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Review

Agricultural products and by-products as a low cost adsorbent for heavy metal removal from water and wastewater: A review

Upendra Kumar

Department of Civil Engineering, National Institute of Technology, Silchar 788 010, Assam, India. E-mail: upendra_kumar72@rediffmail.com.

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The use of agricultural products and by-products has been widely investigated as a replacement for current costly methods of removing heavy metals from water and wastewater. Some of the agricultural materials can be effectively used as a low-cost sorbent. Modification of agricultural by-product could enhance their natural capacity and add value to the by-product. In this review, an extensive list of sorbent literature has been compiled to provide a summary of available information on a wide range of low-cost agricultural product and by-product sorbent and their modification for removing heavy metals from water and wastewater.

Key words: Agricultural products, adsorbent, low cost, heavy metals, water, wastewater.

INTRODUCTION

Water pollution due to toxic heavy metals has been a major cause of concern for environmental engineers. The industrial and domestic wastewater is responsible for causing several damages to the environment and adversely affecting the health of the people. Several episodes due to heavy metal contamination in aquatic environment increased the awareness about the heavy metal toxicity. Among these, Minamata tragedy due to mercury poisoning and "Itai-Itai" disease in Japan due to cadmium toxicity are well known. Metals can be distinguished from other toxic pollutants, since they are non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain. A variety of industries are responsible for the release of heavy metals into the environment through their wastewater (Braukmann, 1990). These include iron and steel production, the non-ferrous metal industry, mining and mineral processing, pigment manufacture, the painting and photographic industries and metal working and finishing processes (electroplating). In addition, considerable quantities of heavy metals can be released into the environment through routes other than wastewater. For example, lead is widely used in metallic form and copper is used in electric equipment, water pipes, alloy, as chemical catalysts and in anti-fouling paints on ship hulls.

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 (Dean et al., 1972), membrane processing, and electrolytic methods (Braukmann, 1990). 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 by precipitation processes. On the other hand ion exchange, reverse osmosis and adsorption are more attractive processes because the metals values can be recovered along with their removal from the effluents. Reverse osmosis and ion exchange do not seem to be economically feasible because of their relatively high investment and operational cost. Adsorption has advantages over the other methods because of simple design with a sludge free environment and can involve low investtment in term of both initial cost and land required (Viraraghaban et al., 1993). Activated carbon has been recognized as a highly effective adsorbent for the removal of heavy metal-ion from the concentrated and dilute metal bearing effluents (Netzer and Hughes, 1984; Reed and Arunachalam, 1994). But the process has not been used by small and medium scale industries for the

Table 1. Heavy metal adsorption capacity (mg/g) of agricultural products and by-products

Material	Adsorption capacity (mg/g)						References
	Cd^{+2}	Cr^{+3}	Cr^{+6}	Hg^{+2}	Pb^{+2}	Zn^{+2}	
Douglas fir bark	-	-	-	100	-	-	Masri et al., 1974
Exhausted coffee	1.48	-	1.42	-	-	-	Orhan and Buyukgungor, 1993
Waste tea	1.63	-	1.55	-	-	-	Orhan and Buyukgungor, 1993
Walnut shell	1.5	-	1.33	-	-	-	Orhan and Buyukgungor, 1993
Untreated pinus sylvestris bark	-	8.69	-	-	-	-	Alves et al., 1993
Treated pinus sylvestris bark	-	9.77	-	-	-	-	Alves et al., 1993
Turkish coffee	1.17	-	1.63	-	-	-	Orhan and Buyukgungor, 1993
Black oak bark	25.9	-	-	400	-	-	Teles and Beca, 1994
Sawdust	-	-	10.1, 16.05 4.44	-	-	-	Bryant et al., 1992 Dikshit, 1989 Zarraa, 1995
Redwood bark	27.6, 32	-	-	250	6.8 182	-	Masri et al., 1974 Randall et al., 1974
Pinus pinaster bark	8	19.45	-	-	3.33, 1.59	-	Teles and Beca, 1993-94 Vazquez et al., 1994
Nut shell	1.3	-	1.47	-	-	-	Orhan and Buyukgungor, 1993
Hardwickia binata bark	34	-	-	-	-	-	Deshkar et al., 1990
Formaldehyde-polymerized peanut skins	74	-	-	-	205	-	Randall et al., 1978
Exhausted coffee	1.48	-	1.42	-	-	-	Orhan and Buyukgungor, 1993
Lignin	-	-	-	-	1865	95	Srivastava et al., 1994
Sulfuric acid lignin	-	-	-	150	-	-	Masri et al., 1974
Xanthate sawdust	21.4	-	-	30.1-40.1	31.1-41.4	-	Flynn et al., 1980
Irish sphagnum moss peat	-	-	119, 43.9	-	-	-	Sharma and Foster, 1993, 1995
Sphagnum moss peat	5.8	29	-	-	40	-	McLelland and Rock, 1988
Rastunsuo peat	5.058	4.63	-	16.2	20.038	-	Tummavuori and Aho, 1980a,b
Modified peat	-	76	-	-	230	-	Kertman et al., 1993
Dry redwood leaves	-	-	-	175	-	-	Masri et al., 1974
Dyed bamboo pulp	-	-	-	15.6	15.0	-	Shukla and Sakhardanre, 1992
Undyed bamboo pulp	-	-	-	9.2	8.4	-	Shukla and Sakhardanre, 1992
Dyed jute	-	-	-	13.7	14.1	-	Shukla and Sakhardanre, 1992
Dyed sawdust	-	-	-	18.0	24.0	-	Shukla and Sakhardanre, 1992
Modified wool	87	-	17	632	135	-	Masri and Friedman, 1974
Moss	46.5	-	-	-	-	-	Low and Lee, 1991
Orange peel (white inner skin)	-	-	125	-	-	-	Masri et al., 1974
Orange peel (outer skin)	-	-	275	-	-	-	Masri et al., 1974
Senna leaves	-	-	250	-	-	-	Masri et al., 1974
Undyed sawdust	-	-	-	8.5	7.3	-	Shukla and Sakhardanre, 1992
Copper-coated moss	-	18.9	7.1	-	-	-	Low and Lee, 1995
Petiolar felt-sheath pf palm	10.8	-	5.32	-	11.4	6.0	Iqbal et al., 2002
Black gram husk	49.74	-	-	-	-	-	Saeed and Iqbal., 2003
Rice husk ash	20.24	-	-	66.66	-	-	Kumar and Bandyopadhyay, 2006
Modified hardwickia binata bark	-	-	-	21	-	-	Deshkar et al., 1999

treatment of their metal bearing effluents, because of its high manufacturing cost. For this reason, the use of low cost materials as adsorbent for metal ion removal from the wastewater has been highlighted. However, efforts have been contributed to develop new adsorbent and improving the existing adsorbents to have an alternative to activated carbon. These materials range from industrial products such rubber tyres (Knocke and Hemphill, 1981), industrial wastes and some natural material including agricultural product and by-product.

Agricultural products and by-products as low cost adsorbents

The idea of using various agricultural products and by-products for the removal of heavy metal from solution has been investigated by number of authors. Friedman and Waiss, (1972), Randall et al. (1974) and Henderson et al. (1977) have investigated the efficiency of number of different organic waste materials as sorbents for heavy metals. The obvious advantages of this method compared to other are lower cost involved when organic waste materials are used. Activated carbon adsorption appears to be a particularly competitive and effective process for the removal of heavy metals at trace quantities (Huang and Blankenship, 1984). However, the use of activated carbon is not suitable for developing countries because of its high cost (Panday et al., 1985). For that reason, the uses of low cost materials as possible media for metal removal from wastewater have been highlighted. These materials range from industrial products such rubber tyres (Knocke and Hempill, 1981), industrial wastes and some natural material including agricultural product and by-product as mentioned earlier.

The native exchange capacity and general sorption characteristics of these materials derive from their constituent polymers (in approximately decreasing order of abundance): cellulose, hemicelluloses, pectin, lignin, and protein. Kou et al. (2001) and Houngshan Shang et al. (2003) have proposed the utilization of biomaterials or abandoned biomaterials (BIOM), new name for agricultural product and by-product of which the major component is cellulose $(C_6H_{10}O_5)_n$. Cellulosic surface becomes partially negatively charged when immersed in water and, therefore, possess columbic interaction with cationic species in water (Laszlo, 1994; McKay et al., 1987). The high binding capacities of cationic species on the adsorbents are mainly the results of columbic interactions (Weixing et al., 1998).

Although shown to be effective adsorbent for a wide range of solutes, particularly divalent metals cations, crop residues suffer from at least two major drawback: low exchange or sorption capacity, and poor physical stability (i.e. partial solubility) (Laszlo and Dintzis, 1994). Also some may leach colour into solution; for example peanut skin leaches reddish colour into solution, on contact with water. The soluble coloured compounds were primarily low molecular weight tannins. Also, on prolonged contact with water, peanut skin tends to disintegrate (Randall et al., 1978). In order to overcome these problems, chemical modification and/or activation of the raw adsorbents are required.

Agricultural products and by-products is an abundant waste material, and needs proper disposal. When disposed by burning in situ, it generates CO_2 and other forms of pollutions. This creates a need for the conversion of agricultural products and by-products to useful, and hopeful, value-added products. One possible avenue could be as inexpensive ion exchange or sorbent material, which could remove toxic metal ions from aqueous solutions. The idea of using various agricultural products and by-products for the removal of heavy metal from solution has been investigated by number of authors. The obvious advantages of this method compared to other are lower cost involved when organic waste materials are used. The available literature as summarized in Table 1 shows that some of these non-covenantal adsorbents possess good adsorption capacity for heavy metal removal from industrial effluent.

The parameter which have been investigated for optimizing the use of adsorbent in wastewater treatment include nature of adsorbent and adsorbate metal concentration, temperature and pH of the aqueous solution, kinetics of adsorption, adsorption isotherm and the types of contacting system of the adsorbent with the adsorbate and the contact time. The metal adsorption capacities (mg/g) of some of the agricultural product and by-product are compared with activated carbon and some cation exchange resin (Table 2).

Conclusion

Little efforts seem to have been made to carry out a cost comparison between activated carbon and various non-conventional adsorbents (Nassar and Geundi, 1991). This aspect needs to be investigated further in order to promote large-scale use of non-conventional adsorbents. In spite of the scarcity of consistent cost information, the widespread uses of low-cost adsorbents in industries for wastewater treatment applications today are strongly recommended due to their local availability, technical feasibility, engineering applicability, and cost effectiveness. If low-cost adsorbents perform well in removing heavy metals at low cost, they can be adopted and widely used in industries not only to minimize cost inefficiency, but also improve profitability.

In addition, if the alternative adsorbents mentioned previously are found highly efficient for heavy metal removal, not only the industries, but the living organisms and the surrounding environment will be also benefited from the decrease or elimination of potential toxicity due to the heavy metal. Thus, the use of low-cost adsorbents may

Table 2. Heavy metal adsorption capacities (mg/g) compared with activated carbon and some cation exchange resin.

Adsorbent	Pb^{+2}	Cu^{+2}	Zn^{+2}	Cd^{+2}	Ni^{+2}	Hg^{+2}	Cr^{+6}	References
Granular activated carbon	16.58	5.08	-	3.37	-	-	-	Zacaria et al. 2002
Powdered activated carbon	26.94	4.45	-	3.37	-	-	-	Zacaria et al. 2002
Activated carbon fibers	30.46	11.05	-	-	-	-	-	Zacaria et al. 2002
Peanut hulls	30.04	8.00	8.96	5.96	-	-	-	Zacaria et al. 2002
Corncobs	8.29	7.62	1.96	8.89	13.5	-	-	Zacaria et al. 2002
Cornstarch	28.8	8.57	6.87	8.88	-	-	-	Zacaria et al. 2002
Pine bark	-	9.46	-	14.16	6.28	-	-	Zacaria et al. 2002
Black oak bark	-	-	--	29.9	-	-	-	Teles and Gonzalez 1994
Lignin	1865	-	95	-	-	-	-	Srivastava et al. 1994
Bark	182	-	-	32	-	400	-	Randall et al. 1974
Xanthane	18	-	-	33.27	-	1.149		Flynn et al. 1980
Leaf mould	-	-	-	-	-	-	43	Sharma and Foster, 1994
Sawdust	-	-	-	-	-	-	16.05	Dikshit 1989
CEPI Cotton		-	-	--	-	1000	-	Roberts and Rowland 1973
Duolite GT-73	122.25	61.60	55.59	105.66	56.94	-	-	Zacaria et al. 2002
Amberlite IRC-718	290.08	127.00	156.96	258.32	-	-	-	Zacaria et al. 2002
Amberlite 200	352.24	88.90	85.60	224.8	129.1	-	-	Zacaria et al. 2002
Lewatit TP 207	198.9	85.09	89.60	49.46	88.05	-	-	Zacaria et al. 2002

contribute to the sustainability of the surrounding environment.

Undoubtedly low-cost adsorbents offer a lot of promising benefits for commercial purpose in the future.

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