

Adsorption of Heavy Metals from Water and Waste Water Using Low Cost Adsorbents from Agricultural By-Products

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Abstract: The use of agricultural by-products have been widely investigated as a replacement for current conventional methods for removing heavy metals from waste water, such as chemical precipitation, ion exchange, membrane technologies and electrochemical treatment. Although adsorption process using activated carbon are successfully applied for purification of potable water and the removal of organic pollutants in waste water, the expensive cost of the adsorbent material is still an issue for developing countries. Alternative adsorbents using low cost agricultural by-products are now becoming emergent. The application of low cost adsorbent for treating various adsorbate contaminants such as colour, trace metals, trace organics or chemical oxygen demand have been investigated worldwide. A focus on heavy metals contamination in waste water is a major concern due to their potential toxicity, persistence and tendency to become concentrated in food chains. With sources from more than 100 published papers low cost agricultural by-products have demonstrated outstanding capabilities in adsorbing heavy metal ions from aqueous solution. In this review, an extensive list of adsorbent literature has been compiled to provide a summary of information on a wide range of low-cost agricultural by-product adsorbents. The adsorption capacities depend largely on the characteristics of the adsorbent, pretreatment of the adsorbents, pH and the initial metal concentration.

Key words: Adsorbate, adsorbent, agricultural by-products, heavy metals.

Introduction

The principal objective of wastewater treatment is to allow human and industrial effluents to be disposed off without danger to human health or unacceptable damage to the natural environment.

Water pollution due to toxic heavy metals contamination has been a major issue for environmental engineers. Although many trace metals have a key role in the functioning of metallo-protein enzymes (Stumm, 1996), when a metal ion exceeds its requirement by an organism there is the potential for toxic effects. The toxicity depends on the chemical form of the metal ion (chemical speciation), physiological factors (e.g.

temperature, pH and dissolved oxygen), the biological state of the organism (e.g. stage of the life cycle) and the presence of other metal ions and/or other toxic materials (Davey, 1973; Gillespie, 1978).

Trace metals such as lead, mercury, zinc, copper, nickel and cadmium are released to the environment as a result of human activities. Modern uses of these metals include the production of alloys, photography, paints and dyes, pesticides (e.g. copper oxychloride), textiles, electrical wiring and electroplating. For example the production of printed wiring board (PWB) is estimated to produce about 60% of the soluble metals disposed off into waste waters (Judd, 1987).

Concerns about trace metals primarily result from their potential toxicity, persistence and tendency to become concentrated in food chains (Brierley, 1986; Holan et al., 1993).

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Conventional technologies such as chemical precipitation, ion exchange, membrane technologies and electrochemical treatment are generally employed for heavy metal recovery from waste water. These methods have been found to be limited, since they often involve high capital and operational costs and may be associated with the generation of secondary waste which present treatment problems, such as the large quantity of sludge generated from precipitation processes. Although ion exchange and reverse osmosis are more attractive processes due to their ability to recover adsorbates such as valuable metals along with their removal from the effluents, the cost related technology is still a major issue. Overall these processes appear to be ineffective or extremely expensive at concentrations of 1 to 100 mg/L (Volesky, 1990).

As environmental laws are becoming more stringent a cost-effective water treatment is now becoming crucial (Kadirvelu, 2002).

Recently, adsorption has become one of the alternative treatments (Babel, 2003a). Adsorption has advantages over the other wastewater treatment methods because of simple design with a sludge-free environment and can involve low investment in terms of both initial cost and land required (Viraraghavan, 1993).

Due to its large surface area, high adsorption capacity and surface reactivity, adsorption using activated carbon is able to adsorb various metal adsorbates from inorganic water effluent. However the use of activated carbon might be unsuitable for developing countries (Panday, 1985) due to its expensive cost as much as USD 9/kg (CSIRO, 2004).

In recent years, alternative low-cost adsorbents that have binding capacities have attracted the attention of several investigators for providing alternative treatments. Materials locally available in large quantities such as agricultural products or by-products have been utilized as low-cost adsorbents, rather than simple disposal, which makes both environmental and commercial sense (Bailey, 1999). Some of these materials can be used as adsorbents with little activation or processing. Conversion of these materials into porous materials that can be used as an adsorbent for water purification would improve their economic value i.e. helping industries reduce the cost of waste disposal and providing a potential alternative to activated carbon.

One of the earliest adsorption applications is purification, such as removal of hydrogen sulfide and obnoxious fumes from air and the removal of organic compounds from water (Mackay, 1996). A lot of work has been carried out for further extension of its uses. Fadil

et al. (1994) did research on leachate characteristics and he extended his work to the removal of heavy metals using local materials such as oil palm shell, rice husk/hull that is abundantly available in Malaysia.

Other examples of purification are the removal of odour and colour from edible oil, decolourization in the sugar industry, solute removal in tobacco manufacturing, and the removal of unwanted hydrocarbons from oil refinery industry. For recovery purposes, adsorption has been applied to recover some biological materials and organic compounds as well as precious metals such as gold in mines (Mackay, 1996).

Razivogora et al. (1998) observed the purification of waste water and potable water by activated carbon prepared from apricot stone, lignite and anthracite. Srimurali et al. (1998) carried out their research on the removal of fluoride by activated carbon prepared from nirmali seeds, lignite, kaolinite clay, charfines, and bentonite.

The use of low cost adsorbents for adsorption of various adsorbates have been investigated worldwide including India (Ajmal et al., 2001), Bangladesh (Abul Hossain, 1998), Thailand (Babel, 2003), New Zealand (Djati Utomo, 2006), Malaysia (Tan, 1985), Nigeria (Abia et al., 2003), Italy (Abolino et al., 2003) and USA (Yu et al., 2003).

Table 1 summarizes the potential of several agricultural by-product adsorbents that are capable of reducing the colour, trace metals, and trace organics of effluents. Although many studies have been reported on the potential of low cost adsorbents, most of this work is only at the laboratory level. Very few examples of practical applications at an industrial level have been reported.

Clearly the research study on low cost adsorbents might have a double impact that would benefit both society and the environments from *recycling* of agricultural by-products (tea leaves, coffee grounds, rice husk, coconut shell, oil palm shell, apricot stone, nirmali seeds, peanut hull, hazelnut shell) which currently has no significant usage other than being burned or used for landfill; and *reuse* of the by-product as a low cost treatment system for polluted waste waters. Both of these factors create added value for the waste material.

Agricultural By-products as Low Cost Adsorbent for Heavy Metal Removal from Water

Agricultural by-products are rich sources for low cost adsorbents due to their abundance, naturally availability

Table 1: Adsorption of various adsorbates by agricultural by-product adsorbents

<i>Researchers (Reference)</i>	<i>Adsorbates</i>	<i>Adsorbents</i>
Basar (2006)	malachite green, methylene blue, crystal violet	waste apricot
Nassar and Geundi (1991)	astrazone blue, maxillon red, telon blue	activated carbon, natural clay, bagasse pith, maize cob
Sankar, Sekaran et al. (1999)	direct red 31, acid black 1 and acid blue 16	rice bran based activated carbon
Mohanty, Naidu et al. (2006)	crystal violet	rice husk
Jain, Mathur et al. (2006)	indigo carmine	rice husk, charcoal
Annadurai (2000, 2002)	verofix red, heavy metals	chitosan, banana and orange peels
Inbaraj et al. (2002, 2004)	malachite green, cadmium	jackfruit peel
Rajgopal et al. (2006)	malachite green	rubberwood sawdust
Gupta, Mittal et al. (2006)	dye acid orange 7	bottom ash, de-oiled soya
Deshmukh, Shah et al. (2004)	methylene blue and malachite green	stalk of cajanus cajan
Chuah, Jumariah et al. (2005)	heavy metals and dye	rice husk
Rao, Parwate et al. (2002)	copper and lead	bagasse, fly ash
Djati Utomo and Hunter (2006a)	copper, zinc, lead, cadmium	waste tea leaves, coffee
Rai, Bansal et al. (2000)	magenta	rice husk, fly ash
Kadirvelu et al. (2001a, b)	nickel, cadmium	(boiler feed) coirpith

and ‘minimum to zero’ economic value. Agricultural by-products such as oil palm shell, orange peel and coffee residues pose little economic value and moreover, create serious disposal problems (Selvakumari et al., 2002; Salim et al., 2002).

The potential use of agricultural by-products from food and beverage manufacturing industry such as tea (Djati Utomo, 2006a), coffee grounds (Djati Utomo, 2006b), oil palm shell (Salim et al., 2002) and rice husk (Chuah et al., 2005) are alternatives to synthetic ion-exchange resins or activated carbon for treating metal-containing waste streams.

Adsorption capacity of low cost adsorbents depends on the characteristics of the individual adsorbent, pretreatment of the adsorbents, pH, and the initial concentration of the adsorbate.

Effect of Initial Metal Concentration

Ajmal (2000) and Annadurai (2002) reused orange peel for Ni(II) removal from simulated waste water with initial Ni(II) concentration of 1000 mg L⁻¹ vs 25 mg L⁻¹ respectively. They found that the maximum metal removal occurred at pH 6.0 with metal adsorption capacity of 158.00 mg/g (Table 2).

Djati Utomo (2007) also studied the effects of initial metal ions concentration using Cu(II), Pb(II), Zn(II) and Cd(II) from a suspension containing 10 g/L of used alkaline coffee. They found that at pH 5.0 the percentage of metal ion adsorbed was fairly constant at metal ion concentrations below about 10 mg/L, but at levels above 100 mg/L the adsorptive capacity of the coffee began to be exceeded. The study suggested once the adsorption

process of metal ions onto adsorbent surface site reached a saturation point, the availability of adsorption sites becomes minimum and leads to decrease further adsorption process.

Effect of Pretreatment

The main purpose of pretreatment was to improve the adsorption capacity of raw adsorbents. Agricultural by-products sourced from hazelnut shell, rice husk, coirpith, almond husk, pecan shells, coffee grounds 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 Babel (2003a) have reported that improved adsorption capacity of the adsorbents after additional processing may compensate the cost for such a process.

The application of Coconut Shell Charcoal (CSC) modified with oxidizing agents and/or chitosan for Cr(VI) removal was investigated by Babel (2004) using simulated wastewater. They found that CSC oxidised with nitric acid had higher chromium 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 pretreatment is able to create more adsorption site for CSC.

A comparative study was conducted on heavy metal removals such as Cu(II), Pb(II), Zn(II) and Cd(II) from aqueous solution using coffee grounds pre-washed by deionised water (used coffee) and coffee grounds pre-treated by alkaline water (used alkaline coffee) (Djati Utomo, 2006a, b). Fraction of heavy metal adsorbed by

Table 2: Pretreated and non-pretreated agricultural waste used as adsorbent for heavy metals in water and wastewater

<i>Metal species</i>	<i>Type of adsorbent</i>	<i>Optimum dose</i>	<i>Optimum pH</i>	<i>Initial metal concentration (mg/L)</i>	<i>Adsorption capacity (mg/g)</i>	<i>Reference</i>
Cr (VI)	As-received CSC	24	6.0	20	2.18	Babel and Kurniawan (2004)
	CSC coated with chitosan	18	4.0	20	3.65	
	H ₂ SO ₄ - treated CSC	15	6.0	20	4.05	
	HNO ₃ - treated CSC	12	4.0	20	10.88	
Ni (II)	Orange peel	20	6.0	1000	158.0	Ajmal et al. (2000)
Ni (II)	Orange peel	1	6-8	25	6.01	Anadurai et al. (2002)
Cr (VI)	Sawdust	2.4	2.0	100	15.82	Dakiki et al. (2002)
Ni (II)	Hazelnut shell	NA	3.0	15	10.11	Demirbas et al. (2002)
Cr (VI)	Hazelnut shell	2.5	1.0	1000	170	Koby (2004)
Cr (VI)	Rice husk	12.0	2.0	10	0.79	Bishnoi et al. (2003)
Cd (II)	Rice husk	20	NA	50	2	Ajmal et al. (2003)
Cd (II)	Coirpith	12	4-5	NA	NA	Kadirvelu et al. (2001a)
Ni(II)		10	4-5	996	91.63	
Ni (II)	Coirpith	0.2	5	40	62.50	Kadirvelu et al. (2001b)
Ni(II)	Almond husk	5	5	250	37.17	Hasar (2003)
Cr(VI)	Ethilenediamine-modified rice hull	NA	2.0	301.6	23.40	Tang et al. (2003)

used coffee shows slightly lower than fraction of heavy metal adsorbed by used alkaline coffee. At pH 4.9-5.0, the adsorption capacity of used alkaline coffee on Cu(II) shows 5-10% higher adsorption rate than used coffee (Djati Utomo, 2007). The measurement at pH less than 7 was to ensure that no precipitation in the form of hydroxide is involved.

Enhanced Cu(II) adsorption was achieved using normal soybean hull (ASH) and soybean hull extracted with NaOH and modified with citric acid (SHMC) (Marshall, 1999). Chemical modification of soybean hull with NaOH and citric acid remarkably improved its metal removal (ASH: 24.76 mg/g vs SHMC: 154.9 mg/g).

Effects of Reaction Temperature

Effects of temperature to the heavy metal adsorption on low cost adsorbent have been investigated by several authors. Demirbas et al. (2002) investigated Ni(II) removal from simulated solution using hazelnut shell activated carbon. They found that metal adsorption reduced with an increasing temperature, suggesting that the adsorption was exothermic. Djati Utomo (2007) found that the increasing temperature from 25°C to 80°C on the adsorption of heavy metals by coffee grounds did not significantly improve the adsorption. On the contrary an improvement of adsorption was found when rice husk was used to adsorb Cd(II) at a decreasing temperature,

suggesting that the adsorption was endothermic (Ajmal et al., 2003).

The above research findings on low cost agricultural by-products show a dependency on the nature of adsorbate-adsorbent interaction process. This argument contradicts with an old finding from Young (1962) confirming that all adsorption processes are always exothermic due to a decrease in entropy due to loss of degrees of freedom of the solute in passing from the dissolved state to the adsorbed state, regardless of the nature of the interaction process.

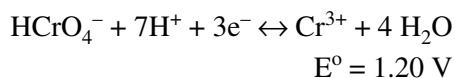
Effects of pH

Optimum pH for adsorption was found to be in intermediate range between pH 4 and 9 for positively charged metal ions adsorbed on various adsorbate surfaces. The uptake of Cd(II), Ni(II) and Cu(II) ions from real industrial wastewater using coirpith activated carbon was studied at pH 4.0-5.0 (Kadirvelu et al., 2001a). Hasar (2003) studied Ni(II) adsorption from simulated solution using almond husk activated carbon and found that the maximum metal removal of 37.17 mg/g occurred at pH 5.0. Djati Utomo (2006a) studied Cu(II), Pb(II), Zn(II) and Cd(II) adsorption from simulated solution using used tea leaves and coffee residues. The results showed that the fraction of metal ion adsorbed decreases significantly at low pH (pH < ca. 4) indicating the H⁺ ions interact competitively with the metal ion-adsorbing

sites on the adsorbents. In addition, for Cd(II) and Zn(II), and to a lesser extent with Pb(II), there is a pronounced decrease in the fraction adsorbed at high pH ($\text{pH} > ca. 10$).

In the case of Pb(II) and Zn(II), this may be due to the competitive formation of anionic hydrolysis products in solution at high pH. However such an explanation is not likely for Cd(II). Another possibility is additional release of soluble metal-binding ligands from the tea or coffee at high pH, which is consistent with an observed increase in colour of the solution at high $\text{pH} > 10$. For higher pH values ($\text{pH} > 6$), it is also difficult to distinguish between adsorption and removal from solution by precipitation of metal hydroxides. For all of the positively charged metal ions, the fraction adsorbed is relatively constant at intermediate pH values.

Negatively charged metal ion such as Cr(VI) was reported to be conveniently adsorbed at as low as pH 2.0. Tang (2003) and Bishnoi (2003) studied the Cr(VI) adsorption by rice hull modified with ethylenediamine and rice husk respectively. Both materials, believed to contain cellulose, lignin, carbohydrate and silica, were investigated for Cr(VI) removal from simulated solution. They found that the maximum Cr(VI) adsorption was reported 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°) in the range of 1.33-1.38 V (Kotas, 2000), implying that Cr(VI) was unstable in the presence of electron donors. The carbon surface of rice hull contains carboxylic and hydroxyl groups play a role as electron donors in the solution (Tan et al., 1993). As a consequent, Cr(VI) oxyanion can be reduced to Cr(III) ions due to the presence of electron donors of rice hulls in acidic solution as detailed below ($\text{pH } 2.0\text{--}6.0$):



Effects of Different Parts of Body Material Used

Low cost adsorbents might source from different parts of the body of material used resulting in different adsorption capacity. Hasar (2003) and Dakiky (2002) studied Ni(II) adsorption from simulated solution using almond husk activated carbon and almond shell respectively. Maximum Ni(II) adsorption of 37.17 mg/g and 10 mg/g is found on almond husk and almond shell respectively. 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. As a consequence almond husk has more hydroxyl groups

and carboxylic groups than almond shell for metal adsorption, resulting in higher metal removal capacity found in almond husk (Hasar, 2003).

Effect of Nature Adsorption Study

There are two common natures of adsorption study adopted by researchers i.e. batch adsorption study and column adsorption study. In batch adsorption experiments, the concentration gradient decreased with increasing contact time while in column studies, 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.

However there was still an agreement between the result from batch and column adsorption study if batch adsorption studies are conducted in enough equilibration time as reported by Djati Utomo (2007) using coffee adsorbent for Cu(II) removal.

Cu(II) adsorption by coffee grounds showed a maximum adsorption density of 15.3 μmol (0.972 mg) per 500 mg of coffee adsorbent, which corresponds to 97 mL of 10 mg/L Cu(II) solution, when calculated using Langmuir equation model. In separate column study using 500 mg of coffee column adsorbent, approximately the first 100 mL of solution passed through the column. There is quantitative adsorption of Cu(II) after which the percentage adsorbed decreases steadily, suggesting that the column adsorbent has become saturated with Cu(II). This agreed very well with the apparent breakthrough of Cu^{2+} at ~ 100 mL actually observed in this case.

Conclusions

Agricultural by-products 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 with high affinity for metal cations.

Chemical pretreatment or surface modification might increase the adsorption capacity of a particular adsorbent. The increasing adsorption capacity might compensate an extra operational cost due to chemical pretreatment.

When the adsorbent reaches a saturation point, regeneration of the spent adsorbent might be the best option, since no solid waste will be generated and no disposal required. In fact, regeneration and desorption could also be done to recover valuable metal from spent adsorbents. However, the economics of this recycling practice depends on the characteristics of the regenerated

adsorbent and on the mass losses incurred during regeneration.

An intermediate pH range of 4-6 are the best pH range to show adsorption phenomenon without precipitation involvement and also convenient aqueous environment for positively charged heavy metal adsorption. Mean-while an acidic pH of 2 is effective for negatively charged ion such as Cr(VI) metal removal by adsorbent from agricultural by-products.

Although low cost adsorbent sourced from agricultural by-products show promising economical adsorbents, little information is still made to carry out a cost comparison between activated carbon and various agricultural by-product adsorbents. This aspect needs to be investigated further in order to promote large-scale use of agricultural by-product adsorbents.

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