Full Length Research Paper

Adsorption kinetics and intraparticulate diffusivities for bioremediation of Co (II), Fe (II) and Cu (II) ions from waste water using modified and unmodified maize cob

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Heavy metals constitute pollution problems to the environment and they are toxic to both man and aquatic organisms. The passive removal of toxic heavy metals such as cobalt (II) (Co(II)), iron (II) (Fe(II)) and copper (II) (Cu(II)) by inexpensive biomaterials, termed biosorption, requires that the substrate displays high metal uptake and selectivity, as well as suitable mechanical properties for applied remediation scenarios. The kinetics and intraparticulate diffusivities for the adsorption of these metal ions onto modified and unmodified maize cob was investigated. The amount of the metal ions adsorbed increased as time increased. The trend of the sorption capacity was found to be Co(II) > Fe(II) > Cu(II) for unmodified and Co(II) > Cu(II) > Fe for EDTA modified maize cob. The mechanism of adsorption of the metal ions followed particle diffusion model. The pseudo-first order and pseudo- second order kinetic equations were used to model the adsorption kinetics, with the second order giving a better fit, as seen from the correlation coefficient (R^2) which ranged from 0.2329 to 0.9958 for pseudo first order and 0.9994 to 1.008 for pseudo-second order model. The applicability of the Elovich equation to the sorption kinetics was also investigated. This work therefore shows that modified and unmodified maize cob could be used to remove Co(II) Fe(II) and Cu(II) ions from waste water and also established their mechanism of sorption.

Key words: Bioremediation, adsorption kinetics, heavy metal, maize cob.

INTRODUCTION

Cobalt, iron and copper are examples of heavy metals. They are very toxic to both man and animal. They also constitute pollution problems to the environment. When these contaminants are found in effluent, they may incre-ase fertility of the sediment and water column and cons-quently lead to euthrophication, which in open waters can progressively lead to oxygen deficiency, algal bloom and death of aquatic life (Asamudo et al., 2005).

Copper have been reported as one of the most widely used heavy metal in electrical and electroplating Indus-tries (Igwe and Abia, 2006). Since copper is an essential metal in a number of enzymes for all forms of life, pro-

blems arise when it is deficient or in excess (Ho et al., 2002). Excess copper accumulates in the liver, brain, skin, pancreas and myocardium (Davis et al., 2000), and the most toxic form of copper is thought to be Cu^+ (Ho et al., 2002). Its toxicity is highly pH dependent and it has been reported to be more toxic to fish at lower pH values (Sharma et al., 1992). Any change in pH of water bodies as a result of influx of effluent, can cause serious change in water chemistry, which can affect resources especially around the coastal areas (Asamudo et al., 2005). These effects on water bodies can be very significant.

The removal and recovery of these metals have be-come very important because of these detrimental effects on the environment. The conventional methods usually employed for the cleanup of these wastes are, sedimen-tation and filtration, flocculation, neutralization, electrodia-

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Table 1. Fraction of amount adsorbed as time increases for unmodified maize cob of 500µm and 850µm particle sizes.

Time (Min)	Ct/Co					
	500 µm			850µm		
	Co	Fe	Cu	Co	Fe	Cu
10	0.4959	0.4380	0.2228	0.4925	0.4269	0.2407
20	0.4961	0.4381	0.2330	0.4977	0.4295	0.2422
30	0.4964	0.4386	0.2363	0.4981	0.4314	0.2464
40	0.4967	0.4387	0.2372	0.4983	0.4335	0.2536
50	0.4969	0.4389	0.2500	0.4988	0.4338	0.2686
60	0.4972	0.4420	0.2501	0.4997	0.4352	0.2807

lysis, reverse osmosis, adsorption, etc (Volesky, 1990; Hussein et al., 2004). Adsorption of these heavy metals on conventional adsorbents such as activated carbon have frequently been employed, but just like the other conventional adsorbents, the use of expensive materials and the necessity to control the discharge of these loaded material makes the processes non-cost effective. Therefore, the past two decades have seen a tremendous upsurge in the search for cost effective and environmentally sound alternatives to the conventional methods for dealing with these wastes. The technologies that have emerged as most promising are those that closely mimics the time tested natural system that have restored environments to their original status following undesirable perturbations. Infact, the self restoring process in nature is what has actually given birth to the concept that the self cleansing ability of nature is infinite (Asamudo et al., 2005).

Of all the technologies investigated in waste cleaning, bioremediation has emerged the most desirable approach for cleaning up many environmental pollutants. Bioremediation is a pollution control technology that uses biological systems to catalyze the degradation of or transformation of various toxic chemicals to less harmful forms. The general approaches to bioremediation may be divided into the following: intrinsic bioremediation, biostimulation and bioaugmentation (Ashaka et al., 2002). Bioremediation is also similar to phytoremediation, that is, the use of plants to restore contaminated sites. Many agricultural by products that are of little or no cost and also of no value to the environment have been utilized in the remediation of metallic contaminants. These includes maize cob and husk (Igwe and Abia, 2003, 2005; Abia et al., 2005) coconut fiber and sawdust (Igwe et al., 2005), sunflower stalks (Gang and Weixing, 1998), sago waste (Quek et al., 1998), cassava waste. (Horsfall and Abia, 2003), banana pith (Low et al., 1995), peanut skin (Randall et al., 1974), *Medicago sativa* (Alfalfa) (Gardea Torresday et al., 1998) sphagnum moss peat (Ho et al., 1995), and so on. In this paper the findings of the studies on the kinetics of adsorption and intraparticulate diffusivities of Co(II), Fe(II) and Cu(II) ions from waste water using modified and unmodified maize cob were reported.

MATERIALS AND METHODS

Materials

All reagents used were analytical grade, purchased and used without further purification. The maize cob used was obtained from a local market in Okigwe, Imo state, Nigeria. The maize cob was washed, crushed in a mill, washed with deionized water and air dried. This was sieved to obtain two different particle sizes of 0.5.mm (500 µm) and 0.85 mm (850 µm). The different sizes of the cob were activated with 2% (v/v) nitric acid over night, washed with de ionized water and air dried.

Methods

The activated maize cob was modified using ethylene diamine tetra acetic acid (EDTA) by a modified method of Okieimen and Orhorhoro (1986). A 30 g sample of the activated maize cob was hydrolyzed with 500 ml of 7% (v/v) aqueous sulphuric acid for 18 h at 65°C. The mixture was filtered, the cob washed with deionized water several times and then dried at 50°C. 17 grams of the hydrolyzed product (cob) was refluxed in a mixture of 300 mL of pyridine and 56.7 g of EDTA for 3 h at 70°C. The mixture was cooled followed by addition of 300 mL of deionized water and then filtered. The filtered product (EDTA – modified) was washed copiously with de ionized water and dried at 50°C for 12 h. This modification was carried out using both particle sizes separately.

To determine the effect of contact time, a 2 g sample of the maize cob (both for modified and unmodified), was put into a 100 mL solution of the metal ions separately at initial concentration of 2000 mg/l. Different samples were left to stand for 10, 20,30,40,50 and 60 min in a rotary shaker at a constant speed of 150 rpm, at 30°C and each time adjusting the pH to 7.5. At the end of each contact time, the samples were filtered rapidly by suction and the metal ions concentration of the filtrates was determined by a buck scientific flame atomic absorption spectrophotometer (FAAS) model 200 A. The amounts of the metal ions adsorbed were gotten by difference between the initial concentration of the metal ions and the final concentration of the filtrate at each contact time.

RESULTS AND DISCUSSION

Sorption capacity

The amount of the heavy metals adsorbed is reported as the fractions of amount (C_t/C_o) at different time intervals and is presented in Table 1 for unmodified maize cob of

Table 2. Fraction of amount adsorbed as time increases for modified maize cob of 500 and 850 μm particle sizes.

Tim (Min)	Ct/Co					
	500 μm			850μm		
	Co	Fe	Cu	Co	Fe	Cu
10	0.4838	0.4771	0.4785	0.4839	0.4776	0.4789
20	0.4838	0.4772	0.4788	0.4840	0.4778	0.4790
30	0.4839	0.4774	0.4791	0.4842	0.4781	0.4792
40	0.4840	0.4775	0.4794	0.4843	0.4782	0.4794
50	0.4839	0.4776	0.4794	0.4845	0.4783	0.4794
60	0.4839	0.4777	0.4793	0.4847	0.4778	0.4796

500 and 850 μm particle sizes. The results for modified maize cob of 500 and 850 μm are shown on Table 2. From Table 1 it is obvious that the amount of the metal ions adsorbed increases with time. Also, the amount of Co is greater than Fe, and then followed by Cu. This trend is the same for both 500 and 850 μm sizes.

From Table 2, it is seen that the amount of the metal ions adsorbed increased with modification of the adsorbent. This effect is more pronounced with copper ion, which increased from about 22% to 47%. For the modified, the trend of the adsorption now became Co > Cu > Fe.

This trend of uptake of the metal ions could be explained based on the ionic diameters of the metal ions. The ionic diameters are Fe^{2+} (92.0); Cu^{2+} (91.0) and Co^{2+} (88.0), all in pico meters (pm). This means that the smaller the ionic diameter the greater the amount adsorbed. The closeness of the ionic diameter of Fe^{2+} and Cu^{2+} gives the reason for the closeness of the amount adsorbed for the two metal ions and possibly even the interchange of the adsorption trend for the modified cob. The formation of chelates between the metal ions and EDTA also plays a major role in the sorption process for the modified cob. There is not much difference in the amount adsorbed for the two particle sizes, with that for 850 μm being a little greater than 500 μm particle size.

Sorption dynamics

The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of Fe^{2+}, Co^{2+} and Cu^{2+} adsorption on modified and unmodified maize cob were analyzed using pseudo first order (Lagergren,1898), pseudo second order (Ho et al., 2000), Elovich (Chien and Clayton, 1980; Sparks, 1986) and intraparticle diffusion (Srivastava et al., 1989; Weber and Morris, 1963) kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2 values close or equal to 1). A relatively high R^2

value indicates that the model successfully describes the kinetics of the adsorption

Pseudo First Order Equation

The pseudo first order equation (Lagergren, 1898) is generally expressed as follows:

$$dq_{t/}dt = k_1 (qe - qt) \qquad (1)$$

Where, q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg g^{-1}), k_1, is the rate constant of pseudo first order adsorption (min^{-1}).
After integration and applying boundary conditions, t = 0 to t = t and q_t = 0 to $q_t = q_t$, the integrated form of Equation (1) becomes:

$$log (q_e - q_t) = log (q_e) - k_1 t/2.303 \qquad (2)$$

The values of log ($q_e - q_t$) were linearly correlated with t. The plots of log ($q_e - q_t$) against t for the metal ions using unmodified maize cob of two particle sizes are shown on Figure 1. From this figure, the values of k_1, and q_e were determined from the slope and intercept of the plots respectively. The pseudo first order plot for the modified maize cob is shown on Figure 2. From these Figures, It could be seen that the plots are fairly linear, except for unmodified cobalt of size 850μm on Figure 1.

The regression equations and R^2 values for the pseudo first order equation are shown on Table 3.The least R^2 value is 0.2329 for Fe(II) on 850μm modified and the highest is 0.9958 for Co(II) on 500μm unmodified. Those with low R^2 values are said to give poor correlation. The values of k_1 and q_e from the slopes and intercepts of the plots respectively are shown on Table 4. The k_1 values are generally higher for Co (II) confirming our initial proposed trend for the sorption process. Also the q_e values increased as Cu> Fe> Co, (that is, opposite to the sorption trend) for the unmodified and Fe > Cu > Co for the modified. Generally, the higher the value of k_1, the greater the adsorption. The opposite is the case for q_e.

Table 3. Regression equations and R^2 values for the pseudo- first order and pseudo- second order rate equations plot for the metal ions adsorption on unmodified and modified maize cob of two particle sizes.

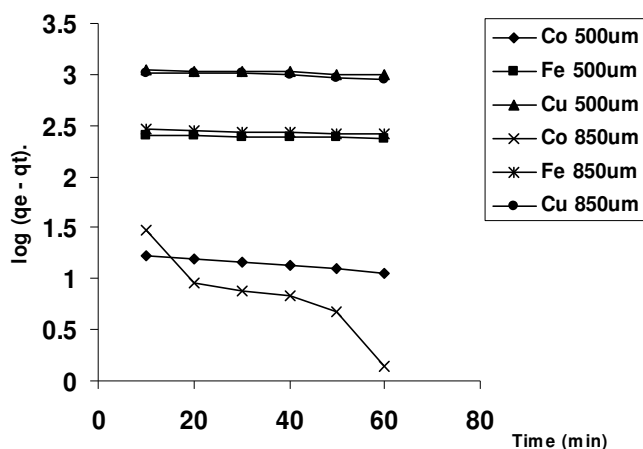| Metal ions	Pseudo –First Order			
	Unmodified		Modified	
	500μm	850μm	500 μm	850 μm
Co	$y = -0.0326x+1.2543$ ($R^2 = 0.9958$)	$Y= -0.2162x+1.5859$ ($R^2 = 0.8766$)	$Y = -7.0x10^{-5}x + 1.8114$ ($R^2 = 0.6857$)	$Y = -0.0005x + 1.8153$ ($R^2 = 0.9932$)
Fe	$Y= -0.0049x+2.4045$ ($R^2 = 0.6756$)	$Y = -0.013x+2.4717$ ($R^2 = 0.9595$)	$Y = -0.0002x + 1.9643$ ($R^2 = 0.9884$)	$Y= -0.0001x + 1.9502$ ($R^2 = 0.0.2329$)
Cu	$Y= -0.0094x+3.0533$ ($R^2=0.9444$)	$Y = -0.0147x+3.0413$ ($R^2 = 0.8990$)	$Y= -0.0004x+ 1.9353$ ($R^2 = 0.7332$)	$Y = -0.0003x + 1.9298$ ($R^2 = 0.9576$)
	Pseudo –Second Order			
Co	$Y = 0.001x + 0.0006$ ($R^2 = 1.006$)	$Y = 0.001x + 0.00005$ ($R^2 = 1.002$)	$Y = 0.001x+ 0.001$ ($R^2 = 1.001$)	$Y = 0.001x + 0.001$ ($R^2 = 1.000$)
Fe	$Y = 0.0011x+0.00017$ ($R^2 = 1.002$)	$Y= 0.00011x+ 0.00038$ ($R^2 = 1.008$)	$Y= 0.001x + 0.001$ ($R^2 = 1.004$)	$Y= 0.001x + 0.002$ ($R^2 = 1.008$)
Cu	$Y = 0.0019x+ 0.0065$ ($R^2 = 0.9994$)	$Y= 0.0017x+ 0.0066$ ($R^2 = 0.9994$)	$Y= 0.001x + 0.002$ ($R^2 = 1.006$)	$Y= 0.001x + 0.002$ ($R^2 = 1.005$)

Figure 1. Pseudo-first order plot for the metal ions adsorption using unmodified maize cob of 500 and 850 μm particle sizes.
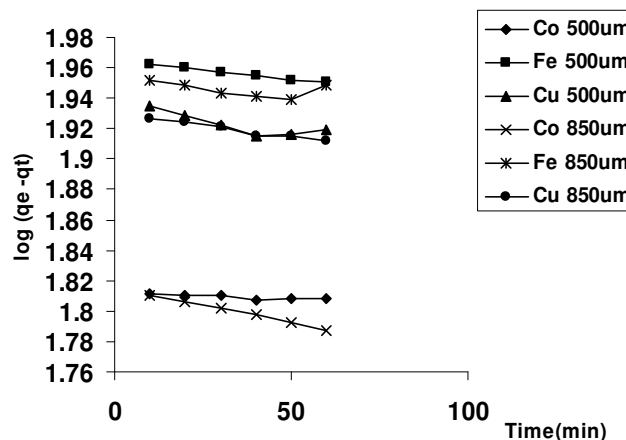

Figure 2. Pseudo-first order plot for the metal ions adsorption using modified maize cob of 500 and 850 μm particle sizes.

Pseudo Second Order Equation

The pseudo second order adsorption kinetic rate equation as expressed by (Ho et al., 2000) is:

$$dq_t/ dt = k_2 (q_e - q_t)^2 \qquad (3)$$

Where:

k_2 is the rate constant of pseudo second order adsorption ($mg^{-1} min^{-1}$) From the boundary conditions t=0 to t=t and

qt=0 to qt=qt, the integrated form of Equation. (3) becomes:

$$1/ (q_e-q_t) = 1/ q_e + kt \qquad (4)$$

This is the integrated rate law for a pseudo second order reaction. Equation (4) can be rearranged to obtain Equation. (5), which has a linear form:

$$t/ q_t = 1/ k_2 q_e^2 + 1 / q_e (t) \qquad (5)$$

If the initial adsorption rate, h_o ($mg. g^{-1} min^{-1}$) is:

Table 4. Kinetic constants for Pseudo First Order Model of the sorption process.

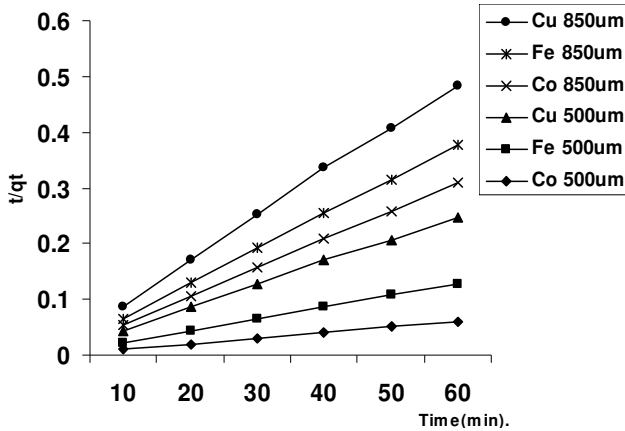| Metal ions	Unmodified				Modified			
	500µm		850µm		500µm		850µm	
	K_1 (min^{-1})	q_e (mg/g)	K_1 (min^{-1})	q_e (mg/g)	K_1 (min^{-1})	q_e (mg/g)	K_1 (min^{-1})	q_e (mg/g)
Co	0.0751	17.96	0.4979	38.54	1.612×10^{-4}	64.77	1.152×10^{-3}	65.36
Fe	0.0113	25.38	0.0237	296.28	4.606×10^{-4}	92.11	2.303×10^{-4}	89.17
Cu	0.0217	1130.58	0.0339	1099.77	9.212×10^{-4}	86.16	6.909×10^{-4}	85.08

Figure 3. Pseudo-second order rate plot for the metal ions adsorption using unmodified maize cob of 500 and 850 µm particle sizes.
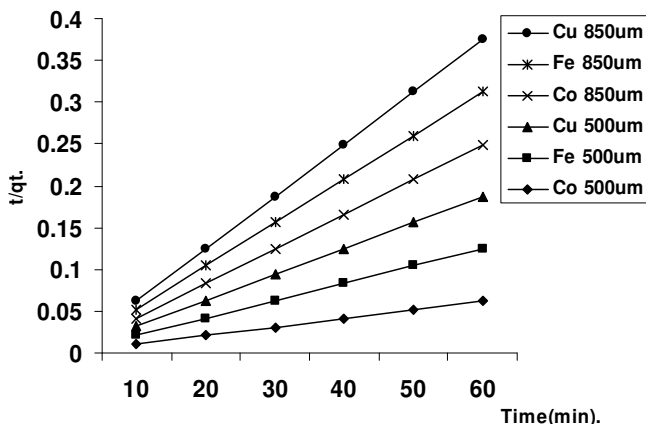

Figure 4. Pseudo-second order rate plot for the metal ions adsorption using modified maize cob of 500 and 850 µm particle sizes.

$$h_o = k_2 q_e^2 \qquad (6)$$

Then Equations (5) and (6) becomes:

$$t/q_t = 1/h_o + 1/q_e (t) \qquad (7)$$

Thus, from Equation (7) plots of (t/q_t) vs. t were made and the values of q_e and k_2 determined from the slopes

and intercepts respectively. The pseudo second order plots for unmodified is shown on Figure 3, and that for modified maize cob is shown on Figure 4. For both modified and unmodified, the two particle sizes and all three metal ions, very good straight lines were obtained. From these figures, it could be seen that unmodified had higher values of (t/q_t) than modified; 850 µm particle size had higher values than 500 µm particle size and that the trend for the metal ions is Cu > Fe > Co. This is also opposite to the trend for the adsorption capacity.

The predictive linear regression equations and R^2 values for the pseudo second order equation is given also on Table 3; while the values of q_e, h_o and k_2 are shown on Table 5. The values of R^2 show that the pseudo second order equation gave a better fit to the sorption process. The least value of R^2 is 0.9994. From Table 5, the values of the initial rate of sorption (h_o) are greater for Co (II) sorption. Also k_2 values are higher for Co (II), which still confirms that Co (II) had higher sorption rate. These results are similar to previous works (Dermirbas et al., 2004; Horsfall et al., 2004)

Elovich equation

The applicability of the Elovich equation to the sorption process was also tested. The Elovich equation is generally expressed as (Chien and Clayton, 1980; Sparks, 1986):

$$dq_t/dt = \alpha \exp(-\beta q_t) \qquad (8)$$

Where, α is the initial sorption rate (mg.g^{-1}. min^{-1}); β is desorption rate constant (mg.g^{-1} min^{-1}) during any one experiment. To simplify the Elovich equation, Chien and Clayton (1980), assumed $\alpha\beta >> t$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Equation (8) becomes:

$$q_t = (1/\beta) \ln(\alpha\beta) + (1/\beta) \ln(t) \qquad (9)$$

Thus, a plot of q_t vs. ln (t) should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta) \ln(\alpha(\beta))$, if the sorption process fits the Elovich equation. The Elovich equation plot for the sorption of the metal ions using two particle sizes of the maize cob is shown on Figure 5 for unmodified and Figure 6 for modified. All

Table 5. Kinetic constants for Pseudo Second Order Model of the sorption process.

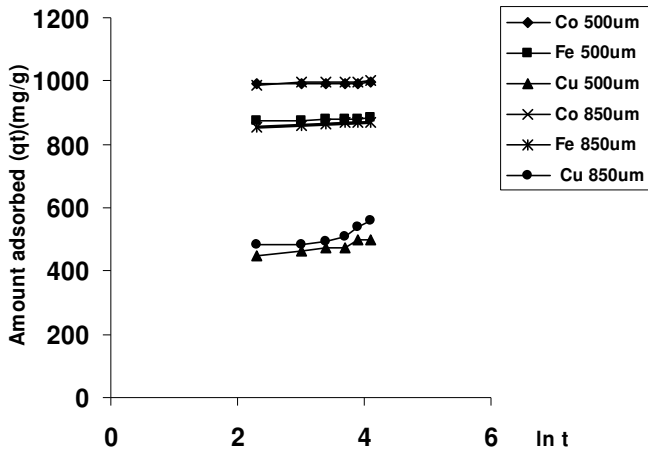| Metal ion	Unmodified						Modified					
	500µm			850 µm			500 µm			850 µm		
	q_e (mg/g)	h_0 (g mg^{-1} min^{-1})	K_2 (g mg^{-1} min^{-1})	q_e (mg/g)	h_0 (g mg^{-1} min^{-1})	K_2 (g mg^{-1} min^{-1})	q_e (mg/g)	h_0 (g mg^{-1} min^{-1})	K_2 (g mg^{-1} min^{-1})	q_e (mg/g)	h_0 (g mg^{-1} min^{-1})	K_2 (g mg^{-1} min^{-1})
Co	1000	16.67×10^3	0.0167	1000	20.0×10^3	0.02	1000	1.0×10^3	1.0×10^{-3}	1000	1.0×10^3	1.0×10^{-3}
Fe	909.1	5.88×10^3	0.0676	909.1	2.63×10^3	3.18×10^3	1000	1.0×10^3	1.0×10^{-3}	1000	0.5×10^3	5.0×10^{-4}
Cu	526.3	0.15×10^3	5.42×10^{-4}	588.2	0.15×10^3	4.34×10^{-4}	1000	0.5×10^3	5.5×10^{-4}	1000	0.5×10^3	5.0×10^{-4}

Figure 5. Elovich equation plot for the adsorption of metal ions using unmodified maize cob of 500 and 850 µm particle sizes.
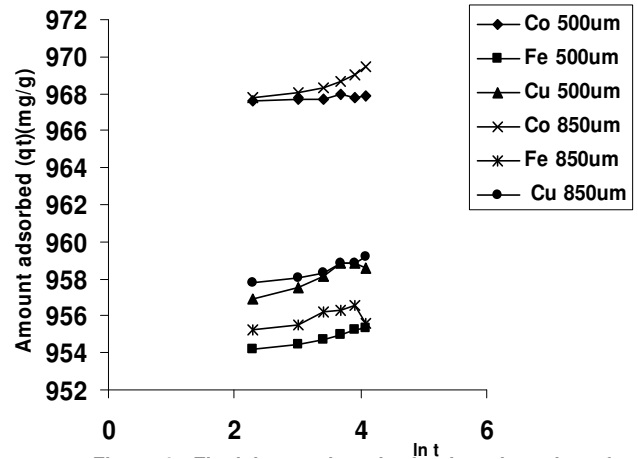

Figure 6. Elovich equation plot for the adsorption of metal ions using modified maize cob of 500 and 850 µm particle sizes.

the plots are fairly linear. The regression equation and R^2 values for the Elovich equation plot are shown on Table 6. The R^2 values are quite high and show good fit except for R^2 value of 0.4801 and 0.4107 for Fe (II) on 500 µm unmodified and 850 µm modified respectively. Thus, the Elovich equation could be said to be a good model for the sorption process.

Intraparticle diffusion model

The sorption rate is shown to be controlled by several factors including 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 or pore diffusion)
(iv)Uptake which can involve several mechanisms, such as physico chemical sorption, ion exchange, precipitation or complexation (Findon et al., 1993; Weber and Digiano, 1996).

The first one is bulk diffusion, the second is external mass transfer resistance and the third is intraparticle mass transfer resistance. When the intraparticle mass transfer resistance is the rate limiting step, then the sorption process is described as being particle diffusion controlled.
One type of equation used to model the intraparticle diffusion is that developed using the linear driving force concept by Chanda et al., as reported by Okieimen and Orhorhoro (1986). This is given as

$$\ln (1-\alpha) = -K_p t \qquad (10)$$

Where, K_p is the rate coefficients for particle diffusion controlled sorption, α (alpha) is the fractional attainment to equilibrium (FATE), which is given as:

$$\alpha = [M^{n+}]_t / [M^{n+}]_{eq} \qquad (11)$$

That is, the amount of metal ion adsorbed at time (t) divided by that at equilibrium (eq). A plot of ln $(1-\alpha)$ vs. t, giving straight lines means that the sorption is intraparticle diffusion controlled, as against film diffusion controlled sorption.
  A second type of intraparticle diffusion equation usually employed to model sorption processes is that by Mckay and Poots (1980). This is given as:

$$q_t = X_i + K^1 t^{0.5} \qquad (12)$$

Where, X_i is the boundary layer diffusion effects, K^1 is the rate constant for intraparticle diffusion. A plot of qt vs. $t^{0.5}$ giving straight line confirms intraparticle diffusion sorption.
  Another type of intraparticle diffusion model is expressed as (Weber and Morris, 1963; Srivastava et al., 1989):

$$R = K_{id} (t)^a \qquad (13)$$

A linearised form of the equation is given as:

$$\log R = \log K_{id} + a \log(t) \qquad (14)$$

Where, R is the fraction of the amount adsorbed, t is the contact time (min) 'a' is the gradient of linear plots; K_{id} is the intraparticle diffusion rate constant (min^{-1}).
  This model was used to analyze the experimental data. The plot of log R vs. log t is shown on Figure 7 for unmodified and Figure 8 for modified maize Cob. The regression equations and R^2 values for intraparticle diffusion model is shown on Table 6.

Table 6. Regression equations and R^2 values for the Elovich equation and the intraparticle diffusion equation plots for the metal ions adsorption on unmodified and modified maize cob of two particle sizes.

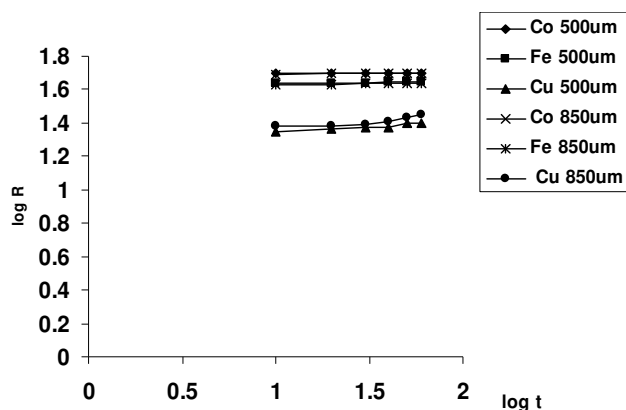| Metal ions	Elovich Equation			
	Unmodified		Modified	
	500μm	850μm	500 μm	850 μm
Co	y = -1.4085x + 988.25 (R^2 = 0.9282)	Y= 7.1148x +970.87 (R^2 = 0.8579)	Y = 0.1503x + 967.27 (R^2 = 0.7458)	Y = 0.9017x + 965.47 (R^2 = 0.8940)
Fe	Y= 3.1499x + 867.41 (R^2 = 0.4801)	Y = 9.3608x +831.64 (R^2 = 0.9877)	Y= 0.6751x + 952.51 (R^2=0.9522)	Y= 0.5168x +954.15 (R^2 = 0.4107)
Cu	Y= 31.195x + 369.47 (R^2=0.9049)	Y = 41.193x + 370.73 (R^2 = 0.7205)	Y= 1.0856x + 954.45 (R^2 = 0.9001)	Y = 0.7941x + 955.80 (R^2 = 0.9136)
Intraparticle diffusion equation				
Co	Y =0.00014x + 1.6939 (R^2 = 0.9265)	Y = 0.0072x + 1.6862 (R^2 = 0.8566)	Y = 0.0002x + 1.6845 (R^2 = 0.5123)	Y = 0.0008x + 1.6839 (R^2 0.8376)
Fe	Y = 0.0035x+1.6374 (R^2 = 0.4862)	Y= 0.0111x + 1.6199 (R^2 = 0.9556)	Y= 0.0008x + 1.6778 (R^2 = 0.9551)	Y= 0.0005x + 1.6786 (R^2 = 0.4790)
Cu	Y = 0.0635x + 1.2829 (R^2 = 0.9127)	Y= 0.0799x + 1.2884 (R^2 = 0.7378)	Y= 0.0011x + 1.6789 (R^2 = 0.9096)	Y= 0.0008x + 1.6794 (R^2 = 0.8471)

Figure 7. Plot of intraparticle diffusion for the metal ions adsorption using unmodified maize cob of 500 and 850 μm particle sizes.
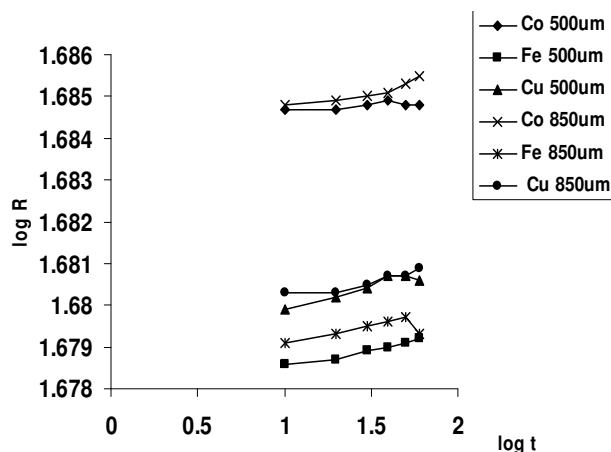

Figure 8. Plot of intraparticle diffusion for the metal ions adsorption using modified maize cob of 500 and 850 μm particle sizes.

The values of the R^2 are quite high with a highest value of 0.9556 for Fe(II) on 500 μm unmodified and lowest of 0.4790 for Fe(II) on 850 μm modified maize Cob.

The values of the constants K_{id} and a, are shown on Table 7. The values of 'a' and K_{id} were calculated from the slopes and intercepts of the plot respectively. The values of 'a' depicts the adsorption mechanism and K_{id} may be taken as a rate factor (Dermirbas et al., 2004). The values of K_{id} increases as Co>Fe>Cu, for unmodified and Co> Cu> Fe, for modified maize Cob. Higher values of K_{id} illustrate an enhancement in the rate of adsorption,

whereas larger 'a' values illustrate a better adsorption mechanism. This means that the sorption process is particle diffusion controlled and that the intraparticle mass transfer resistance is the rate limiting step. This is also similar to results of previous reports (Abia et al., 2005; Dermirbas et al., 2004; Horsfall et al., 2004).

Conclusion

The use of EDTA modified and unmodified maize Cob for the removal of Co(II), Fe(II) and Cu(II) ions from aqueous

Table 7. Kinetic constants for the intraparticle diffusion model of the sorption process.

Metal ions	Unmodified				Modified			
	500µm		850µm		500µm		850µm	
	k_{id}	a	K_{id}	a	K_{id}	a	k_{id}	a
Co	49.42	0.0014	48.55	0.0072	48.36	0.0002	48.30	0.0008
Fe	43.39	0.0035	41.59	0.00111	47.62	0.0008	47.71	0.0005
Cu	19.18	0.0635	19.43	0.0799	47.74	0.0011	47.80	0.0008

solutions is feasible. It was found that modification enhanced the adsorption predominantly due to chelates formation. Co(II) ion was adsorbed more for both unmodified and modified maize cob, than the other two metal ions. The trend of the uptake is Co(II) >Fe(II)>Cu(II) for the unmodified and Co(II)>Cu(II)>Fe(II) for the modified maize Cob. It was found that the pseudo second order equation gave a better fit to the sorption process than the pseudo first order equation. It was also possible to use Elovich equation to model the sorption process. The intraparticle diffusion plot confirmed that the sorption process was particle diffusion controlled. The regression models that were generated for these equations could be used as predictive models for these heavy metals sorption on maize cob at any other contact time. Also, the results of this study could serve as parameters for designs of treatment plants for the treatment of heavy metal bearing effluents using maize cob or even any other agricultural by-products as adsorbents. Therefore, maize cob which is a waste has been employed in treating another waste, which is heavy metal waste water, thereby achieving environmental friendliness.

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