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Short Communication

Sorption kinetics and intraparticulate diffusivities of Cd, Pb and Zn ions on maize cob

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The kinetics of sorption and intraparticulate diffusivities of Zn, Cd and Pb using maize cob was studied. The amount of the metal ions adsorbed increased with time. The highest sorption rates of the three metal ions were 71% for Zn^{2+}, 32% for Cd^{2+}, and 30% for Pb^{2+}. The fractional attainment of equilibrium showed that Zn^{2+} reached equilibrium before Pb^{2+} ion and then Cd^{2+} ion. This study showed that the sorption of Zn^{2+}, Cd^{2+} and Pb^{2+} ions on maize cob is particle diffusion controlled. The rate coefficients for particle diffusion were 0.07 min^{-1} for Zn^{2+}, 0.053min^{-1} for Pb^{2+} and 0.081min^{-1} for Cd^{2+}.

Key words: Adsorption, Kinetics, intraparticulate diffusivity, heavy metal, maize cob.

INTRODUCTION

The research into the utilization of agricultural by-products as adsorbents for the removal of heavy metals from aqueous solutions has been on the increase. This is because these agricultural by-products are naturally occurring; hence they are available at little of no cost. They also have advantage over the conventional adsorbents such as activated carbon particularly because of their low cost and high availability. There is also no need for complicated regeneration processes when using agricultural by-products and they are capable of binding to heavy metals by adsorption, chelation and ion-exchange (Gardea-Torresdey et al., 1996, 1999; Gang and Weixing, 1998). In our previous work, (Abia and Igwe, 2004) we reported the feasibility of utilizing maize cob and husk as adsorbents for removal of cadmium, lead and zinc ions from aqueous solutions. The utilization of other agricultural by-products for adsorption of heavy metals have been reported elsewhere, which includes the use of sun flower stalks as adsorbents (Gang and Wexing 1998), use of polyaminated highly porous chitosan (Wataru and Hiroyuki 1998), use of shea butter seed husks (Eromosele and Otitolaye, 1994), use of chitosan and N-carboxy-methyl chitosan, (Ngah and Liang, 1999) and the use of chemically modified and unmodified cassava waste (Abia et al., 2003).

Maize is abundant in Nigeria, and the cob constitute waste problems. Most of the reported work on the use of agricultural by-products for removal of heavy metals has to do with the capability of such materials in adsorbing heavy metals. There are very few reports on the specific mode of action of the adsorbents. The study of the adsorptive action of metallic ions towards the agricultural by-products may involve metals interactions or co-ordination to functional groups present in natural protein, lipids and carbohydrates positioned on cell wall (Quek et al., 1998).

The fractional attainment of equilibrium is the ratio of the amounts of metal ion removed from solution after a certain time to that removed when sorption equilibrium is attained. It would definitely be expected that factors such as the number of reactive sites on the substrate and the bulkiness of the substrate would affect the rate of sorption of metal ions. However, a great deal of information is gotten from the fractional attainment of equilibrium. The rate of attainment of equilibrium may be either film-diffusion controlled or particle-diffusion controlled, even though this two different mechanism cannot be sharply demarcated (Okieimen et al., 1991).

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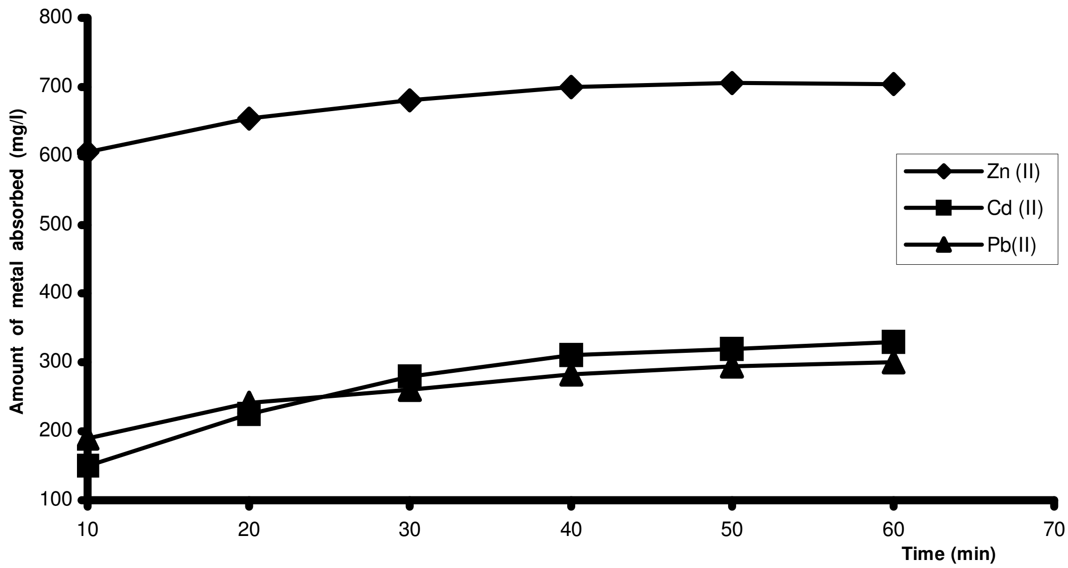

Figure 1. Effect of contact time on sorption of Zn(II), Cd(II) and Pb(II) ions in maize cob.

For particle-diffusion controlled processes, the fractional attainment of equilibrium is a function of D^+/Dr_o^2; where D is the diffusion coefficient of the counter ions in the solvent; D^+, the distribution coefficient of analyte ions and r_o is the particle radius. Therefore, the sorption of a high amount of a metal ion in solution is facilitated by a reduction in the size of the analyte ion. Hence, the time needed to attain a given uptake level is not dependent on variable such as concentration.

The linear driving force concept was used to develop the relationship:

$$\ln (1-\alpha) = -k_p t \qquad 1.0$$

For particle-diffusion controlled sorption processes (Okieimen et al., 1991), α is the fractional attainment of equilibrium, k_p is the rate coefficient for particle diffusion controlled process corresponding to particle size of the sorbent; t is time and $\ln(1- \alpha)$ is a measure of the intraparticulate diffusivity. If a plot of $\ln(1 - \alpha)$ versus time results in a linear relationship, then the sorption process is particle-diffusion controlled and the diffusivity of the metal ions onto the adsorbent surface is independent of the extent of sorption.

In this study the rate of adsorption of Zn (II), Pb (II) and Cd (II) metals ions onto maize cob was investigated at optimum pH of 7.5 and temperature of 30℃. The effect of contact time between the adsorbent and the metal ions were also investigated.

METHODS

The maize (*Zea mays*) cob obtained was washed with de-ionized water, cut into small pieces, air-dried and powdered in a grinder.

The meal obtained was air-dried and first sieved through a 1000 μm mesh and then through 850 μm mesh. The meal retained on the 850 μm mesh was used. It was soaked in dilute nitric acid solution (2% v/v) overnight, rinsed with de-ionized water and air-dried.

To determine the effect of contact time, a 2 g sample of the maize cob was put into a 100 ml solution of the metal ion of initial concentration 2000 mg/l. Different samples were left to stand for 10, 20, 30, 40, 50, and 60 min. 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 gotten by difference. The intraparticulate diffusivity and the fractional attainment of equilibrium were then calculated.

RESULTS AND DISCUSSION

The results of the uptake level of the metal ions as time increase from zero to sixty minutes are shown on Figure 1. It could be seen that the uptake level of the metal ions by maize cob generally increased for all three metal ions especially for Zn with initial increase between zero and ten minutes being very sharp. From Figure 1, it was also observed that the uptake rate gradually decreases with time and most of the curves were almost leveling up, indicating that sorption was rapid and approached maximum at about sixty minutes.

Table 1 gives the fraction or ratio of the amount adsorbed at any given time (C_t) to the initial concentration

Table 1. Fraction of the amount adsorbed for Zn^{2+}, Cd^{2+} and Pb^{2+} on maize cob.

Time (min)	C_t/C_o		
	Zn^{2+}	Cd^{2+}	Pb^{2+}
10	0.61	0.15	0.19
20	0.65	0.23	0.24
30	0.68	0.28	0.26
40	0.70	0.31	0.28
50	0.71	0.32	0.30
60	0.70	0.33	0.30

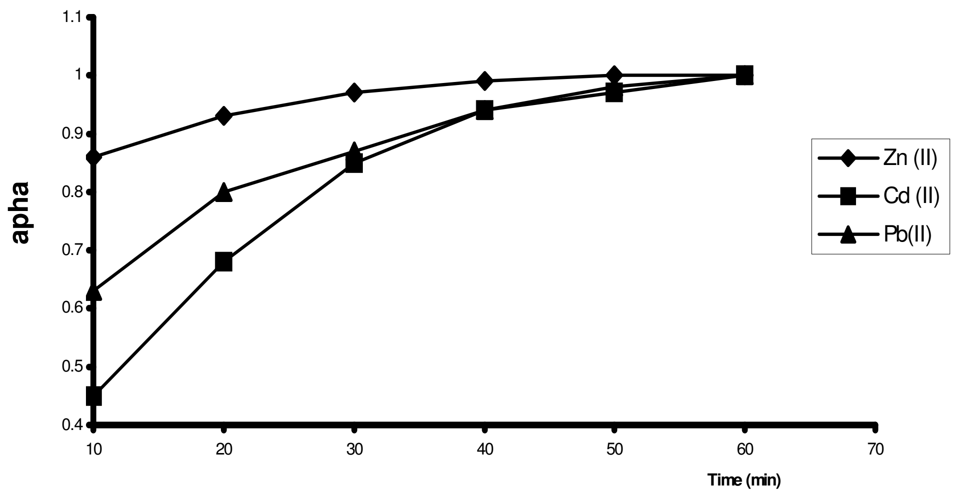

Figure 2. Fractional attainment of equilibrium (alpha) vs time for sorption of Zn(II), Cd(II) and Pb(II) ions in maize cob.

(C_o). From this table it is easy to calculate the percentage of adsorption. The value for Zn (II) ion at 10 min, (61%) is much higher than that for Cd^{2+} ion and Pb^{2+} ion, which are 15 and 19%, respectively. It is also clearly seen that at 60 minutes, 70% of Zn^{2+} has been adsorbed compared to 33% and 30% for Cd^{2+} and Pb^{2+}, respectively.

Differential adsorption of metal ions from solutions by an adsorbent has been generally ascribed to (1) differences in ionic radii of the metal ions, (2) differences in the affinity of the metal ions for active groups on the adsorbent and (3) nature of the anions of the salt of the metal ion. The ionic radii for the metal ion are 0.74 Å for Zn, 0.97 Å for Cd and 1.21 Å for Pb. The adsorption pattern corresponds to the differences in the ionic radii of the metal ions.

The fractional attainment of equilibrium α was calculated from the relationship:

$$\alpha = [M]_t^{n+}/[M]_\infty^{n+} \qquad 2.0$$

Table 2. Rate coefficient for particle-diffusion controlled sorption for Zn^{2+}, Cd^{2+} and Pb^{2+} on maize cob.

Metal ion	Zn^{2+}	Pb^{2+}	Cd^{2+}
Kp $(min)^{-1}$	0.077	0.053	0.081

where $[M]_t^{n+}$ is the concentration of metal ion at anytime t and $[M]_\infty^{n+}$ is the concentration at infinity, that is equilibrium. The plot of α against time is shown on Figure 2. From this figure, it is observed that the value of α with change in time increases from about 5 to 40 min. It can be seen that α is higher for Zn^{2+} than Pb^{2+} and Cd^{2+}; Pb^{2+} and Cd^{2+} have the same value at 40 min, and values of α converge to one at 60 min. This value of α showed that Zn^{2+} ion was adsorbed more, followed by Pb^{2+} and then Cd^{2+}; that also mean that the rate of adsorption of Zn^{2+} ion was faster.

A plot of ln(1-α) against time (not shown) for the three metal ions, showed straight lines. This means that the sorption process for Zn^{2+}, Cd^{2+} and Pb^{2+} ions is particle diffusion controlled. The values of the rate coefficient for particle-diffusion controlled sorption (k_p) are shown in Table 2. The rate coefficient for particle-diffusion controlled sorption for Zn^{2+}, Cd^{2+} and Pb^{2+} are 0.077, 0.081 and 0.053 min^{-1}, respectively. This gives a measure of the diffusion rate of the metal ions indicating that diffusion rate also affects adsorption rate.

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