

Review

# Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals

Tonni Agustiono Kurniawan<sup>a</sup>, Gilbert Y.S. Chan<sup>a,\*</sup>, Wai-hung Lo<sup>a,\*</sup>, Sandhya Babel<sup>b</sup>

<sup>a</sup> Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

<sup>b</sup> Environmental Technology Program, Sirindhorn International Institute of Technology (SIIT), Thammasat University,  
P.O. Box 22 Rangsit, Klong Luang, Pathumthani 12121, Thailand

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## Abstract

In this article, the removal performance and cost-effectiveness of various low-cost adsorbents derived from agricultural waste, industrial by-product or natural material are evaluated and compared to those of activated carbon for the removal of heavy metals (Cd(II), Cr(III), Cr(VI), Cu(II), Ni(II) and Zn(II)) from metals-contaminated wastewater. To highlight their technical applicability, selected information on pH, dose required, initial metal concentration, adsorption capacity and the price of the adsorbents is presented. It is evident from the survey of 102 published studies (1984–2005) that low cost adsorbents derived from agricultural waste have demonstrated outstanding capabilities for the removal of heavy metal (Cr(VI): 170 mg/g of hazelnut shell activated carbon, Ni(II): 158 mg/g of orange peel, Cu(II): 154.9 mg/g of soybean hull treated with NaOH and citric acid, Cd(II): 52.08 mg/g of jackfruit), compared to activated carbon (Cd(II): 146 mg/g, Cr(VI): 145 mg/g, Cr(III): 30 mg/g, Zn(II): 20 mg/g). Therefore, low-cost adsorbents can be viable alternatives to activated carbon for the treatment of metals-contaminated wastewater. It is important to note that the adsorption capacities presented in this paper vary, depending on the characteristics of the individual adsorbent, the extent of surface modification and the initial concentration of the adsorbate. In general, technical applicability and cost-effectiveness are the key factors that play major roles in the selection of the most suitable adsorbent to treat inorganic effluent. © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Agricultural waste; Industrial by-product; Low-cost material; Metal-contaminated water; Wastewater treatment

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\* Corresponding authors. Tel.: +852 2766 5643; fax: +852 2364 9932.

E-mail addresses: [bcyschan@polyu.edu.hk](mailto:bcyschan@polyu.edu.hk) (G.Y.S. Chan), [bctlo@polyu.edu.hk](mailto:bctlo@polyu.edu.hk) (W.H. Lo).

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## 1. Introduction

The objective of water pollution control in the industrial application is to minimize the generation of toxic contaminants such as heavy metals. Many industrial processes in the plating industry involve heavy metals for metal finishing and their effluent must be treated prior to discharge. In this context, a cost-effective treatment for metals-contaminated wastewater is required, as environmental laws become stringent (Kadirvelu et al., 2002).

Although heavy metal removal from inorganic effluent can be achieved by conventional treatment such as chemical precipitation or flotation, each treatment has its inherent limitation. Recently, adsorption has become one of the alternative treatments (Leung et al., 2000; Kurniawan and Babel, 2003a). Basically, adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions (Kurniawan and Babel, 2003b). Due to its large surface area, high adsorption capacity and surface reactivity, adsorption using activated carbon can remove metals such as Ni(II) (Shim et al., 1996), Cr(VI) (Ouki et al., 1997), Cd(II) (Leyva-Ramos et al., 1997), Cu(II) (Monser and Adhoum, 2002) and Zn(II) (Leyva-Ramos et al., 2002), from inorganic effluent and the treated

effluent can meet stringent standards for metal effluent discharge in some countries (Table 1). However, the use of activated carbon may be costly.

In recent years, the search for low-cost adsorbents that have metal-binding capacities has intensified. Materials locally available in large quantities such as natural materials, agricultural waste or industrial by-products can be utilized as low-cost adsorbents. Some of these materials can be used as adsorbents with little processing. Conversion of these materials into activated carbon, which can be used as an adsorbent for water purification, would improve economic value, helping industries reduce the cost of waste disposal and providing a potential alternative to activated carbon.

To achieve an economically effective treatment of metal-contaminated wastewater, various low-cost materials have been investigated worldwide, such as in India (Ajmal et al., 2001), Thailand (Kurniawan, 2002), Nigeria (Abia et al., 2003), Italy (Abollino et al., 2003) and USA (Yu et al., 2003). It was reported that wool (Balkaya, 2002), soya cake (Daneshvar et al., 2002), sawdust (Dakiky et al., 2002), maple saw dust (Yu et al., 2003), distillery sludge (Selvaraj et al., 2003), cocoa shell (Meunier et al., 2003), sugar beet pulp (Reddad et al., 2003) and zeolite (Babel and Kurniawan, 2004a) could bind Cr(VI) with high removal capacity.

Table 1  
Maximum contaminant level (MCL) of heavy metals in surface water and their toxicities

Heavy metal	Toxicities	Maximum effluent discharge standards (mg/L)		
		*EPA (2004) USA	**EPD (2004) (Hong Kong SAR)	***PCD (2004) (Thailand)
Cr(VI)	Headache, nausea, diarrhea, vomiting	0.05	0.05–0.10	0.25
Cr(III)		0.10		0.75
Zn(II)	Depression, lethargy, neurologic signs such as seizures and ataxia, and increased thirst	1.00	0.60–1.00	5.00
Cu(II)	Liver damage, Wilson disease, insomnia	0.25	0.05–0.1	2.00
Cd(II)	Kidney damage, renal disorder, Itai-Itai	0.01	0.001–0.05	0.03
Ni(II)	Dermatitis, nausea, chronic asthma, coughing	0.20	0.10–0.20	1.00

Remarks:

\*Environmental Protection Agency (EPA), USA.

\*\*Environmental Protection Department (EPD), Hong Kong Special Administrative Region (HKSAR).

\*\*\*Pollution Control Department (PCD), The Ministry of Natural Resources and Environment, Thailand.

In this article, a critical overview of various adsorbents derived from agricultural waste, industrial by-products or natural materials that have metal-binding capacity is presented. To highlight their technical applicability for treating metals-contaminated water, selected information on pH, dose required, initial metal concentration, adsorption capacity and the price of the adsorbent is discussed. Low-cost adsorbents that stand out for high metal adsorption capacities are compared to activated carbon.

## 2. Sources of low-cost adsorbents

### 2.1. Agricultural waste

Agricultural waste is one of the rich sources for low-cost adsorbents besides industrial by-product or natural material. Due to abundant availability, agricultural waste such as orange peel poses little economic value and moreover, creates serious disposal problems (Selvakumari et al., 2002).

Without significant processing, Ajmal et al. (2000) employed orange peel for Ni(II) removal from simulated wastewater. They found that the maximum metal removal occurred at pH 6.0 and that the adsorption followed the Langmuir isotherm, indicating that Ni(II) uptake might occur on a homogenous surface by monolayer adsorption. A metal adsorption capacity of 158 mg/g was achieved at 323 K (Table 2a). This result was significantly higher than that of a similar study undertaken by Annadurai et al. (2002) (Table 2a), suggesting that the adsorption capacity of an adsorbent depends on the initial concentration of adsorbate.

To achieve an economically effective treatment of metal-contaminated water, other unused resources such as hazelnut shell, rice husk, coirpith, almond husk, pecan shells and jackfruit can be used as an adsorbent for heavy-metal uptake after chemical modification or conversion by heating into activated carbon. This process can be costly due to energy and chemicals consumption. However, literature surveys conducted by Bailey et al. (1999) and Babel and Kurniawan (2003a) have reported that improved adsorption capacity of the adsorbents after additional processing may compensate the cost for such a process.

For example, coconut shell charcoal (CSC) is an agricultural waste from coconut industry in Thailand at US\$0.25/kg. The applicability of CSC modified with oxidizing agents and/or chitosan for Cr(VI) removal was investigated by Babel and Kurniawan (2004b) using simulated wastewater. They found that CSC oxidized with nitric acid had higher Cr adsorption capacities

(10.88 mg/g) than that oxidized with sulfuric acid (4.05 mg/g) or coated with chitosan (3.65 mg/g). The results suggest that surface modification of CSC with a strong oxidizing agent generated more adsorption sites on its solid surface for metal adsorption.

To make Cr removal by CSC more economical, further work has been done by Kurniawan (2002) to regenerate the spent adsorbent. It was reported that desorption and regeneration of CSC with NaOH and HNO<sub>3</sub> still enabled the same column for multiple uses in subsequent cycle with regeneration efficiency of more than 95% (Kurniawan, 2002).

Cu(II) and Zn(II) removal from real wastewater were studied using pecan shells activated carbon (Bansode et al., 2003). Some treated pecan shells used are: PSA (phosphoric acid-activated pecan shell carbon), PSC (carbon dioxide-activated pecan shell carbon); PSS (steam-activated pecan shell carbon). PSA and PSS had good removal capacities for both ions (Table 2a). The Freundlich isotherm was applicable for the equilibrium sorption of PSA, suggesting that metal uptakes ions took place on a heterogeneous surface by multilayer adsorption.

A comparative study was conducted on Cu(II) removal from simulated solution using phosphoric-modified pecan shells and/or by a SR5 resin (Shawabkeh et al., 2002). At pH 3.6, the adsorption capacity of pecan shells on Cu(II) (95 mg/g) was higher than that of the resins (80 mg/g). At pH higher than 8.5, pecan shells had an adsorption capacity of 180 mg/g, almost two times higher than that at pH 3.6. This measured Cu(II) adsorption capacity was not a reliable result since, at pH higher than 8.5, Cu(II) ions precipitated in the form of hydroxide, thus increasing the metal removal from the solution.

Demirbaş et al. (2002) investigated Ni(II) removal from simulated solution using hazelnut shell activated carbon. They found that metal adsorption improved with an increasing temperature, suggesting that the adsorption was endothermic as indicated by all thermodynamic parameters presented in Table 2b. With an initial metal concentration of 15 mg/L, the optimum Ni(II) removal took place at pH 3.0 with metal adsorption capacity of 10.11 mg/g. In another study, hazelnut shell was also employed for Cr(VI) adsorption from simulated solution with an initial Cr(VI) concentration of 1000 mg/L (Kobyas, 2004). About 170 mg/g of Cr(VI) capacity occurred at pH 1.0. The results indicate that the adsorption capacity of individual adsorbent depends on the initial metal concentration.

Bishnoi et al. (2003) conducted a study on Cr(VI) removal by rice husk activated carbon from aqueous solution. They found that the maximum metal removal

Table 2a

Unmodified/modified agricultural waste utilized for removal of heavy metals by adsorption

Species	Type of adsorbent	Optimum dose (g/L)	Initial metal concentration (mg/L)	Optimum pH	Adsorption capacity (mg/g)	Retail price (US\$/kg)	$\Delta H^\circ$ (kJ/mol)	$\Delta G^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/mol)	References
Cr(VI)	As-received CSC	24	20	6.0	2.18	0.25	NA	NA	NA	Babel and Kurniawan (2004b)
	CSC coated with chitosan	18	20	4.0	3.65	0.25				
	H <sub>2</sub> SO <sub>4</sub> -treated CSC	15	20	6.0	4.05	0.25				
	HNO <sub>3</sub> -treated CSC	12	20	4.0	10.88	0.25				
Cd(II)	Cocoa shell	5	28.10	2.0	4.94	NA	NA	NA	NA	Meunier et al. (2003)
Cr(III)		5	13.00	2.0	2.52					
Cu(II)		5	15.88	2.0	2.87					
Ni(II)		5	14.68	2.0	2.63					
Zn(II)		5	16.35	2.0	2.92					
Cu(II)	Pecan shell	1	500	3.6	95.0	NA	NA	NA	NA	Shawabkeh et al. (2002)
Ni(II)	Orange peel	20	1000	6.0	158.0	NA	10.37	−9.49	−0.06	Ajmal et al. (2000)
	Parthenium	1	70	5.0	54.35	NA	NA	NA	NA	Kadirvelu et al. (2002)
Ni(II)	Orange peel	1	25	6–8	6.01	NA	NA	NA	NA	Annadurai et al. (2002)
Cu(II)		1	25	6–8	3.65					
Zn(II)		1	25	6–8	5.25					
Cr(VI)	Sawdust	2.4	100	2.0	15.82	NA	NA	−2.02	NA	Dakiky et al. (2002)
Cr(VI)	Maple sawdust	50	10	5.0	5.1	NA	NA	NA	NA	Yu et al. (2003)
Zn(II)	PSA	10	32.70	NA	13.9	NA	NA	NA	NA	Bansode et al. (2003)
Cu(II)		10	31.75		6.84					
Zn(II)	PSC	10	32.70		6.62					
Cu(II)		10	31.75		0.001					
Zn(II)	PSS	10	32.70		7.38					
Cu(II)		10	31.75		18.1					

Remarks: \*NA: Not available.

Table 2b

Unmodified/modified agricultural waste utilized for removal of heavy metals by adsorption

Species	Type of adsorbent	Optimum dose (g/L)	Initial metal concentration (mg/L)	Optimum pH	Adsorption capacity (mg/g)	Retail price (US\$/kg)	$\Delta H^\circ$ (kJ/mol)	$\Delta G^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/mol)	References
Cu(II)	Banana peel	1	25	6–8	4.75	NA	NA	NA	NA	Annadurai et al. (2002)
Zn(II)		1	25	6–8	5.80					
Ni(II)		1	25	6–8	6.88					
Ni(II)	Hazelnut shell	NA	15	3.0	10.11	NA	−16.71	+7.089	−30.73	Demirbaş et al. (2002)
Cr(VI)	Hazelnut shell	2.5	1000	1.0	170	NA	56.62	−6.75	0.195	Koby (2004)
Cr(VI)	Activated alumina	6	10	4.0	1.6	NA	NA	NA	NA	Bishnoi et al. (2003)
	Rice husk	12	10	2.0	0.79					
Cd(II)	Rice husk	20	50	NA	2	NA	40.16	−3.98	0.139	Ajmal et al. (2003)
Cd(II)	Coirpith	12	NA	4–5	NA	NA	NA	NA	NA	Kadirvelu et al. (2001a)
Cu(II)		9	126	4–5	10.22					
Ni(II)		10	996	4–5	91.63					
Ni(II)	Coirpith	0.2	40	5.0	62.50	NA	NA	NA	NA	Kadirvelu et al. (2001b)
Ni(II)	Almond husk	5	250	5.0	37.17	NA	NA	NA	NA	Hasar (2003)
Cr(VI)	Almond shell	2.4	100	2.0	10.62	NA	NA	+2.73	NA	Dakiky et al. (2002)
Cr(VI)	Ethylenediamine-modified rice hull	NA	301.6	2.0	23.40	NA	NA	NA	NA	Tang et al. (2003)
Cd(II)	Sugar-cane bagasse pith	2	50	6.0	24.70	NA	+27.52	−3.65	+93.61	Krishnan and Anirudhan (2003)

Remarks: \*NA: Not available.

by rice husk took place at pH 2.0 and multilayer adsorption might occur on the surface of adsorbent, as indicated by the applicability of the Freundlich isotherm for the equilibrium data. However, Ajmal et al. (2003) reported that the Langmuir isotherm was representative for the metal equilibrium data of rice husk. These differences could be due to the extent of surface modification on the individual adsorbent. Bishnoi et al. (2003) employed formaldehyde for pretreatment of rice husk, while  $K_2HPO_4$  was used in Ajmal et al. (2003). The two chemicals have different effects on the extent of surface modification that affects their reactivity in adsorbing heavy metal from solution.

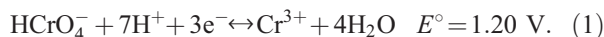
The uptake of Cd(II), Ni(II) and Cu(II) ions from real industrial wastewater using coirpith activated carbon was studied (Kadirvelu et al., 2001a). They reported that the maximum metal removal occurred at pH ranging from 4.0–5.0. Since coirpith was made up of homogenous adsorption patches, monolayer adsorption might occur on the surface, as indicated by the applicability of the Langmuir isotherm for the equilibrium sorption. This result is in agreement with the later study undertaken by Kadirvelu et al. (2001b), who used coirpith for Ni(II) uptake (Table 2b).

Hasar (2003) studied Ni(II) adsorption from simulated solution using almond husk activated carbon. The author found that the maximum metal removal of 37.17 mg/g occurred at pH 5.0. Monolayer adsorption might occur on the adsorbent surface, as indicated by the applicability of the Langmuir isotherm for the equilibrium sorption. Although both originated from almond waste, the Ni(II) adsorption capacity of almond husk (37.17 mg/g) was almost four times higher than that of almond shell (10 mg/g) (Dakiky et al., 2002). This can be due to the fact that the cell walls of almond husk contain a higher concentration of cellulose, silica and lignin than those of almond shell. Consequently, almond husk has more hydroxyl groups and carboxylic groups than almond shell for metal adsorption, resulting in higher metal removal by the almond husk (Hasar, 2003).

Rice hull, containing cellulose, lignin, carbohydrate and silica, was investigated for Cr(VI) removal from simulated solution (Tang et al., 2003). To enhance its metal removal, the adsorbent was modified with ethylenediamine (Table 2b). The maximum Cr(VI) adsorption of 23.4 mg/g was reported to take place at pH 2. This result indicates that an acidic pH range was effective for Cr(VI) removal from the solution. In acidic solution, Cr(VI) demonstrates a very high positive redox potential ( $E^\circ$ ) in the range of 1.33–1.38 V (Kotaš and Stasicka, 2000), implying that Cr(VI) was unstable in the presence of electron donors. The carbon surface of rice hull con-

tains carboxylic and hydroxyl groups, which play a role as electron donors in the solution (Tan et al., 1993). Consequently, Cr(VI) oxyanion is readily reduced to Cr(III) ions due to the presence of electron donors of rice hulls according to the following reaction:

pH 2.0–6.0



This can be observed that the reduction of Cr(VI) oxyanion is accompanied by proton consumption in the acidic solution, confirming the role played by  $H^+$  in the Cr(VI) removal.

Thioglycolic acid-modified cassava waste was explored for the removal of Cd(II), Cu(II) and Zn(II) from simulated solution (Abia et al., 2003). After chemical modification, adsorption kinetics was rapid and equilibrium was attained within 20 min. The adsorption capacities of the adsorbent were 18.05, 11.06 and 56.82 mg/g for Cd(II), Zn(II) and Cu(II) ions, respectively; thus suggesting that the surface modification of cassava waste with thio-glycolic acid improved its metal performance (Table 2c).

Enhanced Cu(II) adsorption was achieved using as-received soybean hull (ASH) and soybean hull extracted with NaOH and modified with citric acid (SHMC) (Marshall et al., 1999). Chemical modification of soybean hull with NaOH and citric acid remarkably improved its metal removal (ASH: 24.76 mg/g; SHMC: 154.9 mg/g). This could be due to the fact that pretreatment increased not only the number of carboxyl groups, but also the negative charges on the hulls.

Peanut hulls were investigated for Ni(II) removal from synthetic solution (Periasamy and Namasivayam, 1995). Maximum Ni(II) removal of 53.65 mg/g took place at pH ranging from 4–5. In another column studies, Periasamy and Namasivayam (1996) explored Cu(II) removal from synthetic solution using peanut hull. Maximum Cu(II) removal of 65.57 mg/g occurred at pH ranging from 6–10. This result is significantly higher than that of Brown et al. (2000), who also employed peanut hulls in batch studies for Cu(II) removal with an adsorption capacity of 10.17 mg/g (Table 2c). This phenomenon could be due to the inherent difference in the nature of both studies. In batch experiments, the concentration gradient decreased with increasing contact time; while in column operation, the adsorbent continuously had physicochemical contact with fresh feeding solution at the interface of the adsorption zone, as the adsorbate solution passed through the column. Consequently, the metal removal by peanut hull in column studies was higher than that in batch studies (Rao et al., 2002).



Table 2c

Unmodified/modified agricultural waste utilized for removal of heavy metals by adsorption

Species	Type of adsorbent	Optimum dose (g/L)	Initial metal concentration (mg/L)	Optimum pH	Adsorption capacity (mg/g)	Retail price (US\$/kg)	$\Delta H^\circ$ (kJ/mol)	$\Delta G^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/mol)	References
Cd(II)	Cassava waste	NA	112.4	4.0–5.0	18.05	NA	NA	NA	NA	Abia et al. (2003)
Cu(II)		NA	63.5	4.0–5.0	56.82					
Zn(II)		NA	65.4	4.0–5.0	11.06					
Cu(II)	Citric-acid modified soybean hulls	10	1270	NA	154.9	NA	NA	NA	NA	Marshall et al. (1999)
Cu(II)	Peanut hulls	10	32	NA	10.17	2.0	NA	NA	NA	Brown et al. (2000)
Cd(II)		10	32	NA	6.00					
Zn(II)		10	33	NA	9.00					
Cu(II)	Peanut hulls pellets	10	32	NA	9.11	11.0–18.5	NA	NA	NA	
Cd(II)		10	32	NA	6.00					
Zn(II)		10	33	NA	10.00					
Ni(II)	Peanut hulls	1	20	4.0–5.0	53.65	NA	NA	NA	NA	Periasamy and
Cu(II)	Peanut hulls	0.6	80	6.0–10.0	65.57	NA	NA	NA	NA	Namasivayam (1996)
Ni(II)	Rubber-wood ash	20	120	5.0–6.0	28.88	NA	–43.47	NA	NA	Hasan et al. (2000)
Ni(II)	Maize cob	6	NA	9.0	57.50	NA	NA	NA	NA	Selvakumari et al. (2002)
Cd(II)	Jackfruit	1.2	40	5.0	52.08	NA	NA	NA	NA	Inbaraj and Sulochana (2004)

Remarks: \*NA: Not available.

Overall, waste from agricultural sources has demonstrated its ability for heavy metal removal. Chemical modification with an oxidizing agent can enlarge its surface area, thus improving its sorptive capacity. This process requires extra operational cost due to the consumption of chemicals. However, improved adsorption capacities of the adsorbents may compensate for the cost of additional processing. Moreover, when an adsorbent from agricultural waste get saturated, regeneration of the spent adsorbent has become one of the most cost effective and sound environmental option, since no solid waste will be generated and disposed of. In fact, regeneration and desorption could be done to recover valuable metal from the spent adsorbent. However, the economics of this practice are dependent on the characteristics of the regenerated carbon and on the mass losses incurred during regeneration. Compared to adsorbents from other sources, those from agricultural waste possess unique characteristics such as ease of regeneration and desorption with basic or acid solutions. This can be due to the fact that they have surface functional groups such as hydroxyl and carboxylic that possesses high affinity for metal cations.

Among the adsorbents derived from agricultural waste, after chemical modification or conversion by heating into activated carbon, hazelnut shell and soybean hull have demonstrated an outstanding metal removal for Cr(VI) (170 mg/g) and/or Ni(II) (154.9 mg/g). These adsorbents can be employed to treat inorganic effluent of concentration less than 100 mg/L, in the

range of 100–1000 mg/L and higher than 1000 mg/L (Tables 2a b and c), providing one of promising alternatives to replace costly activated carbon. An acidic pH ranging 2–6 is effective for metal removal by adsorbents from agricultural waste. The Langmuir isotherm is generally applicable for the equilibrium data of such adsorbents, suggesting monolayer adsorption.

## 2.2. Industrial by-products

Like agricultural waste, industrial by-products such as fly ash (Mavros et al., 1993), waste iron (Lee et al., 2003), metallic iron (Singh and Singh, 2003), hydrous titanium oxide (Ghosh et al., 2003), are inexpensive and abundantly available. They can be chemically modified to enhance its removal performance. However, unlike those from agricultural waste, adsorbents from this source can be obtained from industrial processing only.

Several studies have been conducted on the potential of industrial by-products for metal removal. Zouboulis and Kydros (1993) investigated red mud, a solid by-product from alumina production, for Ni(II) removal from simulated wastewater. Red mud had high cation exchange capacity (CEC) and cation exchange sites. With an initial Ni(II) concentration of 400 mg/L, the maximum Ni(II) uptake of 160 mg/g occurred at pH 9.0, where chemical precipitation of Ni(II) might also occur.

To explore its potential as low-cost adsorbent, Lee et al. (2004) studied green sands, another by-product from the iron foundry industry, for Zn(II) removal from

synthetic solution. Kinetics studies showed that the adsorbent was effective for the metal removal with an adsorption capacity of 32.46 mg/g. Clay and iron in the green sands played major roles for Zn(II) sorption via sorption and precipitation. The adsorption reaction was endothermic, as shown by the positive value of enthalpy change (Table 3).

Blast-furnace slag is an adsorbent generated from steel plants. In 1996, Dimitrova studied the adsorption of Cu(II), Ni(II) and Zn(II) ions from simulated wastewater using blast-furnace slag. Its sorption capacities on Cu(II), Ni(II) and Zn(II) were 133.35, 55.76, and 103.33 mg/g, respectively. The metal sorption was in the form of hydro-oxo complexes and the high sorption capacity was due to the formation of soluble compounds on the internal surface of adsorbent. The Freundlich isotherm was representative for metals adsorption.

Feng et al. (2004) investigated Cu(II) and Pb(II) removal from simulated wastewater using iron slag and/or steel slag. A pH range from 3.5 to 8.5 [for Cu(II)] and from 5.2 to 8.5 [for Pb(II)] was optimum

for both iron and steels slags to maximize metal removal. The sorption of both metals for the two slags corresponded well with the Langmuir isotherm. The adsorption capacities of both slags for the metals are presented in Table 3.

Magnetite (Fe<sub>3</sub>O<sub>4</sub>), the main component of converter slag in the steel industry, was explored for Ni(II) removal from simulated wastewater (Ortiz et al., 2001). The adsorption rates increased with initial metal concentration, but decreased with increasing temperature. The maximum Ni(II) adsorption of 18.43 mg/g occurred at pH ranging from 5.5–6.0. The adsorption equilibrium followed the Freundlich isotherm.

Activated slag, an adsorbent from thermal power plant with a commercial price of US\$ 0.038/kg, was studied for the treatment of synthetic and real wastewater (Gupta, 1998). Using simulated solution (in batch studies), the adsorption capacities of activated slag were 30 mg/g for Ni(II) and 29 mg/g for Cu(II) ions. Using real wastewater (in column study), the capacities of activated slag were 66 mg/g for Ni(II) and 38 mg/g

Table 3  
Removal of heavy metals by adsorption using industrial by-products

Species	Type of adsorbent	Optimum dose (g/L)	Initial metal concentration (mg/L)	Optimum pH	Adsorption capacity (mg/g)	Retail price (US\$/kg)	$\Delta H^\circ$ (kJ/mol)	$\Delta G^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/mol)	References
Ni(II)	Red mud	7	400	9.0	160	NA	NA	NA	NA	Zoubuland Kydros (1993)
	Fly ash	1	50	8.5–9.0	NA	NA	NA	NA	NA	Mavros et al. (1993)
Zn(II)	Green sands	40	100	5.5–6.0	32.46	NA	+15.76	–12.66	+0.168	Lee et al. (2004)
Cu(II)	Blast-furnace slag	NA	214.63	7.5	133.35	NA	NA	NA	NA	Dimitrova (1996)
Ni(II)		NA	205.45	7.5	55.76					
Zn(II)		NA	220.40	9.0	103.33					
Cu(II)	Iron slags	2	200	3.5–8.5	88.50	NA	NA	NA	NA	Feng et al. (2004)
Pb(II)		2	200	3.5–8.5	95.24					
Cu(II)	Steel slags	2	200	5.2–8.5	16.21	NA	NA	NA	NA	
Pb(II)		2	200	5.2–8.5	32.26					
Ni(II)	Activated slag	10	250	4.0	30		+9.28	–18.50	0.091	
Cu(II)	(batch studies)	20	500	5.0	29		+17.99	–15.02	0.108	
Ni(II)	Activated slag	NA	248	NA	66	0.038	NA	NA	NA	Gupta (1998)
Cu(II)	(column studies)	NA	248	NA	38		NA	NA	NA	
Cd(II)	Bagasse	10	14	6.0	2.0	NA	–9.39	–4.95	+14.55	Gupta et al. (2003)
Ni(II)	Fly ash	10	12	6.5	1.70		–12.19	–5.44	+20.89	
Ni(II)	Magnetite	1	20	5.5–6.0	18.43	NA	NA	NA	NA	Ortiz et al. (2001)
Cr(VI)	Bagasse	4	100	6.0	0.03	NA	NA	NA	NA	Rao et al. (2002)
	Fly ash	4	90	6.0	0.01					
Ni(II)	Bagasse	10	90	8.0	0.001					
	Fly ash	10	100	8.0	0.0002					
Ni(II)	Fly ash type	20	25	8.0	1.16					
Cu(II)	Seyitomer	20	25	7.0	1.25					
Ni(II)	Fly ash type	20	25	8.0	0.99	NA	NA	NA	NA	Bayat (2002)
Cu(II)	Afsin-Elbistain	20	25	7.0	1.35					
Cr(VI)	Hydrous titanium oxide	20	0.1	1.5	30.0	NA	NA	NA	NA	Ghosh et al. (2003)

for Cu(II). As shown by the positive values of enthalpy change ( $\Delta H^\circ$ ) and the change in the Gibbs free energy ( $\Delta G^\circ$ ), the adsorption reaction in batch studies was endothermic and spontaneous in nature, indicating that the metal uptake was enhanced with an increasing temperature.

Gupta et al. (2003) explored bagasse fly ash, a solid waste from sugar industry, for Cd(II) and Ni(II) removal from synthetic solution. About 90% of 14 mg/L of Cd(II) and 12 mg/L of Ni(II) were removed at pH ranging from 6.0 to 6.5. The metal removal improved with an increasing temperature, suggesting an endothermic reaction.

Ni(II) and Cu(II) removal from simulated wastewater using Seyitomer and Afsin–Elbistain fly ash was evaluated by Bayat (2002). In Turkey, fly ash is a waste from thermal power plants. The adsorption capacities of Seyitomer fly ash for the two heavy metals were comparable to those of Afsin–Elbistain fly ash (Table 3). As indicated by the applicability of the Langmuir isotherm for the equilibrium data of both metals, monolayer adsorption might occur on the surface of the adsorbent.

As a whole, adsorbents from industrial by-products such as iron/steel slag have some advantages for metal removal. In addition to having a wide pH range (pH 1.5–9.0) effective for metal removal, such adsorbents can be employed to treat inorganic effluent with metal concentration of less than 20 mg/L, in the range of 20–100 mg/L, or higher than 100 mg/L (Table 3). Unlike adsorbents from agricultural waste, no further work has been done on the regeneration of the spent adsorbent from industrial by-products. This could be due to the fact that adsorbents derived from agricultural waste and industrial by-products have different characteristics in nature from each other such as processing conditions, making them difficult for regeneration. As a result, more R and D work needs to be undertaken to enable the adsorbents for commercialization.

Among the adsorbents from industrial by-products, red mud and blast-furnace slag have high metal adsorption capacities (160 mg Ni(II)/g and 133.35 mg Cu(II)/g), respectively. Their capacities were comparable to that of orange peel (158 mg Ni(II)/g) and of soybean hull modified with NaOH and citric acid (154.9 mg Cu(II)/g). However, unlike the two prominent adsorbents, fly ash, a by-product from lignite-burning plants, is not effective for metal removal due to its low metal-binding capacity. Both the Langmuir and Freundlich isotherms can be applicable for the equilibrium data of adsorbents from industrial by-products, suggesting that either monolayer or multilayer adsorption could occur on their surface, depending on the type of by-products.

### 2.3. Natural materials

Like industrial by-product, natural materials locally available in certain region can be employed as low-cost adsorbents. Due to its metal-binding capacity, natural materials such as zeolite and clay have been explored for treating metal-contaminated wastewater.

#### 2.3.1. Zeolite

Among minerals that possess sorbent properties, zeolite appears as one of the most promising for metal purification. Zeolite, an aluminosilicate tetrahedron connected with oxygen atom, has charge-balancing cations that counter-balance the negative charge localized on the aluminosilicate framework (Keane, 1998). In Greece, zeolite has been used for the treatment of metal-contaminated wastewater due to its low cost. Depending on its quality, zeolite is sold at US\$0.03–0.12/kg (Virta, 2001).

Babel and Kurniawan (2003b) studied Cr(VI) uptake from simulated wastewater using natural zeolite. NaCl-treated zeolite had better removal capabilities (3.23 mg/g) for Cr(VI) ions than as-received zeolite (1.79 mg/g) at an initial Cr concentration of 20 mg/L. These results suggest that the Cr adsorption capacities of zeolite varied, depending on the extent of chemical treatment (Wingenfelder et al., 2005). The results were significantly lower than those of Perić et al. (2004), who also used zeolite for Zn(II) and Cu(II) removal (Zn(II): 13.06 mg/g; Cu(II): 25.04 mg/g). The metal removal by zeolite was a complex process, involving ion exchange and adsorption.

When zeolite in the column get exhausted, recovery of the adsorbed material as well as the regeneration of adsorbent becomes necessary. Kurniawan (2002) reported that NaCl was suitable to reuse zeolite with regeneration efficiency of more than 90%. This could be due to the fact that Cr adsorption on zeolite mostly occurred due to ion exchange between Na(I) of zeolite and Cr(III) ions in the solution.

#### 2.3.2. Clay

Another low-cost mineral that has high cation exchange capacity (CEC) in solution is clay. There are three types of clay: montmorillonite, bentonite and kaolinite. Out of the three, montmorillonite has the highest CEC and its current market price (US\$ 0.04–0.12/kg) is twenty-times cheaper than that of activated carbon (Virta, 2002).

A number of studies on metal uptake using montmorillonite have been conducted. The adsorption of Cd(II), Cr(III), Cu(II), Ni(II) and Zn(II) ions on Na-montmoril-



lonite using column operations was investigated by Abollino et al. (2003). As shown in Table 4a, Cu(II) was the least adsorbed of the cations, while Cd(II) ion was the most adsorbed due to its high charge density. Modification of montmorillonite using sodium dodecyl sulfate (SDS) was reported to significantly improve its removal for Cu(II) and Zn(II) (Lin and Juang, 2002). The amount of Cu(II) sorbed was larger (16.13 mg/g) than that of Zn(II) (13.27 mg/g) (Table 4a). These results were four times higher than those of montmorillonite modified with sodium (Abollino et al., 2003). This could be due to the fact that large anionic species such as SDS could easily enter and became strongly fixed in the inter-layer region of montmorillonite, compared to NaOH.

Vengris et al. (2001) reported that pretreatment of clay with HCl significantly improved the removal of Ni(II), Cu(II) and Zn(II) from simulated wastewater. This could be due to the fact that acid treatment changed the chemical composition and mineralogical structure of clay, enhancing its uptake capacity. The maximum adsorption capacities for the cations in the solution were in the order: Cu(II) > Ni(II) > Zn(II) (Table 4a). As indicated by the applicability of the Langmuir isotherm for the equilibrium data of those metals, monolayer adsorption might occur on the surface of adsorbent.

Another material from clay mineral to adsorb metal is bentonite, which consists of clay, silt and sand. This material is valuable for its tendency to absorb water in the interlayer site (Kaya and Oren, 2005). Chakir et al. (2002) studied the uptake of Cr(III) from simulated solution using bentonite and an expanded perlite. Surface complexation played major roles in Cr(III) removal. Kinetics studies showed that the Cr(III) uptake by bentonite was faster than that by perlite. The Cr(III) removal by bentonite (96%) was remarkably higher than that by perlite (40%) at the same Cr concentration of 20 mg/L. Similar results were also obtained by Ulmanu et al. (2002), who compared Cu(II) and Cd(II) removal from synthetic solution using bentonite. Compared to diatomite, bentonite has higher adsorption capacities for both ions (Cu(II): 18.16 mg/g; Cd(II): 9.34 mg/g).

Kaolinite is the other clay, representing a layered alumino-silicate mineral with the structure of a tetrahedral (Si center) and octahedral (Al center). Kaolinite was used for Cu(II), Ni(II), Mn(II) and Co(II) removal from simulated solution (Arias et al., 2002; Yavuz et al., 2003). The metal sorption on kaolinite followed the Langmuir isotherm. Due to their small ionic radius, Cu(II) ions had the highest adsorption affinities compared to other. At 298 K, the change in free energy ( $\Delta G^\circ$ ) was negative (Table 4b), indicating that the

Table 4a  
Heavy metal uptake by natural materials through adsorption

Species	Type of adsorbent	Optimum dose (g/L)	Initial metal concentration (mg/L)	Optimum pH	Adsorption capacity (mg/g)	Retail price (US\$/kg)	$\Delta H^\circ$ (kJ/mol)	$\Delta G^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/mol)	References
Cr(VI)	NaCl-treated zeolite	9	20.0	4.5	3.23					Babel and Kurniawan (2003b)
	As-received zeolite	27	20.0	4.5	1.79	0.75	NA	NA	NA	
Zn(II)	Natural zeolite	10	65.4	6.5	13.06	NA	NA	NA	NA	Perić et al. (2004)
Cu(II)		10	64.3	5.5–6.5	25.04					Abollino et al. (2003)
Cd(II)	Na-Montmorillonite	1274	112.0	5.5	5.20	NA	NA	NA	NA	
Cr(III)		1274	52.0		5.13					
Cu(II)		1274	63.5		3.04					
Ni(II)		1274	58.7		3.63					
Zn(II)		1274	65.4		3.61					
Ni(II)	HCl-treated clay	10	85	6.2	80.9	NA	NA	NA	NA	Vengris et al. (2001)
Cu(II)		10	90	6.2	83.3					
Zn(II)		10	85	6.2	63.2					
Cu(II)	SDS-modified	2.5	2857.5	4.0	16.13	NA	+7.05	−9.66	+9.09	Lin and Juang (2002)
Zn(II)	montmorillonite	2.5	2943.0	4.0	13.27		+7.39	−9.17	+6.39	
Cd(II)	Kaolinite	20	200	6.0	3.04	NA	NA	NA	NA	Ulmanu et al. (2002)
Cu(II)		20	200	6.0	4.47					
Cd(II)	Bentonite	20	200	6.0	9.27					Chakir et al. (2002)
Cu(II)		20	200	6.0	18.16					
Cd(II)	Diatomite	20	200	6.0	3.24					
Cu(II)		20	200	6.0	5.54					
Cr(III)	Bentonite	10	20	5.0	4.29	NA	NA	NA	NA	
	Perlite	10	20	5.0	1.4					

Remarks: \*NA: Not available.

Table 4b

Heavy metal uptake by natural materials through adsorption

Species	Type of adsorbent	Optimum dose (g/L)	Initial metal concentration (mg/L)	Optimum pH	Adsorption capacity (mg/g)	Retail price (US\$/kg)	$\Delta H^\circ$ (kJ/mol)	$\Delta G^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/mol)	References
Cu(II)	Kaolinite	5	20	4.0	1.9	NA	NA	NA	NA	Arias et al. (2002)
	Kaolinite-HA	5	20	4.0	4.8					
Cd(II)	Kaolinite	5	20	4.0	3.7					Chantawong et al. (2003)
	Kaolinite-HA	5	20	4.0	8.6					
Cd(II)	Kaolinite	20	100	6.5	0.75	NA	NA	NA	NA	
	Ball clay	20	100	6.5	2.24					
Cr(III)	Kaolinite	20	100	4.0	1.81					
	Ball clay	20	100	4.0	3.60					
Cu(II)	Kaolinite	20	100	5.0	0.76					Álvarez-Ayuso and García-Sánchez (2003)
	Ball clay	20	100	5.0	1.60					
Ni(II)	Kaolinite	20	100	6.0	0.003					
	Ball clay	20	100	6.0	0.41					
Zn(II)	Kaolinite	20	100	6.5	1.80					
	Ball clay	20	100	6.5	2.88					
Ni(II)	Natural	10	100	6.0	19.3	NA	NA	NA	NA	
Cu(II)	vermiculite	10	100	5.0	26.0					
Ni(II)	Exfoliated	10	100	6.0	5.91					
Cu(II)	vermiculite	10	100	5.0	8.60					
Cu(II)	Kaolinite	10	3159	NA	10.79	NA	+39.52	−4.61	+0.117	
Ni(II)		10	1010	NA	1.70		+37.27	−5.42	+0.107	
Co(II)		10	1000	NA	0.92		+21.52	−5.51	+0.054	
Mn(II)		10	1029	NA	0.45		+36.73	−6.69	+0.101	
Cr(VI)	Pyrite fines	20	100	5.0–6.5	10.00	NA	NA	NA	NA	Zoubulis et al. (1995)
Cd(II)	Glauconite	2	5	4.0–6.5	4.10	NA	NA	NA	NA	Smith et al. (1996)
Zn(II)		2	5	4.0–6.5	1.37					
Cr(VI)	Wollastonite	20	10.4	2.5	0.52	NA	NA	NA	NA	Sharma (2003)

Remarks: \*NA: Not available.

adsorption was an endothermic process with higher removal favored at a higher temperature of 313 K.

Chantawong et al. (2003) studied the adsorption of Cd(II), Cr(III), Cu(II), Ni(II) and Zn(II), on kaolinite and ballclay from simulated solution. Metal adsorption by kaolinite was observed as follows: Cr>Zn>Cu ≈ Cd>Ni>Pb and that by ballclay was: Cr>Zn>Cu>Cd>Ni (Table 4b). Ballclay has higher removal efficiency than kaolinite because illite, the major mineral in the ballclay, has a higher surface charge than kaolinite. Cr(III) ions were the most readily absorbed of the heavy metals, as it had the highest ionic charge compared to the others.

Smith et al. (1996) investigated the sorption of Cd(II) and Zn(II) ions from simulated wastewater using glauconite, a complex clay mineral occurring in marine sediments. Equilibrium was attained within 60 min and Cd(II) ions had a higher adsorption capacity (4.1 mg/g) than Zn(II) (1.37 mg/g). Although the adsorbent is a complex mineral, the Langmuir isotherm was applicable for the equilibrium data.

Other natural materials such as pyrite and vermiculite have been studied less intensively due to its local availability. The Cr(VI) removal from simulated waste-

water using pyrite fines was investigated (Zoubulis et al., 1995). Pyrite is a common mineral associated with sulphide ores and coal. Maximum Cr(VI) removal of 10 mg/g was achieved at pH ranging from 5.5 to 6.5. At higher pH than 9.0, Cr(OH)<sub>4</sub> species were formed, reducing Cr(VI) removal due to interference effects.

Álvarez-Ayuso and García-Sánchez (2003) also studied Ni(II) and Cu(II) removal from synthetic solution and/or real wastewater using natural vermiculite (NV) and exfoliated vermiculite (EF). In batch studies using simulated solution, maximum metal removal occurred at pH ranging from 5 to 6. The Langmuir isotherm was applicable for the equilibrium data (Table 4b). In column operations using real wastewater, at 218 bed volumes (BV), the Ni(II) concentration in the effluent was less than 2 mg/L, the discharge limit established by the European Community (EC).

The applicability of wollastonite for Cr(VI) uptake from synthetic wastewater was investigated by Sharma (2003). Maximum Cr adsorption of 0.52 mg/g occurred at pH 2.5. The metal adsorption was an endothermic reaction, as the removal increased with an increasing temperature from 30–50 °C.

Overall, zeolite and clay have shown their ability to treat inorganic effluent. Among clay minerals, montmorillonite and bentonite have shown reasonable removal for Cu(II) with adsorption capacities of 16.13 and 18.16 mg/g, respectively. The Langmuir isotherm is generally applicable to describe monolayer adsorption on the surface of adsorbent. Adsorbents derived from natural materials perform well at an acidic pH ranging from 2.5–6.5. Montmorillonite and kaolinite generally treat inorganic effluent with metal concentration in the range of 100–1000 mg/L or higher than 1000 mg/L; zeolite and bentonite, however, are usually employed for treating real wastewater with metal concentration of less than 200 mg/L (Table 4b). Compared to that of adsorbents derived from agricultural waste, the price of those originated from natural materials is relatively higher, making them not competitive enough for commercial application.

#### 2.4. Miscellaneous low-cost adsorbents

Other adsorbents such as coal, sludge and peat have been studied less extensively due to its local availability. Karabulut et al. (2000) studied Cu(II) and Zn(II) removal from simulated wastewater with low-rank Turkish coals. Carboxylic acid and hydroxyl functional groups present on the surface of coal were the adsorption sites for metal removal via ion exchange. Maximum Cu(II) removal of 1.62 mg/g and 1.2 mg/g for Zn(II) occurred at pH 4.0. Despite using coal as the adsorbent, the metal

capacities in the study carried out by Karabulut et al. were significantly lower than those of study undertaken by Solé et al. (2003) for Zn(II) removal with an adsorption capacity of 27.2 mg/g at pH 6.0, indicating that the adsorption capacity of an adsorbent depends on the initial concentration of adsorbate (Table 5a).

Sludge is another adsorbent used for Cu(II) and Cd(II) removal from simulated waste-water (Calace et al., 2003). The pH breakthrough curve of Cd(II) was similar to that of Cu(II) ions at pH 4.0. The sorption capacities of Cu(II) and Cd(II) ions were 9.5 and 10.23 mg/g, respectively. It is interesting to note that about 70% regeneration efficiency was achieved for both cations with 0.1 M HCl.

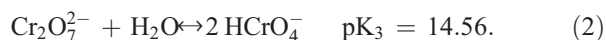
Ni(II) removal from synthetic solution using a combined sludge-ash was also studied (Weng, 2002). As indicated by the applicability of the Freundlich isotherm for equilibrium data, multilayer adsorption might occur on the surface of the adsorbent. The adsorption capacity of the combined adsorbent was 0.32 mg/g, lower than that of fly ash alone (0.65 mg/g) in another study (Weng, 1990). These results were very low compared to those of Zhai et al. (2004), who investigated Cd(II) and Ni(II) removal from simulated wastewater using sewage sludge. Zhai et al. reported that maximum removal of Cd(II) was 16 mg/g and of Ni(II) was 9 mg/g at pH ranging from 5.5 to 6.0, indicating that the characteristics of the individual adsorbent affect the removal capacity of an adsorbent on heavy metal.

Table 5a  
Miscellaneous low-cost adsorbents for metals decontamination using adsorption

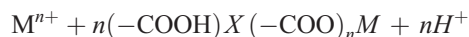
Species	Type of adsorbent	Optimum dose (g/L)	Initial metal concentration (mg/L)	Optimum pH	Adsorption capacity (mg/g)	Retail price (US\$/kg)	$\Delta H^\circ$ (kJ/mol)	$\Delta G^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/mol)	References
Cu(II)	Coal	10	100	4.0	1.62	NA	NA	NA	NA	Karabulut et al. (2000)
Zn(II)		10	100	4.0	1.20					
Zn(II)	Coal	5	500	6.0	27.2	NA	NA	NA	NA	Solé et al. (2003)
Cu(II)	Sludge	1.2	38.1	4.0	9.50	NA	NA	NA	NA	Calace et al. (2003)
Cd(II)			67.4	4.0	10.23					
Ni(II)	Sludge-ash	1	5.1	>8.0	0.32	NA	+30.45	−31.12	0.20	Weng (2002)
Cd(II)	Anaerobic sludge	20	200	6.0	5.82	NA	NA	NA	NA	Ulmanu et al. (2002)
Cu(II)		20	200	6.0	0.25					
Cd(II)	Sewage sludge	10	40	5.5–6.0	16	NA	NA	NA	NA	Zhai et al. (2004)
Ni(II)		20	30	5.5–6.0	9					
Cd(II)	Coffee residue-clay	10	200	7.0–9.0	39.5	NA	−4.66	NA	NA	Boonamnuayvitaya et al. (2004)
Cu(II)			50	7.0–9.0	31.5					
Zn(II)			250	7.0–9.0	13.4					
Ni(II)			100	7.0–9.0	11.0					
Cr(III)	Milled peat	NA	200	4.0	14.04	NA	NA	NA	NA	Dean et al. (1999)
Cr(VI)		NA	200	2.0	30.16					
Cu(II)	Calcined	1	50	5.0	29.8	NA	NA	NA	NA	Aklil et al. (2004)
Zn(II)	phosphate	1	50	5.0	20.6					

Remarks: \*NA: Not available.

Dean et al. (1999) investigated the uptake of Cr(III) and Cr(VI) ions from synthetic solution using peat. Maximum Cr(III) uptake of 14.04 mg/g took place at pH 4.0, while the optimum Cr(VI) uptake of 30.16 mg/g occurred at pH 2.0. Although the oxyanion of dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) was used as the source of Cr(VI) in the synthetic wastewater, under common environmental pH ( $\text{pH} < 6.0$ ), the most dominant species at pH 2.0 and pH 4.0 for metal removal was  $\text{HCrO}_4^-$  (Lalvani et al., 1998; Pradhan et al., 1999). The hydrolysis reaction of  $\text{Cr}_2\text{O}_7^{2-}$  was reported as follows:



Since the acidic functional groups including carboxylic, hydroxyl, and carbonyl groups are present on the surface of peat, the physicochemical interactions that might occur during Cr(VI) removal could be expressed as follows:



where  $(-\text{COOH})$  represents the surface functional group of peat and  $n$  is the coefficient of the reaction component, depending on the oxidation state of metal ions, while  $\text{M}^{n+}$  and  $\text{H}^+$  are Cr(III) and hydrogen ions, respectively.

Boonamnuayvitaya et al. (2004) investigated the removal of Cd(II), Cu(II), Zn(II) and Ni(II) ions from synthetic solution using pyrolyzed coffee residue and clay. The clay was used as a binder for the residue. Adsorption was observed in the order of  $\text{Cd(II)} > \text{Cu(II)} > \text{Zn(II)} > \text{Ni(II)}$  (Table 5a). The Langmuir isotherm was representative for the equilibrium data of the metals, suggesting that monolayer adsorption might occur on the surface of adsorbent.

Gang et al. (2000) studied the Cr(VI) removal from simulated wastewater using a reactive polymer, a long alkyl quaternized poly 4-vinylpyridine (PVP). Metal adsorption by the adsorbent was strongly influenced by pH. Maximum Cr(VI) of 3.5 mg/g occurred at a

pH range of 4.5–5.5 (Table 5b). The Langmuir isotherm was representative for the equilibrium data, indicating monolayer adsorption on the surface of the adsorbent.

Among the adsorbents presented above, peat and wool stand out for high Cr(VI) removal with adsorption capacities of 30.16 and 41.15 mg/g, respectively. An acidic pH range of 2.0–4.0 is effective for Cr(VI) removal with an initial metal concentration ranging from 100–200 mg/L. It is important to note that the adsorption capacities of low-cost adsorbents presented above vary, depending on the characteristics of the individual adsorbent, the extent of surface modification and the initial concentration of adsorbate.

### 3. Activated carbon (AC)

Based on its size and shape, there are four types of activated carbon: powder (PAC), granular (GAC), fibrous (ACF), and cloth (ACC). Due to the different raw materials, the extent of chemical activation, and the physicochemical characteristics; activated carbon has its specific application as well as inherent advantages and disadvantages in wastewater treatment. Depending on its quality, activated carbon is costly at US\$9/kg (CSIRO, 2004).

Netzer and Hughes (1984) studied the adsorption of Cu(II) ions by granular activated carbon (GAC) type Barney Cheney NL 1266 from synthetic solution. At pH 4.0, GAC could remove 93% of 10 mg/L Cu(II) solution. The results were lower than that of GAC type Filtrasorb 400, employed by Sharma and Forster (1996) for Cr(VI) removal from simulated wastewater. They reported that the maximum metal adsorption capacity of 145 mg/g was achieved at pH ranging from 2.5 to 3.0 (Table 6).

The adsorption of Cd(II) ions from synthetic solution using GAC type Filtrasorb 400 was investigated (Leyva-Ramos et al., 1997). The metal adsorption capacity of GAC was 8 mg/g at pH 8.0. This result was

Table 5b  
Miscellaneous low-cost adsorbents for metals decontamination using adsorption

Species	Type of adsorbent	Optimum dose (g/L)	Initial metal concentration (mg/L)	Optimum pH	Adsorption capacity (mg/g)	Retail price (US\$/kg)	$\Delta H^\circ$ (kJ/mol)	$\Delta G^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/mol)	References
Cr(VI)	Soya cake	9.3	44	1.0	0.28	NA	NA	NA	NA	Daneshvar et al. (2002)
Cr(VI)	Wool	2.4	100	2.0	41.15	NA	NA	–2.26	NA	Dakiky et al. (2002)
	Olive cake	2.4	100	2.0	33.44		NA	–0.94	NA	
	Pine needles	2.4	100	2.0	21.50		NA	0.13	NA	
	Cactus	2.4	100	2.0	7.08		NA	+2.80	NA	
Cr(VI)	PVP-coated silica gel	2.5	10.0	4.5–5.5	3.50	NA	NA	NA	NA	Gang et al. (2000)

Remarks: \*NA: Not available.

Table 6  
Heavy metals removal by commercial activated carbon (CAC)

Species	Type of activated carbon	Optimum dose (g/L)	Initial metal concentration (mg/L)	Optimum pH	Adsorption capacity (mg/g)	References
Cu(II)	GAC type Barney Cheney NL 1266	NA	10	4.00	NA	Netzer and Hughes (1984)
Cr(VI)	GAC type Filtrasorb 400	NA	NA	2.5–3.0	145	Sharma and Forster (1996)
Cr(III)		NA	NA	NA	30	Park and Jung (2001)
Cd(II)	Filtrasorb 400	NA	80	8.0	8	Leyva-Ramos et al. (1997)
Cd(II)	Oxidized ACF	20.00	1000	5.0–6.0	146	Rangel-Mendez and Streat (2002)
Ni(II)	As-received ACF	NA	NA	NA	2	Shim et al. (2001)
Cu(II)		NA	NA	NA	9	
Cr(VI)		NA	NA	NA	40	Shim et al. (1996)
Zn(II)	Oxidized	2.5	6.54	9.0	2	Babić et al. (2002)
Cd(II)	ACC	2.5	11.24	3.75		
Zn(II)	GAC type C	2.0	60	7.0	20.00	Leyva-Ramos et al. (2002)
Zn(II)	GAC type	10	32.70	NA	0.29	Bansode et al. (2003)
Cu(II)	Filtrasorb-200	10	31.75	NA	6.10	
	HNO <sub>3</sub> -oxidized GAC	2.0	20	4.0	15.47	
Cr(VI)	H <sub>2</sub> SO <sub>4</sub> -oxidized GAC	4.0	20	4.0	8.94	Babel and Kurniawan (2004b)
	As-received GAC	6.0	20	4.0	4.72	

Remarks: \*NA: Not available.

slightly higher than that of Bansode et al. (2003), who employed GAC type Filtrasorb 200 for Cu(II) removal with an adsorption capacity of 6.10 mg/g, indicating that the initial concentration of adsorbate plays major roles in determining the extent of the adsorption capacity of an adsorbent (Table 6). For Zn(II) removal, the adsorption capacity of GAC type C (Leyva-Ramos et al., 2002) was significantly higher than that of GAC type Filtrasorb 200 (Bansode et al., 2003), as shown in Table 6.

To improve its removal performance on Cr(III) ions, the surface of GAC was chemically modified with nitric acid (Aggarwal et al., 1999). The adsorption capacity on the oxidized carbon for Cr(III) was enhanced three times to 30 mg/g. This could be due to the greater negative charge on the surface of oxidized GAC compared to the non-oxidized material (Goel et al., 2005). Due to electrostatic attraction between the Cr(III) ions and the negatively-charged surface, more adsorption of Cr(III) ions might occur on the carbon surface, resulting in higher metal uptake by the adsorbent. Similar results were obtained by Shim et al. (2001), Park and Jung (2001), Rangel-Mendez and Streat (2002), Monser and Adhoum (2002), Babić et al. (2002), and Babel and Kurniawan (2004b). They also found that electrostatic attraction played a major role in metal adsorption on the surface of carbon.

Overall, chemical modification of activated carbon can improve its removal for heavy metal. Among the various types of activated carbon presented, GAC type

Filtrasorb 400 and HNO<sub>3</sub>-oxidized activated carbon fibre (ACF) stand out high metal removal with adsorption capacities of 145 mg of Cr(VI)/g and 146 mg of Cd(II)/g, respectively. The results were lower than those of adsorbent derived from agricultural waste such as hazelnut shell activated carbon (Cr(VI): 170 mg/g) and chemically modified soybean hull (Cu(II): 154.9 mg/g). It is interesting to note that activated carbon performs effectively at an acidic pH range of 2.5–7.0 and has the ability to treat inorganic effluent with metal concentration ranging from 10 to 1000 mg/L. Due to its high cost, industrial users are reluctant to employ activated carbon for the treatment of metal-contaminated wastewater, opening the way for commercialization of low cost adsorbent derived from agricultural waste (Inbaraj and Sulochana, 2004).

#### 4. Comparison of adsorption capacities among low-cost adsorbents and activated carbon

To justify their viability as effective adsorbents for heavy metal uptake, the adsorption capacities of all low-cost adsorbents need to be compared. Table 7 presents the highest reported metal adsorption capacities of low-cost adsorbents and activated carbon. It is evident that after chemical modification or conversion by heating into activated carbon, the low-cost adsorbents originating from agricultural waste have demonstrated outstanding metal removal capabilities. The removal capacity of such materials (Cr(VI): 170 mg/g



Table 7

Summary of the highest reported adsorption capacities of low-cost adsorbents and activated carbon

Source of adsorbent	Type of adsorbent	Adsorption capacity (mg/g)						References
		Cd(II)	Cr(III)	Cr(VI)	Cu(II)	Ni(II)	Zn(II)	
Agricultural waste	Hazelnut shell			170				Koby (2004)
	Orange peel					158		Ajmal et al. (2000)
	Citric acid-modified soybean hull				154.9			Marshall et al. (1999)
	Jackfruit	52.08						Inbaraj and Sulochana (2004)
Industrial by-products	Red mud					160		Zouboulis and Kydros (1993)
	Blast-furnace slag				133.35		103.33	Dimitrova (1996)
	Titanium oxide			30				Ghosh et al. (2003)
Natural materials	HCl-treated clay				83.3	80.9	63.2	Vengris et al. (2001)
Miscellaneous adsorbent	Wool			41.15				Dakiky et al. (2002)
	Coffe residue-clay	39.5			31.5			Boonamnuayvitaya et al. (2004)
Activated carbon	Coal						27.2	Solé et al. (2003)
	Calcined phosphate				29.8			Aklil et al. (2004)
	GAC type			145				Sharma and Forster (1996)
	Filtrisorb 400		30					Park and Jung (2001)
	HNO <sub>3</sub> -treated ACF	146						Rangel-Mendez and Streat (2002)
	GAC type C						20	Leyva-Ramos et al. (2002)

of hazelnut shell activated carbon, Ni(II): 158 mg/g of orange peel, Cu(II): 154.9 mg/g of soybean hull, Cd(II): 52.08 mg/g of jackfruit) is comparable to that of activated carbon (Cd(II): 146 mg/g, Cr(VI): 145 mg/g, Cr(III): 30 mg/g, Zn(II): 20 mg/g), suggesting the viability of low-cost adsorbents for treating metals-contaminated wastewater.

Among adsorbents derived from agricultural waste, hazelnut shell activated carbon (Cr(VI): 170 mg/g), orange peel (Ni(II): 158 mg/g) and chemically modified soybean hull (Cu(II): 154.9 mg/g) stand out for significantly higher metal adsorption capacities, compared to those from natural material such as clay (Ni(II): 81 mg/g, Cu(II): 83 mg/g, Zn(II): 63 mg/g). This can be due to the fact that most adsorbents derived from agricultural waste contain cellulose, hemicellulose and lignin, with surface functional groups such as carboxylic, carbonyl and hydroxyl, which possess high affinity for heavy metal ions. Tan et al. (1993) reported that metal uptake by adsorbents from agricultural waste might occur through sorption process involving these surface functional groups.

Different characteristics of individual adsorbents can be addressed in different ways to improve its metal removal performance. Low cost adsorbents from agricultural waste can be chemically modified with oxidizing agents to enhance their metal removal performance. This can be due to the increased surface area for metal adsorption and greater negative surface charge, resulting from oxidative treatment. The adsorption capacity is

raised through columbic attractions with metal in the solution (Babel and Kurniawan, 2004b). However, those from natural materials such as zeolite need to be treated with NaCl to improve its metal removal performance. Kurniawan (2002) reported that this treatment rendered the adsorbent in the homoionic form of Na(I). Consequently, the Na(I) of zeolite could be replaced by metal cations [Cr(III)] in the solution through ion exchange process (Kurniawan, 2002).

To evaluate the technical applicability of various low-cost adsorbents, comparative studies are made in terms of pH, optimum dose required (g/L) and maximum concentration of metal used (mg/L). This comparison has a relative meaning due to different conditions (pH, temperature and wastewater composition), type of biomaterial and methods.

It is evident from Tables 2a–c, 3, 4a,b and 5a,b that after chemical modification or conversion by heating into activated carbon, appealing materials such as pecan shell, hazelnut shell or soybean hulls demonstrate outstanding adsorption capacities compared to less attractive materials such as zeolite. An objective evaluation of the commercial potential of any material as an adsorbent should consider its local availability, as this factor is closely related with cost minimization (Bailey et al., 1999). For countries not producing agricultural waste, the cost of transportation of raw material may be involved for the production of activated carbon. Local environmental conditions also affect the removal performance of activated carbon derived from agricultural

waste. In tropical countries, activated carbon shows a favorable removal performance, as adsorption occurs at higher temperature, resulting in higher metal uptake. Moreover, local availability of low-cost adsorbents, fast adsorption rate, reasonable adsorption capacity and sludge-free operation will reduce operational cost and render their use for treating inorganic effluent a very attractive option.

### 5. Cost-effectiveness of low-cost adsorbents

Since the cost-effectiveness of an adsorbent is one of the important issues that must be considered when selecting an adsorbent, the price of low-cost adsorbents has to be compared. The price of low-cost adsorbents listed in Tables 2a–c, 3, 4a,b and 5a,b is not complete due to the unavailability of data from previous studies. Expenditure on individual adsorbents varies, depending on the processing employed and its local availability (Hasan et al., 2000; Shukla and Pai, 2005). Low-cost adsorbents derived from agricultural waste, which are converted chemically or by heating into activated carbon, require extra processing cost. Improved adsorption capacities, however, may compensate the cost for such a process (Bailey et al., 1999; Babel and Kurniawan, 2003a).

Although expenditure on low-cost adsorbents may be negligible, further cost-benefit analysis needs to take into account any spending associated with regeneration or operation including chemicals, electricity, labor, transportation and maintenance (Krishnan and Anirudhan, 2003). If the overall cost remains economically attractive, low-cost adsorbents for metal uptake present promising alternatives to costly activated carbon, as their use can minimize treatment cost.

The cost efficacy of outstanding adsorbents such as hazelnut shell for metal removal from wastewater increases if they can be regenerated for multiple uses. The price of low-cost adsorbents may decrease, as more industries consider their use for treating metals-contaminated wastewater. In spite of the positive trend of the development worldwide, so far no low cost adsorbents have been available for commercialization. This indicates that more R and D work and in-depth study on the mass production of the adsorbents with enhanced removal performance and on the most suitable chemicals for their regeneration, need to be addressed prior to commercialization.

### 6. Concluding remarks

The current global trend towards more stringent environmental standards favors the application of low-cost

systems for the treatment of inorganic effluent. Recently, various low-cost adsorbents derived from agricultural waste, industrial by-products or natural materials, have been investigated intensively for heavy metal removal from metal-contaminated wastewater. It is evident from the literature survey of 102 recent papers (1984–2005) that after chemical modification or conversion by heating into activated carbon, low-cost adsorbents from agricultural waste have demonstrated outstanding removal capability (Cr(VI): 170 mg/g of hazelnut shell activated carbon, Ni(II): 158 mg/g of orange peel, Cu(II): 154.9 mg/g of chemically modified soybean hull, Cd(II): 52.08 mg/g of jackfruit) compared to activated carbon (Cd(II): 146 mg/g, Cr(VI): 145 mg/g, Cr(III): 30 mg/g, Zn(II): 20 mg/g). It is important to note that the metal adsorption capacities of low-cost adsorbents presented above vary, depending on the characteristics of the individual adsorbent, the extent of surface modification and the initial concentration of adsorbate. Overall, technical applicability and cost-effectiveness are two key factors in the selection of the most suitable low-cost adsorbent for treating inorganic effluent.

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