8). It was used by Alomá et al. (2012)

Table 6 A	Adsorption ca	pacities of s	straw materials	s for the remova	al of heavy	y metals from	water/wastewater
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Cellulosic materials	Type of adsorbent	Heavy metals	Adsorption capacity (mg/g)	References
Wheat straw	NB	Cd(II)	14.56	Dang et al. (2009)
Wheat straw	NB	Cr(VI)	47.16	Dhir and Kumar (2010)
Wheat straw	NB	Cu(II)	11.43	Dang et al. (2009)
Wheat straw	NB	Ni(II)	41.84	Dhir and Kumar (2010)
Wheat straw	MB (urea and microwave radiation)	Cd(II)	39.22	Farooq et al. (2011)
Wheat bran	NB	Pb(II)	62.0	Farajzadeh and Monji (2004)
Barley straw	NB	Cu(II)	4.64	Pehlivan et al. (2009a, b, c)
Barley straw	NB	Pb(II)	23.2	Pehlivan et al. (2009a, b, c)

NB natural or unmodified biosorbent, MB modified biosorbent



in the removal of Ni(II) ions from the aqueous solution. The adsorption capacity for Ni(II) ion removal at pH 5 at 25 °C was evaluated. The calculated sorption capacity was approximately 2 mg/g. Adsorption followed Langmuir, Freundlich and sips isotherm models. They also reported that the Langmuir model represented data in a better way, with correlation coefficient greater than 0.95.

Yu et al. (2013) used sugarcane bagasse modified with PMDA and unmodified form for the removal of heavy metals such as  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$ . It was found that adsorption of these four metal ions increased with an increasing solution pH and dosages. Langmuir isotherm model fit with equilibrium results. The adsorption capacities of modified bagasse were 1.06, 0.93, 1.21 and 1.0 mmol/g and for unmodified bagasse 0.04, 0.13, 0.10, and 0.07 mmol/g for Pb<sup>2+</sup>, Cd<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup>, respectively. FTIR and EDX studies also performed showed that the adsorption mechanism and kinetic process, pseudo-first order and pseudo-second order were also used to predict the adsorption rates.

# Stalk

Plant stalks are cellulosic materials consisting of cellulose, hemicelluloses and lignin. Many plant stalk such as corn stalk (Zheng et al. 2012) and sunflower stalk (Sun and Shi 1998) are used for the removal of toxic metals (Table 9). Corn stalk as adsorbent was used after modification by graft polymerization for the removal of Cd(II) metal ion from aqueous solution (Zheng et al. 2012). The maximum adsorption of Cd(II) metal ion was found to be 21.37 mg/g. They also reported that modified corn stalk had better potential of metal ion removal than unmodified corn stalk because of the addition of functional groups (–CN and – OH groups) and the lower crystallinity. Scanning electron microscopy (SEM), energy dispersive spectroscopy (SEM– EDS, X-ray diffraction (XRD) and solid-state CP/MAS C<sup>13</sup> NMR were used for characterization of adsorbents.

The feasibility of sunflower stalks for lead (Pb) and cadmium (Cd) metal ion adsorption has been investigated by Jalali and Aboulghazi (2013). Batch adsorption studies were conducted to study the effect of contact time, initial concentration (50 mg/l), pH (4–9) and adsorbent doses (0.2–1.2 g) on the removal of Cd(II) and Pb(II) metal ions at room temperature. The data fitted well with the modified two-site Langmuir model with maximum sorption capacities for Pb(II) and Cd(II) at optimum conditions of 182 and 70 mg/g. The pseudo-second-order kinetic model fitted well with the rate constant  $8.42 \times 10^{-12}$  and  $8.95 \times 10^2$  g/mg/m for Cd and Pb, respectively.

# Shell

The effectiveness of lignocellulosic material as adsorbent from aqueous solution is due to the affinity between water molecule and cell wall components. These materials are highly porous and have a wide surface area. In the bioadsorbents as shell, coconut, bael fruit, cashew nut, oil palm, wheat and wood apple nd many others are used for various heavy metal removal (Table 10).

The biosorption of Pb(II) ions using hazelnut shells (NHS) and almond shells (AS) was investigated in batch experiments. Alkaline pH (6–7) was found to be favorable for the removal of metal ions. The uptake capacities were

Table 7 Adsorption capacities of fruit peel materials for the removal of heavy metals from water/wastewater

Cellulosic materials	Type of adsorbrnt	Heavy metals	Adsorption capacity(mg/g)	References
Banana peel	NB	Cr(VI)	131.56	Memon et al. (2009)
Banana peel	NB	Cd(II)	35.52	Memon et al. (2008)
Mango peel	NB	Cd(II)	68.92	Iqbal et al. (2009a, b)
Mango peel	NB	Pb(II)	99.02	Iqbal et al. (2009a, b)
Mango peel	NB	Cu(II)	46.09	Iqbal et al. (2009a, b)
Mango peel	NB	Ni(II)	39.75	Iqbal et al. (2009a, b)
Mango peel	NB	Zn(II)	28.21	Iqbal et al. (2009a, b)
Mosambi (Sweet lime) peel	NB	Cr(VI)	250	Saha et al. (2013)
Orange peel	NB	Ni(II)	15.8	Ajmal et al. (2000)
Orange peel	MB (nitric acid)	Cd(II)	13.7	Lasheen et al. (2012)
Orange peel	MB (nitric acid)	Cu(II)	15.27	Lasheen et al. (2012)
Orange peel	MB (nitric acid)	Pb(II)	73.53	Lasheen et al. (2012)
Sugar beet pulp	MB (H <sub>2</sub> SO <sub>4</sub> )	Cr(VI)	24	Altundogan et al. (2007

NB natural or unmodified biosorbent, MB modified biosorbent



Cellulosic materials	Type of adsorbent	Heavy metals	Adsorption capacity	References
Grape bagasse	NB	Cd(II)	0.774 mmol/g	Farinella et al. (2008)
Grape bagasse	NB	Pb(II)	0.428 mmol/g	Farinella et al. (2008)
Sugarcane bagasse	MB (sulfuric acid)	Cd(II)	38.03 mg/g	Mohan and Singh (2002)
Sugarcane bagasse	MB (sulfuric acid)	Zn(II)	31.11 mg/g	Mohan and Singh (2002)
Sugarcane bagasse	NB	Ni(II)	2 mg/g	Alomá et al. (2012)

Table 8 Adsorption capacities of bagasse materials for the removal of heavy metals from water/wastewater

Table 9 Adsorption capacities of stalk materials for the removal of heavy metals from water/wastewater

Cellulosic materials	Type of biosorbent	Heavy metals	Adsorption capacity (mg/g)	References
Corn stalk	AMCS (acryl nitrile)	Cd(II)	12.73	Zheng et al. (2010)
Corn stalk	MB (graft coplymerization)	Cd(II)	21.37	Zheng et al. (2012)
Sunflower stalk	NB	Cu(II)	29.3	Sun and Shi (1998)
Sunflower stalk	NB	Zn(II)	30.73	Sun and Shi (1998)
Sunflower stalk	NB	Cd(II)	42.18	Sun and Shi (1998)
Sunflower stalk	NB	Cr(III)	25.07	Sun and Shi (1998)
Sunflower stalk	NB	Pb(II)	182.90	Jalali and Aboulghazi. (2012)
Sunflower stalk	NB	Cd(II)	69.80	Jalali and Aboulghazi. (2013)

found to be 90 and 68 % for NHS and AS sorbents after 90 min equilibrium time. The adsorption isotherm for Pb(II) fitted well with the Langmuir model, with binding capacities of shell of 28.18 and 8.08 mg/g for NHS and AS, respectively. Doke and Khan (2012) also used H<sub>2</sub>SO<sub>4</sub>modified wood apple shell for the adsorption of Cr(VI) metal in aqueous medium. The maximum adsorption capacity was 151.51 mg/g which is the highest of other shell adsorbents. Oil palm shell was evaluated as a adsorption for the removal of Cu(II) from synthetic wastewater by Chong et al. 2013. An adsorption capacity of 1.756 mg/g was reported for Cu(II). They also used the same adsorbent for Pb(II) removal and reported an adsorption capacity of 3.309 mg/g for Pb(II) metal ion. The material was used for both batch mode and column mode studies. They found that the lower  $pH_{PZC}(4.1)$  is suitable for heavy metal removal at optimum conditions. The Freundlich isotherm was fitted well than Langmuir isotherm. The kinetics of Pb(II) adsorption follow pseudosecond-order kinetic model.

# Leave

Lignocellulosic materials are the structural elements of wood and other plant materials. These are present in the biosphere in abundant form. Leaves come in the category of natural materials. Most of the plants shed their leaves in unfavorable conditions and these leaves can be used as biosorbents (Table 11). The removal of Cu(II) from aqueous solution using dried sunflower leaves was investigated by Benaïssa and Elouchdi (2007). The influence of initial Cu(II) concentrations (10-500 mg/l), pH (5-6), contact time (2.5-7 h) and adsorption amount (0.2 g) was observed. The experimental data were well followed by Langmuir and Freundlich isotherms. The kinetic model and pseudo-first-order also supports the rate of reaction. The maximum metal ion uptake capacities obtained was 89.37 mg/g. Martins et al. (2013) used castor leaf powder as bioadsorbent for the removal of C(II) and Pb(II) metals from an aqueous medium. The adsorption capacities were found to be 0.340 and 0.327 mmol/g for C(II) and Pb(II) metals, respectively.

Mondal et al. (2013) used bamboo leaf powder in the detoxification of Hg(II) ions from water. They used bamboo leaf powder in three forms, viz., unmodified bamboo leaf powder (BPL), modified by using anionic surfactant SDS (BLPS) and non-ionic surfactant Triton X-100 (BLPT). All these materials were characterized by BET and FTIR analysis. The experimental studies were supported by the adsorption isotherm, kinetics, thermo-dynamics and the mechanisms involved in it. The maximum adsorption capacity shown by unmodified, Triton



Cellulosic materials	Type of biosorbent	Heavy metals	Adsorption capacity (mg/g)	References
Almond shell	NB	Pb(II)	8.08	Pehlivan et al. (2009a, b, c)
Bael fruit shell	NB	Cr(VI)	17.27	Anandkumar and Mandal (2009)
Cashew nut shell	NB	Cd(II)	22.11	Kumar et al. (2012a, b)
Chestnut shell	NB	Cu(II)	12.56	Babel and Kurniawan (2004)
Hazelnut shell	NB	Pb(II)	28.18	Babel and Kurniawan (2004)
Hazelnut shell	NB	PB(II)	28.18	Pehlivan et al. (2009a, b, c)
Palm shell	MB (tomatoes)	Hg(II)	83.33	Ismaiel et al. (2013)
Oil palm shell	NB	Cu(II)	1.75	Chong et al. (2013)
Oil palm shell	NB	Pb(II)	3.39	Chong et al. (2013)
Lentil	NB	Cu(II)	9.59	Aydm et al. (2008)
Rice	NB	Cu(II)	2.95	Aydin et al. (2008)
Walnut shell	MB (H <sub>2</sub> SO <sub>4</sub> )	Cr(VI)	200	Kumar et al. (2012a, b)
Wheat	NB	Cu(II)	17.42	Aydm et al. (2008)
Wood apple shell	MB (H <sub>2</sub> SO <sub>4</sub> )	Cr(VI)	151.51	Doke and Khan (2012)

Table 10 Adsorption capacities of shell materials for the removal of heavy metals from water/wastewater

Table 11 Adsorption capacities of leave materials for the removal of heavy metals from water/wastewater

Cellulosic materials	Type of biosorbent	Heavy metals	Adsorption capacity	References
Bamboo leaf powder	NB	Hg(II)	27.11 mg/g	Mondal et al. (2013)
Bamboo leaf powder	MB (anionic surfactant SDS)	Hg(II)	28.1 mg/g	Mondal et al. (2013)
Bamboo leaf powder	MB (Triton X-100)	Hg(II)	31.05 mg/g	Mondal et al. (2013)
Castor leaves	NB	Pb(II)	0.327 mmol g/l	Martins et al. (2013)
Castor leaves	NB	Cd(II)	0.340 mmol g/l	Martins et al. (2013)
Neem leaves	MB (HCl)	Cr(VI)	62.97 mg/g	Babu and Gupta (2008)
Pine leaf powder	NB	As(V)	3.27 mg/g	Shafique et al. (2012)
Sunflower leaves	NB	Cu(II)	89.37 mg/g	Benaïssa and Elouchdi (2007)

NB natural or unmodified biosorbent, MB modified biosorbent

X-modified and SDS-modified BPL was 27.11, 28.1 and 35.05 mg/g, respectively. Very little literature investigation has been done on the use of pine needles (or leaf) in heavy metal removal. Pine needle is novel emerging adsorbent which was examined by Shafique et al. (2012) used chir pine leaves (*Pinus roxburghii*) in the removal of As(V) ions from aqueous solution. The maximum adsorption was reported at pH 4.0 and equilibrium was achieved in 35 min. The pine leaves were tested for various contact times, pH, agitation speed and initial metal concentration to evaluate the optimum conditions which showed the maximum As(V) metal ions uptake of 3.27 mg/g. The experiment was further supported by pseudo-second-order kinetics.



Plant's bark is also used for heavy metal removal in aqueous solution (Table 12). Different concentrations of Cr(VI) and Cr(III) ions were studied by Sarin and Pant 2006. They used eucalyptus bark in the removal of Cr(VI) and Cr(III) metal ions. The experimetal study was performed in a batch process and the influence of the following parameters, pH, contact time and initial concentration, will be investigated. The adsorption was followed by Fruendlich isotherms mainly and first-order Lagergren kinetics. The adsorption capacity was found to be 45 mg/g at pH 2.

Alkali NaOH- and acid  $H_2SO_4$ -pretreated neem barks were used as adsorbent and the influence of initial cation



concentration, temperature and pH was investigated to optimize Zn(II) and Cd(II) metal ion removal from aqueous solutions (Naiya et al. 2009). The maximum adsorption capacity was obtained as 13.29 for Zn(II) ion and 25.57 mg/g for Cd(II) ion at pH 5 for Zn(II) and 6 for Cd(II), respectively. Different parameters such as pH, initial ion concentration, contact time and adsorbent doses were studied to evaluate the equilibrium conditions. Thermodynamic parameters and Gibbs free energy ( $\Delta$ G) values for Zn(II) are -4.76 KJmol<sup>-1</sup> and for Cd(II) are -6.09 KJmol<sup>-1</sup>, respectively, were also studied. Reddy et al. (2011) also used *Moringa oleifera* bark as low-cost adsorbents for the biosorption of Ni(II) metal from aqueous solution. The adsorption capacity was found to be 30.38 mg/g at 6 pH.

# Fiber

In 2010, the removal of heavy metals from wastewater by using Agave Americana fibers was studied by Hamissa et al. 2010. It was indicated that Agave Americana fiber is more effective for Pb(II) and Cd(II) is also exchanged at a satisfactory level. Approximately, 40.0 mg/g of Pb(II) and 12.5 mg/g of Cd(II) were removed. The equilibrium conditions were obtained at 20 °C temperature, pH 5.0, contact time of 30-60 min and 5 g/l biomass adsorbent media. Infrared scopy revealed that the functional groups were involved in Pb(II) and Cd(II) ion bins on adsorbent media. Scanning electron microscopy (SEM) also gives proof of the adsorption surface area. Thermodynamic parameters such as enthalpy change ( $\Delta H^{o}$ ), free energy change ( $\Delta G^{o}$ ) and entropy change ( $\Delta S^{o}$ ) were calculated from Langmuir and Freundlich isotherm constant. The positive value of  $\Delta H^{\circ}$  indicates that the sorption process is endothermic in nature. Hydrogen peroxide-modified coir was also used in metal removal from aqueous solutions. It was found that coir fibers with chemical modification were found to be more effective than unmodified coir fibers. Heavy metals

such as Ni(II), Zn(II) and Fe(II) could be eliminated with a removal capacity of 4.33, 7.88 and 7.49 mg/g for chemically modified adsorbents, respectively, and unmodified coir fiber uptake capacity were 2.51, 1.53 and 2.84 mg/g. It was also found that metal capacity decreases with lowering of pH. Desorption study was also carried with dilution of NaOH solution with loaded metal ions (Shukla et al. 2006). It was reported the adsorption process decreased with lowering of pH and the Langmuir model fitted for modified jute fibers. Plant fibers such as those of *Agave americana*, kenaf, coir, banana, remie and jute were used for heavy metal removal (Table 13).

In 2005, the use of modified jute fibers to remove heavy metals was investigated (Shukla and Pai 2005). It was observed that modified jute fibers were used in the synthetic waste water containing toxic heavy metals, viz., Cu(II), Ni(II) and Zn(II). They used two types of fibers in the metal ion sequestration. The dye-loaded jute fibers showed the metal uptake value of 8.4, 5.26 and 5.95 mg/g for Cu(II), Ni(II) and Zn(II), respectively. The other adsorbent modified with hydrogen peroxide showed the metal uptake values of 7.73, 3.37 and 3.55 mg/g for unmodified jute fibers.

# Fruit stone/waste

Fruit containing stones (stone fruit) are used adsorbent for metal removal after removing their central fleshy parts. Peach stones, olive stones and palm fruit bunches' inner and outer hard parts are used as adsorbents for metal removal. The raw material obtained from the fruit stone part is dried and washed with organic solvents (Ali 2014). Rashed (2006) carried out a comparative study of fruit stones (peach and apricot) and found their adsorption potential. The equilibrium time for lead adsorption was 3–5 h (%Pb adsorption 93 % for apricot and 97.64 % for peach). The lead adsorption onto peach stone was found to be higher than onto stone up to 3.36 % at 3 h. The

Table 12 Adsorption capacities of bark materials for the removal of heavy metals from water/wastewater

Cellulosic materials	Type of biosorbents	Heavy metals	Adsorption capacity (mg/g)	References
Acacia leucocephala	NB	Cu(II)	147.1	Munagapati et al. (2010)
Acacia leucocephala	NB	Cd(II)	167.7	Munagapati et al. (2010)
Acacia leucocephala	NB	Pb(II)	185.2	Munagapati et al. (2010)
Moringa oleifera	NB	Ni(II)	30.38	Reddy et al. (2011)
Moringa oleifera	NB	Pb(II)	34.6	Reddy et al. (2010)
Neem bark	NB	Zn(II)	13.29	Naiya et al. (2009)
Neem bark	NB	Cd(II)	25.57	Naiya et al. (2009)

NB natural or unmodified biosorbent, MB modified biosorbent



Cellulosic materials	Type of biosorbent	Heavy metals	Adsorption capacity (mg/g)	References
Agave americana	NB	Pb(II)	39.7	Hamissa et al. (2010)
	NB	Cd(II)	12.5	Hamissa et al. (2010)
Coir fibers	NB	Ni(II)	2.51	Shukla et al. (2006)
	NB	Zn(II)	1.53	Shukla et al. (2006)
	NB	Fe(II)	2.84	Shukla et al. (2006)
	MB (H <sub>2</sub> O <sub>2</sub> )	Ni(II)	4.33	Shukla et al. (2006)
	MB (H <sub>2</sub> O <sub>2</sub> )	Zn(II)	7.88	Shukla et al. (2006)
	MB (H <sub>2</sub> O <sub>2</sub> )	Fe(II)	7.49	Shukla et al. (2006)
Hemp fibers	NB	Co(II)	13.58	Tofan et al. (2013)
Jute fibers	NB	Cu(II)	4.23	Shukla and Pai (2005)
	NB	Ni(II)	3.37	Shukla and Pai (2005)
	NB	Zn(II)	3.55	Shukla and Pai (2005)
	MB (H <sub>2</sub> O <sub>2</sub> )	Cu(II)	7.73	Shukla and Pai (2005)
	MB (H <sub>2</sub> O <sub>2</sub> )	Ni(II)	5.57	Shukla and Pai (2005)
	MB (H <sub>2</sub> O <sub>2</sub> )	Zn(II)	8.02	Shukla and Pai (2005)
	CB (dye loaded)	Cu(II)	8.4	Shukla and Pai (2005)
	CB (dye loaded)	Ni(II)	5.26	Shukla and Pai (2005)
	CB (dye loaded)	Zn(II)	5.95	Shukla and Pai (2005)

Table 13 Adsorption capacities of fiber materials for the removal of heavy metals from water/wastewater

suitable pH was observed to be 7–8. The heavy metal removal capacities of fruit stone/waste are shown in Table 14.

Alslaibi et al. (2013) determined the potential of microwaved olive stone-activated carbon (OSAC) for removal of cadmium metal ion. The maximum cadmium uptake obtained using OSAC was 95.32 %. The adsorption process was followed by Langmuir isotherm with 11.72 mg/g adsorption capacity. Mohammadi et al. (2010) examined the efficacy of modified sea-buckthorn stone to adsorb Pb(II) metal ions. Activated carbons have been prepared using phosphoric acid and zinc chloride chemical activation. The maximum adsorption of Pb(II) on activated carbon was 51.81 mg/g with  $H_3PO_4$  and 25.91 mg/g with activated ZnCl<sub>2</sub>.

# Peat

Peat moss is used as an inexpensive and naturally available low-cost adsorbent. Lignin and cellulose are the chief components of peat. Due to having polar functional groups, peat works effectively in metal detoxification from aqueous solutions. Ho and Mckay (2004) investigated sorption of Cu(II) by peat moss. The adsorption was maximum at pH 5, and the maximum adsorption capacity was 0.199 mmol/ g at 20 °C. The mechanism behind Cu(II) uptake was cation exchange. The cupper ion was exchanged with



hydrogen ions in the presence of humic and fulvic acids. Gupta et al. (2009) described adsorption of Cu and Ni ions onto Irish peat moss. The adsorption of Cu(II) and Ni(II) from aqueous solutions on peat moss was studied over a range of 2–8 (pH) and 5–100 mg/l (concentration). The maximum biosorption capacity of Iris peat moss was found to be 17.6 mg/g for Cu(II) and 14.5 mg/g for Liu et al. (2009) studied the use of peat for removal of nickel from aqueous solutions at different pH values. It was observed that metal ion removal increases with increase in pH value. The first-order model favored the experimental data. Table 15 represents the metal removal capacities of different types of peat biomass.

Janaki et al. (2015) reported the removal of Ni(II) ions from an aqueous solution of Indian peat moss (sphagnum) as adsorbent. The effects of pH, adsorbent dosage and initial concentrations were studied in batch experiment. The experimental results revealed that 99.5 % of Ni(II) ion removal occurs at pH 6. The authors also described the interaction between the metal ions and peat mosses by Fourier transform infrared spectroscopy.

# Vegetable waste

The applicability of vegetable waste as low-cost adsorbent leads to zero waste discharge in the environment. Vegetable wastes are easily available and have no

Cellulosic materials	Type of biosorbent	Heavy metals	Adsorption capacity (mg/g)	References
Apricot stone	MB (H <sub>3</sub> PO <sub>4</sub> )	Pb(II)	111.11	Abbas et al. (2014)
Date pit	NB	Cu(II)	35.9	Mohammad et al. (2010)
Date pit	NB	Cd(II)	39.5	Mohammad et al. (2010)
Olive stone	NB	Pb(II)	92.6	Fiol et al. (2006)
Peanut hull	NB	Cu(II)	21.25	Zhu et al. (2009)

Table 14 Adsorption capacities of fruit stone for the removal of heavy metals from water/wastewater

 Table 15
 Adsorption capacities of peat for the removal of heavy metals from water/wastewater

Cellulosic materials	Type of biosorbent	Heavy metals	Adsorption capacity (mg/g)	References
Peat	MB (thermal activated)	Pb(II)	81.3	Lee et al. (2015)
Peat	MB (thermal activated)	Cu(II)	18.2	Lee et al. (2015)
Peat	MB (thermal activated)	Cd(II)	39.8	Lee et al. (2015)
Peat	MB (NaCl)	Cr(III)	18.75	Henryk et al. (2016)
Peat	MB (NaCl)	Cr(VI)	8.02	Henryk et al. (2016)
Sphagnum peat moss	MB (thermally activated)	Cu(II)	12.6	Ho and Mckay (2004)

NB natural or unmodified biosorbent, MB modified biosorbent

economic use (Table 16). Gill et al. (2013) reported the removal of Ni(II) onto a mixture of vegetable waste as adsorbent. The mixture of vegetable waste was prepared in the ratio of 1:1 (potato:carrot peels). The effects of various operating variables, viz., initial pH, temperature, contact time, initial metal concentration and biosorbent dose, were studied. The maximum adsorption of nickel (79.32 %) was found with 75 min of contact time and 3.0 g of biosorbent at 35 °C and ph 4. FTIR spectrophotometer and X-ray flourescence spectrophotometer techniques confirm the adsorption process. Bhatti et al. (2010) studied the adsorption of chromium on Daucus carota L. waste biomass. The maximum removal capacity for Cr(III) and Cr(VI) was 85.65 and 88.27 mg/g, respectively. The maximum removal rate occurred at biosorbent dose 0.1 g, biosorbent size 0.250 mm, initial concentration 100 mg/l, temperature 30 °C and contact time 240 min.

Aksu and Isoglu (2005) examined the biosorption equilibria and kinetics of copper(II) metal ion via agricultural waste sugar beet pulp. The highest biosorption capacity was 28.5 mg/g for Cu(II) at 25 °C and initial pH value 4. The biosorption rates were found to follow pseudo-first order and pseudo-second order.

# Grass

Grass is considered to be of low cost and abundant because of mowing lawns, gardens, parks and open fields

(Table 17). Grasses are major organic components of solid waste and comprise about 14.6 % of total municipal solid waste (MSW) and about 50 % organic content of the MSW (Yu et al. 2002). Koroki et al. (2010) used culm of bamboo treated with concentrated sulfuric acid for grass Cr(V) metal ion removal from aqueous solutions. They found that the Cr(VI) requestration was highly correlated with pH and favored physicochemical sorption mechanism. The Cr(VI) sorption was observed irreversible due to strong bonding of HCrO<sub>4</sub><sup>-</sup> and the presence of active sites. Zuo et al. (2012) tried to evaluate the applicability of sodium hydroxide solution (NaOH) immersed lemon grass (ILG) for the removal of cupper(Cu), zinc(Zn) and cadmium(Cd) from single and multi-metal solutions. According to the authors, maximum removal was 13.93 mg Cu, 15.87 mg Zn and 39.53 mg Cd per gram ILG. FTIR studies showed that NaOH modification leads to increase in the number of sorption sites for metal uptake.

Pandey et al. (2015) explored NaOH-treated kush grass leaves and bamboo leaves for Cd(II) removal from aqueous media. NaOH-modified *Desmostachya bipinnata*, Kush grass leaves (MDBL) and *Bambusa arundinacea* (bamboo) leaves (MBAL) were used in batch experiments. Langmuir isotherm fitted well than Freundlich isotherm and the maximum adsorption capacity was found to be 15.22 mg/g for MBDL and 19.70 mg/g for MBAL at room temperature. Desorption studies were also carried out using 0.1 N HNO<sub>3</sub>; 94.18 and 92.98 % recovery of metals was obtained



Cellulosic materials	Type of biosorbent	Heavy metals	Adsorption capacity (mg/g)	References
Cabbage waste	NB	Pb(II)	60.57	Hossain et al. (2014)
Cabbage waste	NB	Cd(II)	20.57	Hossain et al. (2014)
Cassava peelings	MB (mercapto acetic acid)	Cu(II)	127.3	Horsfall et al. (2004)
Cassava peelings	NB	Cd(II)	119.6	Horsfall et al. (2004)
Cauliflower waste	NB	Pb(II)	47.63	Hossain et al. (2014)
Cauliflower waste	NB	Cd(II)	21.32	Hossain et al. (2014)
Fluted pumpkin seed shell	MB (H <sub>3</sub> PO <sub>4</sub> )	Pb(II)	14.286	Okoye et al. (2010)
Potato peel	Mb (thermally activated)	Cu(II)	84.74	Guechi and Hamdaowio (2015)

Table 16 Adsorption capacities of vegetable waste for the removal of heavy metals from water/wastewater

Table 17 Adsorption capacities of grass for the removal of heavy metals from water/wastewater

Cellulosic materials	Type of biosorbent	Heavy metals	Adsorption capacity (mg/g)	References
Alfa grass	MB (H <sub>2</sub> SO <sub>4</sub> )	Cr(VI)	75.8	Tazrouti and Amrani (2009)

NB natural or unmodified biosorbent, MB modified biosorbent

for Cd(II) ions from MDBL and MBL, respectively. Hossain et al. (2012) utilized garden grass (GG) for removal of copper(II) from aqueous solutions. The maximum adsorption and desorption capacities were 58.34 and 319.03 mg/ g, respectively, for 1 g dose. From the results, it was revealed that GG occupied high surface area and functional groups on the surface area.

# Cake

The cakes of olive, cotton seed and jatropha are agricultural wastes and applied as cellulosic adsorbents for heavy metal removal (Table 18). Malathi et al. (2015) examined the ability of activated carbon prepared from sulfuric acidtreated cottonseed cake (SCSC) by chemical activation. According to the authors, the equilibrium time and optimum pH range were observed to be 3 h and 4.0-6.0, respectively. SCSC exhibit a higher adsorption capacity of 115.86 mg/g than commercial activated carbon (21.69 mg/ g) at 300 K. Bose et al. (2011) evaluated a biodiesel waste of jatropha seed press cake (JPC) for the elimination of hexavalent chromium ion from aqueous solutions. The chromium metal removal increases with increase in pH as well as concentration. The peak biosorption capacity was observed at 22.727 mg of Cr(VI)/g of biosorbent at 30 °C. The activation energy for the adsorption process was 27.114 kJ/mol, showing a physical process.

Konstantinou et al. (2007) investigated the sorption ability of olive cake for Cu(II) and Eu(II) ions in a batch study. They observed that the sorption process takes place due to formation of an inner-sphere complex with active



sites of the surface. Elouear et al. (2008) studied the removal of toxic metal ions from aqueous solutions using exhausted olive cake ash (EOCA). The optimum removal occurred up to 2 h contact time for Ni(II) and Cd(II) onto EOCA at pH 6. Langmuir isotherm correlated well than Freundlich isotherm. The adsorption capacities were 8.34 and 7.32 mg/g for Ni(II) and Cd(II), respectively. Khan et al. (2012) utilized oil cake in the removal of nickel from aqueous medium. Metal removal favored pseudo-second order model. The breakthrough capacities for 5 and 10 mg/l were 0.25 and 4.5 mg/g and exhausted capacities for 5 and 10 mg/l were 4.5 and 9.5 mg/g for Ni(II) metal ion, respectively.

# Others adsorbents

Different cellulosic material used in the removal of heavy metals such as cactus cladodes, castor seed hull, *Eichhornia crassipes* roots, hemp fibers, meranti wood and *Prosopis juliflora* seed were found to be efficient as low-cost bioadsorbents (Table 19).

# Conclusion

Adsorption is an efficient technique in heavy metal removal rather than coagulation, flocculation, ion exchange, precipitation, osmosis and flotation. These conventional techniques are not suitable for the removal of heavy metal ions from wastewater at trace concentrations. The use of commercially activated carbons for wastewater

1	1	5		
Cellulosic materials	Type of biosorbent	Heavy metals	Adsorption capacity (mg/g)	References
Gingelly oil cake	MB (thermal activated)	Pb(II)	105.26	Nagashanmugam and Srinivasan (2010)
Gingelly oil cake	MB (H <sub>2</sub> SO <sub>4</sub> )	Pb(II)	114.94	Nagashanmugam and Srinivasan (2010)
Moringa seed cake	MB (n-hexane)	Cr(VI)	3.191	Meneghel et al. (2013)
Soya cake	NB	Cr(VI)	0.288	Daneshwar et al. (2002)

Table 18 Adsorption capacities of cake for the removal of heavy metals from water/wastewater

Table 19 Adsorption capacities of different cellulosic materials for the removal of heavy metals from water/wastewater

Cellulosic materials	Type of biosorbent	Heavy metals	Adsorption capacity (mg/g)	References
Cactus cladodes	MB	Cd(II)	30.42	Barka et al. (2013)
Cactus cladodes	MB	Pb(II)	98.62	Barka et al. (2013)
Castor seed hull	MB	Zn(II)	6.72	Mohammod et al. (2011)
Coir pith	MB	Co(II)	12.82	Parab et al. (2006)
	MB	Cr(II)	11.56	Parab et al. (2006)
	MB	Ni(II)	15.95	Parab et al. (2006)
Eichhornia crassipes root	MB	Cu(II)	32.51	Li et al. (2010)
Eichhornia crassipes root	MB	Cr(III)	33.98	Li et al. (2010)
Meranti wood	MB	Cd(II)	175.43	Rafatullah et al. (2012)
Prosopis juliflora seed	MB	Pb(II)	40.32	Jayaram and Prasad (2009)

NB natural or unmodified biosorbent, MB modified biosorbent

treatment leads to increase in the cost of treatment, and, hence, researchers are focusing on the use of feasible cellulosic low-cost adsorbents for metal adsorption. Cellulosic waste materials are promising adsorbents for wastewater treatments, because of their abundance and renewability. Most of these cellulosic wastes are rich in cellulose, hemicelluloses and lignin content which adhere to toxic pollutants on the surface. In this review, the emerging cellulosic low-cost adsorbents are utilized for the removal of various kinds of metals from different types of aqueous solutions. It is evident that most of the cellulosic adsorbents applied for metal sequestration exhibited efficient adsorption capacity. So, these materials can serve as an alternative to commercially available activated carbons. Further research requires investigation of structural studies of adsorbents, multi-metal studies, immobilization of adsorbent, reuse of adsorbent, recovery of metals and pilotscale studies.

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