Int. J. Environ. Sci. Technol. (2012) 9:379–394
DOI 10.1007/s13762-012-0041-y

ORIGINAL PAPER

Applications on agricultural and forest waste adsorbents for the removal of lead (II) from contaminated waters

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Received: 28 March 2011 / Revised: 21 July 2011 / Accepted: 24 November 2011 / Published online: 2 March 2012

Abstract At present, there is growing interest in using low cost, commercially available materials for the adsorption of heavy metals. The major advantages of adsorption technologies are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive adsorbent materials. In this review, agricultural and forest waste adsorbents were used to remove Pb^{2+} ions in wastewater treatment, and their technical feasibilities were reviewed in studies mainly from 2000 to 2010. They all were compared with each other by metal binding capacities, metal removal performances, sorbent dose, optimum pH, temperature, initial concentration and contact time. Although commercial activated carbon is widely used in wastewater treatment applications, it has high costs. The use of agricultural by-products as adsorbent material to purify heavy metal contaminated water has become increasingly popular through the past decade because they are less expensive, biodegradable, abundant and efficient. Instead of activated carbon, this study was focused on the inexpensive materials such as agricultural and forest waste. It was shown that these alternative adsorbents had sufficient binding capacity to remove Pb^{2+} ions from wastewater.

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Keywords Adsorbents · Adsorption · Agricultural wastes · Forest wastes · Lead

Introduction

Major environmental pollutants from waste may include heavy metals and persistent organic pollutants, such as high production volume chemicals, polychlorinated biphenyls, dioxins and furans. The wastes may be infectious, toxic or radioactive (Njoroge 2007).

Heavy metals are present in nature and industrial wastewater. Heavy metal contamination exists in aqueous wastes of many industries, such as metal plating, mining operations, tanneries, chloralkali, radiator manufacturing, smelting, alloy industries, storage batteries industries, etc. The removal of heavy metals from contaminated water has become a major research topic due to the toxicological problems. Lead, copper (Cu), cadmium (Cd), zinc (Zn) and nickel (Ni) are among the most common pollutants found in industrial effluents.

The enormous damage caused by water pollution have led to numerous investigations having as their objective to protect the threatened environment and living creatures through new methods (Kadirvelu et al. 2001; Frisbie et al. 2002; Antonio and Corredor 2004). Among heavy metals, lead is one of the most widely distributed and largely found in aqueous wastes. Lead has a long history of beneficial use to human kinds, but now been known as a widespread threat to humans and wildlife. Lead is a pollutant that is present both in drinking water and in air. In air, it is derived from lead emissions from automobiles. The problem attains alarming proportions in industrialized countries and in big urban conglomerates. In water, lead is released from lead treatment and recovery industries, such as metal plating, tanneries, oil refining and mining by effluents. Lead poisoning can cause hypertension, nephritis, abdominal pain, constipation, cramps, nausea, vomiting, behavioral changes, learning disabilities, reading problems, development defects and language difficulties (Kapoor et al. 1999; Lo et al. 1999; Ake et al. 2001; Tunali et al. 2006; Farrag et al. 2009; Gupta et al. 2009a, b). Lead (II) ion (Pb^{2+}) concentration approach 200–500 mg/L in the industrial wastewaters. This value is very high in relation to the water quality standards and it should be reduced to a range of 0.1–0.05 mg/L (Ucun et al. 2003; Vilar et al. 2005; Özaçar et al. 2008).

Several treatment processes such as chemical precipitation, adsorption, ion exchange and membrane filtration have been developed over the years to remove the heavy metals dissolved in industrial wastewaters. However, most of these techniques have some disadvantages, such as complicated treatment process, high cost and energy consumption. Adsorption of heavy metals from aqueous solutions is a relatively new process that has proven very promising in the removal of contaminants from aqueous effluents. The most popular adsorbent for the adsorption process is activated carbon. It has a high surface area, high adsorption capacity and high degree of surface reactivity, whereas it is very expensive and there is a need for its regeneration after each adsorption experiment. In order to decrease the cost of treatment process, the scientists have been attempted to investigate inexpensive, efficient adsorbent materials. The major advantages of adsorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive adsorbent materials. The major advantages of adsorption over conventional treatment methods include low cost, high efficiency, minimization of chemical and/or biological sludge, regeneration of biosorbent, no additional nutrient requirement and possibility of metal recovery. Therefore, it is necessary to develop some adsorbents with low cost and high efficiency for heavy metals including also Pb^{2+} ions. Adsorbent materials derived from low-cost agricultural wastes can be used for the effective removal and recovery of heavy metal ions from wastewater (Holan and Volesky 1994; Volesky and Holan 1995; Ake et al. 2001; Ahalya et al. 2003; Özcan et al. 2004; Tunali et al. 2006). The basic components of the agricultural waste biomass include hemicelluloses, lignin, extractives, lipids, proteins, simple sugars, water hydrocarbons and starch-containing variety of functional groups (Bailey et al. 1999). In general, raw lignocellulosic biosorbents were modified with physical or chemical treatments to increase their sorption capacities, because metal-ion binding by lignocellulosic biosorbents is believed to take place through chemical functional groups, such as carboxyl, amino or phenolics (Demirbaş 2008).

Activated carbon is usually prepared by using one of the two basic activation methods, namely *physical activation and chemical activation.* In comparison to physical activation, there are two important advantages of chemical activation: the first one is the lower temperature at which the process is accomplished, and the second one is that the global yield of the chemical activation tends to be greater, since burn-off char is not required. Physical activation is a process in which the precursor is developed into activated carbons using gases. Carbonization is the first stage where the precursor is pyrolyzed in the temperature range 600–900°C in an inert atmosphere (nitrogen, argon). The activation is the process in which the material is exposed to oxidizing atmospheres (carbon dioxide, oxygen or steam) usually in the temperature range 600–1,200°C, which results in the removal of the more disorganized carbon and the formation of a well-developed porous structure, leading to high surface area. Chemical activation is used for the preparation of activated carbons by using chemicals, such as H_3PO_4, KOH, $ZnCl_2$ or NaOH, followed by heating under a gas (usually nitrogen) flow in the temperature range 450–900°C (Ahmadpour and Do 1997; Boudrahem et al. 2009; Gupta et al. 2009a, b).

The use of agricultural by-products as biosorbent material to purify heavy metal contaminated water has become increasingly popular through the past decade, because they are less expensive, biodegradable, abundant and efficient. Cost is an important parameter for comparing the sorbent materials. The expense of individual sorbents varies depending on the degree of processing required and local availability. It is stated that an adsorbent can be termed as a low-cost adsorbent if it requires little processing, is abundant in nature, or is a by-product or waste material from some selected industries. Thus, there is an urgent need that all possible sources of agro-based inexpensive adsorbents should be explored and their feasibility for the removal of heavy metals should be studied in detail (Bailey et al. 1999; Demirbaş 2008; Gupta et al. 2009a, b). The objective of this study is to contribute in the search for less expensive adsorbents and their utilization possibilities for various agricultural waste by-products, which are in many cases also pollution sources.

These low-cost adsorbent materials recently studied can be classified into four categories as natural minerals (coal, peat, clays, etc.), industrial wastes (fly ash, biogas slurry, sludge, furnace slag, etc.), agricultural wastes (shell, banana pith, peel, hazelnut shell, rice husk, etc.) and forest wastes (barks, leaves and sawdust of certain timber trees) (Örnek et al. 2007).

Adsorption of metal cation on adsorbent depends upon the nature of adsorbent surface and species distribution of the metal cation. Surface distribution mainly depends on pH of the system (Namasivayam and Ranganthan 1995).

The pHzpc (zero point charge) plays an important role in the adsorption process. The nature and concentration of the carbon surface charge, which is a positive charge below pHzpc and a negative charge above pHzpc, up to a certain range of pH values can be modified by changing the pH of the carbon-solution system. The organic functional groups on the adsorbent surface may acquire a negative or positive charge depending on the solution pH. At pH above pHzpc, the surface of activated carbon is negative due to the ionization of acidic carbon-oxygen surface groups, and there is a strong electrostatic attraction between surface groups and metal species. Thus, the adsorption of metal ions mainly involves electrostatic attractive and repulsive interactions between metal ionic species in the solution and the negative sites on the carbon surface produced by the ionization of acidic groups. The decrease in the adsorption process observed at pH values less than pHzpc could be attributed to the presence of basic surface groups, the excessive protonation of the surface at low pH values and to graphene layers that act as Lewis bases resulting in the formation of acceptor–donor complexes important for the adsorption of many organic compounds from aqueous solutions. The surface is positive and may result in a repulsive force between positively charged surfaces (Bansal and Goyal 2005).

The adsorptive removal of organic and inorganic substances from wastewater by activated carbons depends upon the surface area, the pore volume and the pore-size distribution in carbons. However, the effectiveness of the adsorption depends not only on the properties of the adsorbent, but also on various parameters (pH, temperature, initial concentration, contact time, particle size of adsorbent, etc.) used for the adsorption process. These parameters should also be taken into account while examining the potential of low-cost adsorbents.

Agricultural and forest adsorbents as low-cost adsorbents

Forest and agricultural products are generating the most abundant renewable resources available worldwide. Agriculture is one of the richest sources for low-cost adsorbents. The use of agriculture and forest waste for adsorption shows great promise. The basic components of the agricultural waste materials include hemicellulose, lignin, lipids, proteins, simple sugars, water, hydrocarbons and starch, containing variety of functional groups (acetamido, alcoholic, carbonyl, phenolic, amido, amino, sulphydryl groups). These groups have the ability to some extent to bind heavy metal ions by the donation of an electron pair from these groups to form complexes with the metal ions in solution. The functional groups present in agricultural waste biomass have affinity for heavy metal ions to form metal complexes or chelates that immobilize the contaminants through reactions of chemisorption, complexation, adsorption on surface, diffusion through pores and ion exchange. Agricultural waste materials being economic and eco-friendly due to their unique chemical composition, availability in abundance, renewable nature and low cost are viable option for water and wastewater remediation (Ahmedna et al. 2000; Pagnanelli et al. 2003; Gupta et al. 2009a, b).

Most of the known methods for removing metal ions from solution are expensive. It has been shown that wood, bark and other agricultural residues remove metal ions from solution with varying efficiencies. The abundance and availability of agricultural by-products make them good sources of adsorbents (Bansode et al. 2003).

In the last several decades, several agricultural and forest wastes have been explored as low-cost adsorbent. Agricultural adsorbents such as orange peels wastes, olive stones, coconut shell, cocoa shell, apricot stone, palmyra palm, peach stone, pecan nuts, hazelnut husk, almond, beech and poplar woods, rice husk, rice husk ash, plant maize, corn, fly ash, bagasse, leaves, sago waste, sawdust, seed hull, tea waste, coffee, leaf powder, sunflower waste, sunflower seed peel pistachio, palm kernel fiber, wheat bran, peat, palm shell, oil palm tree, onion skins, etc. have been evaluated for their adsorption properties (Table 1). Reviews of some agricultural and forest waste adsorbents for the removal of Pb^{2+} ions from wastewater are presented as follows. Different adsorbents that used for the removal of Pb^{2+} ions are given in Table 1 with parameters method type, uptake capacity, removal (%) of Pb^{2+} ions, sorbent dose, optimum pH, temperature, initial concentration and contact time.

Shells

Activated carbons are produced from agricultural wastes, such as bagasse, hard shells of apricot stones, almond, walnut and hazelnut shells. Activated carbons from the hard shells have the best adsorption properties and the highest surface area (Dolas et al. 2011; Özdemir et al. 2011; Saka 2012). Activated carbons could be used in the separation of metal ions from wastewaters. Shells consist of cellulose, hemicellulose and lignin. Cellulose is a common material in plant cell walls and lignin is relatively hydrophobic and aromatic in nature (Pehlivan et al. 2009). Dolas et al. (2011) reported that activated carbon having high surface area were produced from pistachio shells that were chemically activated using $ZnCl_2$ at room temperature and then activated in carbon dioxide gas that was saturated in water vapor. As a result, the activated carbon produced from pistachio shells treated with 40% $ZnCl_2$ then with 40% HCl in room temperature and then activated

Table 1 Summary of adsorbents

Adsorbent	Uptake capacity (mg/g)	Removal (%)	Optimum pH	Sorbent dose(g)	Concentration (mg/L)	Temperature (°C)	References
Activated charcoals (bamboo)	53.76	83.01	5.0	0.1	50–90	29	Lalhruaitluanga et al. (2010)
Almond		99.8	6–10	0.1	30	Ambient	Kazemipour et al. (2008)
Almond	8.08	68	6–7	0.5	0.001 mol/L	25 ± 1	Pehlivan et al. (2009)
Antep pistachio		90 ± 2	5.5	1.0	30	30	Yetilmezsoy and Demirel (2008)
Apricot stone		89.6	6–10	0.1	30	Ambient	Kazemipour et al. (2008)
Apricot stone	1.31 (mg/kg)	93	7–8	2	200		Rashed (2006)
Arca shell			1.0–7.0		10–500	25 ± 2	Dahiya et al. (2008)
Bagasse fly ash	3.8	95–96	6.0	10	5.0–70.0	30	Gupta and Ali (2004)
Bamboo dust	2.151	66.73	7.2	28	600	30° + 1°	Kannan and Veemaraj (2009)
Banana peels	72.79		5	1	200	25 ± 2	Gupta et al. (2009a, b)
Banana peels	2.18	85.3	5	2.0	30–80	25	Anwar et al. (2010)
Biomass of *Spirulina maxima*	Intact 21, pretreated 23	Intact 84, pretreated 92	5.5	2	50	20	Gong et al. (2005)
Black gram husk	49.97		5				Saeed et al. (2005)
C. demersum	44.8		5–6	2	10	25	Keskinkan et al. (2007)
Capsicum annuum seeds		90	5.0	0.1	100	20	Özcan et al. (2007)
Carpobrotus edulis	175.6	98	5.84	25	100	25	Benhimaa et al. (2008)
Ceiba pentandra hulls	25.5	99.5	6.0	0.1	50	30 ± 1	Rao et al. (2008)
Cephalosporium aphidicola	92.322		1.0–6.0		100–400	20–40	Tunali et al. (2006)
Cereal chaff	12.5		5.5	0.1–0.6	8 g/L	20	Han et al. (2005)
Charcoals raw (bamboo)	10.66	13.63	5.0	0.1	50–90	29	Lalhruaitluanga et al. (2010)
Chitin natural	264		4	1	100–300	35	Kim et al. (2006)
Chitin, phosphorylated	258		4	1	100–300	35	Kim et al. (2006)
Chitosan	8.31		6	1.5	50	30	Zulkali et al. (2006)
Citrus peels original and protonated	~400	90	5	0.1	300		Schiewer and Balaria (2009)
Cocoa shells	161 mmol/kg	95	2	15	3.66 mmol/L		Meunier et al. (2003)
Coconut	4.38	60	4	6	100	60	Gueu et al. (2007)
Coconut shell	26.50	75	4.5		50 mg/50 ml		Sekar et al. (2004)
Coconut shell granular activated carbon	21.88		5.0		5–70	37 ± 2	Goel et al. (2005)
Coffee	0.1247 (L/g)		5.0	1.8	10	170–220	Utomo and Hunter (2006)
Coffee residue activated with zinc chloride	62.57	75	5.8	1	10	25	Boudrahem et al. (2009)
Coir	0.127	86.98	4.9	1	0.56 mmol/dm^3	30	Shukla and Roshan (2005)
Coir fibers	52.03		4	1	200	25 ± 2	Gupta et al. (2009a, b)
Copolymer-grafted orange peel		99	5	0.12			Lugo-Lugo et al. (2009)
Corncobs chemically modified	Hydrolyzed 0.2095 Esterified 0.0381		5	0.2	0.1 mmol/L	25	Tana et al. (2010)
Corncobs native	0.0783 (mmol/g)		5	0.2	0.1 mmol/L	25	Tana et al. (2010)
Eucalyptus camaldulensis Dehn. bark	0.89 mmol/g		5	0.1	0.1–10 mmol/L	60	Patnukao et al. (2008)

Table 1 continued

Adsorbent	Uptake capacity (mg/g)	Removal (%)	Optimum pH	Sorbent dose(g)	Concentration (mg/L)	Temperature (°C)	References
Euphorbia echinus	165.1		5.84	25	100	25	Benhimaa et al. (2008)
Fly ash, bagasse	2.50	95–96	6	10	5.0–70	30	Gupta and Ali (2004)
Fly ash, modified, activated	98 mmol/100 g	98	5	0.5–2	0.0027 mol/L	25	Woolard et al. (2000)
Grape stalk	0.241 mmol/g		5.5	0.1	0.96 mmol/L	20	Martınez et al. (2006)
Grass clippings	29.05		5	1	200	25 ± 2	Gupta et al. (2009a, b)
Groundnut shells	0.106 mmol/g	82.81	4.9	1		30	Shukla and Roshan (2005)
Hazelnut husks	13.05		5.7	0.3	200	18	Imamoglu and Tekir (2008)
Hazelnut shell		96.9	6–10	0.1	30	Ambient	Kazemipour et al. (2008)
Hazelnut shells	28.18	90	6–7	0.5	0.001 mol/L	25 ± 1	Pehlivan et al. (2009)
Horticultural peat	0.145 mmol/g	96	4.5–7.0	1	100	25	Ulmanu et al. (2008)
Jute	0.090 mmol/g	73.37	4.9	1		30	Shukla and Roshan (2005)
Launaea arborescens	129.9		5.84	25	100	25	Benhimaa et al. (2008)
Lawny grass modified	1.55		5.0–5.8	0.025	0.001 mol/L		Lu et al. (2009)
Leaf powder *Azadirachta indica* (neem)	300	93	7.0	0.4	100	27	Bhattacharyya and Sharma (2004)
Leaf powder *Hevea brasiliensis*	46.73		5.0	0.1	50	30	Hanafiah et al. (2006)
Leaves bael	104	97	4.0	0.2	50	30	Chakravarty et al. (2010)
Leaves *Ficus religiosa*	37.45		4	0.5	100	25.4	Qaiser et al. (2009)
Leaves neem		41.45	5	1	20.00	25	Oboh et al. (2009)
Leaves peepul	127.34		4	1	200	25 ± 2	Gupta et al. (2009a, b)
Leaves, *Casuarina glauca* tree	97.37		6.5		25		Abdel-Ghani et al. (2008)
Lignin modified from alkali glycerol	8.2–9.0	95.8	5.0	10.0		57	Demirbaş (2004)
M. spicatum	46.49		5–6	2	10	25	Keskinkan et al. (2007)
Maize bran	142.86	98.4	6.5		100	20	Singh et al. (2006)
Maize cobs		≈80	4.5	1	25	25	Abdel-Ghani et al. (2007)
Mango leaves	31.54		4	1	200	25 ± 2	Gupta et al. (2009a, b)
Mango peel waste	99.05	98.85 ± 1.78	5	2.5	50	25 ± 2	Iqbal et al. (2009)
Meranti sawdust	34.246	97	6	5	1–200	30	Rafatullah et al. (2009)
Meranti tree sawdust		90.4	7	0.25	25–250	25	Ahmad et al. (2009)
Mustard husk	30.48		6				Meena et al. (2008)
Natural condensed tannin	114.9	91	4.2				Zhana and Zhao (2003)
Neurospora crassa	43.29		4.0		5–300	25	Kiran and Akar (2005)
Nile rose plant		98.66	8.5	0.5	50	25	Abdel-Ghani et al. (2007)
Oil palm tree chemically modified		70	6.2	0.5	50	28	Abia and Asuquo (2006)
Oil palm tree unmodified		70 + 2	6.2	0.5	50	28	Abia and Asuquo (2006)
Okra waste	5	99	5		240	25	Hashem (2007)
Olive cake	18.14	82.5	6.00	1	2.5 and 50 mg/50 mL	30	Doyurum and Celik (2006)

Table 1 continued

Adsorbent	Uptake capacity (mg/g)	Removal (%)	Optimum pH	Sorbent dose(g)	Concentration (mg/L)	Temperature (°C)	References
Olive oil	1.10×10^{-4} (mol/g)		5	0.5		25	Martín-Lara et al. (2009)
Olivestone waste		80 ± 2	5.5	0.2	2.3×10^{-4}	20	Fiol et al. (2006)
Orange peel formaldehyde treated		99	5	0.12			Lugo-Lugo et al. (2009)
Orange peel natural	46.61	99	5	0.12	150 30		Lugo-Lugo et al. (2009)
Orange peel xanthate	204.50		5.0	0.05	100	30	Liang et al. (2009)
Palm kernel fiber			5.0	0.6	120	36 ± 3	Ho and Ofomaja (2006)
Palm kernel husk		88	5	4			Iyagba and Opete (2009)
Palm kernel shell		81	5	4			Iyagba and Opete (2009)
Palm shell	95.2		3 and 5		10–700	27	Issabayeva et al. (2008)
Palm shell polyethyleneimine-impregnated	0.258 mmol/g		5	2	60 g/L	25	Yin et al. (2008)
Palm shell unpretreated	92.6		5				Issabayeva et al. (2008)
Palmyra palm fruit seed	24.6	100	4	0.2		30	Kannan and Thambidurai (2007)
Peach stone	2.33 mg/kg	97.64	7–8	2	200		Rashed (2006)
Peanut hulls	69.75		5	1	200	25 ± 2	Gupta et al. (2009a, b)
Peanut shells modified	0,63 mmol/g		4.6–5				Chamarthy et al. (2001)
Pecan nutshell	0.946 mmol/g		5.5	4.0	100	25	Vaghetti et al. (2009)
Pistachio shell		83	6–10	0.1	30	Ambient	Kazemipour et al. (2008)
Plant maize	2.3		4.0				Zhang and Banks (2006)
Plant powder	9×10^{-5} mol/g	80	6	0.1	85		Abdel-Halim et al. (2003)
Onion skins	200	93	6	0.15	25–200	30	Saka et al. (2011a, b)
Pomegranate peel			5.6	0.25	10–50	26 ± 1	El-Ashtoukhya et al. (2008)
Pomegranate peel activated carbon			5.6–7.6	0.25	10–50	26 ± 1	El-Ashtoukhya et al. (2008)
Pomegranate peel chemically treated			5.6–7.6	0.25	10–50	26 ± 1	El-Ashtoukhya et al. (2008)
Ponkan peel	112.1		5.0	0.2	15.0 mmol/L	25	Pavan et al. (2008)
Rice stem	49.57		5	1	200	25 ± 2	Gupta et al. (2009a, b)
Rice husk	5.69		5	2.0	50	60	Zulkali et al. (2006)
Rice husk	31.13		5	1	200	25 ± 2	Gupta et al. (2009a, b)
Rice husk ash	10.86		5.60–5.80	2	40	15	Feng et al. (2004)
Rice husk ash	91.74	99.3	5	5	3–100	30	Naiya et al. (2009)
Rice husks		98.15	4.5	1	25	25	Abdel-Ghani et al. (2007)
Rose petals chemically modified	118.40		5	0.1	100	30	Nasir et al. (2007)
Sago waste cooled orbital shaker	46.6		4.5–5.5		50–100	25 ± 5	Quek et al. (1998)
Sargassum glaucescens			5.0	1		20 ± 2	Naddafi et al. (2007)
Sawdust	13.9	98.8	2–5	40	5	23	Yu et al. (2001)
Sawdust	0.087 mmol/g	70.94	4.9	1		30	Shukla and Roshan (2005)
Sawdust		≈80	4.5	1	25	25	Abdel-Ghani et al. (2007)
Sawdust activated carbon	0.223 mmol/g	90.1	5.0	2	0.5 mmol/L	30 ± 2	Sreejalekshmi et al. (2009)

Table 1 continued

Adsorbent	Uptake capacity (mg/g)	Removal (%)	Optimum pH	Sorbent dose(g)	Concentration (mg/L)	Temperature (°C)	References
Sawdust of *Pinus sylvestris*	22.22	98	5.5	0.1	100	25	Taty-Costodes et al. (2003)
Sawdust waste generated in the timber industry	0.646 mmol/g	88.6	6.5–	1.0	0.5 mmol/dm^3	30	Krishnan et al. (2003)
Seaweed *Ascophyllum nodosum*	117.3		4.0		10		Zhang and Banks (2006)
Seaweed, brown	1.35		4	2.0		30	Vieira et al. (2007)
Seed hull of the palm tree	3.77		4	6	100	60	Gueu et al. (2007)
Seed powder of *Prosopis juliflora* DC	40.322	85.1	6.0	0.1	20	28	Jayaram and Prasad (2009)
Senecio anteuphorbium	149.6	98	5.84	25	100	25	Benhimaa et al. (2008)
Sphagnum moss immobilised	32.5		4.0		10		Zhang and Banks (2006
Staphylococcus saprophyticus		100	4.5		100	27	Ilhan et al. (2004)
Sugarcane bagasse chemically modified	189		6.2	0.1	200–400		Karnitz et al. (2007)
Sunflower seed peel		99	6			60	Özdemir et al. (2004)
Sunflower waste	33.2		4.0		10		Zhang and Banks (2006)
Tea waste	73	96	5	0.5	5–100	30	Ahluwalıa and Goyal (2005)
Tea leaves discarded	35.89		5	1	200	25 ± 2	Gupta et al. (2009a, b)
Tea waste		92.8 ± 1.3	7		100	28	Ghaffar (2008)
Teak saw dust	40.70		4	1	200	25 ± 2	Gupta et al. (2009a, b)
Tree fern	38.1		4.9	6.8	200	20	Ho (2005)
Ulva lactuca	34.7		2.0–8.0		10–400	20–50	Sarı and Tuzen (2008)
Valonia tannin resin	138.3		4	2		25	Özaçar et al. (2008)
Viscum album leaves	769.23	92.2	3.0	0.5	50	25	Erentürk and Malkoç (2007)
Walnut shell		96.2	6–10	0.1	30	Ambient	Kazemipour et al. (2008)
Waste tea and coffee adsorbents	0.0712		5.0	2.0	10	170–220	Utomo and Hunter (2006)
Wheat bran	86.96		4–7	0.5	200–500	20	Bulut and Baysal (2006)
Wheat bran acid treated	79.37	82.8	6.0	0.1	100	25	Özer (2007)

at 900°C for 90 min has 3,256 m^2/g of Brunauer–Emmett–Teller (BET) surface area, 3,822 m^2/g of Dubinin–Radushkevich (DR) surface area and 1.36 cm^3/g of DR micropore volume. It was found that the activated carbon produced from pistachio shells treated with 40% of sodium chloride and activated at 900°C for 90 min has 3,895 m^2/g of BET surface area, 5,235 m^2/g of DR surface area and 1.86 cm^3/g of DR micropore volume.

The potential of shells of hazelnut (HNS) and almond (AS) to remove Pb^{2+} from aqueous solutions was investigated in batch experiments (Pehlivan et al. 2009). The influences of initial Pb^{2+} ion concentration (0.1–1.0 mM), pH (2–9), contact time (10–240 min) and adsorbent amount (0.1–1.0 g) have been investigated. The equilibrium sorption capacities of HNS and AS were 28.18 and 8.08 mg/g, respectively, after equilibrium time of 2 h. The binding of metal ions involved three mechanisms: the first is adsorption, the second of these being simple ion exchange and the third one is through the formation of complexes.

Kazemipour et al. (2008) developed the adsorption of Pb^{2+}, Zn^{2+}, Cu^{2+} and Cd^{2+} onto the carbon produced from nutshells of walnut, hazelnut, pistachio, almond and apricot stone. All the agricultural shells or stones used were ground, sieved to a defined size range and carbonized in an oven. Time and temperature of heating were optimized at 15 min and 800°C, respectively, to reach maximum removal efficiency.

Issabayeva et al. (2006) reported the palm shell activated carbon to remove Pb^{2+} ions from aqueous solutions at pH 3.0 and 5.0. Palm shell activated carbon showed high adsorption capacity for Pb^{2+} ions at pH of 5 with an ultimate uptake of 95.2 mg/g. Quite low pHpzc value (1.43) of palm shell carbon suggested higher uptake of metal ions, especially at higher pH. The authors reported that palm shell activated carbon is characterized by a high concentration of acidic surface groups. This result indicated that palm shell activated carbon exhibited higher adsorption capacity, since high acidity was responsible for the higher adsorption of metal ions on the carbon surface. However, phenols and carbonyls were not detected in the palm shell activated carbon used in experiments.

Issabayeva et al. (2008) also reported the continuous adsorption of Pb^{2+} ions from aqueous solution on commercial, granular and unpretreated palm shell activated carbon at the presence of complexing agents (malonic and boric acids). The breakthrough period was longer at pH 5 than at pH 3 indicating higher adsorption capacity of Pb^{2+} ions at higher pH. The authors showed that complexing agents did not improve adsorption uptake of Pb^{2+} ions. However, presence of malonic acid resulted in smoother pH stabilization of solution compared to single Pb^{2+} and Pb^{2+} with boric acid systems. Continuous adsorption of Pb^{2+} ions showed that the breakthrough period was shorter at the pH of 3 than at the pH of 5.

Husks

Rice is one of the major crops grown throughout the world. Rice husk is a by-product generally obtained from rice mill. Rice husk ash is a solid obtained after burning of rice husk. Naiya et al. (2009) reported the adsorption of Pb^{2+} from aqueous solution on rice husk ash in batch studies. Optimum conditions for Pb^{2+} removals were found to be pH 5, adsorbent dosage 5 g/L of solution and equilibrium time 1 h. Adsorption of Pb^{2+} was followed pseudo-second-order kinetics. The adsorption capacity of rice husk ash for Pb^{2+} ions was 91.74 mg/g. The authors indicated that the adsorption process was chemical in nature. pHpzc was 8.5. Thermodynamic parameter studies showed that the Pb^{2+} ions adsorption are spontaneous in nature.

Meena et al. (2008) reported the adsorption of Pb^{2+} and Cd^{2+} ions using mustard husk as an adsorbent. Maximum removal of Pb^{2+} and Cd^{2+} ions on mustard husk was at the pH of 6 and 4, respectively. The adsorption capacities of mustard husk for Cd^{2+} and Pb^{2+} ions are 42.85 and 30.48 mg/g, respectively.

Bran

Bran is the hard outer layer of grain, such as rice, corn (maize), wheat, oats, barley and millet. It is an integral part of whole grains, and is often produced as a by-product of milling in the production of refined grains.

Wheat bran is a by-product of wheat milling industries and may be considered as a raw material to produce an effective adsorbent. The adsorption of Pb^{2+} ions from aqueous solutions on wheat bran was investigated by Bulut and Baysal (2006). The maximum Pb^{2+} ions sorption capacities on wheat bran at 20, 40 and 60°C are 69.0, 80.7 and 87.0 mg/g, respectively. The sorption process was found to be endothermic.

Sulfuric acid-treated wheat bran was used as an adsorbent to remove Pb^{2+} ions from aqueous solution (Özer 2007). At pH 6.0, adsorption percentage for an initial Pb^{2+} ion concentration of 100 mg/L was found to be 82.8% at 25°C for contact time of 2 h. The equilibrium data obtained at different temperatures fitted to the non-linear form of Langmuir, Freundlich and Redlich–Peterson and linear form of Langmuir and Freundlich models. The maximum adsorption capacity which was obtained as linear form of Langmuir model increased from 55.56 to 79.37 mg/g with increasing temperature from 25 to 60°C.

Maize bran as a low-cost biosorbent for the removal of Pb^{2+} ions from an aqueous solution was reported by Singh et al. (2006). Optimum removal at 20°C was found to be 98.4% at pH 6.5, with an initial Pb^{2+} ion concentration of 100 mg/L. The authors showed that the reaction was spontaneous and exothermic in nature. The adsorption data fitted the Langmuir isotherm. In addition, authors showed that the adsorption in the initial stages was due to the boundary layer diffusion, whereas in the later stages adsorption was due to intraparticle diffusion.

Sawdust

Sawdust is composed of fine particles of wood. The meranti sawdust is found to be cost effective and has good efficiency to remove these toxic metal ions from aqueous solution. Rafatullah et al. (2009) showed that meranti sawdust was able to adsorb Cu^{2+}, Cr^{3+}, Ni^{2+} and Pb^{2+} ions from aqueous solutions in the concentration range of 1–200 mg/L. The amount of Cu^{2+}, Cr^{3+}, Ni^{2+} and Pb^{2+} ions adsorbed into the meranti sawdust increased with an increase in concentration and dosage of adsorbent. The maximum adsorption capacity for Pb^{2+} ions is 34.246 mg/g. The maximum adsorption percentage for Pb^{2+} ions at the pH of 6 is 97% in 120 min of contact between the sawdust and the solution at 30°C.

The removal of Pb^{2+} ions and Pb^{2+}–citric acid (Pb^{2+}–CA) from aqueous solutions by sawdust activated carbon (SDAC) was investigated by Sreejalekshmi et al. (2009) in batch adsorption experiments. The higher adsorptive removal of Pb^{2+} from aqueous solutions containing Pb^{2+}–CA than Pb^{2+} only was observed due to the presence of CA in the former system. The adsorption was maximum for the initial pH in the range of 6.5–8.0 and 2.0–5.0 for Pb^{2+} and Pb^{2+}–CA, respectively. The kinetic and equilibrium adsorption data were well modeled using pseudo-first-order kinetics and Langmuir isotherm model, respectively. The pHzpc value was found to be 5.3. The authors showed that surface properties of SDAC under investigation are: particle size, 0.096 mm; ash content, 5.31%; apparent density, 1.02 g/mL; cation-exchange capacity, 3.16 meq/g; total acidic sites, 4.02 meq/g and carboxylic acid content, 1.95 meq/g. Also, the authors reported that at pH <5.3, the predominant Pb^{2+} species is Pb^{2+} and other species, such as $Pb(OH)^+$, $Pb_2(OH)^{3+}$, $Pb_3(OH)_4^{2+}$ and $Pb_4(OH)_4^{4+}$ are present only in very small amounts. Therefore, the uptake of metal in the pH range of 2.0–5.3 for SDAC will be predominantly H^+–Pb^{2+} exchange process.

Leaves

It has been reported that wood wastes, such as sawdust, barks and tree leaves effectively adsorb Cd species from aqueous systems (Kumar and Dara 1982). Gupta et al. (2009a, b) investigated the adsorption of Pb^{2+} with adsorbents peepul leaves ($q_{max} = 127.34$ mg/g), banana peels (72.79 mg/g), peanut hulls (69.75 mg/g), coir fibers (52.03 mg/g), rice stem (49.57 mg/g), teak saw dust (40.70 mg/g), discarded tea leaves (35.89 mg/g), mango leaves (31.54 mg/g), rice husk (31.13 mg/g) and grass clippings (29.05 mg/g). Kinetics of Pb^{2+} sorption by the selected biomass types, excepting peepul leaves, were very fast with >90% sorption occurring within 10 min. The isotherm data of Pb^{2+} biosorption are more significantly fitted to Langmuir model. External diffusion, rather than intraparticle diffusion, was the dominant mechanism for Pb^{2+} sorption by all the test plant materials Pb^{2+} sorption attained maxima at the pH of 4 (peepul leaves, mango leaves, rice stem and coir fibers) or 5 (grass, tea leaves, banana peels, teak saw dust, peanut hulls and rice husk).

Bhattacharyya and Sharma (2004) developed an adsorbent from the mature leaves of the neem (*Azadirachta indica*) tree for removing Pb^{2+} from wastewater. The adsorbent had a considerably high Langmuir monolayer capacity of 300 mg/g. The maximum adsorption percentage is 93% for Pb^{2+} in 300 min from a solution of concentration 100 mg/L at 300 K with a small amount of the adsorbent of 1.2 g/L. The adsorption continuously increased in the pH range of 2.0–7.0. The adsorption was exothermic at ambient temperature. Also, neem leaves for the adsorption of Cu^{2+}, Ni^{2+}, Zn^{2+} and Pb^{2+} ions from wastewater under various experimental conditions was investigated by Oboh et al. (2009) with contact time of 120 min. The results showed that neem leaves achieved the percent removal of 76.8, 67.5, 58.4 and 41.45 for Cu^{2+}, Ni^{2+}, Zn^{2+} and Pb^{2+} ions, respectively.

Biosorption of Pb^{2+} ions on bael leaves (*Aegle marmelos*) was investigated by Chakravarty et al. (2010). The maximum capacity of the bael leaves was 104 mg/g at 50 mg/L initial Pb^{2+} ion concentration at the pH of 5.1. The authors showed that the adsorption of Pb^{2+} occurs inside the wall of the hollow tubes present in the bael leaves and carboxylic acid, thioester and sulfonamide groups are involved in the process. The sorption process was best described by pseudo-second-order kinetics.

Peels

Orange peel is mostly composed of cellulose, pectin, hemicellulose, lignin, chlorophyll pigments and other low molecular weight hydrocarbons. Many of these contain several hydroxyl functional groups, which make the orange peel a potential substrate for the synthesis of xanthates. Application of orange peel xanthate for the adsorption of Pb^{2+} ions from aqueous solutions was investigated by Liang et al. (2009) in batch experiments. Pristine orange peel was chemically modified by introducing sulfur groups with the carbon disulfide treatment in alkaline medium. At 30°C and the pH of 5.0, the maximum adsorption capacity of orange peel xanthate was 204.50 mg/g, which found to increase by about 150% compared to that of pristine orange peel. The adsorption process can attain equilibrium within 20 min, and kinetics was found to be best-fit pseudo-second-order equation. The adsorption mechanism was suggested to be a type of complexation.

The uptake of Pb^{2+} ions by processed orange peels, which is a pectin-rich by-product of the fruit juice industry, was presented by Schiewer and Balaria (2009) with acidic groups around pH 4, 6 and 10. Depending on the particle size, equilibrium was achieved in 30 min to 2 h. The first-order model was inferior to second- or third-order models. The Pb^{2+} ions uptake of ~400 mg/g was observed for citrus peels in this study. The authors noted that the maximum uptake capacity was not yet reached at the experimental conditions. This means metal uptake could be even higher: the extrapolated maximum capacity according to the Langmuir model was 658 mg/g. This value is, however, only an estimate not experimentally confirmed.

The ponkan fruit is cultivated on a large scale in Brazil and it has an agronomic importance, because the fruits are widely used in nature or in a processed form as concentrated juice. Ponkan peel is a pectin-rich fruit waste whose basic composition is lignin, hemicellulose, cellulose and principally pectin, containing hydroxyl and carboxyl groups. Pavan et al. (2008) reported the ponkan peel as biosorbent to remove Pb^{2+} ions from aqueous solution in batch method at 25°C with optimal pH value of 5.0. Based on the Langmuir-type isotherms, the maximum uptake capacity of Pb^{2+} ions on ponkan peel was 112.1 mg/g. The authors show that ponkan peel is a good biosorbent for removing Pb^{2+} ions from aqueous solution and does not need any chemical or physical pretreatment.

Mango peel waste as a new sorbent for the removal of Cd^{2+} and Pb^{2+} ions from aqueous solution was evaluated by Iqbal et al. (2009). The maximum sorption capacity of Cd^{2+} and Pb^{2+} ions was found to be 68.92 and 99.05 mg/g, respectively. The kinetics of sorption of both metals was reached at equilibrium in 60 min. Sorption kinetics and equilibria followed pseudo-second-order and Langmuir adsorption isotherm models. The authors stated that carboxyl and hydroxyl functional groups were mainly responsible for the sorption of Cd^{2+} and Pb^{2+} ions. Chemical modification of mango peel waste for the blocking of carboxyl and hydroxyl groups showed that 72.46 and 76.26% removal of Cd^{2+} and Pb^{2+} ions, respectively, was due to the involvement of carboxylic group, whereas 26.64% and 23.74% was due to the hydroxyl group.

Seeds

Biosorption potential of *Prosopis juliflora* seed powder for Pb^{2+} ions from aqueous solution was investigated by Jayaram and Prasad (2009) in batch experiments. The maximum uptake of metal ions was obtained at pH 6.0. Adsorption equilibrium was established at 360 min. The pseudo-second-order kinetic model provided the best correlation. The maximum uptake of Pb^{2+} ions was found to be 40.322 mg/g. The isotherm data of Pb^{2+} ions biosorption are more significantly fitted to Langmuir model. The adsorption process was spontaneous and exothermic in nature.

An adsorption method using *Capsicum annuum* seeds as adsorbent for the removal of Pb^{2+} ions from aqueous solutions in a batch system was developed by Özcan et al. (2007). The authors showed that mechanism involved in adsorption of Pb^{2+} ions by seeds of *C. annuum* was mainly attributed to Pb^{2+} binding of amino and hydroxyl groups. The maximum adsorption capacity was 1.87×10^{-4} mol/g with adsorption equilibrium of 40 min. The reaction rate was better described by pseudo-second-order kinetic model.

Coffee

Lignocellulosic materials are good precursors for the production of activated carbon. The coffee residue has been used by Boudrahem et al. (2009) as raw material in the preparation of powder activated carbon using the method of chemical activation with $ZnCl_2$ for the sorption of Pb^{2+} from dilute aqueous solutions. The optimum experimental condition for preparing predominantly microporous activated carbons with high pore surface area (890 m^2/g) and micropore volume (0.772 cm^3/g) is an impregnation ratio of 100%. Thus, 75% represents the optimal impregnation ratio. The maximum uptake of Pb^{2+} at 25°C was about 63 mg/g at the pH of 5.8 and initial Pb^{2+} concentration of 10 mg/L.

Stones

The use of peach and apricot stones as adsorbents for the removal of Pb^{2+} ions from aqueous solution was presented by Rashed (2006). The results revealed that adsorption of Pb^{2+} ions onto peach stone was stronger than onto apricot stone up to 4% at 5 h adsorption times. Suitable equilibrium time for the adsorption was 3–5 h. Pb^{2+} adsorption percentages for apricot and peach were 95 and 97.64%, respectively. The maximum uptakes of Pb^{2+} apricot and peach stones were about 1.31 and 2.33 mg/kg, respectively.

Martín-Lara et al. (2009) reported three different olive oil wastes for Pb^{2+} biosorption removal from aqueous solutions: olive stone, the two-phase olive mill solid and olive tree pruning. The maximum uptake of Pb^{2+} on olive oil wastes was about 1.10×10^{-4} mol/g. The authors stated that carboxylic group is the main active site present in these olive oil wastes and constitutes the highest percentage of titratable sites (>50%).

Black gram

The removal of heavy metals (Pb^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}) when present singly or in binary and ternary systems using agrowaste of *Cicer arietinum* (chickpea var. black gram) as the biosorbent from aqueous solutions was developed by Saeed et al. (2005). Biosorption equilibrium was established within 30 min. The maximum amount of heavy metals adsorbed at equilibrium was 49.97, 39.99, 33.81, 5.73 and 19.56 mg/g for Pb^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+} and Ni^{2+}, respectively.

Rose petals

The removal of Pb^{2+} and Zn^{2+} from aqueous solutions was studied by Nasir et al. (2007) using chemically modified distillation sludge of rose (*Rosa centifolia*) petals by pretreatment with NaOH, $Ca(OH)_2$, $Al(OH)_3$, C_6H_6, C_6H_5CHO and $HgCl_2$. NaOH pretreated biomass showed remarkable increase in sorption capacity. Maximum adsorption of both metal ions was observed at the pH of 5. Maximum adsorption capacity of biomass tends to be in the order Pb^{2+} (87.74 mg/g) >Zn^{2+} (73.8 mg/g) by NaOH pretreated biomass.

Corncobs

Corncobs biomass as an adsorbent to remove Pb^{2+} from aqueous solution under different conditions, including solution pH, contact time and metal concentration was investigated by Tana et al. (2010). Ground corncobs were modified with CH_3OH and NaOH to investigate the effect of chemical modification on Pb^{2+} binding capacity. The maximum Pb^{2+} binding capacity calculated from Langmuir isotherm was 0.0783 mmol/g. After base hydrolysis of the biomass, Pb^{2+} binding capacity increased from 0.0783 to 0.2095 mmol/g (about 43.4 mg/g). However, Pb^{2+} binding capacity on the esterified corncobs decreased greatly from 0.0783 to 0.0381 mmol/g. The authors showed that hydroxyl and carboxylic groups on the biomass play an important role in Pb^{2+} binding process.

Kapok (*Ceiba pentandra*) hulls

The ability of low-cost activated carbon prepared from *C. pentandra* hulls for the removal of Pb^{2+} and Zn^{2+} from aqueous solutions has been investigated by Rao et al. (2008) in the batch tests, including solution pH, contact time, adsorbent dose and initial metal ion concentration. Maximum removals of Pb^{2+} and Zn^{2+} with 10 g/L of sorbent at 50 mg/L sorbate concentration were 99.5 and 99.1% at the pH of 6.0, respectively. Removals of about 60–70% occurred in 10 min, and equilibrium was attained at around 50 min for both metals. The functional groups (–CO, –SO, –OH) present on the carbon surface were responsible for the adsorption of metal ions. The adsorption capacities for Pb^{2+} and Zn^{2+} were 25.5 and 24.1 mg/g, respectively. Maximum desorption of 85% for Pb^{2+} and 78% for Zn^{2+} were attained with 0.15 M HCl.

Mistletoe (*Viscum album* L.)

The removal efficiency of *V. album* L. from Pb^{2+} containing aqueous solutions was investigated by Erentürk and Malkoç (2007) using a batch adsorption technique. The optimum pH for Pb^{2+} ions adsorption was found as 3.0 with maximum adsorption percentage of 92.2% and adsorbent of 0.5 g/L. The monolayer saturation capacity is 769.23 mg/g at 25°C. The adsorption process was found to be endothermic and spontaneous.

Plants *Myriophyllum spicatum* and *Ceratophyllum demersum*

Keskinkan et al. (2007) reported the comparison of the adsorption properties of two aquatic plants *M. spicatum* and *C. demersum* for Pb^{2+}, Zn^{2+} and Cu^{2+} with batch studies conformed well to the Langmuir Model. The maximum adsorption capacities achieved with *M. spicatum* were 10.37 mg/g for Cu^{2+} and 15.59 mg/g for Zn^{2+} as well as 46.49 mg/g for Pb^{2+}, and with *C. demersum* they were 6.17 mg/g for Cu $^{2+}$, 13.98 mg/g for Zn^{2+} and 44.8 mg/g g for Pb^{2+}. It was found that *M. spicatum* has a better adsorption capacity than *C. demersum* for each metal tested.

Acorn waste

Acorn shell is an agriculture waste as a no-cost and profoundly accessible potential adsorbent (Saka et al. 2012). Örnek et al. (2007) reported the adsorption of Pb^{2+} onto formaldehyde or sulfuric acid-treated acorn waste using a batch sorber. The optimum pH for Pb^{2+} ions adsorption was found as 5.0. Maximum Pb^{2+} ions adsorption percentages for formaldehyde-treated acorn waste and sulfuric acid-treated acorn waste with 1 g/100 mL of the adsorbent were 93.1 and 96.8%. The authors show that the pseudo-second-order equation provides the best correlation for the adsorption process.

Dehn

Powdered activated carbon prepared from *Eucalyptus camaldulensis* Dehn. bark for the adsorption of Cu^{2+} and Pb^{2+} was developed by Patnukao et al. (2008). The best adsorption of Cu^{2+} and Pb^{2+} occurred at the pH of 5 where the adsorption reached equilibrium within 45 min for the whole range of initial heavy metal concentrations (0.1–10 mmol/L). The maximum adsorption capacities for Cu^{2+} and Pb^{2+} at 60°C were 0.85 and 0.89 mmol/g, respectively. Nature of the adsorption was endothermic.

Condensed tannin

Zhana and Zhao (2003) suggested an adsorption method for removing Pb^{2+} from wastewater on a new adsorbent synthesized from natural condensed tannin using a series of batch adsorption experiments. The Pb^{2+} removal efficiency was up to 71, 87 and 91% with initial solution pH at 3.0, 3.6 and 4.2, respectively. The maximum adsorption capacity of Pb^{2+} was 57.5, 76.9 and 114.9 mg/g, respectively.

Beech and poplar woods

Adsorptions of toxic metal ions Pb^{2+} and Cd^{2+} onto modified lignin from beech and poplar woods by alkali glycerol delignification were presented by Demirbaş (2004). The maximum adsorption capacities are 8.2–9.0 and 6.7–7.5 mg/g of the modified lignin for Pb^{2+} and Cd^{2+} at the pH of 5, respectively. The maximum adsorption percentage is 95.8 for Pb^{2+} for 4 h at 330 K using 10 g of adsorbent.

Olive cake

Olive cake is a waste of olive factory and usually used for heating, and as fertilizer and feeding material. Its structure contains organic compounds like lignocellulosic material, polyphenols and also amino acid, protein, oil and tannins. Doyurum and Celik (2006) investigated the removal of heavy metals from wastewater using olive cake as an adsorbent in batch method. The optimum sorption conditions were determined for two elements. The maximum adsorption capacities are 18.14 mg/g (80.62%) and 9.05 mg/g (45.25%) of the olive cake for Pb^{2+} and Cd^{2+}, respectively. Maximum desorption of the Pb^{2+} and Cd^{2+} ions were found to be 95.92 and 53.97% by 0.5 M HNO_3 and 0.2 M HCl, respectively.

Sugarcane bagasse

Karnitz et al. (2007) showed the preparation of new chelating materials derived from sugarcane bagasse for the adsorption of heavy metal ions in aqueous solution. The first part of this report deals with the chemical modification of sugarcane bagasse with succinic anhydride. The carboxylic acid functions introduced into the material were used to anchor polyamines. The second part of this report features the comparative evaluation of the adsorption capacity of the modified sugarcane bagasse materials for Cu^{2+}, Cd^{2+} and Pb^{2+} ions in aqueous single metal solution by classical titration. The maximum adsorption capacity is 189 mg/g for Pb^{2+}.

Bamboo charcoal

Bamboo charcoal has application in food, pharmaceutical and chemical industries. Lalhruaitluanga et al. (2010) prepared the activated charcoal from *Melocanna baccifera* charcoal with chemical pretreatment in batch experiments. The optimum conditions for Pb^{2+} biosorption are pH of 5.0, contact time 120 min and adsorption capacity 10.66 mg/g (raw charcoal) and 53.76 mg/g (activated charcoal). The authors showed that –OH, C–H bending, –C=O stretching vibration and –C=O functional groups were mainly responsible for Pb^{2+} biosorption. Chemical activation was carried out using H_3PO_4 and KOH at various concentrations.

Lawny grass

Lawny grass is a familiar and abundant waste during the process of city beautifying or garden building. Lawny grass principally contains protein, crude fiber, amylum, polysaccharides, pectin, chlorophyll, etc. Removal of Pb^{2+} ions from aqueous solution using the modified lawny grass was examined by Lu et al. (2009). The optimum pH is in the range of 5.0–5.8 for all adsorbents. The sorption system follows pseudo-second-order kinetic model and equilibrium time is obtained after 60 min. The maximum adsorption capacities obtained from Langmuir–Freundlich model are 1.55 and 1.26 mol/kg by using one lawny grass modified by 1 and 0.6 mol/L citric acid, respectively.

Tree fern

The sorption of Pb^{2+} ions from water onto tree fern was examined by Ho (2005) as a function of pH using an agitated and baffled system. Application of the pseudo-second-order kinetics model produced very high coefficients of determination. The optimum pH for Pb^{2+} ions removal was between 4 and 7. Ion exchange occurred in the initial reaction period. The maximum adsorption capacities are 38.1 mg/g for Pb^{2+}.

Onion skins

Onion skins are a new adsorbent. Adsorption applications of onion skins have been carried out by various assays (Saka et al. 2011a, b; Saka and Şahin 2011). Saka et al. (2011b) reported the adsorption characteristics of Pb^{2+} ions prepared from preboiled and formaldehyde-treated onion skins were evaluated. The point of zero net charge was 6.53. The optimum pH for the maximum removal of Pb^{2+} ions was 6.0. The maximum amounts of Pb^{2+} ions adsorbed, as evaluated by Langmuir isotherm, was 200 mg/g. With increasing pH, the adsorption of Pb^{2+} ions was increased and maximum removal was 93.6% at 50 mg/L. This study concluded that onion skins, a waste material, have good potential as an adsorbent to remove toxic metals like Pb^{2+} ions from wastewater.

The other agricultural and forest-based adsorbents used for the removal of Pb^{2+} ions are shown in Table 1 (Abdel-Ghani et al. 2007, 2008; Abdel-Ghani and Elchaghaby 2007; Abdel-Halim et al. 2003; Ahluwalıa and Goyal 2005; Benhimaa et al. 2008; Chamarthy et al. 2001; Dahiya et al. 2008; El-Ashtoukhya et al. 2008; Feng et al. 2004; Fıol et al. 2006; Ghaffar 2008; Goel et al. 2005; Gong et al. 2005; Gueu et al. 2007; Han et al. 2005; Hanafiah et al. 2006; Hashem 2007; Ho and Ofomaja 2006; Ho 2005; Ilhan et al. 2004; Imamoglu and Tekir 2008; Iyagba and Opete 2009; Kannan and Thambidurai 2007; Kannan and Veemaraj 2009; Kim et al. 2006; Kiran and Akar 2005; Krishnan et al. 2003; Liao et al. 2010; Lugo-Lugo et al. 2009; Martınez et al. 2006; Meunier et al. 2003; Naddafi et al. 2007; Özdemir et al. 2004; Qaiser et al. 2009; Quek et al. 1998; Sarı and Tuzen 2008; Sekar et al. 2004; Shukla and Roshan 2005; Taty-Costodes et al. 2003; Kadirvelu et al. 2001; Ulmanu et al. 2008; Utomo and Hunter 2006; Vaghetti et al. 2009; Vieira et al. 2007; Woolard et al. 2000; Yetilmezsoy and Demirel 2008; Yin et al. 2008; Yu et al. 2001; Zhang and Banks 2006; Zulkali et al. 2006).

Discussion

The objective of this review is to contribute in the search for less expensive adsorbents and their utilization possibilities for various agricultural waste by-products, such as wood leaves, stones of fruits, husks, hulls, seeds, shells, etc. for the elimination of the Pb^{2+} ions from wastewater. As presented at Table 1, various agricultural adsorbents have been reported to show high removal efficiency for Pb^{2+} ions The review indicate that use of commercially available activated carbon for the removal of the Pb^{2+} ions can be replaced by the utilization of inexpensive, effective and readily available agricultural by-products as adsorbents. Thus, the sources of agro-based inexpensive adsorbents were explored and their feasibility for the removal of the Pb^{2+} ions should be studied in detail. The main experimental parameters to evaluate the adsorption behavior are metal binding capacities, metal removal performances, sorbent dose, optimum pH, temperature, initial concentration, contact time, etc. However, sorption efficiency for the removal of Pb^{2+} ions is highest only at pH values higher than 7 due to the formation of insoluble hydroxide. The pHzpc plays an important role in the adsorption process. The nature and concentration of the carbon surface can be modified by changing the pH of the carbon-solution system. The time data is generally fitted to pseudo-first-order and pseudo-second-order kinetics. Various isothermic models such as Langmuir, Freundlich and Temkin have been used. The sorption capacity is dependent on the type of the adsorbent investigated and the nature of the wastewater treated (Khan et al. 2004). More studies on the carbon for the removal of the Pb^{2+} ions should be carried out to better understand the process of low-cost adsorption and to demonstrate the technology effectively.

Conclusion

Several treatment processes have been developed over the years to remove the lead dissolved in wastewaters. However, most of these techniques have some disadvantages, such as complicated treatment process, high cost and energy consumption. Adsorption of heavy metals from aqueous solutions is a relatively new process that has proven very promising in the removal of contaminants from wastewaters. The most popular adsorbent for the adsorption process is activated carbon, but it is very expensive and there is a need for its regeneration after each adsorption experiment. Adsorbent materials derived from low-cost agricultural wastes can be used for the effective removal and recovery of lead ions from wastewater. Cost is an important parameter for comparing the sorbent materials. The expense of individual sorbents varies depending on the degree of processing required and local availability. The effectiveness of the adsorption depends not only on the properties of the adsorbent, but also on various parameters (pH, temperature, initial concentration, contact time, particle size of adsorbent, etc.) used for the adsorption process. These parameters should also be taken into account while examining the potential of low-cost adsorbents.

This review shows that agricultural waste adsorbents have equal or greater adsorption capacities than activated carbon. Some of the adsorbents with uptake sorption capacities (>90 mg/g) are: citrus peels, cocoa shells, leaf powder *A. indica* (neem), leaves peepul, leaves, *Casuarina glauca* tree, maize bran, mango peel waste, orange peel, palm shell, onion skins, ponkan peel, rice husk ash, rose petals, seaweed *Ascophyllum nodosum*, *Senecio anteuphorbium*, sugarcane bagasse, valonia tannin resin, *V. album* leaves and wheat bran.

It has also been recommended that additional studies are required to predict the performance of the adsorption processes for the removal of Pb^{2+} ions from wastewater.

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