Full Length Research Paper

The role of pH in heavy metal detoxification by bio-sorption from aqueous solutions containing chelating agents

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The high level of toxic metal pollution in the environment is a result of increased human activities. The hydrogen ion concentration of solutions has been known to affect reactions in solutions. The role of pH in As(V), Pb(II) and Hg(II) ions detoxification by bio-sorption from aqueous solutions using coconut fiber and sawdust waste biomass, containing chelating agents was studied. pH characteristically influenced adsorption. Maximum adsorption occurred at pH 2 and 12 whereas minimum adsorption occurred at pH 6-8. Modification of the adsorbent by carboxymethylation and thiolation decreased the absorption capacity. As(V) metal ion was adsorbed more than Hg(II), then followed by Pb(II) ion. A model was proposed for the action of pH on the adsorption pattern of the metal ions on the adsorbents used. Desorption studies was investigated using NaOH and H_2PO_4. Therefore, these results can serve as parameters for design of treatment plants for heavy metal detoxification using agricultural by-products, such as sawdust and coconut fiber.

Key words: pH, heavy metal, bio-sorption, adsorbents, detoxification.

INTRODUCTION

Environmental pollution problems caused by heavy metals cannot be over emphasized. Heavy metals are very toxic and pose a threat to man and the environment. The United States environmental protection Agency has classified some heavy metals such as lead, cadmium and mercury as priority pollutants because of their toxicity (Keith and Telliard, 1978). The amount of these heavy metals in our environment increases as a result of industrialization. The anthropogenic sources of heavy metals include waste from the electroplating and metal finishing industries, metallurgical industries, tannery operations, chemical manufacturing, mine drainage, battery manufacturing, leachates from land fills and contaminated ground water from hazardous waste sites (Reed et al., 1994; Neal et al., 1990). As a result of these,

the need to remove, and/or recover these heavy metals have been on the increase.

The removal and recovery of toxic and/or valuable metals from aqueous effluents have received much attention in recent years. A great deal of interest has been given to the utilization of agricultural by-products as adsorbents for the removal of trace amounts of toxic and valuable heavy metals from industrial and municipal waste water effluents. Precipitation and ion-exchange, the two removal/recovery techniques that have found wide application, require the use of chemicals and synthetic resins which are expensive. Many agricultural by-products that are available at little or no cost have been reported to be capable of removing substantial amounts of metal ions from aqueous solutions (Abia et al., 2003; Ngah and Liang, 1999; Igwe and Abia 2003; Gang and Weixing, 1998; Eromosele and Otitolaye, 1994; Wataru and Hiroyuki, 1998; Findon et al., 1993; Gardea-Torresdey et al., 1996, Okieimen et al., 1988; Volesky and Holan, 1995; Mckay and Poots, 1980; Igwe

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et al., 2005a).

More recently, we reported on the use of sawdust and coconut fiber for the removal of heavy metal ions from waste water (Igwe et al., 2005a,b). We found that coconut fiber and sawdust meal were capable of removing heavy metal ions from wastewater. Also, recently we used another cellulosic material, maize cob, to establish the mode of adsorption of the metal ions on the adsorbent (Igwe and Abia, 2005). We found out that the mode of adsorption could be particle diffusion controlled or film diffusion controlled depending on the metal ion type and the adsorbent type.

The pH of aqueous solutions and hence wastewater effluents affects a number of reactions that takes place in these solutions (Hodi et al., 1995; Okieimen et al., 1988; Sadiq et al., 1983; Igwe and Abia, 2003). The effect of pH on heavy metal adsorption from aqueous solutions has been reported (Okieimen et al., 1988; Namasivayam and Senthilkumar, 1998; Igwe and Abia, 2003; Gang and Wiexing, 1998; Zouboulis et al., 1992). It was found that the removal of heavy metal ions was pH dependent at the different pH ranges that was tested. Each result presents a characteristic variation of pH with amount adsorbed depending on the adsorbent type, metal ion and/or initial concentration of metal ions.

In this study, we investigated the role of pH in mercury (II) arsenic (V) and lead (II) metal ions adsorption from aqueous solutions, using coconut fibre and sawdust meal. The effect of incorporation of chelating agents on the adsorbent such as carboxymethyl group ($-COCH_3$) and thiol group ($-SH$), was also investigated. Desorption studies was also investigated to possibly recover the metal ion and regenerate the adsorbent.

MATERIALS AND METHODS

The coconut used was obtained from a local market in Okigwe Imo State, Nigeria. The fibrous parts was removed washed with de-ionizaed water, cut into small pieces, air-dried and powdered in a grinder. Also, sawdust meal was obtained from a timber shade in Okigwe. The sawdust was obtained from freshly cut particular species of wood, to avoid variation in the cellulose content of the wood. The methods of sieving, activation and modification by thiolation and carboxymethylation are essentially the same as that described else where (Igwe and Abia, 2005; Igwe et al., 2005a; Okieimen and Orhorhoro, 1986).

To determine the affect of pH, 100 ml each of the metal ion solution of 2000 mg/l initial concentration, was placed into a conical flask containing 2 g sample of the adsorbent. The solution pH was maintained by the use of buffer solution. The flask was maintained at a constant temperature of 30°C for one hour. The samples were filtered rapidly and the metal content of the filtrates determined by a buck scientific flame Atomic Absorption spectrometer (FAAS) model 200A. The amounts of the metal ions adsorbed were obtained by difference.

RESULTS AND DISCUSSION

The influence of pH of the metal ion solution on the sorption of As (V), Pb (II) and Hg (II) ions by unmodified,

thiolated and carboxymethylated sawdust is presented in Table I, while that for coconut fibre is shown in Table 2. It can be seen that the amount of metal ions removed from the solutions by the adsorbents was minimum at pH range of 6-8, and a maximum at pH 2 and 12. It means that at around neutral pH, the adsorption was minimum and maximum at acidic and alkaline medium. The uptake of metal ions from aqueous solutions by cellulosic materials is usually accompanied by a reduction in the pH of the metal ion solution (Okieimen et al., 1988). This is generally believed to be due to the exchange of the hydrogen atom in the substrate by metal ions. The extent of hydrogen ion exchange would depend on the relative concentration of the exchangeable hydrogen and the hydrogen ion concentration of the medium. It is thought that the presence of a relatively high concentration of H^+ ions in the medium would influence the exchange of hydrogen on the substrate.

The observed reduction in the levels of metal ions removed from solution by the cellulosic materials associated with the increase in the hydrogen ion concentration (i.e. pH 2-6) of the metal ion solution, indicates that the contribution of hydrogen atom exchange to the overall sorption process at these pH values may be insignificant. The pH dependence of As (V), Pb (II) and Hg (II) ions sorption by coconut fiber and sawdust meal, suggest that at about pH 6-8, a large proportion of adsorbed metal ions may be recovered.

From Tables 1 and 2, it is seen that As (V) was adsorbed more than Hg (II), then followed by Pb(II) ion. This trend could be explained based on the modes of adsorption on cellulosic materials. The adsorption of metal ions on cellulosic materials can be attributed to two main terms; intrinsic adsorption and coulombic interaction (Gang and Weixing, 1998). The coulombic term results from the electrostatic energy of interactions between the adsorbents and adsorbate. The charges on both substrates as well as softness or hardness of charge on both sides are mostly responsible for the intensity of the interaction. Coulombic interaction can be observed from adsorption of cationic species versus anionic species on adsorbents (Gang and Weixing, 1998). The intrinsic adsorption of the materials is determined by their surface areas which can be observed by the effect of different sizes of adsorbents on adsorption capacity (Igwe and Abia, 2003).

Also, from Tables 1 and 2, it is seen that modification by thiolation and carboxymethylation decreased the adsorptive capacity of the cellulosic materials. This confirms our earlier suggestion that what took place was intrinsic adsorption. The decrease in the amount adsorbed on modification indicates that the carboxymethyl and the thiol groups blocks the site of attachment by replacing the hydrogen atom on the hydroxyl group of the cellulose. The introduction of these functional groups reduces the ease with which the hydrogen ions was lost hence, decreasing the

Table 1. Amount of metal adsorbed (mg/g) as pH of the metal ion solutions increases for modified and unmodified sawdust.

pH	Amount adsorbed (mg/g)								
	Unmodified sawdust			Thiolated sawdust			Carboxymethylated sawdust		
	As^{5+}	Pb^{2+}	Hg^{2+}	As^{5+}	Pb^{2+}	Hg^{2+}	As^{5+}	Pb^{2+}	Hg^{2+}
2	927.0	933.0	705.0	506.0	350.0	390.0	407.9	376.6	394.2
4	926.0	921.0	659.0	450.0	361.0	384.0	402.7	365.3	383.6
6	914.0	693.5	545.0	408.0	325.0	398.0	121.3	199.5	236.2
8	913.0	687.0	530.0	412.0	393.0	120.6	103.7	229.3	229.4
10	923.0	822.0	634.0	486.0	464.0	442.0	366.4	347.4	358.3
12	940.0	886.5	739.0	528.0	487.0	612.0	405.3	368.3	390.0

Table 2. Amount of metal adsorbed (mg/g) as pH of metal ions solution increases for modified and unmodified coconut fiber.

pH	Amount adsorbed (mg/g)								
	Unmodified coconut fibre			Thiolated coconut fibre			Carboxymethylated coconut fibre		
	As^{5+}	Pb^{2+}	Hg^{2+}	As^{5+}	Pb^{2+}	Hg^{2+}	As^{5+}	Pb^{2+}	Hg^{2+}
2	986.0	672.3	926.0	923.0	907.0	921.0	928.1	677.3	924.3
4	977.0	679.5	974.0	954.0	912.0	919.0	912.7	500.7	867.2
6	926.0	495.9	885.0	926.0	885.5	909.0	833.0	434.0	799.5
8	924.0	495.4	880.0	948.0	887.0	912.0	800.7	432.7	801.6
10	975.0	564.3	974.0	974.0	978.0	979.0	926.1	676.5	894.1
12	974.0	541.3	975.0	975.0	972.5	981.0	953.7	656.5	965.5

contribution by coulombic interaction of the metal ions with the surface groups, to the adsorptive capacity.

Furthermore, for example, the oxy-anions of arsenic (V) exist in four different arsenate species as H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} in the pH range <2, 3-6, 8-10 and >12, respectively (Sadiq et al., 1983). Namasivayam and Senthilkumar (1998), reported that in the pH range 3-7, $H_2AsO_4^-$ is the predominant species and apparently, this species is adsorbed. Thus the adsorbent acquires a net positive charge in the pH range and adsorption may be facilitated by coulombic interactions. In the pH range of 7-10 specific interactions seem to occur, since dissociation of arsenic acid is expected. The transfer of proton to the hydroxyl groups of the (β-D-glucose units of the cellulose is also possible (Ghosh and Yuan, 1987).

Specific adsorption (ligand exchange mechanism) or chemi-sorption of arsenic on Fe oxide/hydroxide surfaces has been reported in the literature (Sadiq, 1997). Grossl et al. (1997) have proposed a mechanism for the specific adsorption of arsenic (V) on goethite in a two-step process resulting in the formation of an inner-sphere mono-dentate surface complex at low surface coverage and an inner-sphere bi-dentate surface complex at high surface coverage. A surface complexations model has also been proposed recently by Manning and Golderg (1997) for As (V) adsorption on clay minerals. Based on the model, the following reactions are proposed for the

adsorption of heavy metals on cellulosic materials. Using As (V) as an example, we proposed the following mechanism.

Surface acid-base reactions:

$$SOH + H^+ \rightleftharpoons SOH_2^+ \quad (1)$$

$$SOH \rightleftharpoons SO^- + H^+ \quad (2)$$

Mononuclear As (V) adsorption:

$$SOH + H_3AsO_4 \rightleftharpoons SH_2AsO_4 + H_2O \quad (3)$$

$$SOH + H_3AsO_4 \rightleftharpoons SHAsO_4^- + H_2O + H^+ \quad (4)$$

$$SOH + H_3AsO_4 \rightleftharpoons SHAsO_4^{2-} + H_2O + 2H^+ \quad (5)$$

Binuclear As (v) adsorption:

$$2SOH + H_3AsO_4 \rightleftharpoons S_2AsO_4 + 2H_2O \quad (6)$$

$$2SOH + H_3AsO_4 \rightleftharpoons S_2AsO_4^- + 2H_2O + H^+ \quad (7)$$
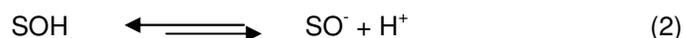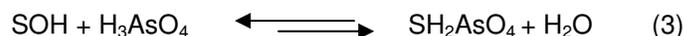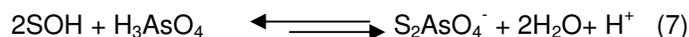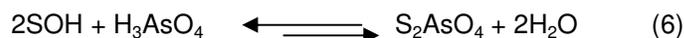
SOH represents one reactive surface hydroxyl group bound to the glucose unit. The above model can also be applied to lead and mercury. Thus, the modification by thiolation and carboxymellylation removes the H-atom from the surface hydroxyl group, thereby altering the

reactions on the surface. Therefore, this reduces the amount of metal adsorbed on modification.

Attempts were made to regenerate the adsorbent as well as re-solubulize the metal ions from the spent adsorption at a neutral pH of about 7.0. Although some amount of metal ions were adsorbed at that pH, it was possible to desorbe the metal ions using NaOH, at concentrations of 10^{-3} to 10^{-2} M. This was used to maintain the pH from acidic to neutral by regulating the volume of the NaOH added. The percent de-sorption improved from 20 to 50% when the concentration was increased from 10^{-3} to 10^{-2} M. Further increase in concentration of the NaOH to I M did not improve the de-sorption. For adsorption at a higher pH, phosphoric acid was used to maintain the pH to about neutral pH of 7.0. This is in agreement with the observation of Hodi et al. (1995). This implies the suitability of this treatment for the safe disposal of arsenic, lead and mercury-laden sawdust and coconut fiber, taking into consideration the relatively high initial concentration of these metal ions tested.

In conclusion, coconut fiber and sawdust waste biomass was successfully used to remove arsenic, lead and mercury from aqueous solution. The removal of these metal ions was characteristically pH dependent within the range of 2-12. Adsorption was very low at around neutral pH. This was used to carry out de-sorption studies to recover the metal ions and regenerate the adsorbents. A model was proposed for the adsorption of these metal ions based on proton exchange reactions on the surface of the adsorbent. This confirmed our findings that modification caused a stearic hindrance on the adsorption, hence reduced the amount adsorbed. This is similar to previous results (Igwe et al., 2005c). Since the adsorbents are disposed as waste material, treatment of arsenic, lead and mercury contaminated waste water using sawdust and coconut fibre is expected to be economical.

REFERENCES

Abia AA, Igwe JC (2005). Sorption kinetics and intraparticulate diffusivities of Cd, Pb, and Zn ions on maize cob. Afr. J. Biotechnol. 4(6): 509 – 512.

Abia AA, Horsfall Jr M, Didi O (2003). The use of chemically modified and unmodified cassava waste for the removal of Cd, Cu and Zn ions from aqueous solution. Bioresour. Technol. 90: 345 – 348.

Eromosele IC, Otitolaye OO (1994). Binding of iron, zinc and lead ions from aqueous solution by shea butter (*Butyrospermnm Parkii*) seed husk. Bull. Environ. Contam. Toxicol. 52: 530 – 537.

Findon A, Mckay G, Blair HS (1993). Transport studies for the sorption of copper ions by chitosan. J. Environ. Sci. Health. A28: 173 – 185.

Gang S, Weixing S (1998). Sunflower stalk as adsorbents for the removal of metal ions from waste water. Ind. Eng. Chem. Res. 37(4): 1324 – 1328.

Gardea-Torresdey JL, Gonzalez JH, Tiemann KJ, Rodrignuez O, Gamez G (1998). Phytofiltration of Hazardous cadmium, chromium, lead and zinc ions by biomass of medicago sativa (Alfalfa). J. Hazard. Matter 57: 29 – 39.

Ghosh MM, Yuan JR (1987). Adsorption of inorganic arsenic and organoarsenicals on hydrous oxide. Environ. Prog. 6: 150-156

Grossl PR, Eick MJ, Sparks DL, Goldberg S, Ainsworth CC (1997). Arsenate and Chromate retention mechanisms on goethite. 2 Kinetic evaluation using a pressure-jump relaxation technique. Environ. Sci. Technol. 31: 321-325

Hodi M, Polyak K, Htavay J (1995). Removal of Pollutants from drinking water by combined ion-exchange and adsorption methods. Environ. Int. 21: 325---328.

Igwe JC, Abia AA (2003). Maize cob and husk as Adsorbents for removal of cadmium, lead and zinc ions from wastewater. The physical scientist 2: 210-215.

Igwe JC, Ekeghe EMN, Abia A.A. (2005a). Binding of Hg^{2+}, Ni^{2+} and Pb^{2+} ions unto thiolated and carboxymethylated sawdust. *Intern. J. Chem. India*. (in press).

Igwe JC, Ibeh CA, Abia AA (2005b). Sorption Kinetics and Intraparticulate diffusivities of Hg, As and Pb on modified coconut fibre. J. Appl. Sci. Environ. Managt. (In Press).

Igwe JC, Iroh CU, Abia AA, (2005c). Removal of Hg^{2+}, Ni^{2+} and Pb^{2+} ions from wastewater using modified Grannular Activated carbon (GAC): Adsorption and kinetic studies. J. Environ. Managt. (In press).

Keith LH, Telliard WA (1979). Priority Pollutants. Environ. Sci. Tech., 13: 416-424.

Manning BA, Goldberg S (1997). Adsorption and stability of arsenic (III) at the clay mineral-water interface. Environ. Sci. Technol. 31: 2005-2011.

Mckay G, Poots VJ, (1980).Kinetics and diffusion processes in colour removal from effluent using wood as an adsorbent. J. Chem. Technol. Biotechnol. 30: 279 – 292.

Namasivayam C, Senthilkumar S (1998). Removal of Arsenic (V) from Aqueous solution using industrial Solid waste: Adsorption rates and Equilibrium studies. Ind. Eng. Chem. Res. 37: 4816 – 4822.

Neal BG, Lawrence EB, Wendt JL (1990). Alkali metal partitioning in Ash from pulverized coal combustion. Combust. Sci. Tech. 74: 211-214.

Ngah WS, Liang KH, (1991). Adsorption of Gold (III) ions onto chitosan and N-Carboxymetthyl chitosan: Equilibrium studies. Ind. Eng. Chem. Res., 38(4): 1411-1414.

Okieimen FE, Maya AO, Oriakhi CO (1988). Sorption of cadmium, lead and zinc ions on sulphur containing chemically modified cellulosic materials. Intern. J. Environ. Anal. Chem. 32: 23-27.

Okieimen FE, Orhorhoro F.; (1986) Binding cadmium and copper ions with chemically modified cellulosic materials. Int. J. Environ. Anal. Chem. 24: 319-325.

Reed BF, Arunnachalam S, Thomas B (1994). Removal of lead and cadmium from aqueous waste streams using Granular activated carbon (GAC) columns. Environ. Prog. 13: 60-65.

Sadiq M (1997). Arsenic chemistry in soils: An overview of thermodynamic predictions and field observations. Water Air Soil Pollut. 93: 117-121.

Sadiq M, Zaida JH, Mian AA (1983). Water, Air, soil Pollut. 20:369-???.

Volesky B, Holan ZR (1995). Biosorption of heavy metals. Biotechnol. Prog. 11: 235-250.

Wateru T, Hiroyuki Y (1998). Adsorption of Organic acids on polyaminated Highly porous chitosan: Equilibra. Ind. Eng. Chem. Res. 37(4): 1300 – 1309.

Zouboulis AI, Matis KA, Stalidis GA (1992). Flotation methods and techniques in wastewater. Innovations in Flotation Technology. Mavros P, Matis KA (Eds.) Kluwer Academic Dordrecht, NL. pp. 96-104.