Heavy metal removal from wastewater using various adsorbents: a review

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ABSTRACT

Heavy metals are discharged into water from various industries. They can be toxic or carcinogenic in nature and can cause severe problems for humans and aquatic ecosystems. Thus, the removal of heavy metals from wastewater is a serious problem. The adsorption process is widely used for the removal of heavy metals from wastewater because of its low cost, availability and eco-friendly nature. Both commercial adsorbents and bioadsorbents are used for the removal of heavy metals from wastewater, with high removal capacity. This review article aims to compile scattered information on the different adsorbents that are used for heavy metal removal and to provide information on the commercially available and natural bioadsorbents used for removal of chromium, cadmium and copper, in particular.

Key words | adsorbents, adsorption capacity, heavy metal, wastewater

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INTRODUCTION

Discharge from industry contains various organic and inorganic pollutants. Among these pollutants are heavy metals which can be toxic and/or carcinogenic and which are harmful to humans and other living species (MacCarthy *et al.* 1993; Clement *et al.* 1995; Renge *et al.* 2012). The heavy metals of most concern from various industries include lead (Pb), zinc (Zn), copper (Cu), arsenic (As), cadmium (Cd), chromium (Cr), nickel (Ni) and mercury (Hg) (Mehdipour *et al.* 2015). They originate from sources such as metal complex dyes, pesticides, fertilisers, fixing agents (which are added to dyes to improve dye adsorption onto the fibres), mordants, pigments and bleaching agents (Rao *et al.* 2010). In developed countries, legislation is becoming increasingly stringent for heavy metal limits in wastewater. In India, the current maximum contaminant level (ppm–mg/mL) for heavy metals is 0.05, 0.01, 0.25, 0.20, 0.80, 0.006, 0.00003, 0.050 for chromium, cadmium, copper, nickel, zinc, lead, mercury and arsenic, respectively (Gopalakrishnan *et al.* 2015). Various treatment technologies employed for the removal of heavy metals include chemical precipitation, ion exchange, chemical oxidation, reduction, reverse osmosis, ultrafiltration, electrodialysis and adsorption (Fu & Wang 2011). Among these methods, adsorption is the most efficient as the other techniques have inherent limitations such as the generation of a large amount of sludge, low efficiency, sensitive operating conditions and costly disposal. The adsorption method is a relatively new process and is emerging as a potentially preferred alternative for the removal of heavy metals because it provides flexibility in design, high-quality treated effluent and is reversible and the adsorbent can be regenerated (Fu & Wang 2011). The specific sources of chromium are leather tanning, electroplating, nuclear power plants and textile industries. Chromium(VI) is an oxidising agent, is carcinogenic in nature and is also harmful to plants and animals (Barnhart 1997). Exposure to chromium(VI) can cause cancer in the digestive tract and lungs, epigastric pain, nausea, severe diarrhoea, vomiting and haemorrhage (Mohanty *et al.* 2005). Although chromium can access

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many oxidation states, chromium(VI) and chromium(III) are the species that are mainly found in industrial effluents (Mohan & Pittman 2006). Chromium(VI) is more toxic than chromium(III) and is of more concern (Al-Othman *et al.* 2012). The United States Environmental Protection Agency (USEPA) has set the maximum chromium levels in drinking water at 0.1 ppm. The USEPA has classified cadmium as a human carcinogen and it is known to cause deleterious effects to health and bone demineralisation either through direct bone damage or as a result of renal dysfunction (Fu & Wang 2011). The major sources of cadmium include metal refineries, smelting, mining and the photographic industry and it is listed as a Category-I carcinogen by the International Agency for Research on Cancer (IARC) and a group B-I carcinogen by the USEPA (Friberg *et al.* 1992). Copper is an essential element and is required for enzyme synthesis as well as tissue and bone development. Copper(II) is toxic and carcinogenic when it is ingested in large amounts and causes headache, vomiting, nausea, liver and kidney failure, respiratory problems and abdominal pain (Ren *et al.* 2008; Hu *et al.* 2013; Lan *et al.* 2013). The USEPA has set the copper limit at 1.3 ppm in industrial effluents. Industrial sources of copper include smelting, mining, electroplating, surface finishing, electric appliances, electrolysis and electrical components (Yin *et al.* 2012; Bilal *et al.* 2013; Lan *et al.* 2013). Nickel is a human carcinogen in nature and causes kidney and lung problems, gastrointestinal distress, skin dermatitis and pulmonary fibrosis (Borba *et al.* 2006). Zinc is essential for human health but large quantities of zinc can cause skin irritation, stomach cramps, vomiting and anaemia (Oyaro *et al.* 2007). Similarly, lead is harmful to human health and can damage kidney, liver, reproductive system and brain functions (Naseem & Tahir 2001). Mercury is also harmful and it is a neurotoxin that can affect the central nervous system. If it is exceeded in concentration it can cause pulmonary, chest pain and dyspnoea (Namasivayam & Kadirvelu 1999). Arsenic can cause skin, lung, bladder and kidney cancer, muscular weakness, loss of appetite, and nausea (Mohan & Pittman 2007).

Due to stringent regulations for heavy metals, their removal has become a serious environmental problem. This review surveys the various commercially available adsorbents and natural biosorbents used over the past decades for the removal of chromium, cadmium and copper ions from wastewater. Commercial adsorbents are those adsorbents which are produced commercially on a large scale, such as activated carbon, silica gel, alumina, etc., however they are costly. Natural bioadsorbents are those obtained from biological material and are comparatively cheap. However, cost analysis is an important criterion for selection of an adsorbent for heavy metal removal from wastewater. The cost of the adsorption process depends on the cost of the adsorbent. For instance, the cost of commercial activated carbon is Rs. 500/kg; however, the cost of bioadsorbents is in the range of Rs. 4.4–36.89/kg, which is much less as compared to the commercial adsorbents (Gupta & Babu 2008). A comprehensive approach has been followed to cover all significant work done in this field to date, and a final evaluation has been made on the most efficient adsorbent(s) to date.

ADSORBENTS USED FOR REMOVAL OF HEAVY METALS FROM WASTEWATER

There are a number of types of adsorbent that are used for the efficient removal of heavy metal removal from wastewater that are both commercial and/or bioadsorbents. These are described as follows.

Commercially available adsorbents for chromium removal

Graphene

Nanomaterials are efficient adsorbents for the removal of heavy metals from wastewater because of their high surface area, enhanced active sites and the functional groups that are present on their surface (Gopalakrishnan *et al.* 2015). Graphene is a carbon-based nanomaterial with a two-dimensional structure, high specific surface area and good chemical stability. It is available in various forms such as pristine graphene, graphene oxide and reduced graphene oxide. Graphene may be oxidised to add hydrophilic groups for heavy metal removal (Thangavel & Venugopal 2014). Yang *et al.* (2014a) adsorbed chromium onto the surface of graphene oxide and the maximum adsorption capacity found was around 92.65 mg/g at an optimum pH

of 5. This adsorption of chromium on graphene oxide was found to be endothermic and spontaneous. Gopalakrishnan *et al.* (2015) have also oxidised graphene for the addition of −COOH, −C=O and −OH functional groups onto the surface using a modified Hummer's method (Hummers & Offeman 1958). The novelty of their work is that only 70 mg of graphene oxide has been utilised for 100% removal of chromium from wastewater effectively at an optimum pH of 8. Graphene composite materials have been developed by a number of authors for the removal of heavy metals. Li *et al.* (2013) functionalised graphene oxide with magnetic cyclodextrin chitosan for the removal of chromium since magnetic cyclodextrin chitosan has favourable properties such as high adsorption capacity and magnetic property which assists in the separation process. Guo *et al.* (2014) functionalised graphene with a ferro/ferric oxide composite for chromium removal with a maximum adsorption capacity of 17.29 mg/g which is higher as compared to the adsorption capacity of other magnetic adsorbents, such as Fe@Fe_2O_3 core-shell nanowires (Ai *et al.* 2008), chitosan-coated $MnFe_2O_4$ nanoparticles (Xiao *et al.* 2013) and Fe_3O_4-polyethyleneimine (PEI)-montmorillonite (Larraza *et al.* 2012), i.e., 7.78 mg/g, 15.4 mg/g, 8.8 mg/g, respectively. Table 1 summarises the graphene-related work that has been reported in this area.

Activated carbon

Modern industries began production of active carbon in 1900–1901 to replace bone char in the sugar refining industry (Bansal *et al.* 1988) and powdered activated carbon was first produced commercially in Europe in the early 19th century, using wood as a raw material (Mantell 1968). Activated carbon can be obtained from any material which has high carbon content. Activated carbon is a good adsorbent for chromium removal because it has a well-developed porous structure and a high internal surface area for adsorption (Anirudhan & Sreekumari 2011). However, because coal-based activated carbon is expensive, its use has been restricted and further efforts have been made to convert cheap and abundant agricultural waste into activated carbon (Anirudhan & Sreekumari 2011). Activated carbon is now prepared from various agricultural wastes such as rubber wood sawdust (Karthikeyan *et al.* 2005), moso and

Table 1 | Chromium removal using graphene, graphine oxide and modified graphine as an adsorbent

Adsorbent	Metal concentration (ppm-mg/L)	Optimum pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorbent capacity (mg/g)	Removal per cent (%)	References
Graphene oxide based inverse spinel nickel ferrite composite	1,000	4	Langmuir	120	0.125–2.5	45	–	Lingamdinne *et al.* (2015)
Zero-valent iron assembled on magnetic Fe_3O_4/graphene nanocomposites	40–100	3	Langmuir	120	–	101	83.8%	Lv *et al.* (2014)
Zero-valent iron decorated on graphene nanosheets	15–35	3	Langmuir	90	1.0	–	70%	Li *et al.* (2016)
Copolymer of dimethylaminoethyl methacrylate with graphene oxide	–	1.1	–	45	–	82.4	93%	Ma *et al.* (2015)
Graphene sand composite (GSC)	8–20	1.5	Langmuir	90	10	2859.38	93%	Dubey *et al.* (2015)
Graphene oxide	52	5	Langmuir	12	–	43.72	92.65%	Yang *et al.* (2014a)
Modified graphene (GN) with cetyltrimethylammonium bromide	50, 100	2	Langmuir	60	400	21.57	98.2%	Wu *et al.* (2013)

ma bamboo (Lo *et al.* 2012), viticulture industry wastes, grape stalk, lex, pomace (Sardella *et al.* 2015), hazelnut shell activated carbon (Kobya 2004), coconut tree sawdust (Selvi *et al.* 2001), coconut shell carbon (Babel & Kurniawan 2004), sugarcane bagasse (Sharma & Forster 1994), treated sawdust of Indian rose wood (Garg *et al.* 2004), wood activated carbon (Selomulya *et al.* 1999), tyre activated carbon (Hamadi *et al.* 2001), coconut shell activated carbon (Selomulya *et al.* 1999) and palm shell (Saifuddin & Kumaran 2005; Owlad *et al.* 2010; Kundu *et al.* 2015; Nizamuddin *et al.* 2015, 2016; Sabzoi *et al.* 2015; Thangalazhy-Gopakumar *et al.* 2015), etc.

Karthikeyan *et al.* (2005) removed chromium from wastewater using activated carbon derived from rubber wood sawdust and 44 mg/g maximum adsorption capacity was obtained at an optimum pH 2. Maximum adsorption capacity obtained in their work was higher as compared to other adsorbents such as coconut tree sawdust (Selvi *et al.* 2001), coconut shell carbon (Babel & Kurniawan 2004), sugarcane bagasse (Sharma & Forster 1994) and treated sawdust of Indian rose wood (Garg *et al.* 2004), which were only 3.60 mg/g, 10.88 mg/g, 13.40 mg/g and 10 mg/g, respectively. Lo *et al.* (2012) derived activated carbon from moso and ma bamboo, and 100% removal was obtained using once activated maa bamboo and 91.7% removal using twice activated maa bamboo. Removal efficiency decreases for once activated moso bamboo and twice activated moso bamboo by 20–77% because their average pore diameter is less than 2 nm and major pores were mesopores. Kobya (2004) prepared activated carbon using hazelnut shell and maximum adsorption capacity of 170 mg/g was obtained at an optimum pH 1 which is higher than adsorption capacity of other adsorbents such as wood activated carbon (Selomulya *et al.* 1999), tyre activated carbon (Hamadi *et al.* 2001) and coconut shell activated carbon (Selomulya *et al.* 1999) which is only 87.6 mg/g, 58.5 mg/g and 107.1 mg/g, respectively. Table 2 summarises the reported use of activated carbon for chromium removal from wastewater.

Carbon nanotubes

Carbon nanotubes are efficient adsorbents for heavy metal removal because they possess chemical stability, large surface area, excellent mechanical and electrical properties, adsorption property and well-developed mesopores (Gupta *et al.* 2011; Mubarak *et al.* 2014a; Al-Khaldi *et al.* 2015). They can also be further modified by chemical treatment to increase

Table 2 | Chromium removal using activated carbon as an adsorbent

Adsorbent derived from	Metal concentration (mg/L)	Optimum pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorbent capacity (mg/g)	Removal per cent (%)	References
Acrylonitriledivinylbenzene copolymer	30	2	Freundlich	420	0.6	101.2	80%	Duranoğlu *et al.* (2010)
Syzygium jambolanum nut carbon	20–100	2	Langmuir	240	5	–	100%	Muthukumaran & Beulah (2011)
Green alga *Ulva lactuca*	5–50, 5–250	1	Langmuir	40	2	10.61 112.36	98%	El-Sikaily *et al.* (2007)
Jatropha wood	30–100	2–10	Langmuir	360	0.6–2	106.4–140.8	–	Gueye *et al.* (2014)
Tamarind wood	10–50	6.5	Langmuir Freundlich	40	2	–	28%	Acharya *et al.* (2009)
Pterocladia capillacea	5–100	1	Langmuir	120	3–10	66	100%	El Nemr *et al.* (2015)
Zizania caduciflora	10–50	2–3	Freundlich	48	0.8	2.7	84.8%	Liu *et al.* (2014)
Prawn shell	25–125	–	Langmuir Freundlich	31.4	–	100	98%	Arulkumar *et al.* (2012)

adsorption capacity (Chen *et al.* 2009; Mubarak *et al.* 2013, 2015a, 2015b, 2015c, 2016a, 2016c; Ruthiraan *et al.* 2015b). Hu *et al.* (2009) removed chromium using oxidised multi-walled carbon nanotubes and 100% maximum removal was achieved at an optimum pH of 2.88. Gupta *et al.* (2011) combined the adsorptive property of multi-walled carbon nanotubes with the magnetic property of iron oxide. The advantages of this composite are high surface area, can be used for contaminant removal and can be controlled and removed from the medium using a simple magnetic process. A maximum removal of 88% at pH 6 was obtained. Luo *et al.* (2013) prepared manganese dioxide/iron oxide/acid oxidised multi-walled carbon nanotube nanocomposites for chromium removal. Manganese dioxide is a scavenger of aqueous trace metals because of its high adsorption capacity but the use of pure manganese dioxide is not favoured because of the high cost and its unfavourable physical and chemical properties. The maximum adsorption capacity of the above nanocomposite was 186.9 mg/g with a maximum removal of 85% at an optimum pH of 2. Mubarak *et al.* (2014b) functionalised carbon nanotubes for chromium removal using nitric acid and potassium permagnate in 3:1 volume ratio and compared the removal capacity with non-functionalised carbon nanotubes. They found that maximum adsorption capacity for functionalised carbon nanotubes was 2.517 mg/g while for non-functionalised carbon nanotubes it was 2.49 mg/g, and removal capacity for functionalised carbon nanotubes (87.6%) was higher compared to non-functionalised carbon nanotubes (83%). Mubarak *et al.* (2016b) produced carbon nanotubes using microwave heating for comparative study of the removal of chromium with another heavy metal (i.e., lead). Microwave heating provides a fast and uniform heating rate and it accelerates reaction and gives a higher yield. The maximum adsorption capacity obtained for chromium was 24.45 mg/g and removal efficiency obtained was 95% at an optimum pH 8. Table 3 summarises the reported use of carbon nanotubes for chromium removal from wastewater.

Bio-adsorbents for chromium removal from wastewater

Rice husk

Rice husk consists of cellulose (32.24%), lignin (21.44%), hemicellulose (21.34%) and mineral ash (15.05%) (Rahman *et al.* 1997). This material is not soluble in water and possesses a granular structure, chemical stability and good mechanical strength (Chuah *et al.* 2005). Silica is derived from rice husk using sol gel technique and has an affinity for chromium (Adam *et al.* 2006). Thus, Oladoja *et al.* (2013) incorporated iron oxide into silica derived from rice husk, calling it modified rice husk derived silica. This modified rice husk derived silica has higher adsorption (63.69 mg/g) as compared to the silica derived from raw rice husk. Rice husk in its natural form and in modified form (activated carbon modified using ozone) was used for the removal of chromium(VI) and results compared (Bishnoi *et al.* 2004; Sugashini & Begum 2015). It was found that ozone modified rice husk shows a higher removal capacity than raw rice husk. Sugashini & Begum (2015) modified rice husk by treating it with ozone to produce activated carbon for chromium removal with 86% removal being reported. Ozone was used for activation because it is a strong oxidising agent, stable and can be regenerated. Rice husk can also be modified by preparation of biochar. Biochar is a carbon-rich solid by-product resulting from the pyrolysis of rice husk under oxygen-free and low temperature conditions (Lehmann 2007; Woolf *et al.* 2010; Mubarak *et al.* 2013, 2014c; Agrafioti *et al.* 2014; Ruthiraan *et al.* 2015a, 2015b). Biochar has the ability to adsorb heavy metals because of electrostatic interactions between the negative surface charge and the metal cations, as well as ion exchange between biochar surface protons and metal cations (Machida *et al.* 2006; Lehmann 2007; Woolf *et al.* 2010; Xu *et al.* 2013; Thines *et al.* 2014, 2015). Agrafioti *et al.* (2014) modified rice husk by pyrolysis for chromium removal with 95% removal reported. Table 4 summarises the reported use of rice husk for chromium removal from wastewater.

Surfactant modified waste

Various agricultural wastes have been modified using surfactants (Bingol *et al.* 2004; Namasivayam & Sureshkumar 2008; Nadeem *et al.* 2009; Jing *et al.* 2011; Min *et al.* 2013). Surfactants are amphipathic substances with both lyophobic and lyophilic groups with the capability of forming self-associated clusters. Depending upon the nature of their hydrophilic group they can be cationic (positive charge), anionic (negative charge), non-ionic (no apparent charge)

Table 3 | Chromium removal using carbon nanotubes as an adsorbent

Adsorbent	Metal concentration (mg/L)	Optimum pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorbent capacity (mg/g)	Removal per cent (%)	References
Nitric acid oxidised carbon nanotube	1	7	–	2	150	0.5	18%	Atieh *et al.* (2010)
Composite of carbon nanotubes and activated alumina	100	2	Langmuir Freundlich	240	2.5	264.5	>95%	Sankararamakrishnan *et al.* (2014)
Nitrogen-doped magnetic CNTs	12.82	8	Langmuir	720	0.2	638.56	>97%	Shin *et al.* (2011)
CNT supported by activated carbon	0.5	2	Langmuir	60	0.04	9	72%	Atieh (2011)
Cigarette filter with MWCNT and graphene	4	–	–	–	4	–	63–79%	Yu *et al.* (2015)
Oxidised multi-walled carbon nanotubes	2.88	<2	Langmuir adsorption isotherm	9,900	75–1.25	4.2615	100%	Hu *et al.* (2009)
Composite of multi-walled carbon nanotubes and iron oxide	20	6	–	10–60	0.1–2	–	88%	Gupta *et al.* (2011)
Manganese dioxide/iron oxide/acid oxidised multi-walled carbon nanotube nanocomposites	50–300	2	Langmuir	150	5	186.9	85%	Luo *et al.* (2013)
Carbon nanotubes functionalised using nitric acid and potassium permagnate	1	9	Langmuir and Freundlich	120	0.1	2.47, 2.48	87.6%	Mubarak *et al.* (2014b)
Carbon nanotube produced using microwave heating	2	8	Langmuir and Freundlich	60	9	24.45	95%	Mubarak *et al.* (2016b)

Table 4 | Chromium removal using rice husk as an adsorbent

Adsorbent	Metal concentration (mg/L)	Optimum pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorbent capacity (mg/g)	Removal per cent (%)	References
Iron oxide incorporated into silica derived from rice husk	50–300	2	Langmuir	120	2.0	63.69	71%	Oladoja *et al.* (2013)
Ozone-treated rice husk	50, 100	2	Freundlich	150	4.0	8.7–13.1	86%	Sugashini & Begum (2015)
Modified rice husk	190, 850	6.8	Freundlich	5,760	1–16	–	95%	Agrafioti *et al.* (2014)

and zwitterionic (both charges are present); because of these characteristics surfactant modified adsorbents are superior in removal efficiency and promote selective adsorption (Nadeem *et al.* 2006; Rosen & Kunjappu 2012). These researchers modified carbon powder obtained from the husks and pods of *Moringa oleifera* using the surfactant cetyltrimethyl ammonium bromide. This process improved the removal efficiency of the carbon powder with an adsorption capacity of 27 mg/g being reported at an optimum pH of 8. Similarly, Namasivayam & Sureshkumar (2008) modified coconut coir pith by using hexadecyltrimethyl ammonium bromide surfactant to increase the removal efficiency of chromium. They reported a maximum adsorption capacity of 76.3 mg/g at an optimum pH of 2. Table 5 summarises the reported use of surfactant modified waste as an adsorbent for chromium removal.

Modified sugarcane bagasse

Sugarcane bagasse is a by-product of agricultural wastes that consists of cellulose (50%), polyoses (27%) and lignin (23%). Due to these biological component polymers, sugarcane bagasse is rich in hydroxyl and phenolic groups and these groups can be chemically modified to improve adsorption capacity (Ngah & Hanafiah 2008). Sugarcane bagasse is obtained from the fibrous material left after cane stalk crushing and juice extraction. Sugarcane bagasse originates from the outer rind and inner pith (Ullah *et al.* 2013) and has been used in the natural form as well as in a modified form. Ahmad *et al.* (2013) reported chromium removal using chromium-resistant reducing bacteria *Acinetobacter haemolyticus* inside sugarcane bagasse; this bacteria converts Cr(VI) into Cr(III) which is less toxic and less soluble as compared to Cr(VI), and a removal of more than 90% was obtained. Chemicals used for modification of sugarcane bagasse are succinic anhydride, EDTA dianhydride (EDTAD), xanthate, pyromellitic anhydride, sulphuric acid, citric acid, sodium bicarbonate, ethylenediamine, etc. These acids work as good chelating agents, so they become polymerised with sugarcane bagasse because it increases the number of chelating sites and helps in heavy metal removal from wastewater. Garg *et al.* (2009) used succinic acid for modification of sugarcane bagasse and reported 92% removal obtained at an optimum pH of 2. Cronje *et al.* (2011) removed chromium by activating sugarcane bagasse with zinc chloride, and >87% chromium was reported at an optimum pH of 8.58. Table 6 summarises the reported use of sugarcane bagasse as an adsorbent for chromium removal.

Modified wheat bran

Wheat bran is an agricultural by-product which can be used for the removal of heavy metals and is obtained from the shell of flour mill wheat seeds. It is economically viable, biodegradable and consists of many nutrients such as protein, minerals, fatty acids and dietary fibres (Kaya *et al.* 2014). It has various organic functional groups with a surface area of 441 m^2/g and a fixed carbon content of 31.78% (Singh

Table 5 | Chromium removal using surfactant modified waste as an adsorbent

Adsorbent	Metal concentration (mg/L)	Optimum pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorbent capacity (mg/g)	Removal per cent (%)	References
Coconut coir pith modified by using surfactant cetyltrimethyl ammonium bromide	30	8	Langmuir	120	1	29.96	98%	Nadeem *et al.* (2006)
Coconut coir pith modified by using hexadecyltrimethyl ammonium bromide surfactant	20–60	2	Langmuir, Freundlich, Dubinin–Radushkevich	90	0.5–6.0	76.3	96%	Namasivayam & Sureshkumar (2008)

Table 6 | Chromium removal using modified sugarcane bagasse as an adsorbent

Adsorbent	Metal concentration (mg/L)	Optimum pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorbent capacity (mg/g)	Removal per cent (%)	References
Acinetobacter haemolyticus bacteria inside sugarcane bagasse	10–100	7	–	2,880	–	–	>90%	Ahmad *et al.* (2013)
Succinic acid modified sugarcane bagasse	50	2	–	60	20	–	92%	Garg *et al.* (2009)
Sugarcane bagasse activated with zinc chloride	77.5	8.58	–	60	6.85	–	>87%	Cronje *et al.* (2011)

et al. 2009). It has various functional groups, such as methoxy, phenolic hydroxyl and carbonyl, that have the ability to bind heavy metals (Ravat *et al.* 2000). Farajzadeh & Monji (2004) demonstrated the removal of chromium using wheat bran with a maximum adsorption capacity of 93 mg/g and a maximum removal of 89%. Wheat bran can be modified by using different acids to increase removal capacity (Al-Khaldi *et al.* 2015). The thermo-chemical interaction between wheat bran and acids increases with temperature. Thus, Özer & Özer (2004) modified wheat bran using sulphuric acid and demonstrated chromium removal with an adsorption capacity of up to 133 mg/g at an optimum pH of 1.5. Kaya *et al.* (2014) used tartaric acid for modification of wheat bran and reported a 51% removal without modification, while after modification, removal was up to 90% at pH 2 and the maximum adsorption capacity was reported to be 4.53 mg of Cr(VI)/g and 5.28 mg of Cr(VI)/g at pH 2.2, without and with modification, respectively. Table 7 summarises the reported use of modified wheat bran as an adsorbent for chromium removal.

Modified coconut waste

Coconut waste is also used as an adsorbent for chromium removal. Its sorption properties are due to the presence of coordinating functional groups such as hydroxyl and carboxyl (Tan *et al.* 1993). Coconut coir pith and coconut shell are coconut wastes suitable for heavy metal removal. Coir pith is a light fluffy biomaterial and is generated during the separation process of fibre from coconut husk (Namasivayam & Sureshkumar 2008). Notably, 7.5 million tons per year of coconut is produced in India (Chadha 2003). Raw coir pith consists of 35% cellulose, 1.8% fats, 25.2% lignin and resin, 7.5% pentosans, 8.7% ash content, 11.9% moisture content and 10.6% other substances (Dan 1992). Namasivayam & Sureshkumar (2008) modified coir pith using the surfactant hexadecyltrimethylammonium bromide for chromium removal. The maximum removal obtained with this material was reported as being higher than 90% at an optimum pH of 2 and the maximum adsorption capacity was 76.3 mg/g. This was higher than the

Table 7 | Chromium removal using modified wheat bran as an adsorbent

Adsorbent	Metal concentration (mg/L)	Optimum pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorbent capacity (mg/g)	Removal per cent (%)	References
Wheat bran	20	5	–	20	80	93	89%	Farajzadeh & Monji (2004)
Wheat bran modified using sulphuric acid	50, 100	1.5	Langmuir	300	2.0	133	99.9%	Özer & Özer (2004)
Wheat bran modified using tartaric acid	52	2, 2.2	Freundlich	15–1,440	20	5.28	90%	Kaya *et al.* (2014)

maximum adsorption capacity obtained using raw coir pith which was only 1.24 mg/g (Sumathi *et al.* 2005). This demonstrates that the adsorption capacity obtained after modification was much higher. Similarly, Shen *et al.* (2012) removed chromium using coconut coir and derived char and reported a maximum removal of 70%. Table 8 summarises the reported use of modified coconut waste as an adsorbent for chromium removal.

Modified orange peel waste

Orange peel is used as an adsorbent for the removal of chromium from wastewater because it contains cellulose, hemicelluloses, pectin (galacturonic acid) and lignin (Feng *et al.* 2011). These components also have various coordinating functional groups including carboxylic and phenolic acid groups which can bind heavy metals. Orange peel is an attractive adsorbent because of its availability and low cost (Feng *et al.* 2011). Marín *et al.* (2010) studied the role of three major functional groups (amine, carboxyl and hydroxyl) on chromium removal where the bioadsorbent (orange peel) was chemically modified by esterification, acetylation and methylation in order to selectively block the functional groups. Thus, esterification decreased removal capacity, which indicates that the carboxylic groups present in the adsorbent are important for chromium removal and that the amine and hydroxyl groups have a negligible effect. The maximum adsorption capacity reported by these researchers was 40.56 mg/g. Lugo-Lugo *et al.* (2012) biosorbed chromium on pre-treated orange peel in both single (presence of chromium only) and binary mixtures (presence of chromium along with iron). It was observed that in the binary mixture, removal of chromium was interfered with by the presence of iron as more than one heavy metal in the mixture may increase, decrease or may not affect removal performance of the adsorbent. The removal per cent and adsorption capacity obtained in single phase (presence of chromium only) was 51% and 4.79 mg/g while for the binary system (presence of chromium along with iron) it was 79% and 7.60 mg/g. López-Téllez *et al.* (2011) removed chromium by preparing a composite that incorporates iron nanoparticles into orange peel pith. It was found that for this composite the percentage removal and adsorption capacity were 71% and 5.37 mg/g, respectively, as compared to raw orange peel, i.e., 34% and 1.90 mg/g, respectively. Table 9 summarises the reported use of modified orange peel waste as an adsorbent for chromium removal from wastewater.

Modified sawdust

As a solid waste, sawdust is produced in large quantities at sawmills. It contains primarily lignin and cellulose. Sawdust has been used as an adsorbent for heavy metal removal and shows good removal (Shukla *et al.* 2002). Sawdust is obtained by cutting, grinding, drilling, sanding or by pulverising wood with a saw or other tool producing fine wood particles. Argun *et al.* (2007) used hydrochloric acid modified oak sawdust (*Quercus coccifera*) for the removal of chromium. This treatment increases the proportion of active surfaces and prevents the elution of tannin compounds that would stain treated water. The maximum removal efficiency reported was 84% for Cr(VI) at pH 3 and the maximum adsorption capacity was 1.70 mg/g for Cr(VI) at pH 3. Politi & Sidiras (2012) used pine sawdust modified with 0.11–3.6 N sulphuric acid for the removal of

Table 8 | Chromium removal using modified coconut waste as an adsorbent

Adsorbent	Metal concentration (mg/L)	Optimum pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorbent capacity (mg/g)	Removal per cent (%)	References
Modified coir pith using the surfactant hexadecyltrimethylammonium bromide	20–100	2	Langmuir, Freundlich and Dubinin–Raduskevich	30–90	50	76.3, 1.24	>90%	Namasivayam & Sureshkumar (2008)
Coconut coir and derived char	10–500	3	–	7,200	1.0	70.4	70%	Shen *et al.* (2012)

Table 9 | Chromium removal using modified orange peel waste as an adsorbent

Adsorbent	Metal concentration (mg/L)	Optimum pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorbent capacity (mg/g)	Removal per cent (%)	References
Modified orange peel	0–500	4	Langmuir	4,320	4.0	40.56	82%	Marín *et al.* (2010)
Pre-treated orange peel	10	3	Langmuir model	260	10.0	4.79, 7.60	51%, 79%	Lugo-Lugo *et al.* (2012)
Composite of iron nanoparticles into orange peel pith	10–50	1	Langmuir	60	5.0	1.90, 5.37	34%, 71%	López-Téllez *et al.* (2011)

chromium and reported a maximum adsorption capacity of 20.3 mg/g and 86% removal at pH 2. Table 10 summarises the reported use of modified sawdust as an adsorbent for chromium removal from wastewater.

Modified egg shell

Although chicken eggs are a worldwide daily food they also pose environmental problems. For example, in the United States, about 150,000 tons of this material is disposed of in landfills every year (Toro *et al.* 2007). Egg shell has an outstanding mechanical performance, such as an excellent combination of stiffness, strength, impact resistance and toughness. The composition is about 95% calcium carbonate (which occurs in two crystal forms: hexagonal calcite and rhombohedral aragonite) and 5% organic materials. The amine and amide groups of the proteins on the surface of particulate egg shell are a potential source of hardening agent and help in chromium removal via chelation (Guru & Dash 2013) and this hardening agent (providing strength to the adsorbent) has an affinity for chromium. Egg shells have been used for the removal of chromium from water in both modified and non-modified forms. Modification is carried out by calcinating at high temperatures. After calcination the structure changes due to the development of pores via the emission of carbondioxide gas (Rohim *et al.* 2014). Daraei *et al.* (2015) used egg shell for chromium removal and reported 93% removal at an optimum pH 5 and 1.45 mg/g of maximum adsorption capacity. Liu & Huang (2011) modified egg shell using PEI. The PEI functionalises the eggshell membrane (ESM) via cross-linking reactions between various functional groups. The prepared bioadsorbent is reported as interacting strongly with chromium(VI), and the uptake capacity of the PEI–ESM was increased by 105% compared with the unmodified egg shell with a maximum removal of 90% and a maximum adsorption capacity of up to 160 mg/g at an optimum pH of 3. Table 11 summarises the reported use of modified egg shell as an adsorbent for chromium removal from wastewater.

Table 10 | Chromium removal using modified sawdust as an adsorbent

Adsorbent	Metal concentration (mg/L)	Optimum pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorbent capacity (mg/g)	Removal per cent (%)	References
Hydrochloric acid modified oak sawdust (*Quercus coccifera*)	0.1–100	3	Langmuir, D–R isotherms	0–720	60	1.70	84%	Argun *et al.* (2007)
Sulphuric acid modified pine sawdust	15–75	2	Freundlich	240	4	20.3	–	Politi & Sidiras (2012)

Table 11 | Chromium removal using modified egg shell as an adsorbent

Adsorbent	Metal concentration (mg/L)	Optimum pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorbent capacity (mg/g)	Removal per cent (%)	References
Egg shell	5–30	5	Freundlich	90	3.5	1.45	93%	Daraei *et al.* (2015)
Egg shell modified using PEI	100	3	Langmuir	10–1,440	10–40	160	90%	Liu & Huang (2011)

Commercially available adsorbents for cadmium removal from wastewater

Mesoporous silica

Mesoporous silica is a highly ordered material which possesses a regular two-dimensional hexagonal array of channels. Mesoporous silica is efficient for cadmium removal because of its high surface area and 2–10 nm pore size (Bhattacharyya *et al.* 2006). Mesoporous silica may be chemically modified via the attachment of groups including carboxylic acid, sulfonic acid and amino-carbonyl. Javadian *et al.* (2014) prepared polyaniline/polypyrrole/hexagonal type mesoporous silica for cadmium removal and reported a removal of 99.2% cadmium at an optimum pH of 8. Hajiaghababaei *et al.* (2011) modified SBA-15 nanoporous silica by functionalising it with ethylenediamine. SBA-15 is a highly ordered material with a regular two-dimensional hexagonal array of channels with a pore diameter of the order of 7–10 nm. The reported removal was 98% at pH > 4.5. Similarly, Burke *et al.* (2009) also used aminopropyl and mercaptopropyl, functionalised and bi-functionalised, large pore mesoporous silica spheres for the removal of chromium from wastewater. These researchers reported a maximum sorption capacity of 43.16 mg/g for Cr. Pérez-Quintanilla *et al.* (2007) modified silica and amorphous silica using 2-mercaptopyridine and reported maximum adsorption capacities of 205 mg/g and 97 mg/g, respectively. Table 12 documents the available data for mesoporous silica for cadmium removal from wastewater.

Chitosan

Chitosan is a derivative of the N-deacetylation of chitin which is a naturally occurring polysaccharide obtained from

Table 12 | Cadmium removal using mesoporous silica as an adsorbent

Adsorbent functionalised with	Metal concentration (mg/L)	Optimum pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorbent capacity (mg/g)	Removal per cent (%)	References
Silica functionalised with mono amino and mercapto groups	25	<8	Langmuir	1,440–2,880	20	12.36, 14.61, 28.10	80%	Machida *et al.* (2012)
Amino functionalised silica	50	5	Langmuir	120	5	18.25	90%	Heidari *et al.* (2009)
Amino functionalised mesoporous silica	5–300	–	Langmuir	1,440	1.11	93.30	100%	Aguado *et al.* (2009)
Iminodiacetic acid-modified mesoporous SBA-15	50–1,000	5.6	Langmuir	1,440	4.0	–	99.8%	Gao *et al.* (2007)
Polyamine-functionalised	100	5.5–7	–	2,880	–	–	70%	Alothman & Apblett (2010)

crustaceans. Chitosan is an efficient adsorbent for the removal of heavy metals (Ren *et al.* 2008). Chitosan is cheap, hydrophilic and biodegradable and it also offers ease of derivatisation. It contains amino and hydroxyl groups that may form chelates with heavy metals (Huo *et al.* 2009; Hu *et al.* 2011). Chitosan has the advantage of being cheap yet effective, but has the disadvantages of being mechanically weak, soluble under acidic conditions and may leach carbohydrate when used in raw form (Ren *et al.* 2008; Huo *et al.* 2009). Various efforts have been made to stabilise chitosan using cross-linking agents, but this results in a decrease in adsorption capacity (Wang *et al.* 2011). Thus, Chen *et al.* (2012) have developed 'ion imprint technology' for achieving higher adsorption capacity and stability. This involves the development of a novel adsorbent that is a thiourea-modified magnetic ion imprinted chitosan/TiO_2 composite for the removal of cadmium. The maximum adsorption capacity obtained for this material was reported to be 256.41 mg/g at an optimum pH of 7. Chitosan has also been modified by a coating process involving ceramic alumina. Coating helps increase accessibility of binding sites and improves mechanical stability. Maximum adsorption capacity obtained was reported to be 108.7 mg/g at an optimum pH of 6 and the maximum removal reported was 93.76% (Wan *et al.* 2004). Similarly, Hydari *et al.* (2012) modified chitosan by coating with activated carbon and reported an adsorption capacity of 52.63 mg/g adsorption capacity at an optimum pH of 6 with 100% removal. Table 13 presents cadmium removal data for chitosan as an adsorbent from wastewater.

Zeolite

Zeolites are among the best adsorbents for the removal of cadmium because they are composed of hydrated aluminosilicate minerals made from the interlinked tetrahedra of alumina (AlO_4) and silica (SiO_4) moieties (Choi *et al.* 2016). Zeolite has good ion exchange properties, a high surface area and a hydrophilic character which makes them suitable for sequestration of cadmium. Modified zeolite provides a higher adsorption capacity compared to natural zeolite. There are different methods for zeolite modification. For example, nanosized zeolite has more accessible pores which make it more suitable for heavy metal removal. Among nanosized zeolite adsorbents, NaX nanozeolite (Ansari *et al.* 2014) (in molar ratio of 5.5 Na_2O:1.0 Al_2O_3:4.0 SiO_2:190 H_2O) is widely used for cadmium removal from wastewater (Erdem *et al.* 2004; Jha *et al.* 2008; Ibrahim *et al.* 2010; Aliabadi *et al.* 2013;

Table 13 | Cadmium removal using chitosan as an adsorbent

Adsorbent	Metal concentration (mg/L)	Optimum pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorption capacity (mg/g)	Removal (%)	References
α-Ketoglutaricacid-modified magnetic chitosan	100–500	6	Langmuir	90	0.04	201.2	93%	Yang *et al.* (2014b)
Electrospun nanofibre membrane of PEO/chitosan	50–1,000	5	Freundlich, Langmuir and Dubinin–Radushkevich	120	–	248.1	72%	Aliabadi *et al.* (2013)
Nano-hydroxyapatite/chitosan composite	100–500	5.6	Freundlich and Langmuir	90	5.0	92, 122	92%	Salah *et al.* (2014)
Polyaniline grafted cross-linked chitosan beads	40–220	6	Langmuir	120	4.5	145	99.6%	Igberase & Osifo (2015)
O-carboxymethyl functionalisation of chitosan	675	10	–	1,440	–	–	95%	Borsagli *et al.* (2015)
Multi-walled carbon nanotubes modified with chitosan	–	6–7	–	–	–	–	>90%	Salam *et al.* (2011)

Rad *et al.* 2014). Rad *et al.* (2014) synthesised NaX nanozeolite using a microwave heating method, and then polyvinylacetate polymer/NaX nanocomposite nanofibres were prepared using electrospinning method; the potential of these composite nanofibres was then investigated for cadmium. The reported maximum adsorption capacity was 838.7 mg/g with 80% removal at an optimum pH of 5. Choi *et al.* (2016) modified zeolite by replacing Si(IV)and Al(III) sites in the lattice with exchangeable cations such as sodium, magnesium, potassium, or calcium, leading to a net negative charge. Mg-modified zeolite has certain advantages such as non-toxicity, low cost, abundance (and hence availability) and large pore size of 40–50 nm compared to the non-modified adsorbent. This Mg-modified adsorbent has a cadmium removal of more than 98% at an optimum pH of 7. In addition, the adsorption capacity of Mg-zeolite was found to be 1.5 times higher than that of zeolite modified with Na or K and 1.5 to 2.0 times higher than that of natural zeolite.

Coal, which is used in many industries as a fuel, produces fly ash as a by-product which causes air pollution and presents disposal problems. Due to its low cost fly ash can be used for zeolite formation using the hydrothermal process (Hui *et al.* 2005). Javadian *et al.* (2015) converted fly ash into amorphous aluminosilicate adsorbent and reported a maximum adsorption capacity for cadmium of 26.246 mg/g with 84% removal at an optimum pH of 5. Similarly, Visa (2016) converted fly ash into zeolite for cadmium removal through a hydrothermal process using sodium hydroxide. These researchers reported that this product has high surface area and is rich in micropores and demonstrates more than 80% cadmium removal at an optimum pH of 7–8. Table 14 summarises the removal parameters for the sequestering of cadmium using zeolite.

Red mud

Red mud is a waste material from the aluminium industry that may be converted into an efficient adsorbent for cadmium removal from waste water (Gupta & Sharma 2002). Red mud has the advantage of being cheap and available and possesses a high capacity for cadmium removal; however, it also has some disadvantages including the difficulty of dealing with the wastewater produced during red mud activation before application, and regeneration/recovery of red mud is difficult after application (Zhu *et al.* 2007). However, Zhu *et al.* (2007) developed red mud as a novel adsorbent for cadmium removal from wastewater. In this regard, the adsorption process onto granular red mud was found to be spontaneous and endothermic in nature. A maximum adsorption capacity of 52.1 mg/g was reported at a pH of 3 to 6. Similarly, Gupta & Sharma (2002) also used red mud for cadmium removal from wastewater and complete removal was obtained at the lower concentration (1.78×10^{-5} to 1.78×10^{-4} Molar) while 60–65% removal was obtained at the higher concentration (1.78×10^{-4} to 1.78×10^{-3} Molar) at an optimum pH between 4 and 5. Ma *et al.* (2009) used $CaCO_3$-dominated red mud (red mud containing substantial amounts of $CaCO_3$) for cadmium removal from wastewater. With increase in saturation degree of binding sites on red mud particles by the heavy metal, the proportion of HCH_3COO-extractable Cu fraction

Table 14 | Cadmium removal using using zeolite as an adsorbent

Adsorbent	Metal concentration (mg/L)	Optimum pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorbent capacity (mg/g)	Removal (%)	References
Synthetic zeolite A	100–2,000	–	Freundlich and D–R	180	1.0	315.65	–	El-Kamash *et al.* (2005)
Zeolite	25–100	6	Freundlich	90	25	–	76%	Rao *et al.* (2006)
Zeolite from fly ash	1124.1–3372.3	6.6	Langmuir	1,440	10	57–195	95.6%	Izidoro *et al.* (2013)
Oil shale into zeolite	100	7	Sips	60–1,440	–	95.6	–	Shawabkeh *et al.* (2004)
Natural zeolite	9–90	5	Freundlich	1,440	–	9	71%	Hamidpour *et al.* (2010)

(acetic acid-extractable Cu fraction) increased accordingly. Cadmium increasingly bound with HCH_3COO-extractable forms until adsorption capacity of red mud was depleted. Ju *et al.* (2012) mixed 2–8% w/w granular red mud with cement and reported an adsorption capacity of 9 mg/g. It was also found that an increase in temperature increases the equilibrium adsorption which suggests that this adsorption process is endothermic in nature.

Bio-adsorbents for the removal of cadmium

Coffee residue

Coffee residue has been reported as an efficient adsorbent for the removal of cadmium from wastewater. For example, Boonamnuayvitaya *et al.* (2004) used coffee residues for cadmium removal and also blended them with clay to prepare an adsorbent with a negative charge which promotes cadmium complexation and removal. The prepared adsorbent contains hydroxyl, carbonyl and amine groups and has a pyrolysis temperature of 500 °C (this temperature gives maximum adsorption capacity) and a particle size diameter of 4 mm. A weight ratio of coffee residue to clay of 80:20 was found to be the most suitable blend. Oliveira *et al.* (2008) employed coffee husks that comprise the dry outer skin, pulp and parchment as these are likely to represent the major residue obtained from the handling and processing of coffee. For this material, the maximum adsorption capacity was reported to be 6.9 mg/g at an optimum pH of 4 with a removal of 65–85%. Kaikake *et al.* (2007) soaked and degreased coffee beans (DCB) in water and methanol to produce an adsorbent. The prepared DCB material behaved as a cation exchanger with 90% removal at an optimum pH 8. Azouaou *et al.* (2010) used waste material from cafeterias as an adsorbent for cadmium removal and reported an adsorption capacity of 15.65 mg/g with more than 80% removal at an optimum pH of 7. Table 15 presents cadmium removal data for coffee residue as an adsorbent.

Rice husk

Rice husk is an agricultural waste obtained from rice mills and it consists of cellulose, hemicelluloses, mineral ash, lignin and a high percentage of silica (Rahman *et al.* 1997). It contains groups such as –OH, Si-O-Si and -Si-H which have an affinity for cadmium coordination and hence removal. It may be useful as an adsorbent for cadmium removal because it is cheap and easily available. Chemicals that are used for the modification of rice husk in order to increase adsorption capacity include the bases sodium hydroxide, epichlorohydrin and sodium carbonate (Kumar & Bandyopadhyay 2006). Ye *et al.* (2010) modified rice husk by constant stirring with sodium hydroxide for 24 hours and reported an adsorption capacity for cadmium removal of 125.94 mg/g, which is higher than the non-modified rice husk at 73.96 mg/g, at an optimum pH of 6.5. Kumar & Bandyopadhyay (2006) modified rice husk using epichlorohydrin, sodium hydroxide and sodium bicarbonate, and the adsorption capacity increased from 8.58 mg/g for raw rice husk to 11.12 mg/g, 20.24 mg/g and 16.18 mg/g, respectively, with the removal increasing

Table 15 | Cadmium removal using coffee residue as an adsorbent

Adsorbent	Metal concentration (mg/L)	Optimum pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorbent capacity (mg/g)	Removal per cent (%)	References
Coffee residues blended with clay	25–250	1.6–2.5	Langmuir	30	10	17.5–17.9	88–92%	Boonamnuayvitaya *et al.* (2004)
Coffee husks	50–100	4	Langmuir	4,320	6.7	6.9	65–85%	Oliveira *et al.* (2008)
Coffee beans	6–202	8	Langmuir	1,440	10	3.80	90%	Kaikake *et al.* (2007)
Coffee grounds from cafeterias	10–700	7	Langmuir	120	9	15.65	>80%	Azouaou *et al.* (2010)

from 75% to 86.2%, 97% and 97.2%, respectively, at an optimum pH of 9. It was also reported that the equilibrium time was reduced from 600 min to 120 min, 240 min and 60 min, respectively. Ajmal *et al.* (2003) treated rice husk using phosphate, and a maximum removal of 99% was reported at an optimum pH of 12. Srivastava *et al.* (2006) used mesoporous rice husk with an 80% pore area (ratio of rice husk's unoccupied area to its total area) and reported a 23.3% cadmium removal along with some other heavy metals at an optimum pH of 6. Sharma *et al.* (2009) used polyacrylamide grafted rice husk for cadmium removal from wastewater, and 85% removal was reported at an optimum pH of 9. Table 16 summarises the removal parameters for the sequestering of cadmium using rice husk.

Powdered olive stones

Olive stones form part of the waste produced from the oleic industry and are available in olive oil producing countries (Bohli *et al.* 2015). Thus, the olive stone is a plentiful by-product of the olive oil industry and is a candidate for use as an adsorbent for the removal of cadmium. Olive stones can be modified using succinic anhydride, sulphuric acid, nitric acid or sodium hydroxide to increase adsorption (Blázquez *et al.* 2005; Aziz *et al.* 2009a). Aziz *et al.* (2009a) modified olive stones using succinic anhydride that chemically functionalises it with succinate moieties that have an affinity for cadmium. This adsorbent was synthesised by esterifying the lignocellulosic matrix of the olive stone with succinic anhydride in the presence of toluene in basic medium. The adsorption capacity reported for this material was 200 mg/g at an optimum pH of 4. Aziz *et al.* (2009b) modified olive stones using concentrated sulphuric acid at room temperature followed by neutralisation with 0.1 N sodium hydroxide solution, and the maximum adsorption capacity was reported to be 128.2 mg/g at an optimum pH range of 5–10. Blázquez *et al.* (2005) used olive stones for cadmium removal and observed the effect of different parameters on the percentage removal. Thus it was found that for a smaller size of adsorbent particles (250–355 nm) the removal capacity increases up to 90% at an optimum pH of 11, and the maximum adsorption capacity was reached within 20 minutes, which is fast compared to the equilibrium time achieved in cadmium removal using olive stones prepared by $ZnCl_2$ activation (Kula *et al.* 2008) and by using olive cake (Al-Anber & Matouq 2008). Olive stone can also be used as an adsorbent by converting it into activated carbon using chemicals such as $ZnCl_2$, H_3PO_4 and H_2O_2 with a subsequent improvement in pore distribution that increases the surface area of the adsorbent. Kula *et al.* (2008) used 20% zinc chloride as an olive stone activating agent for cadmium removal and 95% removal was reported and compared with raw olive stone (43%) at an optimum pH of 9. Obregón-Valencia & del Rosario Sun-Kou (2014) prepared activated carbon from carbon aguaje and olive fruit stone using phosphoric acid solution, and a maximum adsorption capacity of 8.14 mg/g and 9.01 mg/g and a removal capacity of 61% and 68% was obtained for aguaje and olive fruit stones, respectively. Hamdaoui (2009)

Table 16 | Cadmium removal using rice husk as an adsorbent

Adsorbent	Metal concentration (mg/L)	Optimum pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorption capacity (mg/g)	Removal per cent (%)	Reference
Rice husk ash	10–100	6	Freundlich, Redlich–Peterson	5	1–10	3.04	29.8%	Srivastava *et al.* (2008)
Sulphuric acid-treated rice husk	50, 100	4	Langmuir	60	1.0	41.15 and 38.76	–	El-Shafey (2007)
Activated rice husk	8.9–89 M	6	Freundlich, Langmuir and Dubinin–Radushkevish	20	4.0	–	97%	Akhtar *et al.* (2010)

compared the adsorption capacity of olive stone in the absence of ultrasound (42.19 mg/g) and in the presence of ultrasound (55.87 mg/g) and with combined ultrasound/stirring (64.94 mg/g). Ultrasound increases adsorption capacity of olive stone due to acoustic power which enhances mass and heat transfer at films and within the pore. Further, combination of stirring with ultrasound leads to intensification of the removal of cadmium. Table 17 summarises the removal parameters for the sequestering of cadmium using powdered olive stones.

Apple pomace

Apple pomace is a waste product from the apple juice industry and is usually dumped at industrial sites in very large quantities (Chand *et al.* 2015). An apple (solid residue part) consists of the flesh 95% (wt%), seed 2–4% (wt%) and stem 1% (wt%) (Chand *et al.* 2014). Apple pomace is the solid residue part of the apple which is obtained during its processing (Chand *et al.* 2014). Apple pomace contains 7.24 g kg^{-1} of total polyphenol which includes epicatechin (0.64 g/kg), caffeic acid (0.28 g/kg), 3-hydroxyphloridzin (0.27 g/kg), phloretin-20-xyloglucoside (0.17 g/kg), phloridzin (1.42 g/kg), quercetin-3-galactoside (1.61 g/kg), quercetin-3-galucoside (0.87 g/kg), quercetin-3-xyloside (0.53 g/kg), quercetin-3-arbinoside (0.98 g/kg) and quercetin-3-rhamnoside (0.47 g/kg). Thus, apple pomace behaves as a metal chelator because of these polyphenols, amine and carboxyl groups (Foo & Lu 1999; Lu & Foo 1998). Chand *et al.* (2014) chemically modified apple pomace with succinic anhydride via a simple ring opening mechanism that provides a larger surface area on the material. The surface area is reported to increase by 18%, and consequently, 50 times less apple pomace was required as an adsorbent. The adsorption capacity of modified apple pomace (91.74 mg/g) was increased 20 times compared to non-modified apple pomace (4.45 mg/g) and for the modified apple pomace a removal of 90% was obtained compared to 70% for non-modified apple pomace at an optimum pH of 4. Similarly, in other work, these researchers prepared an adsorbent by introducing the xanthate moiety into apple pomace. The maximum adsorption capacity obtained for the xanthate modified material was reported to be 112.35 mg/g with a maximum removal of 99.7% at an optimum pH of 4. This research suggests that chemically modified apple pomace is best for cadmium removal and the introduction of xanthate gives higher removal than succinic anhydride. Table 18 presents cadmium removal data for apple pomace as an adsorbent.

Modified coconut waste

Seven and a half million tons of coconut per year is produced in India alone and the waste by-products have been used as adsorbents for cadmium removal (Chadha 2003).

Table 17 | Cadmium removal using powdered olive stone as an adsorbent

Adsorbent functionalised/ composite with/ modified	Metal concentration (mg/L)	Optimum pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorption capacity (mg/g)	Removal per cent (%)	Reference
Olive cake	100	6	Langmuir and Freundlich	1,440	0.3	65.4	66%	Al-Anber & Matouq (2008)
Zinc chloride activated olive stone	15–45	9	Langmuir and Freundlich	60	20	–	95%	Kula *et al.* (2008)
Microwaved olive stone activated carbon	20	5	Langmuir	7	0.25–2	11.72	95.32%	Alslaibi *et al.* (2013)
Activated carbon from olive stones	56–562	5	Redlich–Peterson	200	6	17.665	23%	Bohli *et al.* (2015)
Olive stone waste	33–16,861	5.5–6	Langmuir and Freundlich	60	13.33	–	49.2%	Fiol *et al.* (2006)

Table 18 | Cadmium removal using apple pomace as an adsorbent

Adsorbent	Metal concentration (mg/L)	Optimum pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsor bent capacity (mg/g)	Removal per cent (%)	References
Succinic anhydride modified apple pomace	10–80	4	Langmuir	10–180	0.8 and 40	4.45, 91.74	70%, 90%	Chand *et al.* (2014)
Xanthate moiety into apple pomace	10–120	4	Langmuir	5–60	0.2–8	112.35	99.7%	Chand *et al.* (2015)

The sorption properties are due to the presence of functional groups such as hydroxyl and carboxyl and this material demonstrates a high affinity for metal ions (Tan *et al.* 1993). Coconut coir pith and coconut shell are waste by-products that can be used for cadmium removal. Coir pith is a light fluffy biomaterial generated during the separation of the coconut fibre from the husk (Namasivayam & Sureshkumar 2008). Raw coir pith consists of 35% cellulose, 1.8% fats, 25.2% lignin and resin, 7.5% pentosans, 8.7% ash, 11.9% moisture and 10.6% other substances (Dan 1992). Kadirvelu & Namasivayam (2003) prepared activated carbon using coconut coir pith and reported a maximum adsorption capacity of 93.4 mg/g at a pH of 5. For cadmium removal, along with some other heavy metals, Jin *et al.* (2013) converted coconut into activated carbon and then grafted it with tetraoxalyl ethylenediamine melamine chelate using a pressure relief dipping ultrasonic method. The maximum adsorption capacity reported was 26.41 mg/g at an optimum pH of 5.5. Pino *et al.* (2006) used green coconut shell powder and reported removal of cadmium over a large concentration range of 20 to 1,000 ppm with a maximum adsorption capacity of 285.7 mg/g and 98% removal at pH 7. Similarly, Sousa *et al.* (2010) used green coconut shell for cadmium removal, along with other heavy metals, and the maximum adsorption capacity found for the single component system (presence of cadmium only) was reported to be 37.78 mg/g and for the multicomponent system (presence of lead, nickel, zinc and copper along with cadmium), 11.96 mg/g at pH 5. Table 19 presents cadmium removal data for modified coconut waste as an adsorbent.

Commercially available adsorbents for copper removal from wastewater

Magnetic adsorbents

Various magnetic adsorbents have been used or show potential for the effective removal of copper from wastewater, including 'magnetic' adsorbent micro- and nano-sized particles (Yin *et al.* 2012). These latter adsorbents

Table 19 | Cadmium removal using modified coconut waste as an adsorbent

Adsorbent	Metal concentration (mg/L)	Optimum pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorbent capacity (mg/g)	Removal per cent (%)	References
Activated carbon from coconut shell	5–40	5	Langmuir, Freundlich	120	0.3921	93.4	98%	Kadirvelu & Namasivayam (2003)
Activated carbon from coconut shell	1,124	5.5	Langmuir	240	2	26.41	93.4%	Jin *et al.* (2013)
Green coconut shell	20–1,000	7	Langmuir	120	5	285.7	98%	Pino *et al.* (2006)
Green coconut shell	100	5	–	1.33–9.98	1.620	37.38, 11.96	–	Sousa *et al.* (2010)

show high adsorption capacity and can be harvested from aqueous solution in the presence of a suitable magnetic field. In addition, such material is potentially reusable (Mehta *et al.* 2015). A problem with the use of unmodified magnetic particles is the formation of aggregates due to magnetic dipolar attraction between the particles. To prevent this, a layer of various polymer compounds or the inorganic oxide may be coated on the surface of the particles (Yin *et al.* 2012). Ren *et al.* (2008) prepared a novel adsorbent by using waste fungal mycelium obtained from industry (industries dealing with fungal products such as antibiotics, citric acid and enzymes), chitosan and iron oxide nanoparticles utilising metal imprinting technology. Fungal mycelium has been used because of its low cost, abundance and high efficiency. However, its direct use is difficult because of its limited reusability, relative low adsorption and low mechanic intensity (mechanical strength). Chitosan is considered useful since it is a polysaccharide and contains $-NH_2$ and -OH functional groups, which have an affinity for copper removal, and iron oxide is used because it is magnetic. In metal ion imprinting technology, selective binding sites are made on synthetic polymer using metal ion templates, and after removal of these templates, polymer become more selective for heavy metal removal from wastewater. Thus, binding of chitosan and industrial waste fungal mycelium on iron oxide nanoparticles produces a novel adsorbent known as magnetic Cu(II) ion imprinted composite adsorbent (Cu(II)-MICA). Ren *et al.* (2008) reported that the Langmuir isotherm fits the experimental data well and a maximum adsorption capacity of 71.36 mg/g was reported. It was also shown that this adsorbent can be reused up to five times with a regeneration loss of 14–15%. Lan *et al.* (2013) used hyaluronic acid supported magnetic microspheres for copper removal, and their adsorption capacity is reported to increase from 6 mg/g to 12.2 mg/g as the pH is increased from 2 to 6.8, and slowly decreases to 11.6 mg/g up to pH 8. The corresponding adsorption equilibrium study showed that the copper adsorption of the hyaluronic acid-supported magnetic microspheres had the best fit to the Freundlich isotherm model. Gong *et al.* (2012) used a pectin-coated iron oxide magnetic nanocomposite as an adsorbent for removal of copper from wastewater. This nanocomposite adsorbent was synthesised using an iron salt co-precipitation method followed by direct encapsulation with a coating of pectin and in the absence of calcium cross linking. The experimental data are reported to fit both Langmuir and Freundlich models and a maximum adsorption capacity of 48.99 mg/g was reported. The adsorbent can be further regenerated using EDTA and a removal of 93.70% was obtained after the first regeneration cycle and a removal of 58.66% remained even after a fifth cycle. Hu *et al.* (2013) used sulfonated graphene oxide for removal of copper from wastewater. The introduction of the sulfo functional group to graphene oxide is reported to increase the copper adsorption with an adsorption capacity of 62.73 mg/g at pH 4.68 and the experimental data fit the Langmuir isotherm.

Alumina

Alumina may be used for copper removal from wastewater and several authors have utilised alumina for this purpose either in nanoparticulate form or via loading with cation exchangers (Mahmoud *et al.* 2010; Fouladgar *et al.* 2015). For example, Fouladgar *et al.* (2015) used Ɣ-alumina nanoparticles for removal of copper along with nickel. Nanoparticles are useful because of their high adsorption capacity due to the high number of metal coordination sites. These researchers have a best fit for the Freundlich isotherm and a maximum adsorption capacity of 31.3 mg/g for copper removal from wastewater. Ghaemi (2016) used a phase inversion method to prepare a mixed matrix membrane using PES (polyethersulfone) and varying amounts (1 wt%) of alumina nanoparticles. Such mixed matrix membranes have shown higher water permeation compared to a pristine PES membrane that is facilitated by the addition of small amounts of nanoparticles. This results in an increase in porosity and hydrophilicity. The mixed matrix membrane has shown the highest removal of copper from wastewater of 60% compared to the PES membrane (around 25%). Mahmoud *et al.* (2010) removed copper from wastewater using three new alumina adsorbents of acidic, neutral and basic nature and their surface was modified by loading with 1-nitroso-2-napthol as a cation exchanger. After modification, alumina adsorbent become stronger towards acid leaching and thermal decomposition. The adsorption capacities obtained were

27.96 mg/g, 28.58 mg/g and 28.59 mg/g for the acidic, neutral and basic adsorbents, respectively. Conventional porous solids such as fly ash, clay and silica materials have the disadvantage of having non-uniform pores and low adsorption capacity. Thus, Rengaraj *et al.* (2004) prepared aminated and protonated mesoporous alumina for copper removal from wastewater. Mesoporous alumina have several advantages over conventional porous solids such as a large surface area, uniform pore size distribution with a sponge-like interlinked pore system, high stability and high metal uptake capacity (Lee *et al.* 2001). Ion exchange takes place between copper and the hydrogen ions that are present on the surface of mesoporous alumina, and the maximum adsorption capacity obtained for aminated mesoporous alumina is 7.9239 mg/g compared to 14.5349 mg/g for protonated mesoporous silica.

Clay

Clay may be used for removal of copper from wastewater and has a number of advantages over other adsorbents, such as high surface area, excellent physical (plasticity, bonding strength, shrinkage)/chemical properties (large zeta potential, cation exchange property, shows monobasicity) and structural/surface properties (load bearing strength, resistance to wear, resistance to chemical attack) (Singh *et al.* 2001; Krikorian & Martin 2005; Aşçı *et al.* 2007). Thus, researchers have studied different types of clay, either in raw form or after its modification, for copper sequestration. For example, Bertagnolli *et al.* (2011) employed bentonite clay after calcination at 400–500 °C. Bentonite has several advantageous properties as an adsorbent including low cost, good ion exchange capacity, selectivity and regenerability. After calcination, the chemical morphology and composition of clay does not change although the resulting structural changes alter its behaviour towards water and enables it to use infixed bed columns with no expansion. This material showed a maximum adsorption capacity of 11.89 mg/g. de Almeida Neto *et al.* (2014) reported copper removal in a fixed bed using Bofe bentonite calcinated clay, and a maximum adsorption capacity of 19.0638 mg/g was reported. The equilibrium time was increased from 120 to 400 minutes which is much less compared to equilibrium time obtained by copper removal using chitosan immobilised on bentonite clay (Futalan *et al.* 2011). Furthermore, the bed was regenerated using NaCl/HCl solution at pH 5 that gave 50% elution efficiency. It increases removal capacity because the bed becomes free from heavy metals after contact with the eluent. Vengris *et al.* (2001) modified clay using hydrochloric acid followed by neutralisation of resultant solution with sodium hydroxide for copper removal from wastewater. Initially, the chemical composition (wt%) of clay was: iron oxide 6.9, silicon oxide 44.2, aluminium oxide 15.3, calcium oxide 13.8 and magnesium oxide 4. After treatment with hydrochloric acid, aluminium, iron and magnesium compounds of clay had increased because acid treatment causes dissolution of iron, calcium, magnesium and aluminium oxides and during the neutralisation process many dissolved metals (except calcium) reprecipitate in the form of hydroxides and their amount in the modified adsorbent increases. This leads to an increase in metal uptake capacity of modified clay compared to unmodified clay. This acidic treatment led to the decomposition of the montmorillonite structure. The maximum adsorption capacity obtained for single component solutions was 0.75 mg/g, for ternary component solutions 0.80 mg/g and the experimental data fitted the Langmuir isotherm. Similarly, Oubagaranadin *et al.* (2010) modified montmorillonite-illite clay using sulphuric acid for copper removal from wastewater. The Brunauer–Emmett–Teller (BET) model fitted well with the experimental data and the shape of the isotherm indicated that copper adsorption was multilayer.

Bio-adsorbents for copper removal from wastewater

Fungal biomass

Fungal biomass has been explored by several researchers for its potential to remove copper from wastewater. The use of fungal biomass for such purposes has been hindered due to problems such as small particle size, poor mechanical strength, low density and rigidity (Akar *et al.* 2009; McHale & McHale 1994; Volesky & Holan 1995). However, the use of a suitable matrix can potentially overcome these problems. Thus, Iqbal & Edyvean (2004) used a low cost, physically strong and highly porous matrix, namely 'loofah sponge' for the immobilised biomass of *Phanerochaete chrysosporium*,

and a maximum adsorption capacity of 50.9 mg/g at pH 6 with 98% removal reported. Formaldehyde inactivated *Cladosporium cladosporioides*, *Gliomastix murorum* and *Bjerkandera* fungi, at optimum conditions, can also be used for copper removal. These fungi are highly porous, their mesh structure provides ready access and a large surface area for the biosorption of copper. Thus, Li *et al.* (2009) obtained maximum adsorption capacities of 7.74 mg/g, 9.01 mg/g and 12.08 mg/g, and removals of 93.79%, 85.09% and 81.96%, for *C. cladosporioides*, *G. murorum* and *Bjerkandera* fungi, respectively. The biosorption data of all fungal species fitted well with the Langmuir model. Ertugay & Bayhan (2010) used *Agaricus bisporus* fungi and 73.3% removal was obtained at pH 5 with a preferred fit to the Freundlich model compared to other adsorption models. Table 20 summarises the parameters for the sequestration of copper using fungal biomass.

Yeast

Yeast has been successfully used as an adsorbent for the sequestration of copper. Yeast is a fungus and has a larger size than bacteria and, like other eukaryotic organisms, has a nucleus and associated cytoplasmic organelles. The cytoplasm present in living cells is important for the living cells because it interacts with metal ions and after entering into the cells, the heavy metal ions are separated into compartments for removal (Wang & Chen 2009). Waste beer yeast is a by-product of the brewing industry that is a cheap and promising adsorbent for copper removal from wastewater (Han *et al.* 2006). These researchers reported a maximum uptake of copper of 1.45 mg/g with a preferred fit to the Langmuir and Freundlich isotherms; bisorption was reached in equilibrium in 30 minutes. The sorption capacity of beer yeast was found to be a function of the

Table 20 | Copper removal using fungal biomass as an adsorbent

Adsorbent	Intial metal concentration (mg/L)	pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorption capacity (mg/g)	Removal per cent (%)	References
Aspergillus niger	10–100	6	Langmuir and Freundlich	–	–	23.6	–	Mukhopadhyay (2008)
Mucor rouxii	10–1,000	5–6	Langmuir, adsorption	4,320	0.25	52.6	96.3%, 94.8%, 95.7%, 96.2%	Majumdar *et al.* (2008)
Fungal cells (dead) and (living)	20–100	5–9	–	4,320	0.2	–	95.27%	Hemambika *et al.* (2011)
Aspergillus niger	25–100	5	–	10, 200	15	15.6	–	Dursun *et al.* (2003)
Rhizopus oryazae filamentous fungus	20–200	4–6	Langmuir	200	1	19.4	–	Bhainsa & D'Souza (2008)
Pleurotus pulmonarius CCB019 and *Schizophyllum commune*	5–200	4	Langmuir	12	3	6.20, 1.52	–	Veit *et al.* (2005)
Chlorella sp. and *Chlamydomonas* sp.	5	7	–	12	25	33.4	–	Maznah *et al.* (2012)
Trametes versicolor	37–80	5.51	Plackett–Burman	80	1	60.98	–	Şahan *et al.* (2010)
Aspergillus niger	10–100	6	Langmuir, Freundlich	30	2–5	23.62	30%	Mukhopadhyay *et al.* (2007)
Penicillium citrinum	10–90	5	Langmuir, Freundlich	30	1.5	–	76.2%	Verma *et al.* (2013)

initial metal ion concentration, the adsorbent dose, pH, contact time and the amount of salts added and the process best fits the Langmuir and Freundlich adsorption models (Han *et al.* 2006). Table 21 summarises the parameters for the sequestration of copper using yeast.

Algal biomass

Algae may be used for the removal of copper because of their high capacity, low cost, renewability and ready abundance (Chen 2012). There are different types of marine algae, such as red algae, green algae and brown algae, that are used for copper removal from wastewater, and the main difference in these algae is in their respective cell walls where biosorption occurs (Romera *et al.* 2007). The cell walls of brown algae contain cellulose (as a structural support), alginic acid and polymers of mannuronic and guluronic acids complexed with metals such as sodium, magnesium, potassium, calcium and other polysaccharides (Romera *et al.* 2007). Green algae mainly have cellulose in the cell wall with a high content of bonded proteins. Therefore, this material contains various functional groups such as carboxyl, amino, sulfate and hydroxyl. Red algae contain cellulose in the cell wall, but their biosorption capacity is attributed mainly to the presence of sulfated polysaccharides called galactans (Romera *et al.* 2007). Brown algae, *Turbinaria ornate,* and green algae, *Ulothrix zonata,* have shown a maximum copper removal of 176.20 mg/g and 147.06 mg/g from wastewater at pH 6 and pH 4.5, respectively (Nuhoglu *et al.* 2002; Vijayaraghavan & Prabu 2006). Industrial algal waste has also been used for copper removal with a maximum adsorption of 16.7 mg/g at pH 5.3 (Vilar *et al.* 2008). Under hydrated and dehydrated conditions, micro algae *Spirulina platensis* has also been reported to remove up to 90% of copper from aqueous solution (Solisio *et al.* 2006). The dried biomass of *Spirogyra neglecta* has a reported maximum adsorption capacity for copper of 115.5 mg/g at pH 4.5–5 (Singh *et al.* 2007). Table 22 summarises the removal parameters for the sequestering of copper using algal biomass as an adsorbent.

Microbial (bacteria)

Bacteria and cyanobacteria remove heavy metal because the cell wall has the ability to capture the heavy metals due to negatively charged groups within its fabric (Uslu & Tanyol 2006). There are several processes to remove heavy metals, such as transport across the cell membrane, biosorption to cell walls, entrapment in extra cellular capsules, precipitation, complexation and oxidation/reduction (Rai *et al.* 1981; Brady *et al.* 1994; Veglio *et al.* 1997). Bacteria are the most abundant and versatile of microorganisms (Mann 1990) and bacteria species such as *Bacillus* sp., *Micrococcus luteus*, *Pseudomonas cepacia*, *Bacillus subtilis* and *Streptomyces coelicolor* have been used for copper removal from wastewater (Nakajima 2002; Öztürk *et al.* 2004; Hassan *et al.* 2009). Veneu *et al.* (2013) used *Streptomyces lumalinharesii* for copper removal from wastewater and a removal of 81% was reported at an optimum pH of 5 with best fit to the Freundlich model.

Table 21 | Copper removal using yeast biomass as an adsorbent

Adsorbent	Initial metal concentration (mg/L)	pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorption capacity (mg/g)	Removal per cent	References
Caustic-treated *Succharomyces cerevisiae* yeast biomass	16–18	5	Freundlich, Langmuir	2,160	2.0	9.01	–	Lu & Wilkins (1996)
Saccharomyces cerevisiae biomass	25–200	3–4	Freundlich, Langmuir, Redlich–Peterson	–	15	2.59	43.08%	Cojocaru *et al.* (2009)
Baker's yeast	100	2.7–6	Langmuir	250	1	65	–	Yu *et al.* (2008)

Table 22 | Copper removal using algal biomass as an adsorbent

Adsorbent	Intial metal concentration (mg/L)	pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorption capacity (mg/g)	Removal per cent (%)	References
Sargassum sp., *Padina* sp., *Ulva* sp. and *Gracillaria* sp.	64	5	Langmuir	60	1	62.91, 72.44	90%	Sheng *et al.* (2008)
Padina sp.	127	5	Langmuir	30	2	50.87	90%	Kaewsarn (2002)
Sargassum	25	4–5	Equilibrium	–	1.2	2.3 meq/g	–	Kratochvil & Volesky (1998)
Macroalga, *Sargassum muticum*	15–190	4.5	Modified competitive Langmuir sorption	240	5	71	75%	Herrero *et al.* (2011)
Gelidium	317	5.3	Freundlich	60	1–20	31.137	97%	Vilar *et al.* (2007)
Cystoseira crinitophylla biomass	25, 40, 50	4.5	Langmuir, Freundlich	720	2.5	160	100%	Christoforidis *et al.* (2015)
Sargassum, *Chlorococcum* and GAC	1–100	4.5	Langmuir, Freundlich	60, 90, 300	0.1	71.4, 19.3, 11.4	87.3%	Jacinto *et al.* (2009)
Codium vermilara	10–150	5	Langmuir	120	0.5	16.521	–	Romera *et al.* (2007)
Spirogyra insignis	10–150	4	Langmuir	120	5	19.063	–	Romera *et al.* (2007)
Spirulina platensis	100–400	–	Langmuir, Freundlich	–	1–4	92.6–96.8	91%	Solisio *et al.* (2006)
Dried micro-algal/ bacterial biomass	10–1,000	4	Langmuir	120	0.4	18–31	80–100%	Loutseti *et al.* (2009)

Öztürk *et al.* (2004) used *S. coelicolor* for copper removal and reported 21.8% removal at an optimum pH of 5 with a good fit to the Langmuir model. Uslu & Tanyol (2006) used *P. putida* for copper removal as a single component (in the presence of copper only) or as binary component (in the presence of copper along with other heavy metal, i.e., lead here) and reported an endothermic and spontaneous process with 50% copper removal from wastewater. Lu *et al.* (2006) used *Enterobacter* sp. J1 for copper removal and an adsorption capacity of 32.5 mg/g and a removal of 90% of copper removal was reported at pH >2. Even after four repeated adsorption and desorption cycles, the *Enterobacter* sp. J1 biomass achieved 79% removal. Nakajima (2002) studied removal of copper using *Arthrobacter nicotianae* bacteria from wastewater by electron spin resonance method, and found that copper ions present in bacterial cells are of octahedral structure with nitrogen and oxygen as ligand atoms and most copper in bacterial cells is combined with amino acid residues present in cell surface protein. Table 23 summarises the removal parameters for the sequestering of copper using bacteria as an adsorbent.

FACTORS AFFECTING ADOPTION OF HEAVY METALS

There are many factors which affect heavy metal removal efficiency of adsorbents from wastewater. These factors are initial concentration, temperature, adsorbent dose, pH, contact time and stirring speed. Heavy metal removal per cent increases with increase in initial concentration, temperature, adsorbent dose, contact time and stirring speed (Sahu *et al.* 2009).

Table 23 | Copper removal using bacteria as an adsorbent

Adsorbent	Initial metal concentration (mg/L)	pH	Best model fit	Contact time (min)	Adsorbent dose (g/L)	Adsorption capacity (mg/g)	Removal per cent (%)	References
Paenibacillus polymyxa	25–500	6	Langmuir	120	–	112, 1,602	–	Acosta *et al.* (2005)
Escherichia coli	32–64	–	–	–	–	8.846, 10.364	–	Ravikumar *et al.* (2011)
Pseudomonas stutzeri	30–100	5	Langmuir, Freundlich	30	1	36.2	–	Hassan *et al.* (2009)
Pseudomonas putida	0.1	5	Langmuir	10	1	6.6	80%	Pardo *et al.* (2003)
Sphaerotilus natans	100	6	Langmuir	150	3	60	–	Beolchini *et al.* (2006)
Sphaerotilus natans (Gram-negative bacteria)	–	–	Langmuir	30	1	44.48	–	Pagnanelli *et al.* (2003)
Bacillus sp. (bacterial strain isolated from soil)	100	5	Langmuir	30	2	16.25. 1.64	–	Tunali *et al.* (2006)
Lactobacillus sp. (DSM 20057)	0.398–39.8	3–6	Langmuir	5–1,440	0.3–10	0.046	–	Schut *et al.* (2011)

FUTURE PERSPECTIVE AND CHALLENGES IN REMOVAL OF HEAVY METALS

In this review paper, the bioadsorbents used for removal of chromium, cadmium and copper are low cost adsorbents and are beneficial replacements for commercially available adsorbents. In some studies, removal efficiency of adsorbents for heavy metal removal from wastewater has been reported to increase after modification. However, less work has been carried out in this direction. Hence, our future perspectives are to increase removal efficiency of bioadsorbents after modification (at minimum requirements of acid, bases and heat), regeneration of adsorbents, recovery of metal ions and application of bioadsorbents at commercial level. The challenge in heavy metal removal from wastewater is that it may require large amounts of bioadsorbents and extra chemicals to maintain a pH that provides suitable conditions for adsorption.

CONCLUSIONS

This review shows the potential of commercial and agricultural adsorbents for the removal of chromium, cadmium and copper from wastewater. A wide range of adsorbents has been studied for removal of heavy metals from wastewater. A few adsorbents that stand out for their maximum adsorption capacities are: graphene sand composite (2,859.38 mg/g), composite of carbon nanotubes and activated alumina (264.5 mg/g), PEI functionalised eggshell (160 mg/g) for chromium, chitosan/TiO_2 composite (256.41 mg/g), chitosan-coated ceramic alumina (108.7 mg/g), α-ketoglutaric acid-modified magnetic chitosan (201.2 mg/g), electrospun nanofibre membrane of PEO/chitosan (248.1 mg/g), NaX nanozeolite (838.7 mg/g), green coconut shell powder (285.7 mg/g), succinic anhydride modified olive stones (200 mg/g) for cadmium, green coconut shell powder (285.7 mg/g), *Paenibacillus polymyxa* bacteria (1,602 mg/g) for copper. Further, optimum values of parameters such as pH, contact time and adsorbent dose were also compared for chromium, cadmium and copper removal from wastewater. It was found that the optimum value of pH is in the range of 1–2 for chromium, 4–7 for cadmium and 4.5–6 for copper. Similarly, the optimum value of contact time for maximum removal is in the range of 120–9,900 minutes for chromium, 5–120 minutes for cadmium and 120 minutes–12 hours for copper. However, the optimum value of adsorbent dose is in the range of 0.75–10 g/L for

chromium, 0.01–4.5 g/L for cadmium and 0.25–1 g/L for copper. Overall, the adsorption data have been found to fit the Langmuir and Freundlich models, which indicates single and multilayer adsorption behaviour. Further, the cost of both commercial adsorbents and bioadsorbents was compared. The cost of commercial activated carbon is Rs. 500/kg; however, the cost of bioadsorbents is in the range of Rs. 4.4–36.89/kg, which is much less compared to the commercial adsorbents (Gupta & Babu 2008). Bioadsorbents have the benefits of being cheap, easily available, no sludge generation, can be regenerated, possess technical feasibility, engineering applicability and affinity for heavy metal removal.

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