

Review Article

Removal of Heavy Metal Ions from Wastewater by Chemically Modified Agricultural Waste Material as Potential Adsorbent-A Review

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Abstract

Heavy metal remediation of aqueous streams is of special concern due to recalcitrant and persistency of heavy metals in environment. Conventional treatment technologies for the removal of these toxic heavy metals are not economical and further generate huge quantity of toxic chemical sludge. Agricultural waste materials being economic and eco-friendly due to their unique biochemical composition, availability in abundance, renewable, low in cost and more efficient are seem to be viable option for heavy metal remediation. The major advantages of biosorption over conventional treatment methods include: low cost, high efficiency, minimization of chemical or biological sludge, regeneration of biosorbents and possibility of metal recovery. 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. The functional groups present in agricultural waste biomass viz. acetamido, alcoholic, carbonyl, phenolic, amido, amino, sulphhydryl groups etc. Have affinity for heavy metal ions to form metal complexes or chelates. Some of the treated adsorbents show good adsorption capacities for Cd, Cu, Pb, Zn and Ni. Rice husk as a low-value agricultural by-product can be made into sorbent materials which are used in heavy metal removal. The mechanism of biosorption process includes chemisorptions, complexation, adsorption on surface, diffusion through pores and ion exchange etc. Agricultural residues are lignocelluloses substances which contain three main structural components: hemicelluloses, cellulose and lignin. Lignocellulosic materials also contain extractives. Generally, three main components have high molecular weights and contribute much mass, while the extractives is of small molecular size, and available in little quantity, which announce in heavy metal removal.

Keywords: Agricultural waste material; Heavy metals; Adsorption; Wastewater treatment

1. Introduction

Heavy metals constitute a very heterogeneous group of elements widely varied in their chemical properties and biological functions. The term heavy metals defined as commonly held for those metals, which have specific weights more than 5g cm^{-3} (Holleman and Wiberg *et al*, 1985). Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater. Some of the heavy metals i.e. arsenic (As), Cadmium (Cd), Lead (Pb), Mercury (Hg) are cumulative poison. The high concentration intake of cadmium cause itai itai disease and mercury intake lead to minamita disease and other heavy metals cause poisoning due to drinking water contamination. The contamination of water due to toxic heavy metal ions is accountable for

causing several damages to the environment and adverse effects on the health of the people like mental retardation, reduction in hemoglobin production and interference with normal cellular metabolism and consequently may damage nervous system.

Strong exposure may cause gastric pain, nausea, vomiting, severe diarrhea, hemorrhage and even cancer in the digestive tract and lungs. Metals and other poisons like chemicals, mold toxins and the toxic waste from bacteria and other parasites are fat soluble. They dissolve in and move through fat. If they gain entrance to the body they end up in the cell walls. Residing in the fat, they cause some of the fat to change shape. The new fats are too long, have the wrong connections between elements or have a funny shape or all of the above. They are square pegs trying to fit into round holes. The new shapes change the ability of the fats to fit into the anatomy of the cell or function in the action steps or physiology necessary to sustain cell life. So the action or physiology of the body is slowed down and illness results or the action stops and death

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results. Results of studies on the adverse effects on human health have been summarized in numerous reports published by international organizations, e.g. the World Health Organization (WHO) and the International Agency for Research on Cancer (IARC), or governmental agencies such as the Centers for Disease Control and Prevention (CDC) in the United States.

The presence of heavy metals in waste and surface waters is becoming a severe environmental problem and because of their non-biodegradability, they can accumulate in the food chain posing a significant danger to human health. The main techniques, which have been utilized to reduce the heavy metal ion content of effluents, include lime precipitation, ion exchange, adsorption into activated carbon, membrane process and electrolytic methods. All these methods are generally expensive (Kumar and Bandyopadhyay et al, 2006) . Recently, agricultural waste materials

have been proposed as economic and eco-friendly adsorbents (D. Sud et al, 2008) . Agricultural materials, particularly those containing cellulose, show a high potential in metal biosorption capacity (D. Ranjan et al, 2009) . Adsorption process of heavy metals present in aqueous solution by low-cost adsorbents from plant wastes can be carried out with or without chemical modifications. In general, chemically modified plant wastes exhibit higher adsorption capacities than unmodified forms (W. S. WanNgah et al, 2008). Living as well as dead (metabolically inactive) biological materials have been sought to remove metal ions. It was found that various functional groups present on their cell wall offer certain forces of attractions for the metal ions and provide a high efficiency for their removal (R. Ashkenazy et.al 1995-97; N. Kuyucak, and B. Volesky et al,1988) .

Some methods to remove metal ions from Wastewaters

Methods	Advantages	Disadvantages
Chemical Precipitation	<ul style="list-style-type: none"> • Simple • Inexpensive • Most of metals can be removed 	<ul style="list-style-type: none"> • Large amounts of sludge produced • Disposal problems
Chemical coagulation	<ul style="list-style-type: none"> • Sludge settling • Dewatering 	<ul style="list-style-type: none"> • High cost • Large consumption of chemicals
Ion-exchange	<ul style="list-style-type: none"> • High regeneration of materials • Metal selective 	<ul style="list-style-type: none"> • High cost • Less number of metal ions removed
Electrochemical method	<ul style="list-style-type: none"> • Metal selective • No consumption of chemicals • Pure metals can be achieved 	<ul style="list-style-type: none"> • High capital cost • High running cost • Initial solution pH and Current density
Adsorption Using activated carbon	<ul style="list-style-type: none"> • Most of metals can be removed • High efficiency (>99%) 	<ul style="list-style-type: none"> • Cost of activated carbon • No regeneration • Performance depends upon adsorbent
Using natural zeolite	<ul style="list-style-type: none"> • Most of metals can be removed • Relatively less costly materials 	<ul style="list-style-type: none"> • Low efficiency
Membrane process and ultrafiltration	<ul style="list-style-type: none"> • Less solid waste produced • Less chemical consumption • High efficiency (>95% for single metal) 	<ul style="list-style-type: none"> • High initial and running cost • Low flow rates • Removal (%) decreases with the presence of other metals

Source: (O’Connell et a., 2008; Farooq et al, 2010)

2. Low cost adsorbent wastes materials

Biosorption is the removal of materials (compounds, metal ions, etc.) by inactive, non-living biomass (materials of biological origin) due to “high attractive forces present between the two (B. Volesky et al, 1995.)^[9]. Several recent publications utilized different inexpensive and locally abundantly available adsorbents like barley straw (V. J. Larsen et al, 1981). waste tea leaves (T. W. Tee et al, 1981). sago waste(S. Y. Quek et al, 199). peanut hulls(P. Brown et al, 2000). hazel nut shell (G. Cimino et al, 2014). saw dust (A. Sukla et al, 2002; T. K. Naiya et al, 2008). neem bark (T. K. Naiya et al, 2008). chitin beads (D. Zhou et al, 2004), thermally treated rice husk ash (G. Doner, et al, 2004). waste banana (G. Annadurai et al, 2003). orange peels (G. Annadurai et al, 2003). cocoa shells (N. Meunier et al, 2003) tree fern (Y. S. Ho et al, 2004). coffee residue (V. Boonamnuyvitaya et al, 2004). rice husk(T. C. Chuah, et al, 2005 ; palm kernel fibre Y. S. Ho et al, 2005) , olive stone waste (N. Fiol et al, 2006),

orange peel (Z. Xuan et al, 2006). grape stalk (M. Martinez et al, 2006). (coir S. Y. Quek et al, 1998; K. Conrad et al, 2007). Tea waste (B. M. W. P. K. Amarasinghe et al, 2007), bagasse fly ash(V. K. Gupta et al, 2004; V. K. Gupta at al, 1998). rice husk (Q. Feng et al, 2004,) etc. Some of the advantages of using plant wastes for wastewater treatment include simple technique, requires little pro- cessing, good adsorption capacity, selective adsorption of heavy metal ions, low cost, free availability and easy regeneration.

3. Chemically modified plant

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. Pretreatment of plant wastes can extract soluble organic compounds and enhance chelating efficiency

[33]. Pretreatment methods using different kinds of modifying agents such as solutions sodium hydroxide, calcium hydroxide, sodium carbonate, Sulfuric acid, Thioglycolic acid, Hydrochloric acid, Tartaric acid, formaldehyde, epichlorohydrin 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.

Dubey and Gopal *et al*, 2006; Abia *et al*, 2006; Ozer *et al*, 2004; Ozer and C. Pirince *et al*, 2006; Min *et al*, 2004; Shukla and Pai *et al*, 2005a; Low *et al*, 2000; Chubar *et al*, 2004; Memon *et al*, 2007; Bulut and Tez *et al*, 2003; Shukla and Pai *et al*, 2005b; Argun *et*

al, 2007; Hanafiah *et al*, 2006a; Ganji *et al*, 2005; Pehlivan *et al*, 2006; Gupta and Ali *et al*, 2004; Wankasi *et al*, 2006; Mohanty *et al*, 2005; Wong *et al*, 2003b; Kumar and Bandyopadhyay *et al*, 2006; Bansal *et al*, 2009; J. Cruz-Olivaresa *et al*, 2010; The types of chemicals used for modifying plant wastes and their maximum adsorption capacities are shown in Table 1. Pretreatment of rice husks can remove lignin, hemicellulose, reduce cellulose crystallinity and increase the porosity or surface area. Cellulose is a crystalline homo-polymer of glucose with $\beta \rightarrow 4$ glycosidic linkage and intra-molecular and intermolecular hydrogen bonds.

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

Adsorbent	Modifying agent(s)	Heavy metal	Qmax (mg/g)	Source
Groundnut husk	Sulfuric acid followed by silver	Cr(VI)	11.4	(Dubey and Gopal <i>et al</i> , 2006)
Cassava waste	Thioglycolic acid	Cd(II)	NA	(Abia <i>et al</i> , 2006).
Wheat bran	Sulfuric acid	Cu(II)	51.5	(Ozer <i>et al</i> , 2004).
Wheat bran	Sulfuric acid	Cd(II)	101	(Ozer and Pirinc <i>et al</i> , 2006).
Juniper fibre	Sodium hydroxide	Cd(II)	29.54	(Min <i>et al</i> , 2004).
Indian barks Sal, mango, jackfruit	Hydrochloric acid	Cu(II)	51.4 42.6 17.4	(Shukla and Pai <i>et al</i> , 2005a).
Spent grain	Hydrochloric acid	Cd(II)	17.3	(Low <i>et al</i> , 2000).
Cork powder	Calcium chloride, Sodium chloride Sodium hydroxide Sodium iodate	Cu(II)	15.6 18.8 18.0 19.0	(Chubar <i>et al</i> , 2004).
Sawdust (cedrus deodar wood)	Sodium hydroxide	Cd(II)	73.62	(Memon <i>et al</i> , 2007).
Walnut sawdust	Formaldehyde in sulfuric acid	Pb(II)	4.48	(Bulut and Tez <i>et al</i> , 2003).
Sawdust	Reactive Orange 13	Cu(II), (Ni(II) Cr(VI)	8.07	(Shukla and Pai <i>et al</i> , 2005b).
Sawdust (Oak tree)	Hydrochloric acid	Pb(II)	3.60 3.37 1.74	(Argun <i>et al</i> , 2007).
Imperata cylindrica leaf powder	Sodium hydroxide	Cu(II)	13.50	(Hanafiah <i>et al</i> , 2006a).
Azolla filiculoides (aquatic fern)	Hydrogen peroxide-Magnesium Chloride	Cu(II)	62	(Ganji <i>et al</i> , 2005).
Sugarbeet pulp	Hydrochloric acid`	Pb(II)	0.15	(Pehlivan <i>et al</i> , 2006).
Bagasse fly ash	Hydrogen peroxide	Pb(II) Cu(II)	2.50	(Gupta and Ali <i>et al</i> , 2004).
Nipah palm shoot biomass	Mercaptoacetic acid	Cu(II)	52.86, 66.71	(Wankasi <i>et al</i> , 2006).
Terminalia arjuna nuts	ZnCl ₂	Cu(II)	28.43	(Mohanty <i>et al</i> , 2005).
Rice husk	Tartaric acid	Cd(II)	31.85	(Wong <i>et al</i> , 2003b).
Rice husk	Water washed Sodium hydroxide Sodium bicarbonate Epichlorohydrin	Cd(II)	8.58 20.24 16.18 11.12	(Kumar <i>et al</i> , 2006).
Rice husk	BRH. FRH	lead(II)	8.5, 10.4	(M. Bansal <i>et al</i> , 2009).
De-Oiled Allspice Husk	nitric acid, ethanol	lead(II)	20.07 mg/gm- 1 (95%)	(J. Cruz-Olivaresa <i>et al</i> , 2010).

4. Rice husk as a novel adsorbent

Rice husk was selected due to its local availability in abundance, chemical stability and insolubility in water (M. Akhtara *et al*, 2010). Rice which is cultivated in more than 75 countries in the world is the essential food for over half the world's population. The worldwide annual rice husk output is about 80 million tones and over 97% of the husk is generated in the developing countries (L. Armesto *et al*, 2002). Previous researches in the utilization of rice husk as novel adsorbents for different applications. The findings will provide a twofold advantage with respect to environmental management. First, large volume of rice husk waste could be partly reduced, converted to useful, value-added adsorbents, and second, the low-cost adsorbent, if developed, may overcome the wastewaters and air pollution at a reasonable cost, solving part of the global agricultural wastes and wastewater treatment problem. Developing countries; approximately 100 million tons of rice husk is available annually for utilization in these countries alone.

Conclusion

In this review the toxic metal ion biosorption on inexpensive and efficient biosorbents from agricultural waste materials have been investigated as replacement strategy for existing conventional systems. Agricultural waste material being highly efficient, low cost and renewable source of biomass can be exploited for heavy metal remediation. 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. A wide range of low-cost adsorbents obtained from chemically modified plant wastes has been studied and most studies were focused on heavy metal ions such as Cd, Cu, Pb, Ni and Cr(VI) ions (S. Chen *et.al* 1993).

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