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Review

Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review

W.S. Wan Ngah *, M.A.K.M. Hanafiah

School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia

Abstract

The application of low-cost adsorbents obtained from plant wastes as a replacement for costly conventional methods of removing heavy metal ions from wastewater has been reviewed. It is well known that cellulosic waste materials can be obtained and employed as cheap adsorbents and their performance to remove heavy metal ions can be affected upon chemical treatment. In general, chemically modified plant wastes exhibit higher adsorption capacities than unmodified forms. Numerous chemicals have been used for modifications which include mineral and organic acids, bases, oxidizing agent, organic compounds, etc. In this review, an extensive list of plant wastes as adsorbents including rice husks, spent grain, sawdust, sugarcane bagasse, fruit wastes, weeds and others has been compiled. Some of the treated adsorbents show good adsorption capacities for Cd, Cu, Pb, Zn and Ni.
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1. Introduction

Heavy metals have been excessively released into the environment due to rapid industrialization and have created a major global concern. Cadmium, zinc, copper, nickel, lead, mercury and chromium are often detected in industrial wastewaters, which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries, etc., (Kadirvelu et al., 2001a; Williams et al., 1998). Unlike organic wastes, heavy metals are non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders; therefore they must be removed before discharge. Research interest into the production of cheaper adsorbents to replace costly wastewater treatment methods such as chemical precipitation, ion-exchange, electroflotation, membrane separation, reverse osmosis, electrodialysis, solvent extraction, etc. (Namasivayam and

Ranganathan, 1995) are attracting attention of scientists. Adsorption is one the physico-chemical treatment processes found to be effective in removing heavy metals from aqueous solutions. According to Bailey et al. (1999), an adsorbent can be considered as cheap or low-cost if it is abundant in nature, requires little processing and is a by-product of waste material from waste industry. Plant wastes are inexpensive as they have no or very low economic value. Most of the adsorption studies have been focused on untreated plant wastes such as papaya wood (Saeed et al., 2005), maize leaf (Babarinde et al., 2006), teak leaf powder (King et al., 2006), lalang (*Imperata cylindrica*) leaf powder (Hanafiah et al., 2007), rubber (*Hevea brasiliensis*) leaf powder (Hanafiah et al., 2006b,c), *Coriandrum sativum* (Karunasagar et al., 2005), peanut hull pellets (Johnson et al., 2002), sago waste (Quek et al., 1998), saltbush (*Atriplex canescens*) leaves (Sawalha et al., 2007a,b), tree fern (Ho and Wang, 2004; Ho et al., 2004; Ho, 2003), rice husk ash and neem bark (Bhattacharya et al., 2006), grape stalk wastes (Villaescusa et al., 2004), etc. Some of the advantages of using plant wastes for wastewater treatment include simple technique, requires little pro-

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* Corresponding author. Tel.: +604 6533888; fax: +604 6574854.
  E-mail address: wsaime@usm.my (W.S. Wan Ngah).

cessing, good adsorption capacity, selective adsorption of heavy metal ions, low cost, free availability and easy regeneration. However, the application of untreated plant wastes as adsorbents can also bring several problems such as low adsorption capacity, high chemical oxygen demand (COD) and biological chemical demand (BOD) as well as total organic carbon (TOC) due to release of soluble organic compounds contained in the plant materials (Gaballah et al., 1997; Nakajima and Sakaguchi, 1990). The increase of the COD, BOD and TOC can cause depletion of oxygen content in water and can threaten the aquatic life. Therefore, plant wastes need to be modified or treated before being applied for the decontamination of heavy metals. In this review, an extensive list of adsorbents obtained from plant wastes has been compiled and their methods of modification were discussed. A comparison of adsorption efficiency between chemically modified and unmodified adsorbents was also reported.

2. Chemically modified plant wastes

Pretreatment of plant wastes can extract soluble organic compounds and enhance chelating efficiency (Gaballah et al., 1997). Pretreatment methods using different kinds of modifying agents such as base solutions (sodium hydroxide, calcium hydroxide, sodium carbonate) mineral and organic acid solutions (hydrochloric acid, nitric acid, sulfuric acid, tartaric acid, citric acid, thioglycollic acid), organic compounds (ethylenediamine, formaldehyde, epichlorohydrin, methanol), oxidizing agent (hydrogen peroxide), dye (Reactive Orange 13), etc. for the purpose of removing soluble organic compounds, eliminating colouration of the aqueous solutions and increasing efficiency of metal adsorption have been performed by many researchers (Hanafiah et al., 2006a; Reddy et al., 1997; Taty-Costodes et al., 2003; Gupta et al., 2003; Namasivayam and Kadirvelu, 1997; Šćiban et al., 2006a; Min et al., 2004; Kumar and Bandyopadhyay, 2006; Baral et al., 2006; Acar and Eren, 2006; Rehman et al., 2006; Abia et al., 2006; Shukla and Pai, 2005a, Low et al., 1995; Azab and Peterson, 1989; Lazlo, 1987; Wankasi et al., 2006). The types of chemicals used for modifying plant wastes and their maximum adsorption capacities are shown in Table 1.

2.1. Rice husks/rice hulls

Rice husk consists of cellulose (32.24%), hemicellulose (21.34%), lignin (21.44%) and mineral ash (15.05%) (Rahman et al., 1997) as well as high percentage of silica in its mineral ash, which is approximately 96.34% (Rahman and Ismail, 1993). Rice husk is insoluble in water, has good chemical stability, has high mechanical strength and possesses a granular structure, making it a good adsorbent material for treating heavy metals from wastewater. The removal of heavy metals by rice husk has been extensively reviewed by Chuah et al. (2005). Among the heavy metal ions studied include Cd, Pb, Zn, Cu, Co, Ni and Au.

Rice husk can be used to treat heavy metals in the form of either untreated or modified using different modification methods.

Hydrochloric acid (Kumar and Bandyopadhyay, 2006), sodium hydroxide (Guo et al., 2003; Kumar and Bandyopadhyay, 2006), sodium carbonate (Kumar and Bandyopadhyay, 2006), epichlorohydrin (Kumar and Bandyopadhyay, 2006), and tartaric acid (Wong et al., 2003a; Wong et al., 2003b) are commonly used in the chemical treatment of rice husk. Pretreatment of rice husks can remove lignin, hemicellulose, reduce cellulose crystallinity and increase the porosity or surface area. In general, chemically modified or treated rice husk exhibited higher adsorption capacities on heavy metal ions than unmodified rice husk. For example, Kumar and Bandyopadhyay (2006) reported that rice husk treated with sodium hydroxide, sodium carbonate and epichlorohydrin enhanced the adsorption capacity of cadmium. The base treatment using NaOH for instance appeared to remove base soluble materials on the rice husk surface that might interfere with its adsorption property. Tarley et al. (2004) found that adsorption of Cd increase by almost double when rice husk was treated with NaOH. The reported adsorption capacities of Cd were 7 and 4 mg g^{-1} for NaOH treated and unmodified rice husk, respectively.

Meanwhile, most of the acids used for treatment of plant wastes were in dilute form such as sulfuric acid, hydrochloric acid and nitric acid. According to Esteghlalian et al. (1997), dilute acid pretreatment using sulfuric acid can achieve high reaction rates and improve cellulose hydrolysis. Concentrated acids are powerful agents for cellulose hydrolysis but they are toxic, corrosive and must be recovered (Sivers and Zacchi, 1995). However, in some cases, hydrochloric acid treated rice husk showed lower adsorption capacity of cadmium than the untreated rice husk (Kumar and Bandyopadhyay, 2006). When rice husk is treated with hydrochloric acid, adsorption sites on the surface of rice husk will be protonated, leaving the heavy metal ions in the aqueous phase rather than being adsorbed on the adsorbent surface. Wong et al. (2003a) carried out an adsorption study of copper and lead on modified rice husk by various kinds of carboxylic acids (citric acid, salicylic acid, tartaric acid, oxalic acid, mandelic acid, malic and nitrilotriacetic acid) and it was reported that the highest adsorption capacity was achieved by tartaric acid modified rice husk. Esterified tartaric acid modified rice husk however significantly reduced the uptake of Cu and Pb. The maximum adsorption capacities for Pb and Cu were reported as 108 and 29 mg g^{-1}, respectively. Effect of chelators on the uptake of Pb by tartaric acid modified rice husk was also studied. It was reported that higher molar ratios of chelators such as nitrilotriacetic acid (NTA) and ethylenediamine tetraacetic acid (EDTA) caused significant suppressing effect on the uptake of Pb. Dyestuff treated rice hulls using Procion red and Procion yellow for the removal of Cr(VI), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II) were studied by Suemitsu et al. (1986). More than 80% of

Table 1
Summary of modified plant wastes as adsorbents for the removal of heavy metal ions from aqueous solution

Adsorbent	Modifying agent(s)	Heavy metal	Q_{max} (mg g^{-1})	Source
Rice husk	Water washed	Cd(II)	8.58	Kumar and Bandyopadhyay (2006)
	Sodium hydroxide		20.24	
	Sodium bicarbonate		16.18	
	Epichlorohydrin		11.12	
Rice husk	Tartaric acid	Cu(II)	31.85	Wong et al. (2003b)
		Pb(II)	120.48	
Sawdust (cedrus deodar wood)	Sodium hydroxide	Cd(II)	73.62	Memon et al. (2007)
Sawdust (S. robusta)	Formaldehyde	Cr(VI)	3.6	Baral et al. (2006)
Sawdust (Poplar tree)	Sulfuric acid	Cu(II)	13.95	Acar and Eren (2006)
Sawdust (Dalbergia sissoo)	Sodium hydroxide	Ni(II)	10.47	Rehman et al. (2006)
Sawdust (Poplar tree)	Sodium hydroxide	Cu(II)	6.92	Šćiban et al. (2006a)
		Zn(II)	15.8	
Sawdust (Fir tree)		Cu(II)	12.7	
		Zn(II)	13.4	
Sawdust (Oak tree)	Hydrochloric acid	Cu(II)	3.60	Argun et al. (2007)
		Ni(II)	3.37	
		Cr(VI)	1.74	
Sawdust (Pinus sylvestris)	Formaldehyde in Sulfuric acid	Pb(II)	9.78	Taty-Costodes et al. (2003)
		Cd(II)	9.29	
Walnut sawdust	Formaldehyde in sulfuric acid	Cd(II)	4.51	Bulut and Tez (2003)
		Ni(II)	6.43	
		Pb(II)	4.48	
Sawdust	Reactive Orange 13	Cu(II)	8.07	Shukla and Pai (2005b)
		Ni(II)	9.87	
		Zn(II)	17.09	
Peanut husk	Sulfuric acid	Pb(II)	29.14	Li et al. (2006a)
		Cr(III)	7.67	
		Cu(II)	10.15	
Groundnut husk	Sulfuric acid followed by silver impregnation	Cr(VI)	11.4	Dubey and Gopal (2006)
Cassava waste	Thioglycollic acid	Cd(II)	NA	Abia et al. (2006)
Cassava tuber bark waste	Thioglycollic acid	Cd(II)	26.3	Horsfall Jr. et al. (2006)
		Cu(II)	90.9	
		Zn(II)	83.3	
Wheat bran	Sulfuric acid	Cu(II)	51.5	Özer et al. (2004)
Wheat bran	Sulfuric acid	Cd(II)	101	Özer and Pirinçci (2006)
Juniper fibre	Sodium hydroxide	Cd(II)	29.54	Min et al. (2004)
Indian barks	Hydrochloric acid	Cu(II)		Reddy et al. (1997)
– sal			51.4	
– mango			42.6	
– jackfruit			17.4	
Jute fibres	Reactive Orange 13	Cu(II)	8.40	Shukla and Pai (2005a)
		Ni(II)	5.26	
		Zn(II)	5.95	
	Hydrogen peroxide	Cu(II)	7.73	
		Ni(II)	5.57	
		Zn(II)	8.02	
	Unmodified	Cu(II)	4.23	
		Ni(II)	3.37	
		Zn(II)	3.55	
Banana pith	Nitric acid	Cu(II)	13.46	Low et al. (1995)
Banana stem	Formaldehyde	Pb(II)	91.74	Noeline et al. (2005)
Spent grain	Hydrochloric acid	Cd(II)	17.3	Low et al. (2000)
	Sodium hydroxide	Pb(II)	35.5	

Table 1 (*continued*)

Adsorbent	Modifying agent(s)	Heavy metal	Q_{max} (mg g^{-1})	Source
Cork powder	Calcium chloride	Cu(II)	15.6	Chubar et al. (2004)
	Sodium chloride		19.5	
	Sodium hydroxide		18.8	
	Sodium hypochlorite		18.0	
	Sodium iodate		19.0	
Corncorb	Nitric acid	Cd(II)	19.3	Leyva-Ramos et al. (2005)
	Citric acid		55.2	
Imperata cylindrica leaf powder	Sodium hydroxide	Pb(II)	13.50	Hanafiah et al. (2006a)
Alfalfa biomass	Sodium hydroxide	Pb(II)	89.2	Tiemann et al. (2002)
Azolla filiculoides (aquatic fern)	Hydrogen peroxide–Magnesium chloride	Pb(II)	228	Ganji et al. (2005)
		Cd(II)	86	
		Cu(II)	62	
		Zn(II)	48	
Carrot residues	Hydrochloric acid	Cr(III)	45.09	Nasernejad et al. (2005)
		Cu(II)	32.74	
		Zn(II)	29.61	
Sugarcane bagasse	Sodium bicarbonate	Cu(II)	114	Junior et al. (2006)
		Pb(II)	196	
		Cd(II)	189	
	Ethylenediamine	Cu(II)	139	
		Pb(II)	164	
		Cd(II)	189	
	Triethylenetetramine	Cu(II)	133	
		Pb(II)	313	
		Cd(II)	313	
Sugarbeet pulp	Hydrochloric acid	Cu(II)	0.15	Pehlivan et al. (2006)
		Zn(II)	0.18	
Bagasse fly ash	Hydrogen peroxide	Pb(II)	2.50	Gupta and Ali (2004)
		Cr(III)	4.35	
Nipah palm shoot biomass	Mercaptoacetic acid	Pb(II)	52.86	Wankasi et al. (2006)
		Cu(II)	66.71	
Groundnut shells	Reactive Orange 13	Cu(II)	7.60	Shukla and Pai (2005b)
		Ni(II)	7.49	
		Zn(II)	9.57	
Terminalia arjuna nuts	ZnCl$_2$	Cr(VI)	28.43	Mohanty et al. (2005)
Coirpith	ZnCl$_2$	Cr(VI)	NA	Namasivayam and Sangeetha (2006)
		Ni(II)		
		Hg(II)		
		Cd(II)		Kula et al. (2007)
	Sulfuric acid and ammonium persulphate	Hg(II)	154	Namasivayam and Kadirvelu (1999)
		Cu(II)	39.7	Namasivayam and Kadirvelu (1997)
		Hg(II)	NA	Kadirvelu et al. (2001a)
		Pb(II)		
		Cd(II)		
		Ni(II)		
		Cu(II)		
		Ni(II)	62.5	Kadirvelu et al. (2001b)

NA – not available.

Cd(II), Pb(II) and Hg(II) ions were able to be removed by the two types of treated adsorbents, while Cr(VI) recorded the lowest percentage removal (<40%).

2.2. Spent grain

Spent grain obtained from brewery can be used to treat Pb(II) and Cd(II) ions as demonstrated by Low et al., 2000.

Treatment of spent grain with NaOH greatly enhanced adsorption of Cd(II) and Pb(II) ions, whereas HCl treated spent grain showed lower adsorption than the untreated spent grain. The increase in adsorption of heavy metal ions after base treatment could be explained by the increase in the amount of galactouronic acid groups after hydrolysis of *O*-methyl ester groups. The best pH range for metal adsorption was 4–6. Kinetic study reveals that the equilib-

rium time of adsorption was 120 min for both metal ions and adsorption followed pseudo-second-order model. The maximum adsorption capacity for lead was two times higher than cadmium. The effect of organic ligands (EDTA, nitrilotriacetic acid and salicylic acid) on adsorption efficiency was assessed and adsorption was greatly reduced by EDTA and nitrilotriacetic acid at molar ratio of 1:1 (metal:ligand). EDTA and nitrilotriacetic acid could chelate the heavy metal ions, therefore more metal ions would remain in the solutions rather than being adsorbed (Jeon and Park, 2005). Salicylic acid on the other hand slightly reduced the percentage of cadmium adsorption but did not affect adsorption of lead.

2.3. Sugarcane bagasse/fly ash

Junior et al. (2006) reported the use of succinic anhydride modified sugarcane bagasse for treatment of Cu, Cd and Pb from aqueous solutions. Sugarcane bagasse consists of cellulose (50%), polyoses (27%) and lignin (23%). The presence of these three biological polymers causes sugarcane bagasse rich in hydroxyl and phenolic groups and these groups can be modified chemically to produce adsorbent materials with new properties. The authors reported that the hydroxyl groups in sugarcane bagasse could be converted to carboxylic groups by using succinic anhydride. The carboxylic groups were later reacted with three different chemicals mainly $NaHCO_3$, ethylenediamine and triethylenetetramine to produce new properties of adsorbent materials which showed different adsorption capacities for metal ions. It was found that sugarcane bagasse treated with ethylenediamine and triethylenetetramine shows a remarkable increase in nitrogen content compared to untreated sample, and triethylenetetramine modified sugarcane bagasse has a higher increasing extent. The presence of amide group was also detected in ethylenediamine and triethylenetetramine modified sugarcane bagasses as a result of the reaction between –COOH and –NH_2 groups. Kinetic studies showed that equilibrium time for adsorption of Cu, Cd and Pb onto tethylenediamine and triethylenetetramine modified sugarcane bagasses were slower than that for adsorbent modified with $NaHCO_3$. Triethylenetetramine modified sugarcane bagasse was the best adsorbent material for removal of Cd and Pb since the adsorption capacities for both metals are two times higher than unmodified sugarcane bagasse. This was probably caused by the higher number of nucleophilic sites introduced in triethylenetetramine modified sugarcane bagasse. When sugarcane bagasse was modified with methanol, however, the resulting adsorbent did not show a good uptake of cadmium as the maximum adsorption capacity was 6.79 mg g^{-1} (Ibrahim et al., 2006).

The performance of hydrogen peroxide treated bagasse fly ash, a solid waste of sugar industry for removal of lead and chromium was explored by Gupta and Ali (2004). Hydrogen peroxide is a good oxidizing agent and used to remove the adhering organic matter on the adsorbent. It was found that hydrogen peroxide treated bagasse fly ash was able to remove chromium in a shorter period of time (60 min) compared to lead (80 min). The isotherm study also revealed maximum adsorption capacity for chromium was higher than lead. However, the recorded values of maximum adsorption capacities for both metals were low (2.50 and 4.35 mg g^{-1} for Pb and Cr, respectively). The detail mechanism of adsorption by the treated bagasse fly ash was not discussed, but it was thought that adsorption was controlled by film diffusion at lower metal concentration and particle diffusion at higher concentration of metal ions.

2.4. Sawdust

Sawdust, obtained from wood industry is an abundant by-product which is easily available in the countryside at negligible price. It contains various organic compounds (lignin, cellulose and hemicellulose) with polyphenolic groups that could bind heavy metal ions through different mechanisms. An experiment on the efficiency of sawdust in the removal of Cu^{2+} and Zn^{2+} ions was conducted by Šćiban et al. (2006a). Two kinds of sawdust, poplar and fir wood were treated with NaOH (fibre-swelling agent) and Na_2CO_3 solutions and the adsorption capacities were compared with the untreated sawdusts. For unmodified sawdust, both types of woods showed higher uptakes of Cu^{2+} ions than Zn^{2+} ions, and adsorption followed Langmuir isotherm model. Equivalent amounts of adsorption capacities were recorded by both types of sawdust for Zn^{2+} and Cu^{2+} ions, although these two adsorbents have different anatomical structure and chemical composition. After treating with NaOH, a marked increase in adsorption capacity was observed for both heavy metal ions, especially for Zn^{2+} ions (2.5 times for Cu^{2+} and 15 times for Zn^{2+}). The adsorption capacities shown by Langmuir model were 6.92 mg g^{-1} (poplar sawdust) and 12.70 mg g^{-1} (fir sawdust) for Cu^{2+}, and 15.83 mg g^{-1} (poplar sawdust) and 13.41 mg g^{-1} for Zn^{2+} (fir sawdust), respectively. In another experiment, Šćiban et al. (2006b) found that the leaching of coloured organic matters during the adsorption can be eliminated by pretreatments with formaldehyde in acidic medium, with sodium hydroxide solution after formaldehyde treatment, or with sodium hydroxide only. According to Šćiban et al. (2006a), NaOH improved the adsorption process by causing the liberation of new adsorption sites on the sawdust surface. An increase in the concentration of NaOH for modification purpose however did not cause a significant increase of the adsorption capacity. The authors suggest that no greater than 1% of concentration of NaOH solution should be used for modification. The temperature of modification was also not a significant factor for the main increase of adsorption capacities of modified sawdusts. It was observed that only a slight increase in Cu^{2+} and Zn^{2+} adsorption occurred when the fir sawdust was treated with NaOH at higher temperature (80 °C). The study on adsorption capacity by

treatment with Na_2CO_3 revealed the modified sawdusts had two times higher adsorption for Cu^{2+} ions and six times higher for Zn^{2+} ions compared to unmodified sawdusts. The application of Na_2CO_3 for chemical modification is less efficient than the use of NaOH. This is due to higher number of Na^+ ions in 1 g of NaOH compared to 1 g of Na_2CO_3. In general, three possible reasons for the increase in adsorption capacities of heavy metal ions were given by the authors:

(i) Changes on wood surface-increase in surface area, average pore volume and pore diameter after alkaline treatment. The surface area and average pore diameter increased about 1.5–2 times after modification.
(ii) Improvement in ion-exchange process especially with Na^+ ions.
(iii) Microprecipitation of metal hydroxides–$Cu(OH)_2$ and $Zn(OH)_2$ in the pores of sawdust.

Although the work on adsorption of copper and zinc ions onto sawdust of poplar tree was reported by Šćiban et al. (2006a), they did not carry out a detail experiment on the kinetic of adsorption.

The effect of sulfuric acid treatment on sawdust of poplar tree was studied by Acar and Eren (2006). Sulfuric acid poplar sawdust possessed good removal of 92.4% Cu^{2+} at pH 5, while untreated sawdust could only removed 47%. The kinetic of copper binding indicated that it is a rapid process and about 70–80% of copper ions removed from the solution in 10 min. The percent of copper removal however decreases as the metal concentration increases. The increase in percent of adsorption with adsorbent dose could be due to the increase in surface area and availability of more active sites. The treated poplar sawdust showed maximum adsorption capacity of 13.945 mg g^{-1} against 5.432 mg g^{-1} for untreated sawdust which followed Langmuir isotherm model. The maximum adsorption capacity for sulfuric acid treated poplar sawdust is higher than to the value recorded by NaOH treated poplar sawdust reported by Šćiban et al. (2006a). Concentrated sulfuric acid was also used to modify coconut tree sawdust for removing mercury and nickel (Kadirvelu et al., 2003). It was reported that 100% removal of mercury was achieved compared to 81% for nickel and adsorption occurred in 1 h.

Rehman et al. (2006) reported the removal of Ni^{2+} ions by using sodium hydroxide treated sawdust of *Dalbergia sissoo*, a byproduct of sawmills. The treatment of sawdust with NaOH results in the conversion of methyl esters which are the major constituents in cellulose, hemicellulose and lignin to carboxylate ligands. The adsorption time study revealed that nickel ions were removed fast in the first 20 min due to extra-cellular binding. The maximum adsorption capacity of Ni^{2+} ions was found to be 10.47 mg g^{-1} at 50 °C. Adsorption was more favourable at higher temperature and adsorption followed both Langmuir and Freundlich isotherm models.

A comparative study on the adsorption efficiency of untreated and NaOH treated sawdust of cedrus deodar wood was conducted by Memon et al. (2007). They reported that cedrus deodar sawdust mainly consists of acid detergent fibre (cellulose and lignin), hydroxyl groups (tannins) and phenolic compounds. The acidimetric–alkalimetric titration study revealed that sawdust has four major groups responsible for cadmium binding which were carboxylic, phosphoric, amines and phenolic. Cadmium removal was more favoured by NaOH treated sawdust as the value of adsorption capacity was four times greater than untreated sawdust. Maximum removal of cadmium occurred at pH above 4 for both types of adsorbents. When the pH of the solution is greater than 4, carboxylic groups will be deprotonated and the adsorbent surface will be negatively charged resulting in higher adsorption of cadmium. However; at pH less than 3, carboxylic groups become protonated and adsorption sites are unable to attract Cd^{2+} ions. NaOH treated sawdust also shows good settling property, making it easy to filter or separate the adsorbent from the solution. Ion-exchange was considered as the predominant mechanism of cadmium adsorption as the values of adsorption energy (E) determined from Dubinin–Radushkevic plots are in the range of 9–16 kJ mol^{-1}. Maximum adsorption capacity recorded at temperature of 20 °C was 73.62 mg g^{-1}.

A detail analysis on the ideal concentration of NaOH for modifying juniper fibre for adsorption of cadmium ions was carried out by Min et al. (2004). Sodium hydroxide treatment of lignocellulosic materials can cause swelling which leads to an increase in internal surface area, a decrease in the degree of polymerization, a decrease in crystallinity, separation of structural linkages between lignin and carbohydrates and disruption of the lignin structure. Sodium hydroxide is a good reagent for saponification or the conversion of an ester group to carboxylate and alcohol, as shown in the equation below:

$$RCOOR' + H_2O \overset{OH^-}{\rightarrow} RCOO^- + R'OH \qquad (1)$$
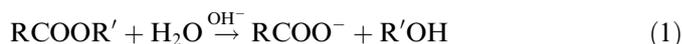
Based on the FTIR analysis, it was found that as the concentration of NaOH increases (from 0 to 1.0 M), the amount of carboxylate was also increased. A maximum concentration of 0.5 M of NaOH was suitable to carry out saponification process. After base treatment, the maximum adsorption capacity of cadmium increased by about three times (from 9.18 to 29.54 mg g^{-1}) compared to untreated juniper fibre despite a decrease in specific surface area for the treated adsorbent. Data obtained from pseudo-second-order kinetic study also revealed that base treated juniper fibre had higher values of adsorption capacity, q_e (mg g^{-1}) and initial adsorption rate constant, h (mg g^{-1} min^{-1}) when compared to untreated adsorbent.

Hexavalent chromium adsorption by formaldehyde treated sawdust was studied by Baral et al., 2006. Formaldehyde is a common compound used to immobilize colour and water soluble compounds from sawdust (Garg et al.,

2004). The adsorption capacity of Cr(VI) determined from Langmuir isotherm was low (3.60 mg g^{-1}) and equilibrium adsorption time took about 5 h. Adsorption process was strongly affected by several physico-chemical parameters such as pH, adsorbent dose, temperature and initial concentration of chromium solution. Maximum adsorption occurred at pH range 3–6 and reduced significantly beyond pH 6. The percentage adsorption of Cr(VI) increased with increase in adsorbent dose, but decreased with increase in metal concentration and temperature. Adsorption rate tends to increase with increase in adsorbent dose due to higher number of available adsorption sites. As concentration of Cr(VI) increases with fixed amount of adsorbent dose, more Cr(VI) ions will remain in the aqueous phase, thus percentage adsorption will be small. The decrease in adsorption rate with increase in temperature indicates exothermic nature of adsorption, in which adsorption is more favourable at lower temperatures.

According to Taty-Costodes et al. (2003), treatment with formaldehyde induces a stabilization of the hydrosoluble compounds of adsorbent by creating covalent bonds on the constitutive units. This could eliminate the problem associated with the release of polyphenolic compounds which could cause an increase in COD in wastewater. A research on the adsorption of Pb(II) and Cd(II) onto formaldehyde treated sawdust of *Pinus sylvestris* shows that the two metal ions were successfully removed in less than 20 min at low concentrations (<10 mg l^{-1}). It was reported that metal ions could form complexes with the oxygen atom on carbonyl and hydroxyl groups (acting as a Lewis base). The maximum adsorption capacities of Pb(II) and Cd(II) were 9.78 and 9.29 mg g^{-1}, respectively. Adsorption kinetic indicates that pseudo-second-order model was better fitted than pseudo-first-order and intraparticle diffusion is one of the rate determining steps. Nickel, cadmium and lead adsorption by walnut sawdust treated with formaldehyde in sulfuric acid was studied and it was found that adsorption is dependent on contact time, metal concentration and temperature (Bulut and Tez, 2003). Equilibrium time was established in about 60 min for all heavy metals. The kinetic study reveals that adsorption followed pseudo-second-order model better than pseudo-first-order. The maximum adsorption capacities were 6.43, 4.51 and 4.48 mg g^{-1} for Ni, Cd and Pb, respectively. Based on temperature study, adsorption was favaourable at higher temperatures as the values of $\Delta G°$ become more negative.

Chubar et al. (2004) studied the performance of various kinds of chemically treated cork powder obtained from cork oak tree for the removal of Cu, Zn and Ni. Treatment of cork powder with salts such as NaCl and CaCl$_2$ causes the conversion of active binding sites from the H$^+$ form to Na$^+$ and Ca^{2+} form. The salt modified cork powder shows greater adsorption capacity than the unmodified cork especially at higher heavy metal concentrations. It was also noted that the Na$^+$ form cork recorded a higher adsorption capacity value than the Ca^{2+} form. This observation can be explained in terms of the different charge of

cations whereby the interaction of cork powder binding sites with divalent calcium ions is stronger than the monovalent sodium ions. Hence, the biosorption reaction of copper will be hindered. Treatment of cork powder with an alkaline solution (NaOH) at high temperature increased the sorption capacity toward heavy metals by about 33%. A high concentration of NaOH however causes a decrease in copper removal due to the destruction of the biomass. Besides NaCl, CaCl$_2$ and NaOH, modification of cork powder could be carried out using commercial laundry detergent and the amount of copper removed was found to increase, probably due to the exposure of new binding sites. The use of NaClO and NaIO$_3$ will increase the number of active binding sites by oxidation of the some of functional groups of cork to carboxylic groups, hence more copper ions could be sorbed. An increase of 70–80% in cork capacity for copper was achieved after treating cork powder with NaClO containing 7% of active chlorine.

2.5. Wheat bran

Wheat bran, a by-product of wheat milling industries proved to be a good adsorbent for removal of many types of heavy metal ions such as Pb(II), Cu(II) and Cd(II). The application of a strong dehydrating agent like sulfuric acid (H$_2$SO$_4$) can have a significant effect on the surface area of the adsorbent, which eventually results in better efficiency of adsorption of copper ions as reported by Özer et al. (2004). It was found that upon treatment with sulfuric acid, wheat bran had a much higher surface area. The authors suggested that acid treatment caused changes in surface area by increasing the conversion of macropores to micropores. Maximum adsorption capacity for Cu(II) ions was reported as 51.5 mg g^{-1} (at pH 5) and equilibrium time of adsorption was achieved in 30 min. Özer and Pirinçci (2006) conducted a study on the removal of lead ions by sulfuric acid treated wheat bran. It was reported that maximum lead removal (82.8%) occurred at pH 6 after 2 h of contact time. Three isotherm models were analyzed for determining the maximum adsorption capacity of wheat bran particularly Langmuir, Freundlich and Redlich-Peterson. Based on the non-linear plots, it was found that adsorption fitted well to the Redlich-Peterson than Langmuir and Freundlich models. The Langmuir plots indicate that maximum adsorption capacities increased with an increase in temperature (79.37 mg g^{-1} at 60 °C and 55.56 mg g^{-1} at 25 °C). The decrease in the values of $\Delta G°$ suggests that adsorption was more favourable at higher temperatures and adsorption was endothermic in nature. The kinetic study showed that lead adsorption could be described well with *n*th-order kinetic model. Özer (2006) also examined the sulfuric acid treated wheat bran for cadmium ion removal from aqueous solution. After 4 h of contact time, the maximum adsorption capacity that could be achieved for cadmium was 101 mg g^{-1} at pH 5. Therefore, in general the order of maximum removal of the above three metals follows: Cd(II) > Pb(II) > Cu(II).

2.6. Corncobs

Besides carbonization at high temperature, an adsorbent can be activated by chemical treatment using a concentrated acid. This method was demonstrated by Khan and Wahab (2006) in the study of adsorption of copper by concentrated sulfuric acid treated corncobs. It was reported that upon treatment of corncobs with sulfuric acid and heated at 150 °C, the pH_{zpc} of the adsorbent reduced from 5.2 (untreated) to 2.7 (treated), and the functional groups present in the adsorbent are mainly oxygen containing groups such as –OH, –COOH and –COO$^-$. The maximum adsorption capacity obtained from Langmuir isotherm was 31.45 mg g^{-1}. Adsorption was more favoured at higher pH value (4.5) due to low competing effect of protons for the adsorption sites. Effect of interfering ions such as Zn(II), Pb(II) and Ca(II) was also studied. It was noticed that copper removal efficiency was reduced by 53%, 27% and 19% in the presence of Pb(II), Ca(II) and Zn(II), respectively. Regeneration study indicates that sulfuric acid treated corncobs can be regenerated by acidified hydrogen peroxide solution and as much as 90% copper could be recovered.

The study on oxidation of corncob by citric acid and nitric acid was carried out by Leyva-Ramos et al. (2005). Upon oxidation of corncob, a significant increase in the surface area of the adsorbent was observed. An increase in the amount of oxygen found in corncob was due to more oxygenated groups being introduced on the adsorbent surface after oxidation. After oxidation, a higher proportion of acidic sites (carboxylic, phenolic and lactonic) was detected, which results in a reduction in the pH_{ZPC} value. It was also reported that the adsorption capacities for citric acid and nitric acid oxidized corncob were much higher than unmodified corncob.

2.7. Weeds

The study on effectiveness of lead adsorption by sodium hydroxide treated lalang (one of the ten worst weed of the world) or *Imperata cylindrica* leaf powder was carried out by Hanafiah et al. (2006a). Maximum adsorption of lead occurred at pH range 4–5 and an adsorbent dose of 4 g l^{-1}. Temperature study indicates that chemisorption was the main rate limiting step and pseudo-second-order kinetic model was fitted well. The value of maximum adsorption capacity obtained by NaOH treated *Imperata cylindrica* (13.50 mg g^{-1}) is much higher than untreated adsorbent (5.89 mg g^{-1}) (Hanafiah et al., 2007). A faster equilibrium time (20 min) was observed for treated *Imperata cylindrica* compared to untreated (120 min). The effect of metal concentration and thermodynamics on the sorption of Pb(II) and Cd(II) ions by nitric acid treated wild cocoyam (*Caladium bicolor*) biomass was investigated by Horsfall and Spiff (2005). The biomass was first reacted with nitric acid before washed with distilled water, then suspended in hydroxylamine to remove all *O*-acetyl groups.

It was noticed that the amount of Pb(II) sorbed was higher than Cd(II) ions. The smaller ionic radii of Cd(II) (0.97 Å) compared to Pb(II) (1.20 Å) means greater tendency of Cd(II) to be hydrolyzed, leading to reduced sorption. Sorption capacity increased with increasing metal concentrations for both cations. The maximum sorption capacities were 49.53 and 48.20 mM g^{-1} for Pb(II) and Cd(II), respectively. Freundlich and Langmuir models were found to be fitted well. The sorption was reported to occur by ion-exchange mechanism involving hydroxyl groups as represented by the following equation:

$$M^{2+} + 2BOH \leftrightarrow M(BO)_2 + 2H^+ \qquad (2)$$
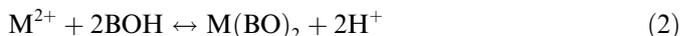
Spontaneous sorption of Pb(II) and Cd(II) was noticed as the negative values of $\Delta G°$ were obtained in all concentrations studied.

2.8. Fruit/vegetable wastes

Adsorption of divalent heavy metal ions particularly Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+} and Pb^{2+} onto acid and alkali treated banana and orange peels was performed by Annadurai et al. (2002). The acid and alkali solutions used for modification of adsorbents were HNO_3 and NaOH. In general, the adsorption capacity decreases in the order of $Pb^{2+} > Ni^{2+} > Zn^{2+} > Cu^{2+} > Co^{2+}$ for both adsorbents. Banana peel exhibits higher maximum adsorption capacity for heavy metals compared to orange peel. The reported maximum adsorption capacities were 7.97 (Pb^{2+}), 6.88 (Ni^{2+}), 5.80 (Zn^{2+}), 4.75 (Cu^{2+}) and 2.55 mg g^{-1} (Co^{2+}) using banana peel; and were 7.75 (Pb^{2+}), 6.01 (Ni^{2+}), 5.25 (Zn^{2+}), 3.65 (Cu^{2+}) and 1.82 mg g^{-1} (Co^{2+}) using orange peel. Acid treated peels showed better adsorption capacities followed by alkali and water treated peels. Based on regeneration studies, it was reported that the peels could be used for two regenerations for removal and recovery of heavy metal ions.

Besides NaOH, $Ca(OH)_2$ is another good saponifying agent for the conversion of ester groups to carboxyl groups as demonstrated by Dhakal et al. (2005). In the study, orange waste (consists of cellulose, hemicellulose, pectin, limonene and other low molecular weight compounds) was treated with $Ca(OH)_2$ to form saponified gel (SOW). Two forms of saponified gels were prepared (Ca^{2+}-form and H$^+$-form) and their removal efficiency for six heavy metal ions particularly Fe(III), Pb(II), Cu(II), Zn(II), Cd(II) and Mn(II) were compared. The authors suggested that cation exchange was the main mechanism for the removal of heavy metal ions as the pH of solutions decreased after adsorption. The order of removal for Ca^{2+}-form SOW gel was Pb(II) > Fe(III) > Cu(II) > Cd(II) > Zn(II) > Mn(II). In the case of H$^+$-form SOW gel, the order of removal was Pb(II) > Fe(III) > Cu(II) > Zn(II) > Cd(II) > Mn(II). As the pH of solutions increases, the percent removal of heavy metal ions also increased except Fe(III). The percent removal of Fe(III) greatly reduced beyond pH 3 due to formation of soluble iron

complexes such as $Fe(OH)^+$, $Fe(OH)_2^+$, $Fe(OH)_2^{4+}$ and $Fe(OH)_4^-$. The authors also suggested that ion-exchange mechanism involves oxygen atom in the pyranose ring of pectin acids cooperating with carboxylic group to form a stable five-membered chelate ring. This study indicates that both types of SOW gels are effective for removing heavy metal ions in acidic solution.

Chemical modification of cornelian cherry, apricot stone and almond shell by using concentrated sulfuric acid for the removal of Cr(VI) has been studied (Demirbas et al., 2004). All the three types of fruit wastes showed highest removal of Cr(VI) at pH 1. It was also reported that adsorption was highly dependent on the initial metal concentration as the lowest concentration recorded fastest removal rate (shortest equilibrium time). The equilibrium time for cornelian cherry was 20 h at 53 mg l^{-1} Cr(VI) concentration, increased to 70 h as the concentration increased to 203 mg l^{-1}. The removal rate increased with a decrease in adsorbent size, which indicates that smaller particle size has larger surface area. Four different kinetic models particularly pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion were evaluated and results showed that pseudo-second-order model correlated well with the experimental data. Recently, Kula et al. (2007) reported the application of ZnCl$_2$ (a dehydrating agent) in the activation of olive stone for removal of Cd(II) ions. It was reported that treated olive stone shows a remarkable increase in surface area compared to untreated olive stone. However, the activated olive stone did not show good adsorption capacity for Cd(II) as the reported maximum adsorption capacity was only 1.85 mg g^{-1}.

Li et al. (2006b) investigated orange peels as an adsorbent for cadmium adsorption and the effect of different citric acid concentrations on the adsorbent characters was studied. Upon treatment with more concentrated citric acid solutions, orange peels showed lower values of pH of zero point charge (pH$_{zpc}$) due to the increase number of total acidic sites while the total number of basic sites decreased. The increase in citric acid concentration results in more oxygenated groups being introduced to the adsorbent surface. Orange peels washed with 0.6 M citric acid at 80 °C has a much lower pH$_{ZPC}$ value indicating that the adsorbent surface becomes more negative due to dissociation of weakly acidic oxygen-containing groups. Chemical treatment with citric acid at high temperature produced condensation product and citric acid anhydride. The reactive citric acid anhydride can react with cellulosic hydroxyl groups to form an ester linkage and introduce carboxyl groups to the cellulose (Marshall et al., 1999). The presence of more carboxyl groups will increase more cadmium ions to bind on the adsorbent surface. It was also reported that cadmium adsorption occurred via ion-exchange mechanism as the pH of the solution decreases after adsorption, which indicates the presence of more protons in the effluents. Desorption experiment revealed that Cd(II) ions could be removed when the concentration of hydrochloric acid was increased and maximum percentage recovery of cadmium was 94% with 0.15 M HCl solution. The reported value of maximum adsorption capacity was 101.16 mg g^{-1}. The untreated orange waste however could only adsorb 0.43 mmol g^{-1} or 48.33 mg g^{-1} Cd (Pérez-Marín et al., 2007). Previously, Wartelle and Marshall (2000) reported an interesting finding in which a linear relationship between total negative charge and amount of copper ions adsorbed was observed for 12 types of agricultural by-products (sugarcane bagasse, peanut shells, macadamia nut hulls, rice hulls, cottonseed hulls, corn cob, soybean hulls, almond shells, almond hulls, pecan shells, English walnut shells and black walnut shells) after modification with citric acid. It was found that after washing with base (NaOH) and modified with citric acid, the total negative charge of all 12 types of agricultural by-products increased significantly. Among the 12 adsorbents, soybean hulls (a low density material) showed the highest copper uptake and had a high total negative charge value, which can be explained by the increase in carboxyl groups after thermo-chemical reaction with citric acid. On the other hand, nutshells (high density materials) such as English walnut shells and black walnut shells displayed low total negative charge values indicating low number of carboxyl groups. Due to the high bulk density, the lignin in nutshells may block or allowed little penetration of citric acid to reactive sites, hence lower copper ion uptake was observed. Wafwoyo et al. (1999) also reported that citric acid treated peanut shells showed higher removal of Cu, Cd, Ni, Zn and Pb ions compared to untreated shells. The metal uptake gets even larger when the shells were treated first with NaOH followed by citric acid. Treatment with NaOH will de-esterify and removes tannins, leaving more active binding sites available for metal adsorption.

Heavy metals such as Cr(III), Cu(II) and Zn(II) were able to be removed from wastewater using HCl treated carrot residues. Acid treatment was performed in order to remove tannins, resins, reducing sugars and coloured materials. According to Nasernejad et al. (2005), adsorption of metal ions onto carrot residues was possible due to the presence of carboxylic and phenolic groups which have cation exchange properties. Based on kinetic study, more than 70% metal ions were removed in the first 10 min and equilibrium was achieved in 70 min. More metals were adsorbed at higher pH values of the solutions (pH 4 for Cr(III) and pH 5 for Cu(II) and Zn(II)). Maximum adsorption capacities were 45.09, 32.74 and 29.61 mg g^{-1} for Cr(III), Cu(II) and Zn(II), respectively.

2.9. Cassava waste

Chemically modified adsorbent could also be prepared by thiolation (a process of introducing –SH group) method. Abia et al. (2003) carried out an experiment of determining the optimal concentration of thioglycollic acid (HSCH$_2$COOH) for the removal of Cd(II), Cu(II) and Zn(II) ions by cassava waste. Cassava waste consists of ligands such as hydroxyl, sulfur, cyano and amino which

could bind heavy metal ions. It was noticed that adsorptivity of the cassava waste was greatly improved as the concentration of modifying agent (thioglycollic acid) was increased from 0.5 to 1.0 M due to the increase in sulfhydryl groups, –SH. Adsorption was reported to take place on the cell wall of the biomass. Optimum adsorptions of all three heavy metals were achieved in less than 30 min. The order of maximum adsorption capacity among the three heavy metal ions after treating cassava waste with 1.0 M thioglycollic acid follows: Zn(II) > Cu(II) > Cd(II). The authors however did not conduct a detail experiment on the kinetic model of adsorption.

Effect of concentration of modifying agent on the adsorption of Cd(II) and Zn(II) ions onto thioglycollic acid treated cassava waste was investigated by Horsfall and Abia (2003). Cassava waste treated with 1.0 M thioglycollic acid showed highest removal of Cd(II) and Zn(II) ions compared to 0.5 M and untreated adsorbent but the time to reach equilibrium remained similar for treated and untreated adsorbent. It was observed that treated cassava waste had a much higher adsorption capacity for Cd(II) and Zn(II) ions compared to untreated sample. The adsorption capacities were reported as 86.68 mg g^{-1} Cd, 55.82 mg g^{-1} Zn and 647.48 mg g^{-1}, 559.74 mg g^{-1} for untreated and treated cassava waste, respectively. The increase in adsorption capacity of Cd and Zn after acid treatment could be associated with the formation of microporosity, which leads to enhanced thiol (–SH) groups on the adsorbent surface. The relative ease of exchanging hydrogen atoms of the thiol groups with heavy metal ions results in improved level of adsorption. Desorption studies revealed that untreated cassava waste showed better recovery of Cd(II) and Zn(II). The authors suggest that the low recovery of heavy metal ions by acid treated cassava waste was due to enhancement in binding sites after acid treatment, which enables the metal ions to bind strongly to the adsorbent surface. Abia et al. (2006) explored different kinetic models to account for the transport of Cd(II) from aqueous solution on to the surface of 0.5 and 1.0 M thiolated cassava wastes. Six kinetic models were tested mainly pseudo-first-order, pseudo-second-order, intraparticle diffusion, Elovich, mass transfer and intraparticle diffusivity models. Results indicate that adsorption followed pseudo-second-order better than the other kinetic models.

2.10. Plant fibres

Two types of chemical modifications on jute fibres and their effectiveness in the removal of Cu(II), Zn(II) and Ni(II) ions were reported by Shukla and Pai (2005a). The first modification involved a monochloro triazine type reactive dye, Reactive Orange 13, which was covalently loaded to the cellulosic matrix of jute fibres. Another modification involved oxidation of hydroxyl groups of cellulose present in jute fibres to carboxyl group (a weak cationic ion-exchanger) by using hydrogen peroxide. In the case of dye loaded jute fibres, the dye contains an azo linkage and hydroxyl groups (–OH), a situation favourable for formation of six membered ring chelate with metal ions. The presence of sodium sulphonate groups of the dye molecules attached covalently to the adsorbent also enhanced the metal adsorption capacity. The mechanism of ion-exchange between Na$^+$ of the dyed material and the heavy metal ions can be represented by the following equation:

$$R(SO_3Na)_2 + M^{2+} \rightarrow R(SO_3)M + 2Na^+ \qquad (3)$$
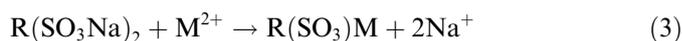
For oxidized jute, the high uptake of heavy metal ions was due to the generation of carboxyl groups (–COOH). The authors reported that oxidation process of jute fibres was carried out under alkaline condition, therefore the carboxyl groups are in the form of carboxylate. The adsorption of heavy metal ions could also take place by ion-exchange mechanism as shown below:

$$2RCOONa + M^{2+} \rightarrow (RCOO)_2M + 2Na^+ \qquad (4)$$

Based on the Langmuir plots, maximum adsorption capacity for Cu(II) ion was achieved by dye loaded jute, followed by oxidized jute and unmodified jute. However, for Ni(II) and Zn(II) ions, maximum adsorption capacities were recorded by oxidized jute and the lowest was by unmodified jute.

Chemical modification of cellulose fibre to improve its removal performance and adsorption capacity for Cu(II), Ni(II) and Zn(II) ions using ethylenediamine was conducted by Torres et al. (2006). Cellulose consists of active hydroxyl groups present on each monomeric unit of cellulose, therefore cellulose can react with carboxyl and amine groups of organic compounds. Based on the isotherm study, it was found that ethylenediamine modified cellulose fibre adsorbed Zn(II) more efficiently than Ni(II) and Cu(II) ions. The reported values of maximum adsorption capacities were 104.1, 308.2 and 69.3 mg g^{-1} for Cu, Ni and Zn, respectively. The modified adsorbent was also capable to adsorb metals 100 times more than unmodified cellulose (Okieimen et al., 2005). Adsorption of heavy metal ions occurred through complexation mechanism in which the amine (–NH$_2$) groups of ethylenediamine take part in the chelation process.

It is well known that adsorption of heavy metals by cellulosic wastes depends on the contact time and temperature. Ho and Ofamaja (2006) found that initial concentration of Cu(II) has great effect on the equilibrium time for copper adsorption onto HCl treated palm kernel fibre. The time to reach equilibrium was only 15 min for 50 mg l^{-1} copper, but increased to 60 min for 200 mg l^{-1}. The study reveals that copper adsorption increases with the increase of temperature which indicates that the mobility of Cu(II) ions increases with a rise in temperature. The value of activation energy of 22 kJ mol^{-1} suggests that chemisorption was an important process in the adsorption of copper onto HCl treated palm kernel fibre. Adsorption follows pseudo-second-order kinetic model at all copper concentrations studied.

2.11. Tree barks

Three different kinds of tree barks mainly sal (*Shorea robusta*), mango (*Mangifera indica*) and jackfruit (*Artocarpus integri floria*) were modified using hydrochloric acid solution in order to remove copper from aqueous solutions (Reddy et al., 1997). Treated barks were able to chelate more copper ions than untreated ones. Extraction of soluble organic compounds which coloured the decontaminated solutions was also avoided after pretreatment process. The highest adsorption capacity of copper ions was shown by sal bark (51.4 mg g^{-1}), followed by mango (42.6 mg g^{-1}) and jackfruit (17.4 mg g^{-1}). Binding of copper to the bark occurred through cation exchange mechanism as the pH of the effluent decreased after copper adsorption. It was reported that hydroxyl and carboxyl groups were involved in the adsorption process and the results indicate that chelation of 1 mol of copper generates about 1.6–1.8 mols of hydronium ions. Regeneration of adsorbent was more successful using higher concentration of HCl solution.

2.12. Azolla (water fern)

Azolla, a small aquatic fern is commonly used as fertilizer in botanical gardens and as green manure in rice fields. Binding or ion-exchange of heavy metal ions is possible due to the presence of charged groups such as carboxyl and phosphate in the Azolla matrix (Ganji et al., 2005). The percentage adsorption values of Pb, Cd, Cu and Zn by Azolla treated with MgCl$_2$ alone were approximately 33, 29, 40 and 24, respectively. These values however increased with increasing concentration of MgCl$_2$ due to better ion-exchange behaviour between heavy metals and Mg^{2+} ions on the cell walls of Azolla. No remarkable effect on the heavy metal removal was observed when Azolla was treated with H$_2$O$_2$ alone. However, the highest metal removal was reported by treating Azolla with 2 M MgCl$_2$ in the presence of 8 mM H$_2$O$_2$. It was thought that upon treatment with H$_2$O$_2$, more hydroxyl groups can be oxidized to carboxyl groups (Robert and Barbati, 2002), which later binds with Mg^{2+} ions. The (RCOO)$_2$Mg can act as a good ion-exchange group, hence more heavy metal ions could be exchanged/removed from wastewater. The maximum adsorption capacities for Pb(II), Cd(II), Cu(II) and Zn(II) were 228, 86, 62 and 48 mg g^{-1}, respectively. Heavy metals could be desorbed from Azolla using HCl solution and the order of desorption follows: Zn(II) > Cu(II) > Cd(II) > Pb(II).

2.13. Alfalfa biomass

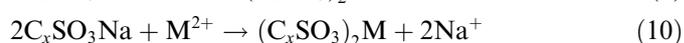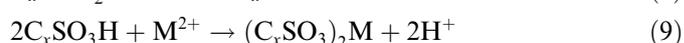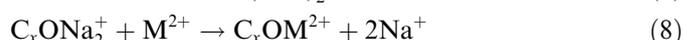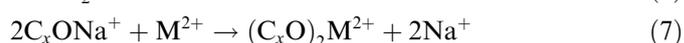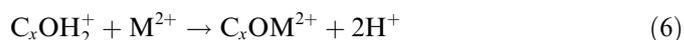Tiemann et al. (2002) investigated the adsorption of lead ions by alfalfa (*Medicago sativa*) biomass. The biomass was modified with a combination of methanol/concentrated HCl solution in order to esterify the carboxyl groups. Binding of lead(II) ions on the biomass was not observed after

esterification, but adsorption capacity increased to 43 mg g^{-1} for unmodified alfalfa and 89.2 mg g^{-1} for hydrolyzed alfalfa by NaOH. This findings indicate that carboxyl groups played a major role for the binding of lead(II) ions from solution by alfalfa biomass. The adsorption mechanism for Pb(II) on alfalfa biomass was established using X-ray absorption near edge structure (XANES) spectroscopy and extended X-ray absorption fine structure (EXAFS) spectroscopy. The EXAFS data demonstrated that Pb(II) ions formed monodentate complex with oxygen atoms via carboxyl groups and the Pb-O bond distance was 2.60 Å.

2.14. Coirpith carbon

The combined application of concentrated sulfuric acid and ammonium persulphate for activation of coirpith for removal of mercury, copper and nickel was carried out by Namasivayam and Kadirvelu (1999); Namasivayam and Kadirvelu (1997); Kadirvelu et al. (2001b). The adsorption equilibrium time for all heavy metal ions studied was less than 60 min and the order of maximum adsorption capacity follows: Hg(II) > Ni(II) > Cu(II). Treatment of coirpith with sulfuric acid and ammonium persulphate introduced more functional groups on the carbon surface and the mechanism of adsorption involves ion-exchange between heavy metal ions and Na$^+$/H$^+$ ions as shown below (Namasivayam and Kadirvelu, 1997):

$$2C_xOH^+ + M^{2+} \rightarrow (C_xO)_2M^{2+} + 2H^+ \tag{5}$$

$$C_xOH_2^+ + M^{2+} \rightarrow C_xOM^{2+} + 2H^+ \tag{6}$$

$$2C_xONa^+ + M^{2+} \rightarrow (C_xO)_2M^{2+} + 2Na^+ \tag{7}$$

$$C_xONa_2^+ + M^{2+} \rightarrow C_xOM^{2+} + 2Na^+ \tag{8}$$

$$2C_xSO_3H + M^{2+} \rightarrow (C_xSO_3)_2M + 2H^+ \tag{9}$$

$$2C_xSO_3Na + M^{2+} \rightarrow (C_xSO_3)_2M + 2Na^+ \tag{10}$$

In another study, chemical activation of coirpith could also be carried out using ZnCl$_2$ for removing Cr(VI), Ni(II) and Hg(II) from wastewater (Namasivayam and Sangeetha, 2006). Coirpith activated with ZnCl$_2$ was found to have a much higher surface area compared to the coirpith prepared in the absence of ZnCl$_2$. Hence, more heavy metal ions were able to be removed from the wastewater.

2.15. Cottonseed hulls and soybean hulls

Marshall and Johns (1996) studied the removal of Zn(II) ions by treating soybean hulls and cottonseed hulls with 0.1 M NaOH and 0.1 M HCl solutions. The results obtained from acid and base treatments were compared with water washed adsorbents. For soybean hulls, a 26% increase in adsorption capacity was observed after NaOH treatment compared with water washing. However, the capacity was greatly reduced (about 78%) after washing

the adsorbent with HCl. For cottonseed hulls, zinc adsorption was also increased by 79% after washing the adsorbent with NaOH, but reduced by 89% after acid treatment. The authors reported that both adsorbents contain pectin substances consisting primarily of galacturonic acid and *O*-methyl esters. Upon treatment with NaOH, the *O*-methyl esters are converted to methanol and additional galacturonic acid. The adsorbent surfaces will have more negative charge sites or greater number of metal adsorption sites, hence greater metal adsorption capacity. Acid-washed hulls however will cause the adsorbent surface to be protonated, causing Zn(II) ions more difficult to be adsorbed (Kumar and Bandyopadhyay, 2006).

3. Conclusion

This review shows that the study on chemically modified plant wastes for heavy metal removal has attracted the attention of more scientists. A wide range of low-cost adsorbents obtained from chemically modified plant wastes has been studied and most studies were focused on the removal of heavy metal ions such as Cd, Cu, Pb, Zn, Ni and Cr(VI) ions. The most common chemicals used for treatment of plant wastes are acids and bases. Chemically modified plant wastes vary greatly in their ability to adsorb heavy metal ions from solution. Chemical modification in general improved the adsorption capacity of adsorbents probably due to higher number of active binding sites after modification, better ion-exchange properties and formation of new functional groups that favours metal uptake. Although chemically modified plant wastes can enhance the adsorption of heavy metal ions, the cost of chemicals used and methods of modification also have to be taken into consideration in order to produce 'low-cost' adsorbents. Since modification of adsorbent surface might change the properties of adsorbent, it is recommended that for any work on chemically modified plant wastes, characterization studies involving surface area, pore size, porosity, pH_{ZPC}, etc. should be carried out. Spectroscopic analyses involving Fourier transform infrared (FTIR), energy dispersive spectroscopy (EDS), X-ray absorption near edge structure (XANES) spectroscopy and extended X-ray absorption fine structure (EXAFS) spectroscopy are also important in order to have a better understanding on the mechanism of metal adsorption on modified plant wastes.

Acknowledgements

References

Abia, A.A., Horsfall Jr., M., Didi, O., 2003. The use of chemically modified and unmodified cassava waste for the removal of Cd, Cu and Zn ions from aqueous solution. Bioresour. Technol. 90, 345–348.

Abia, A.A., Didi, O.B., Asuquo, E.D., 2006. Modelling of Cd^{2+} sorption kinetics from aqueous solutions onto some thiolated agricultural waste adsorbents. J. Appl. Sci. 6, 2549–2556.

Acar, F.N., Eren, Z., 2006. Removal of Cu(II) ions by activated poplar sawdust (Samsun Clone) from aqueous solutions. J. Hazard. Mater. B 137, 909–914.

Annadurai, G., Juang, H.S., Lee, D.J., 2002. Adsorption of heavy metal from water using banana and orange peels. Water Sci. Technol. 47, 185–190.

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

Azab, M.S., Peterson, P.J., 1989. The removal of Cd(II) from water by the use of biological sorbents. Water Sci. Technol. 21, 1705–1706.

Babarinde, N.A.A., Oyebamiji Babalola, J., Adebowale Sanni, R., 2006. Biosorption of lead ions from aqueous solution by maize leaf. Int. J. Phys. Sci. 1, 23–26.

Bailey, S.E., Olin, T.J., Bricka, R.M., Adrian, D.D., 1999. A review of potentially low-cost sorbents for heavy metals. Water Res. 33, 2469–2479.

Baral, S.S., Das, S.N., Rath, P., 2006. Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust. Biochem. Eng. J. 31, 216–222.

Bhattacharya, A.K., Mandal, S.N., Das, S.K., 2006. Adsorption of Zn(II) from aqueous solution by using different adsorbents. Chem. Eng. J. 123, 43–51.

Bulut, Y., Tez, Z., 2003. Removal of heavy metal ions by modified sawdust of walnut. Fresen. Environ. Bull. 12, 1499–1504.

Chuah, T.G., Jumasiah, A., Katayon, S., Thomas Choong, S.Y., 2005. Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: an overview. Desalination 175, 305–316.

Chubar, N., Calvalho, J.R., Correia, M.J.N., 2004. Heavy metals biosorption on cork biomass: effect of the pre-treatment. Colloids Surf. A 238, 51–58.

Demirbas, E., Kobya, M., Senturk, E., Ozkan, T., 2004. Adsorption kinetics for the removal of chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes. Water SA 30 (4), 533–539.

Dhakal, R.P., Ghimire, K.N., Inoue, K., 2005. Adsorptive separation of heavy metals from an aquatic environment using orange. Hydrometallurgy 79, 182–190.

Dubey, S.P., Gopal, K., 2006. Adsorption of chromium(VI) on low cost adsorbents derived from agricultural waste material: a comparative study. J. Hazard. Mater.. doi:10.1016/j.jhazmat.2006.11.04.

Esteghlalian, A., Hashimoto, A.G., Fenske, J.J., Penner, M.H., 1997. Modeling and optimization of the dilute-sulfuric-acid pretreatment of corn stover, poplar and switchgrass. Bioresour. Technol. 59, 129–136.

Gaballah, I., Goy, D., Allain, E., Kilbertus, G., Thauront, J., 1997. Recovery of copper through decontamination of synthetic solutions using modified barks. Met. Metall. Trans. B 28, 13–23.

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

Garg, V.K., Kumar, R., Gupta, R., 2004. Removal of malachite green dye from aqueous solution by adsorption using agro-industry waste: a case study of *Prosopis cineraria*. Dyes Pigments 62, 1–10.

Guo, Y., Yang, S., Fu, W., Qi, J., Li, R., Wang, Z., Xu, H., 2003. Adsorption of malachite green on micro and mesoporous rice husk-based active carbon. Dyes Pigments 56, 219–229.

Gupta, V.K., Ali, I., 2004. Removal of lead and chromium from wastewater using bagasse fly ash – a sugar industry waste. J. Colloid Interface Sci. 271, 321–328.

Gupta, V.K., Jain, C.K., Ali, I., Sharma, M., Saini, V.K., 2003. Removal of cadmium and nickel from wastewater using bagasse fly ash – a sugar industry waste. Water Res. 37, 4038–4044.

Hanafiah, M.A.K., Ibrahim, S.C., Yahya, M.Z.A., 2006a. Equilibrium adsorption study of lead ions onto sodium hydroxide modified Lalang (*Imperata cylindrica*) leaf powder. J. Appl. Sci. Res. 2, 1169–1174.

Hanafiah, M.A.K.M., Ngah, W.S.W., Ibrahim, S.C., Zakaria, H., Ilias, W.A.H.W., 2006b. Kinetics and thermodynamic study of lead adsorption onto rubber (*Hevea brasiliensis*) leaf powder. J. Appl. Sci. 6, 2762–2767.

Hanafiah, M.A.K., Ngah, W.S.W., Zakaria, H., Ibrahim, S.C., 2007. Batch study of liquid-phase adsorption of lead ions using Lalang (*Imperata cylindrica*) leaf powder. J. Biol. Sci. 7, 222–230.

Hanafiah, M.A.K.H., Shafiei, S., Harun, M.K., Yahya, M.Z.A., 2006c. Kinetic and thermodynamic study of Cd^{2+} adsorption onto rubber tree (*Hevea brasiliensis*) leaf powder. Mater. Sci. Forum 517, 217–221.

Ho, Y.S., 2003. Removal of copper ions from aqueous solution by tree fern. Water Res. 37, 2323–2330.

Ho, Y.S., Chiu, W.T., Hsu, C.S., Huang, C.T., 2004. Sorption of lead ions from aqueous solution using tree fern as a sorbent. Hydrometallurgy 73, 55–61.

Ho, Y.S., Ofamaja, A.E., 2006. Kinetic studies of copper ion adsorption on palm kernel fibre. J. Hazard. Mater. B 137, 1796–1802.

Ho, Y.S., Wang, C.C., 2004. Pseudo-isotherms for the sorption of cadmium ion onto tree fern. Process Biochem. 39, 759–763.

Horsfall Jr., M., Abia, A.A., 2003. Sorption of cadmium(II) and zinc(II) ions from aqueous solutions by cassava waste biomass (*Manihot sculenta* Cranz). Water Res. 37, 4913–4923.

Horsfall Jr., Spiff, A.I., 2005. Effect of metal ion concentration on the biosorption of Pb^{2+} and Cd^{2+} by *Caladium bicolor* (wild cocoyam). Afr. J. Biotechnol. 4, 191–196.

Horsfall Jr., M., Abia, A.A., Spiff, A.I., 2006. Kinetic studies on the adsorption of Cd^{2+}, Cu^{2+} and Zn^{2+} ions from aqueous solutions by cassava (*Manihot sculenta* Cranz) tuber bark waste. Bioresour. Technol. 97, 283–291.

Ibrahim, S.C., Hanafiah, M.A.K.M., Yahya, M.Z.A., 2006. Removal of cadmium from aqueous solution by adsorption on sugarcane bagasse. Am-Euras. J. Agric. Environ. Sci. 1, 179–184.

Jeon, C., Park, K.H., 2005. Adsorption and desorption characteristics of mercury(II) ions using aminated chitosan beads. Water Res. 36, 3938–3944.

Johnson, P.D., Watson, M.A., Brown, J., Jefcoat, I.A., 2002. Peanut hull pellets as a single use sorbent for the capture of Cu(II) from wastewater. Waste Manage. 22, 471–480.

Junior, O.K., Gurgel, L.V.A., de Melo, J.C.P., Botaro, V.R., Melo, T.M.S., de Freitas Gil, R.P., Gil, L.F., 2006. Adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugarcane bagasse. Bioresour. Technol. 98, 1291–1297.

Kadirvelu, K., Kavipriya, M., Karthika, C., Radhika, M., Vennilamani, N., Pattabhi, S., 2003. Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions. Bioresour. Technol. 87, 129–132.

Kadirvelu, K., Thamaraiselvi, K., Namasivayam, C., 2001a. Removal of heavy metal from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. Bioresour. Technol. 76, 63–65.

Kadirvelu, K., Thamaraiselvi, K., Namasivayam, C., 2001b. Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from coirpith. Sep. Purif. Technol. 24, 497–505.

Karunasagar, D., Balarama Krishna, M.V., Rao, S.V., Arunachalam, J., 2005. Removal of preconcentration of inorganic and methyl mercury from aqueous media using a sorbent prepared from the plant *Coriandrum sativum*. J. Hazard. Mater. B 118, 133–139.

Khan, M.N., Wahab, M.F., 2006. Characterization of chemically modified corncobs and its application in the removal of metal ions from aqueous solution. J. Hazard. Mater. B 141, 237–244.

King, P., Srivinas, P., Prasanna Kumar, Y., Prasad, V.S.R.K., 2006. Sorption of copper(II) ion from aqueous solution by *Tectona grandis* l.f. (teak leaves powder). J. Hazard. Mater. B136, 560–566.

Kula, I., Uğurlu, M., Karaoğlu, H., Çelik, A., 2007. Adsorption of Cd(II) ions from aqueous solutions using activated prepared from olive stone by $ZnCl_2$ activation. Bioresour. Technol.. doi:10.1016/j.biortech.2007.01.01.

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

Lazlo, J.A., 1987. Mineral binding properties of soy hull. Modeling mineral interactions with insoluble dietary fibre source. J. Agr. Food Chem. 35, 593–600.

Leyva-Ramos, R., Bernal-Jacome, L.A., Acosta-Rodriguez, I., 2005. Adsorption of cadmium(II) from aqueous solution on natural and oxidized corncob. Sep. Purif. Technol. 45, 41–49.

Li, Q., Zhai, J., Zhang, W., Wang, M., Zhou, J., 2006a. Kinetic studies of adsorption of Pb(II), Cr(III) and Cu(II) from aqueous solution by sawdust and modified peanut husk. J. Hazard. Mater. B 141, 163–167.

Li, X., Tang, Y., Xuan, Z., Liu, Y., Luo, F., 2006b. Study on the preparation of orange peel cellulose adsorbents and biosorption of Cd^{2+} from aqueous solution. Sep. Purif. Technol. 55, 69–75.

Low, K.S., Lee, C.K., Liew, S.C., 2000. Sorption of cadmium and lead from aqueous solutions by spent grain. Process Biochem. 36, 59–64.

Low, K.S., Lee, C.K., Leo, A.C., 1995. Removal of metals from electroplating wastes using banana pith. Bioresour. Technol. 51, 227–231.

Marshall, W.E., Johns, M.M., 1996. Agricultural by-products as metal adsorbents: sorption properties and resistance to mechanical abrasion. J. Chem. Tech. Biotechnol. 66, 192–198.

Marshall, W.E., Wartelle, L.H., Boler, D.E., Johns, M.M., Toles, A.A., 1999. Enhanced metal adsorption by soybean hulls modified with citric acid. Bioresour. Technol. 69, 263–268.

Memon, S.Q., Memon, N., Shah, S.W., Khuhawar, M.Y., Bhanger, M.I., 2007. Sawdust – a green and economical sorbent for the removal of cadmium(II) ions. J. Hazard. Mater. B 139, 116–121.

Min, S.H., Han, J.S., Shin, E.W., Park, J.K., 2004. Improvement of cadmium ion removal by base treatment of juniper fiber. Water Res. 38, 1289–1295.

Mohanty, K., Jha, M., Meikap, B.C., Biswas, M.N., 2005. Removal of chromium(VI) from dilute aqueous solutions by activated carbon developed from *Terminalia arjuna* nuts activated with zinc chloride. Chem. Eng. Sci. 60, 3049–3059.

Nakajima, A., Sakaguchi, T., 1990. Recovery and removal of uranium by using plant wastes. Biomass 21, 55–63.

Namasivayam, C., Ranganathan, K., 1995. Removal of Pb(II), Cd(II) and Ni(II) and mixture of metal ions by adsorption onto waste Fe(III)/Cr(III) hydroxide and fixed bed studies. Environ. Technol. 16, 851–860.

Namasivayam, C., Kadirvelu, K., 1997. Agricultural solid wastes for the removal of heavy metals: adsorption of Cu(II) by coirpith carbon. Chemosphere 34, 377–399.

Namasivayam, C., Kadirvelu, K., 1999. Uptake of mercury(II) from wastewater by activated carbon from an unwanted agricultural solid by-product: coirpith. Carbon 37, 79–84.

Namasivayam, C., Sangeetha, D., 2006. Recycling of agricultural solid waste, coirpith: removal of anions, heavy metals, organics and dyes from water by adsorption onto $ZnCl_2$ activated coirpith carbon. J. Hazard. Mater. B 135, 449–452.

Nasernejad, B., Zadeh, T.E., Pour, B.B., Bygi, M.E., Zamani, A., 2005. Comparison for biosorption modeling of heavy metals (Cr(III), Cu(II), Zn(II)) adsorption from wastewater by carrot residues. Process Biochem. 40, 1319–1322.

Noeline, B.F., Manohar, D.M., Anirudhan, T.S., 2005. Kinetic and equilibrium modeling of lead(II) sorption from water and wastewater by polymerized banana stem in a batch reactor. Sep. Purif. Technol. 45, 131–140.

Okieimen, F.E., Sogbaike, C.E., Ebhoaye, J.E., 2005. Removal of cadmium and copper ions from aqueous solution with cellulose graft copolymers. Sep. Purif. Technol. 44, 85–89.

Özer, A., 2006. Removal of Pb(II) ions from aqueous solutions by sulfuric acid-treated wheat bran. J. Hazard. Mater. B 141, 753–761.

Özer, A., Pirinçci, H.B., 2006. The adsorption of Cd(II) ions on sulfuric acid-treated wheat bran. J. Hazard. Mater. B 137, 849–855.

Özer, A., Özer, D., Özer, A., 2004. The adsorption of copper(II) ions onto dehydrated wheat bran (DWB): determination of equilibrium and thermodynamic parameters. Process Biochem. 39, 2183–2191.

Pehlivan, E., Cetin, S., Yanık, B.H., 2006. Equilibrium studies for the sorption of zinc and copper from aqueous solutions using sugar beet pulp and fly ash. J. Hazard. Mater. B 135, 193–199.

Pérez-Marín, A.B., Meseguer Zapata, V., Ortuño, J.F., Aguilar, M., Sáez, J., Lloréns, M., 2007. Removal of cadmium from aqueous solutions by adsorption onto orange waste. J. Hazard. Mater. 139, 122–131.

Quek, S.Y., Wase, D.A.J., Forster, C.F., 1998. The use of sago waste for the sorption of lead and copper. Water SA 24, 251–256.

Rahman, I.A., Ismail, J., 1993. Preparation and characterization of a spherical gel from a low-cost material. J. Mater. Chem. 3, 931–934.

Rahman, I.A., Ismail, J., Osman, H., 1997. Effect of nitric acid digestion on organic materials and silica in rice husk. J. Mater. Chem. 7, 1505–1509.

Reddy, B.R., Mirghaffari, N., Gaballah, I., 1997. Removal and recycling of copper from aqueous solutions using treated Indian barks. Resour. Conserv. Recycl. 21, 227–245.

Rehman, H., Shakirullah, M., Ahmad, I., Shah, S., Hamedullah, 2006. Sorption studies of nickel ions onto sawdust of Dalbergia sissoo. J. Chin. Chem. Soc. 53, 1045–1052.

Robert, R., Barbati, S., 2002. Intermediates in wet oxidation of cellulose: identification of hydroxyl radical and characterization of hydrogen peroxide. Water Res. 36, 4821–4829.

Saeed, A., Waheed Akhter, M., Iqbal, M., 2005. Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent. Sep. Purif. Technol. 45, 25–31.

Sawalha, M.F., Peralta-Videa, J.R., Romero-González, J., Duarte-Gardea, M., Gardea-Torresdey, J.L., 2007a. Thermodynamic and isotherm studies of the biosorption of Cu(II), Pb(II), and Zn(II) by leaves of saltbush (Atriplex canescens). J. Chem. Thermodyn. 39, 488–492.

Sawalha, M.F., Peralta-Videa, J.R., Romero-González, J., Gardea-Torresdey, J.L., 2007b. Biosorption of Cd(II), Cr(III), and Cr(VI) by saltbush (Atriplex canescens) biomass: thermodynamic and isotherm studies. J. Colloid Interface Sci. 300, 100–104.

Šćiban, M., Klašnja, M., Škrbić, B., 2006a. Modified softwood sawdust as adsorbent of heavy metal ions from water. J. Hazard. Mater. B 136, 266–271.

Šćiban, M., Klašnja, M., Škrbić, B., 2006b. Modified hardwood sawdust as adsorbent of heavy metal ions from water. Wood Sci. Technol. 40, 217–227.

Shukla, S.R., Pai, R.S., 2005a. Adsorption of Cu(II), Ni(II) and Zn(II) on modified jute fibres. Bioresour. Technol. 96, 1430–1438.

Shukla, S.R., Pai, R.S., 2005b. Adsorption of Cu(II), Ni(II) and Zn(II) on dye loaded groundnut shells and sawdust. Sep. Purif. Technol. 43, 1–8.

Sivers, M.V., Zacchi, G., 1995. A techno-economical comparison of three processes for the production of ethanol from pine. Bioresour. Technol. 51, 43–52.

Suemitsu, R., Uenishi, R., Akashi, I., Nakano, M., 1986. The use of dyestuff-treated rice hulls for removal of heavy metal ions from waste water. J. Appl. Polym. Sci. 31, 75–83.

Tarley, C.R.T., Ferreira, S.L.C., Arruda, M.A.Z., 2004. Use of modified rice husks as a natural solid adsorbent of trace metals: characterisation and development of an on-line preconcentration system for cadmium and lead determination by FAAS. Microchem. J. 77, 163–175.

Taty-Costodes, V.C., Fauduet, H., Porte, C., Delacroix, A., 2003. Removal of Cd(II) and Pb(II) ions from aqueous solutions by adsorption onto sawdust of Pinus sylvestris. J. Hazard. Mater. B 105, 121–142.

Tiemann, K.J., Gamez, G., Dokken, K., Parsons, J.G., Gardea-Torresdey, J.L., 2002. Chemical modification and X-ray absorption studies for lead(II) binding by Medicago sativa (alfalfa) biomass. Microchem. J. 71, 287–293.

Torres, J.D., Faria, E.A., Prado, A.G.S., 2006. Thermodynamic studies of the interaction at the solid/liquid interface between metal ions and cellulose modified with ethylenediamine. J. Hazard. Mater. B 129, 239–243.

Villaescusa, I., Fiol, N., Martínez, M., Miralles, N., Pocj, J., Serarols, J., 2004. Removal of copper and nickel ions from aqueous solutions by grape stalks wastes. Water Res. 38, 992–1002.

Wafwoyo, W., Seo, C.W., Marshall, W.E., 1999. Utilization of peanut shells as adsorbents for selected metals. J. Chem. Technol. Biotechnol. 74, 1117–1121.

Wankasi, D., Horsfall Jr., M., Spiff, A.I., 2006. Sorption kinetics of Pb^{2+} and Cu^{2+} ions from aqueous solution by Nipah palm (Nypa fruticans Wurmb) shoot biomass. Elec. J. Biotechnol. 9, 587–592.

Wartelle, L.H., Marshall, W.E., 2000. Citric acid modified agricultural by-products as copper ion adsorbents. Adv. Environ. Res. 4, 1–7.

Williams, C.J., Aderhold, D., Edyvean, G.J., 1998. Comparison between biosorbents for the removal of metal ions from aqueous solutions. Water Res. 32, 216–224.

Wong, K.K., Lee, C.K., Low, K.S., Haron, M.J., 2003a. Removal of Cu and Pb by tartaric acid modified **rice husk** from aqueous solutions. Chemosphere 50, 23–28.

Wong, K.K., Lee, C.K., Low, K.S., Haron, M.J., 2003b. Removal of Cu and Pb from electroplating wastewater using tartaric acid modified rice husk. Process Biochem. 39, 437–445.