Full Length Research Paper

Competitive adsorption of Zn (II), Cd (II) AND Pb (II) ions from aqueous and non- aqueous solution by maize cob and husk

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Heavy metals rank as major environmental pollutants. Industrial wastewater effluents carry admixtures of these heavy metals. The competitive adsorption of Zn^{2+}, Cd^{2+} and Pb^{2+} metal ions from aqueous and non-aqueous solutions by unmodified and modified maize cob and husk was investigated. The results showed that maximum adsorption occurred at 495.9 mg/g for Zn^{2+} ion, 456.7 mg/g for Pb^{2+} ion and 493.7mg/g for Cd^{2+} ion without modification. The adsorption in a mixture of the metal ions caused a leveling effect on the adsorption capacity of the maize cob and husk. The adsorption efficiency of each metal ion was influenced by the presence of other metal ions, presence of non -aqueous solvent and modification by carboxymethylation. The study significantly reveals the presence of other heavy metals and chemicals as design parameter in the treatment and management of heavy metal pollutants using cellulosic materials.

Key words: Competitive adsorption, mixed metal ions, aqueous and non-aqueous solution, maize cob and husk.

INTRODUCTION

Recently, a great deal of interest in the research for the removal of heavy metals from industrial effluents have focused on the use of agricultural by-products as adsorbents. The use of agricultural by products in bioremediation of heavy metal ions, which is known as bio-sorption, is an aspect of biotechnology. This is recognized as an emerging technique for the de-pollution of heavy-metal polluted streams (Volesky and Holan, 1995). Bioremediation consists of a group of applications, which involve the detoxification of hazardous substances instead of transferring them from one medium to another by means of microbes and plants (Gavrilescu, 2004). This process is characterized as less disruptive and can be often carried out on site, eliminating the need to transport the toxic materials to treatment sites. The bio-sorption (sorption of metallic ions from solutions by live or dried biomass) offers an alternative to the remediation of industrial effluents as well as the recovery of metals contained in other media (Gavrilescu, 2004).

Biosorbents are prepared from naturally abundant and/or waste biomass. Due to the high uptake capacity and very cost-effective source of raw materials, biosorption is a progression towards a perspective method (Gavrilescu, 2004). These agricultural by-products are capable of binding to heavy metals by adsorption, chelation and ion exchange (Gardea-Torresdey et al., 1996, 1999; Gang and Weixing, 1998). Several sorbents which can be used includes bacterial and algal (Voleskey and Holan, 1995), fungal biomass (Guibal et al., 1992), biopolymers (Deans and Dixon, 1992), sunflower stalks (Gang and Weixing, 1998), maize cob and husk (Igwe and Abia, 2003, 2005; Igwe et al., 2005a,b); chitosan and n-carboxy-methyl chitosan (Ngah and Liang, 1999), chemically modified and unmodified cassava waste (Abia et al., 2003). The use of

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many other sorbents is under study in our laboratory, which include coconut fiber, sugarcane bagasse, tiger nuts waste biomass, great-millet and cocoa pod waste biomass.

In our previous work (Igwe and Abia, 2003, 2005), we investigated the feasibility of using maize cob and husk as adsorbents for the removal of Cd(II), Zn(II) and Pb(II) ions and the mechanism of sorption respectively. In this work we investigated the effect of having a mixture of these metal ions in the waste water. Since the pollution of the environment with toxic metals is essentially a result of many human activities such as mining and metallurgy, it means that these effluents would carry admixtures of heavy metal ions in solution. Also, there could be the presence of other chemicals such as organic solvents and acids. Hence, we investigated the effect of having mixtures of these metal ions, presence of an organic solvent and also the effect of modifying the adsorbent by carboxymethylation.

MATERIALS AND METHODS

All reagents used are analytical grade and was used without further purification. Doubly distilled and de-ionzed water was used in preparation of all sample solutions. The purchase, preparation and activation of the maize cob and husk were essentially the same method as that described earlier (Igwe and Abia, 2005). The particle size used is 425 m. The method of modification by carboxymethylation was the same as that reported by Eromosele et al. (1996).

To determine the adsorption capacity of the adsorbents, initial concentration of 1000 mg/l of all the three metal ions solutions were prepared.100 ml of each of these metal ions were mixed and put in a conical flask containing 2 g of adsorbent. The flask was corked, uniformly agitated at a temperature of 30°C and optimum pH of 7.5 for 10 min. The experimental set-up was repeated for time intervals of 20, 30, 40, 50, and 60 min. At the end of each time, the mixture was rapidly filtered by suction and the metal ions concentrations in the filtrate was determined using a buck scientific Flame Atomic Absorption Spectrometer [FAAS] model 200A. The amounts of the metal ions adsorbed were obtained by difference.

The effect of other chemicals was investigated using iso-propanol. 100 ml of 20% and 50% iso-propanol solutions were introduced separately into the conical flask at each different time interval of the experiment.

RESULTS AND DISCUSSION

It has already been established that maize cob and husk can be used as adsorbent for the removal of Cd(II), Pd(II) and Zn(II) ions from aqueous solutions(Igwe and Abia, 2003). We have also established that the mechanism of sorption is particle diffusion controlled (Igwe and Abia, 2005) and that the sorption follows the Freundlich isotherm model (Igwe and Abia, 2003). Here, we present the results of the amount adsorbed against time for a mixture of the metal ions and other chemicals.

Figures 1 and 2 show the amount of metal adsorbed against time for maize husk and cob respectively, at
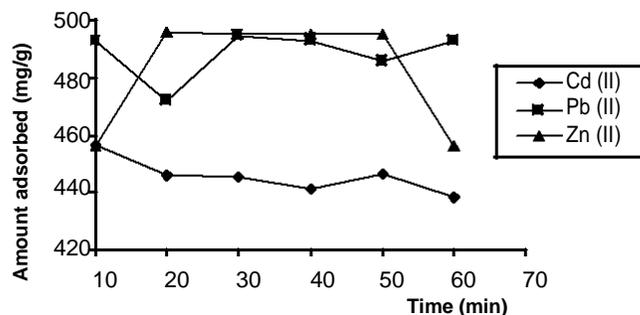
Figure 1. Amount adsorbed (mg/g)against time (min) for Cd (II), Pb (II) and Zn (II) ions on maize husk of 425 m particle size at 1000 mg/l initial mixed metal ion concentration.
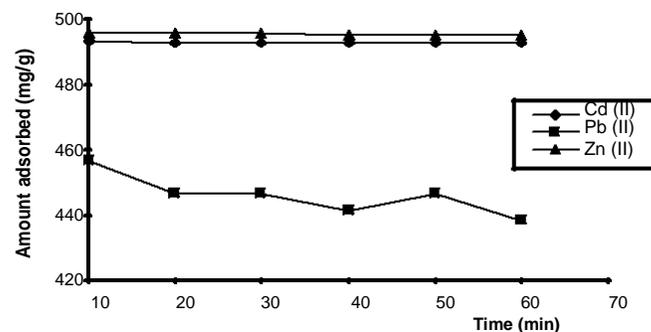
Figure 2. Amount adsorbed (mg/g) against time (min) fpr Cd (II), Pb (II) and Zn (II) ions on maize cob of 425 m particle size at 100 mg/l initial mixed metal ion concentration.
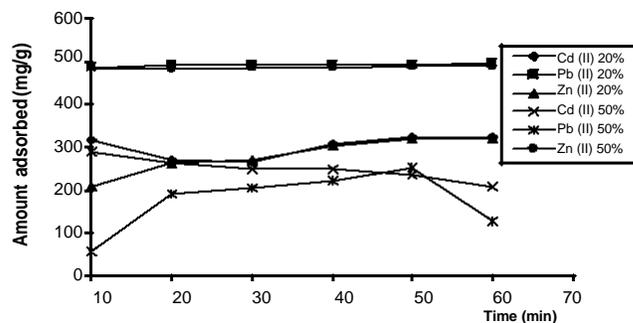
Figure 3. Amount adsorbed (mg/g) against time (min) for Cd (II) ,Pb (II) and Zn (II) ions on maize cobs of 425 m particle size effect of 20% and 50% isopropanol (Initial metal ion concentration is 1000 mg/l).

1000 mg/l initial metal ions concentration and 425 m particle size. Figures 3 and 4 show the amount adsorbed against time for effect of 20% and 50% iso-propanol on maize cob and husk, respectively. Figure 5 show the amount adsorbed against time for carboxymethylated maize cob and husk. Figures 6 and 7 show the
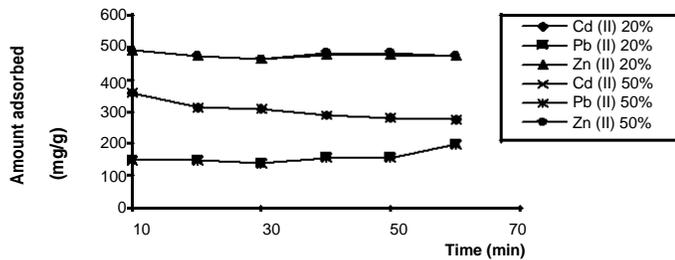
Figure 4. Amount adsorbed (mg/l) against time (min) for Cd (II), PB (II) and Zn (II) ions on maize husk of 425 m particle size with effect of 20 % and 50 % isopropanol . (Initial concentration is 1000 mg/l).
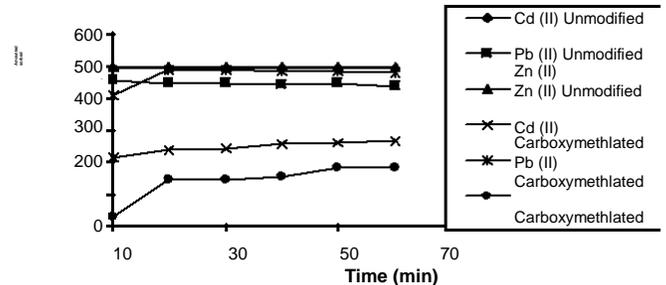
Figure 7. Amounts adsorbed against time (min) for Cd (II), Pb (II) and Zn ions on unmodified and carboxylated maize cob of 425 um particle size. (Initial concentration is 1000 mg/l).

Figure 5. Amount adsorbed (mg/g) against time (min) for Cd (II), Pb (II) and Zn (II) ions on carboxymethlated maize cob and husk of 425 m particle size. (Initial concentration is 1000 mg/l).
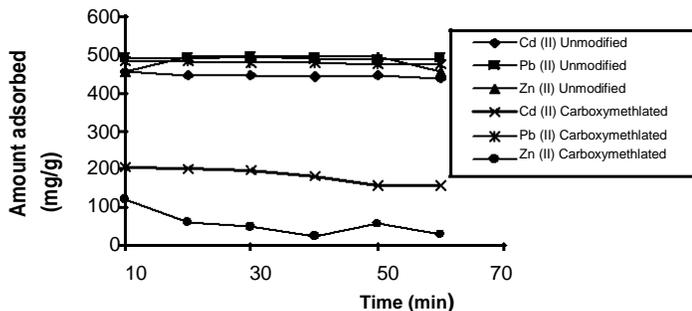
Figure 6. Amount adsorbed (mg/g) against time (min) for Cd (II). Pb (II) and Zn (II) ions on unmodified and carboxylayted maize husk of 425 m particle size. (Initial concentration is 1000 mg/l).

comparison in the amount adsorbed for the unmodified and carboxymethylated for the husk and cob, respectively.

From Figures 1 and 2, we can see that the adsorption was steady for Cd (II) and Zn (II) on maize cob but varied a little for Pb (II) on maize cob and all metal ions on maize husk. On the average, the adsorption was steady, leveling out as time increased. This differs from the result of our previous experiments (Igwe and Abia, 2003, 2005), where the amount adsorbed increased as time increased until equilibrium was attained at about 50-60

min. Since adsorption is particle diffusion controlled (Igwe and Abia, 2005) and this could be effected by the following processes: (i) diffusion of the solute from the solution to the film surrounding the particle; (ii) diffusion from the film to the particle surface (external diffusion); (iii) diffusion from the surface to the internal sites (surface diffusion or pore diffusion), and (iv) uptake which can involve several mechanisms: physicochemical sorption, ion exchange, precipitation or complexation (Findon et al., 1993; Weber and Digiano, 1996). The first process is bulk diffusion, the second is the external mass transfer resistance and the third is intraparticle mass transfer resistance.

When the adsorption is particle diffusion controlled, it means that intraparticle mass transfer resistance is rate limiting. Therefore, in the presence of a mixture of the metal ions, the metal ions justle (i.e compete) for the adsorption sites on the adsorbent. This competition affects the diffusion properties of the metal ions, hence decreases the adsorption capacity of the metal ions. Thus, the metal ion that successfully reaches the adsorption site faster depends on the above factors and also on the ionic radii of the metal ions. Competition among the metal ions for adsorption sites obviously affected the adsorption capacity.

From Figure 5, the amount of metal adsorbed was decreased as a result of modifying the adsorbent by carboxymethylation. This introduces the carboxymethyl group [-COCH$_3$] onto the surface of the adsorbent by attachment to the - D-glucose units. Since the adsorption is particle diffusion controlled, the attached carboxymethyl group acts as a stearic hinderance to the adsorption process. It seems to us that surface attachment might also be taking place on the functional groups on the surface of the adsorbent. More of what happens is volumetric filling of the micro-pores found in the adsorbents

The reduction in the amount adsorbed as affected by modification means that the carboxymethyl group blocks some of these micro-pores making it difficult for the metal ions to reach the adsorption site. Since adsorption takes place in these micro-pores (Motoyuki, 1990), this results in decrease in the amount of metal adsorbed with time,

when compared to that without modification. This is similar to the result obtained with use of granular activated carbon, a conventional adsorbent (Igwe et al., 2005c). The result of the presence of iso-propanol is given on Figure 3 for maize cob and Figure 4 for maize husk. Increase in the concentration of iso-propanol from 20% to 50% decreased the adsorption of Pb(II) and Cd (II) on maize cob, slightly increased the adsorption of Zn(II) on maize cob, but did not affect the adsorption of the metal ions on maize husk. The presence of iso-propanol decreased the amount of metal adsorbed but an increase in the concentration of iso-propanol did not have an appreciable effect on the amount adsorbed. The decrease in the amount adsorbed in the presence of iso-propanol means that it adds to the stearic hindrance to the diffusion processes of the metal ions towards the adsorption sites for subsequent attachment or binding.

From the variation of the amount adsorbed against time for unmodified and carboxymethylated of particle size 425 m for the husk and cob (Figures 6 and 7 respectively), it is clearly seen that the trends and shapes of the figures are the same, indicating that competition is obviously a factor to consider in the adsorption process. It is also clearly seen that the amount of metal adsorbed for the unmodified for each metal ion is always greater than the amount adsorbed for the carboxymethylated cob or husk for the same metal ion. Also, by inspection of the plots, the application of the Lagergren equation (equation 1) shows a zero order reaction. This is true since amount adsorbed remain fairly constant with increased time. The Lagergren equation is given by:

$$\log (q_e-q)=\log q_e - K_{ad} t/2.303. \qquad (1)$$

Where q is amount adsorbed (mg/g) at time t, q_e is amount adsorbed (mg/g) at equilibrium time and K_{ad} is the rate constant of adsorption (min^{-1}).

In conclusion, the amount of Cd(II), Pb(II) and Zn(II) metal ions in aqueous and non-aqueous solutions adsorbed did not increase as time increased as expected from previous work (Igwe and Abia, 2003, 2005). Rather, the amount adsorbed remained fairly constant with time during the competitive sorption. This was attributed to the fact that all the metal ions, will have to be struggling for the same number of adsorption sites at the same time. Modification of the adsorbent by carboxymethylation decreased adsorption because the carboxymethyl group adds to the competition for adsorption site. The presence of iso-propanol decreased the adsorption capacity, but increase in the concentration of iso-propanol did not have any appreciable effect on the adsorption. Therefore, this study significantly reveals that the presence of other heavy metals and chemicals are influential factors and should be design parameters in the treatment and management of heavy metal pollutants using cellulosic materials.

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