A Review on Potential Usage of Modified Agro Waste Adsorbents for Binding Pb(II), Hg(II) & Cr(VI) Ions from Aqueous Solutions

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***Abstract* - Heavy metal pollution is a major problem in the environment. The impact of toxic metal ions can be minimized by different technologies, viz., chemical precipitation, membrane filtration, oxidation, reverse osmosis, flotation and adsorption. But among them, adsorption was found to be very efficient and common due to the low concentration of metal uptake and economically feasible properties. Agro waste materials are of low cost and widely used, and very promising for the future. These are available in abundant quantity, are cheap and have low or little economic value. Different forms of agro waste materials are used as adsorbents such as fibers, leaves, roots, shells, barks, husks, stems and seed as well as other parts also. Natural and modified types of cellulosic materials are used in different metal detoxifications in water and wastewater. In this review paper, the most common and recent materials are reviewed as the efficiency of Pb(II), Hg(II) & Cr(VI) removal from aqueous solution.**

Keywords: Pb(II), Hg(II) & Cr(VI), agricultural wastes adsorbents, adsorption

1 .INTRODUCTION

Environmental pollution due to heavy metals like lead, mercury, cadmium, chromium etc. is of serious concern throughout the world. Due to anthropogenic activities, the concentrations of heavy metals have increased in the environment. Though many methods are available for mercury removal, adsorption is considered as simple, economical and versatile method.

Heavy metals are abundant in our drinking water, air and soil because they are present in every area of modern consumerism like construction materials, cosmetics, medicines, processed foods and personal care products (Abia et al., 2003). In small quantities, certain heavy metals are nutritionally essentially for a healthy life, but in large amounts they may cause acute or chronic toxicity (poisoning). The absorption of this hazardous substance into the bloodstream, distribution to the entire tissues and bioaccumulation in the receptive sites leads to adverse effects, such as potent neurotoxicity, blood vessel congestion and kidney damages (Kidd et al., 2012)

In the present work, we have reviewed the recent articles on the lead (II), mercury(II)and Cr(VI) removal from aqueous solution by considering the effect of various parameters such as pH, temperature, metal ion concentration, contact time, and adsorbent dosage on mercury uptake. These factors are of the utmost significance, as any change in these parameters may considerably change the heavy metals removal efficiency of an adsorbent. In this paper the efficiency of Pb(II), Hg(II) and Cr(VI) removal from aqueous solution using agricultural waste material were reviewed.

2. GENERAL OBSERVATIONS

Most of the studies have been performed in batch mode operation. Synthetic stock solutions were prepared by dissolving lead/mercury compounds (mercury nitrate, mercury chloride etc) and dichromates of chromium for adsorption studies.

2.1 Effect of pH

Adsorption of Pb(II), Hg(II) and Cr(VI) are very sensitive to the pH. The adsorption capacities were found to be low at low pH values and increased with increase in pH for the Pb(II), Hg(II) while, vice-versa in case of Cr(VI) adsorption. The mechanism of adsorption can be explained based on pH. The Pb(II), Hg(II) ions were bound to the adsorbent surfaces mainly by the process of the ion exchange and physico-chemical adsorption as the ionic mobility plays an important role.

2.2 Effect of Contact time and initial metal ion concentration

The initial concentration of metal ions provides an important driving force to overcome all mass transfer resistances of the metal ion between the aqueous and solid phases. Equilibrium time is one of the important parameters for selecting a wastewater treatment system]. Equilibrium concentration increases with increase in adsorbate concentration due to saturation of sorption sites on the adsorbent. This may be due to reduction in immediate solute adsorption, owing to the lack of available active sites on the adsorbents surface compared to the relatively large number of active sites required for high initial concentration of metal ions.

2.4 Effect of Adsorbent Dose

Dosage of adsorbent is a key parameter to control both availability and accessibility of adsorption sites. Adsorption has been found increasing with the increase in dose of adsorbent. But with the higher dose of adsorbent in the solution, the mobility of the ion reduces and there results a decrease in the rate of adsorption. The adsorption capacities, of various modified adsorbents are given in Table 1.

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 6 Issue 10, October - 2017

Table 1. Adsorption properties of modified agro wastes based adsorbents for heavy metal ions.

Adsorbent Material	Modifying agent	Metal ions	Adsorption capacity (mg/g)	References
Pith, saw dust, bagasse	Sulfuric acid	Pb(II)	250.0 200.0 227.3	Ayyappan et al. (2005)
Wheat bran	Sulfuric acid	Pb(II)	55.56 - 79.4	Ozer et al. (2007)
Sugarcane bagasse	Succinic anhydride	Cu(II) Cd(II) Pb(II)	185.2 256.4 500.0	Gurgel et al. (2008)
Militia ferruginea	Sulfuric acid	Pb(II)	97.3	Mengistie et al. (2008)
Orange peel	Formaldehyde-treated	Pb(II)	46.61	Lugo et al. (2009)
Firmiana Simplex leaf	Temperature 100-400 ^{0}C	Pb(II)	379.3	Li et al. (2009)
Cashew nut shells	KOH	Pb(II) Cd(II)	28.9 14.3	Tangjuank et al. (2009)
Ficus religiosa leaves	Polysulfone	Pb(II)	37.4	Qaiser et al. (2009)
Mango peel waste	CH_3OH, conc. HCl & HCHO	Cd(II) Pb(II)	68.9 99.0	Iqbal et al. (2009)
Sugarcane bagasse	Steam treated	Pb(II) Hg(II) Cd(II)	9.3 3.9 1.8	Krishnani et al. (2009)
Lawny grass	Citric acid	Pb(II)	320.9	Lu et al. (2009)
Palm empty fruit bunches	NaOH	Pb(II)	46.7	Ibrahim et al. (2010)
Acacia bark powder	NaOH & H_2SO_4	Cu(II) Cd(II) Pb(II)	147.1 167.7 185.2	Munagapati et al. (2010)
Olive stone	H_2SO_4	Pb(II)	14.03	Hoces et al. (2010)
Cicer arietinum	Steam activation	Cu(II) Cd(II) Pb(II) Zn(II)	18.0 18.0 20.0 20.0	Ramana et al. (2010)
Dates stone	Sulphuric acid	Pb(II) Zn(II)	19.6 10.4	Mouni et al. (2010)
Bamboo activated carbons	Carbonized	Pb(II) Cu(II) Cd(II)	2.0 1.4 0.6	Lo et al. (2011)
Typha angustifolia biomass	EDTA	Pb(II)	263.9	Liu et al. (2011)
Apricot stone	Sulphuric acid	Pb(II)	21.4	Mouni et al. (2011)
Cotton, wood sawdust, buckwheat hull	Thioglycolic acid, acetic anhydride, acetic acid & sulphuric acid	Pb(II)	28.7 43.1 44.8	Wu et al. (2012)
Coconut buttons	Sulphuric acid	Pb(II) Hg(II) Cu(II)	92.7 78.8 73.6	Anirudhan et al. (2011)
Pine cone	H_3PO_4	Pb(II)	27.5	Momcilovic et al. (2011)
Tamarind kernel powder	NaOH & epoxychloropropane	Pb(II) Cu(II) Fe(II) Zn(II) Ni(II)	95.9 94.0 93.9 92.5 92.2	Singh et al. (2011)
Bamboo charcoal	$KMnO_4$	Pb(II)	55.6	Wang et al. (2012)
Mentha piperita carbon	$ZnCl_2$	Pb(II)	53.2	Ahmad et al. (2013)

Orange peel	HNO_3	Pb(II) Cu(II) Cd(II)	73.5 15.3 13.7	Lasheen et al. (2012)
Orange peel	Sodium hydroxide & calcium chloride	Pb(II) Cu(II) Zn(II)	209.8 70.7 56.2	Chuan et al. (2012)
Peach palm waste	NaOH	Pb(II)	65.3	Salvado et al. (2012)
Olive stone	H_2SO_4	Pb(II)	17.7	Lara et al. (2012)
Rice straw Rice bran Rice husk Coconut shell Neem leaves Hyacinth roots	NaOH and H_2SO_4	Pb(II)	24.2 20.5 21.4 24.2 22.3 24.9	Singha et al. (2012)
Muskmelon peel	Calcium hydroxide	Pb(II)	167.8	Huang et al. (2013)
Tamarind	Triethylamine	Fe(II) Zn(II) Cu(II) Pb(II) Cd(II)	93.6 92.5 91.5 90.8 90.0	Singh et al. (2012)
Bamboo charcoal	$NiCl_2$	Pb(II)	142.7	Wang et al. (2013)
Rosa Canina leaves	$FeCl_3.6H_2O$	Pb(II)	833.3	Ghasemi, et al. (2013)
Cattail stem (RC)	NaOH(AC) Citric acid (CC) Malic acid (MC) Tartaric acid (TC)	Pb(II)	CC 1.7 MC 1.4 TC 0.7 RC 0.4 AC 0.6	Li et al. (2013)
Cotton fiber	Citric acid	Cu(II) Zn(II) Cd(II) Pb(II)	6.1 4.5 8.2 21.6	Paulino et al. (2013)
Olive tree pruning waste	Ammonium nitrate	Pb(II) Ni(II)	16.78	Anastopoulos et al. (2013)
Date pedicels	Nitrate-enriched solution	Pb(II)	11.6	Yazid et al. (2013)
Allspice husk	CS_2	Pb(II)	38.3	Blancas et al. (2013)
Banana peels	NaOH, HCl & H_3PO_4	Pb(II)	49.8 to 469.5	Massocatto et al. (2013)
Date palm leaflets	Phosphoric acid	Pb(II)	41.5	EI-Shafey et al. (2013)
Marigold plant leaves	Sulphuric acid	Pb(II)	2.6	Singanan et al. (2013)
Cotton linter	Sulphuric acid	Pb(II)	28.1	Dong et al. (2013)
Peanut hulls, soybean shells and grapefruit peels	epichlorohydrin and ethylenediamine	Pb(II)	47.8, 101.0 and 232.0	Ding, et al. (2014a)
walnut wood	Reflux in nitric acid	Pb(II)	58.8	Ghaedi et al. (2015)
Sugarcane bagasse	Hydrogen peroxide	Pb(II) Cr(VI)	2.5 4.4	Gupta et al. (2004)
Coconut coir Pith	Polyacrylamide-grafted	Cr(VI)	127.3	Unnithan et al. (2004)
Ectodermis of Opuntia	H_2SO_4	Cr(VI) Cr(III)	6.2 11.7	Barrera et al. (2006)
Groundnut husk	Sulphuric acid	Cr(VI)	11.3	Dubey et. al (2007)
Citrus reticulata	HNO_3 and H_2O_2	Cr(III) Cr(VI)	232.5 263.1	Zubair et al. (2008)
Grape waste	Concentrated sulfuric acid	Cr(VI)	1.91 (mol/kg)	Chand et al. (2009)
Wheat residue	Diethylenetriamine (DETA) and Triethylamine	Cr(VI)	322.6	Chen et al. (2010)
Corn stalks	Diethylenetriamine and triethylamine	Cr(VI)	200.0	Chen et al. (2011)
Jatropha seed cake	Hydrochloric acid, phosphoric acid	Cr(VI)	22.7	Bose et al. (2011)

Coir pith	Acrylic acid	Cr(VI)	165.0	Suksabye et al. (2012)
Dalbergia sissoo	Carbonized	Cr(VI)	3.5	Mahajan et al. (2012)
Ricinus communis	Concentrated sulphuric	Cr(VI)	7.7	Thamilarasu et al. (2013)
Ficus carica fiber	H_3PO_4	Cr(VI)	44.8	Gupta et al. (2013b)
Ficus carica fibers	Acylic acid	Cr(VI)	28.9	Gupta et al. (2013c)
Avocado seed	Concentrated sulphuric	Cr(VI)	333.3	Bhaumik et al. (2014)
Spruce bark	Formaldehyde Dilute sulfuric acid Concentrated Sulfuric acid	Cr(VI)	423.0 503.0 759.0	Liang et al. (2014)
Wheat bran	Tartaric acid	Cr(VI)	5.3	Kaya et al. (2014)
Bamboo processing residues	Urea and melamine	Cr(VI)	85.0 89.0	Zhang et al. (2015)
Hardwickia binata bark	Formaldehyde	Hg(II)	21.0	Deshicar et al. (1990)
Peanut hull	Bicarbonate-treated	Hg(II)	20.0	Namasivayam et al. (1993)
Coirpith	Carbon	Hg(II)	154.0	Namasivayam et al. (1999)
Terminalia catappa fruit shell	Sulfuric Acid	Hg(II)	94.4	Inbaraj et al. (2006)
Tamarind fruit shell	Formaldehyde & H_2SO_4	Hg(II)	23.9	Anirudhan et al. (2008)
Walnut shell	$ZnCl_2$	Hg(II)	151.5	Zabihi et al. (2009)
Rice husk	Sulfuric acid	Hg(II)	384.6	EI-Shafey et al. (2010)
Soybean stalk	Phenanthrene	Hg(II)	674.9	Kong et al. (2011)
Pistachio-nut shells and licorice residues	Zinc chloride	Hg(II)	147.1	Asasian et al., (2012)
Mango kernel	$ZnCl_2$	Hg(II)	19.8	Somayajula et al. (2013)
Palm shell	Trioctyl-methyl-ammonium-thiosalicylate	Hg(II)	83.3	Ismaiel et al. (2013)
Bamboo leaf powder	Sodium dodecyl sulphate	Hg(II)	31.0	Mondal et al. (2013)
Rice husk	Sulfur-functionalized Organosilane-grafted	Hg(II)	89.0 118.0	Song et al. (2014)
Banana Stem	Formaldehyde	Hg(II)	132.2	Mullassery et al. (2014)
Peanut Hull Powder	Mercaptoacetic acid	Hg(II)	83.3	Ding et al. (2014)
Raw almond Shell Activated Almond Shell	Ortho-phosphoric acid and H_3PO_4	Hg(II)	3.7 37.1	Taha et al., (2017)

CONCLUSION

The present review has established that adsorption offers a great opportunity for a cheap and highly effective process for the removal of Pb(II), Hg(II) and Cr(VI) ions from aqueous solution. Experimental parameters like temperature, solution pH, heavy metal ions concentration, and adsorbant dose and contact time influence adsorption process. On the basis of evidences presented in this review there exist a significant potential for future research in utilizing the adsorbent in industries, agriculture as well as for domestic purpose.

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International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 6 Issue 10, October - 2017

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