



Adsorption of Lead (II) and Copper (II) ions Onalginat and Kaolinite Activated Charcoal Composite Beads

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ABSTRACT

Heavy metals pollution has become one of the most serious environmental problems today. Biobased adsorbent have attracted the attention of many researchers due to their availability, recyclability, simple modification and cost effectiveness. In this study, alginate composite beads were prepared using kaolinite clay and activated charcoal by simple dripping methods. The prepared beads were tested for the removal of Pb²⁺ and Cu²⁺ ions from aqueous solutions. The adsorption parameters such as initial pH, contact time, initial metal ion concentration and amount of the adsorbent were investigated. The experimental result showed that the adsorption of copper and lead ions followed the pseudo-second order kinetic model when compared to first-order model. Langmuir isotherm model fitted better than Freundlich model based on the correlation coefficient greater than 0.99 for both Pb²⁺ and Cu²⁺ with maximum monolayer adsorption capacity of 73 mg/g and 35mg/g respectively. The results indicate that the composite beads adsorbed Pb²⁺ ions more effectively when compared with Cu²⁺ ions and therefore could be employed as a low-cost alternative adsorbent for Pb²⁺ in waste water treatment.

Keywords: Activated charcoal; alginate; kaolinite; composite; Isotherm; Kinetics

INTRODUCTION

Contamination of toxic metal ions is a serious environmental problem which received a considerable attention nowadays. Their presence endangered the entire ecological environment due to the non-biodegradability and bioaccumulation of such heavy metals (Yazan and Suhail, 2017). Pollution could either be from natural or man-made (anthropogenic) sources, such as combustion, construction, mining, agriculture and manufacturing industries (Fu and Wang, 2011). The toxicity of these heavy metals released into the environment has recently triggered a number of studies, aiming to develop an efficient technology that could be used for the removal of such metal ions from aqueous solutions. The use of low cost materials such as natural polymers and non-conventional adsorbents have been reported as alternatives for industrial wastewater treatment (Crini, 2006). There are several methods to treat metal contaminated effluents, such as chemical precipitation, ion exchange, membrane filtration and adsorption. But the choice of the treatment method usually depends on the concentration of metal ions and the cost of treatment. Adsorption is one of the most popular techniques employed for the removal of heavy metals from the wastewater due its cost effectiveness, clean and sludge free technology and simplicity in design and operation

(Chakir *et al.*, 2002)). Alginate is one of the most investigated biopolymers for the removal of metal ions from dilute aqueous solutions (Chen *et al.*, 1997). It is a polymer consisting of the residues of β-1,4-linked-D-mannuronic acid (M-block) and α-1,4-linked-L-guluronic acid (G-block) (Haug *et al.*, 1966). Clay is another low-cost mineral that has high cation exchange capacity (CEC) in solution. Many clay minerals have been studied for wastewater treatment, e.g. kaolinite (Dawodu and Akpomie, 2014, Jiang *et al.*, 2010), montmorillonite (Sdiri *et al.*, 2011, Zhu *et al.*, 2015) and bentonite (Chen *et al.*, 2012, Ye *et al.*, 2015).

In the present study, the use of kaolinite clay to prepared composite beads with activated charcoal and alginate as a crosslinker is reported. The composite beads were then evaluated for the removal of Pb²⁺ and Cu²⁺ ions from aqueous solutions.

MATERIALS AND METHODS

The kaolinite clay was collected from Kankara town, Katsina State, Nigeria. Alginate was purchased from Sigma Aldrich (U.S.A) and granular activated charcoal (1.5 mm) was obtained from Qualikems (England). Copper nitrate Cu(NO₃)₂ and lead nitrate, Pb(NO₃)₂ salts were purchased from (LobaChemie (England). All other

chemicals were of analytical grade and used without further purification.

Preparation of Composite Beads

The clay was sieved and washed with distilled water to remove dirt and other particulate matters. The resulting slurry was allowed to sediment and later decanted, thereafter dried in an oven to constant weight. The composite beads were then prepared by dispersing sodium alginate (2.00 g), kaolinite clay (3.00 g) and activated charcoal (3.00 g) in 200 mL of deionized water and mechanically stirred. The resultant colloidal solution obtained was added dropwise into a stirred 100 mL of CaCl₂ solution using a syringe. Solid gel beads were immediately formed. The beads were allowed to stay in the CaCl₂ solution for 24 hrs to stabilize. Subsequently, the beads were thoroughly washed with excess deionized water to removed CaCl₂ from the surfaces. Thereafter, the gel beads were dried in the oven until constant weight (Wayne and Fong, 2012).

Batch Equilibrium Experiments

Stock solutions containing heavy metals ions were prepared by dissolving stoichiometric amount of nitrate salts in deionized water to desired concentrations (1000 mg/L). The following metal ions concentrations 50, 100, 150, 200 and 250 and 300mg/L were prepared from stock solution were varied. The pH of solution was adjusted by using 0.1 M NaOH and/or 0.1 M HNO₃. Adsorption studies were carried out using a 250 mL conical flask containing 50 mL of metal solution. In each experiment (0.2 g) of the adsorbent was added in the flask and adjusted to desired pH in the range of 2-8. The conical flasks were agitated using a shaker set at 300 rpm for 90 minutes at 10 minutes intervals. At the end of adsorption, the mixture was centrifuged at 300 rpm and metal solution was decanted in a separate labeled sample bottle. The solutions were analyzed using atomic absorption spectrophotometer (AAS). The removal efficiency and the amount of metal ions adsorbed by the adsorbent at equilibrium were calculated using equation (1) and (2) respectively (Liu *et al.*, 2009).

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e \text{ (mg/g)} = \frac{C_0 - C_e}{W \text{ (g)}} \times V \text{ (L)} \quad (2)$$

where C_0 is the initial metal ions concentration (mg/L), C_e is the t , equilibrium concentration of the metal ions in solution (mg/L), V is the volume of metal ions solution used (L) and w is the weight of the adsorbent used (g).

Adsorption Kinetic Models

The prediction of the batch sorption kinetic is essential for the design of the industrial sorption

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (6)$$

Where q_e and q_t (mg/g) are amounts of what (metal ions) adsorbed at equilibrium and at time t respectively, and k_1 (min⁻¹) is the equilibrium rate constant for pseudo-first-order adsorption process. The plot of $\log(q_e - q_t)$ against t gives a straight

columns. To determine the rate of adsorption, the pseudo-first-order and pseudo-second-order models were employed.

Pseudo-first-order model

Pseudo -first-order kinetic model is expressed using equation (6)

line. From the slope of the straight line, the rate constants k_1 were calculated (Kadirvelu *et al.*, 2001).

Pseudo-second-order model

Pseudo-second-order kinetic model is expressed by the following equation (Ho and McKay, 1999):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

Where q_e and q_t (mg/g) are amounts of the uptake of adsorbate at equilibrium and at time t respectively, and k_2 (g/mg min) is the equilibrium rate constant for pseudo-second order adsorption process. The slope and intercept of the plot of $\frac{t}{q_t}$ versus t can be used directly to calculate the kinetic parameters, q_e and k_2 (Ho and McKay, 1999).

Adsorption Isotherm Models

Langmuir and Freundlich isotherms, were employed to interpret the adsorption mechanism of metal ions onto the adsorbents.

Langmuir Isotherm

The Langmuir isotherm equation employed was reported by Langmuir as expressed in equation (3)

$$\frac{C_e}{q_e} = \frac{1}{q_m Q_L} + \frac{C_e}{q_m} \quad (3)$$

To validate this model, a plot of C_e/q_e vs C_e must be linear. The values of parameters, adsorption capacity (q_m) and Langmuir constant (Q_L) can be obtained from calculation of the slope and the intercept respectively, (Singh *et al.*, 2009).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

Where q_e is the amount of metal ion adsorbed at equilibrium time, C_e is equilibrium concentration of metal ion in solution. K_F and n are isotherm constants indicate the capacity and intensity of the adsorption respectively (Sharma and Gaur, 1995). The Freundlich constants, n and K_F respectively can be calculated from the slope and intercept of a plot of $\log q_e$ against $\log C_e$. The Freundlich adsorption isotherm model assumes that, adsorption takes place on heterogeneous surfaces.

Freundlich Isotherm

The Freundlich isotherm model can be expressed using equation (4) (Freundlich, 1906 and Hasar, 2003).

RESULTS AND DISCUSSION

Effect of pH of Solution

The pH of solution is one of the most important parameters affecting the adsorption of metals in aqueous solutions. It affects the active sites of the adsorbent as well as the solubility of the metal ions in solution. The effect of solution pH on the adsorption of Pb^{2+} and Cu^{2+} using the composite beads was investigated and the results were presented in Fig. 1. The percentage metal ions removal were observed at an optimum pH of 6 as 86% for Pb^{2+} and 82% for Cu^{2+} respectively. However, at pH below 4, the percentage removal were observed to be low. This could be due to increase in positive charges on the adsorbent surface which will lead to repulsion between adsorbent surface and metal ions, resulting to increase in competition between H^+ and metal ions for the available adsorption sites (Lim and Chen, 2007).

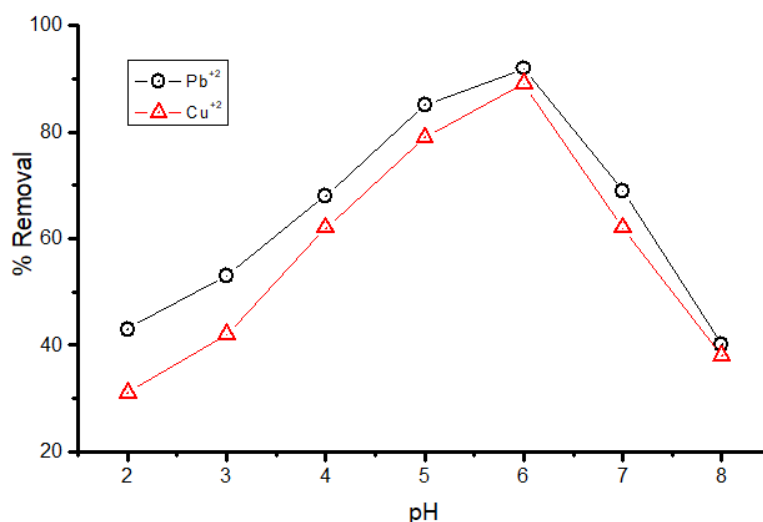


Figure 1 Effect of pH on the adsorption of metal ions by alginate composite beads.

Effect of Metal ions Concentration

The effect of Pb^{2+} and Cu^{2+} ions concentration were examined at varying concentrations (50-300 mg/L) as shown in Fig. 2. It was observed that the percentage removal increased gradually with increasing initial concentrations (up to 200 mg/L), but relatively decreased at 300 mg/L.

At concentrations of 200 mg/L, the percentage removal was nearly the same, 81 % and 79 % for Pb^{2+} and Cu^{2+} respectively. Because at higher concentrations of metal ions, this may result to a greater driving force at the liquid solid interface, which in turn enhances the mass transfer (Mishra *et al.*, 2010). Less competition between the free

adsorptive sites at low initial concentration lead to faster initial adsorption. When the adsorptive sites

were occupied, adsorption became slower until equilibrium was achieved.

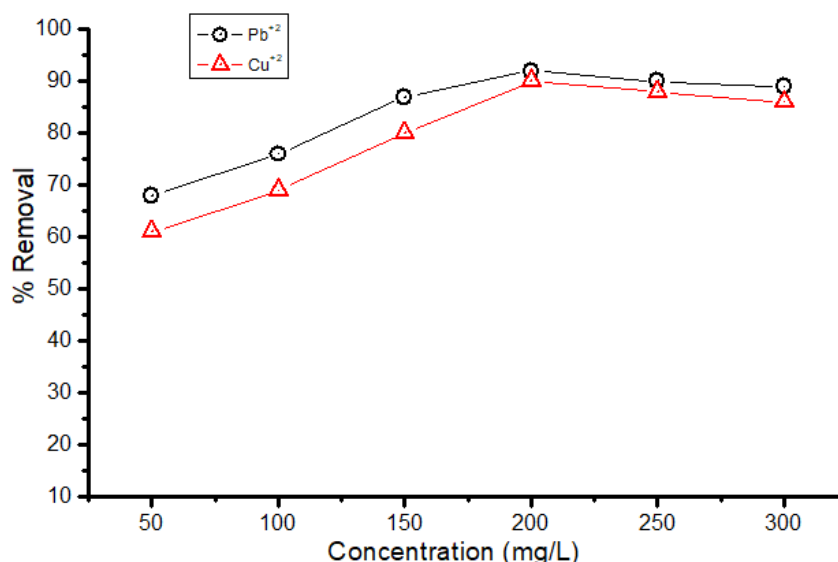


Figure 2. Effect of initial metal ions concentration on adsorption of metal ions by alginate composite beads

Effect of Contact Time

In order to determine the effect of the contact time, 50 mL solution of metal ions of initial concentration 200 mg/L was added to 0.2 g of the adsorbent and stirred for time interval of 10 to 80 minutes at pH6. The experimental results obtained were shown in (Fig.3). It is clear from the graph that the percentage removal increased with increased contact time, and after certain period of

time it reached to a constant value (equilibrium) beyond which no further adsorption took place. The results showed that, the adsorption was fast at the initial stage of contact time and then slowed down as the equilibrium point approached (60 mins). This could be due to the exhaustion of the adsorption sites and monolayer surface coverage. These results are similar to those reported in the literature (Jeonet *et al.*, 2002).

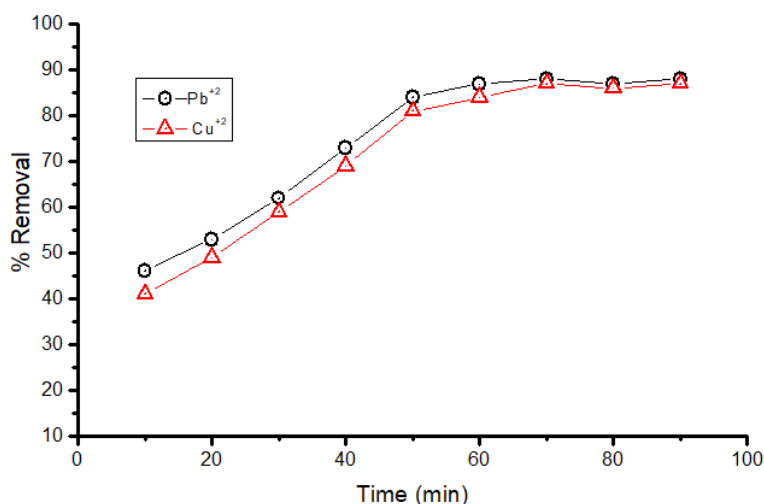


Figure 3. Effect of contact time on adsorption of metal ions by alginate composite beads

Effect of Adsorbents Dose

To study the effect of adsorbent dosage on the adsorption of metal ions, a series of adsorption experiments were carried out with different adsorption dosages, varying from 0.1 to 0.5 g at initial concentration of 200 mg/L. The effect of adsorbent dose for the uptake of metal ions by alginate composite beads was found to increase with an optimum amount at 0.4 g adsorbent dosage

(Fig.4). This could be due to the fact that as the amount of adsorbent is increased, the total surface area available for the adsorption will also increase (Inglezakis *et al.*, 2002; Chen and Yang, 2006). However, it was observed that at higher amount of adsorbent (0.5 g), the metal ions uptake decreased gradually. This could be attributed to either due to the split in a flux or the concentration gradient between the metal ions concentration in the

solution and the concentration of the metal ions on the surface of the adsorbent, leading to decrease in the amount of the metal ions adsorbed onto unit mass of the adsorbent (Dawood and Sen, 2012).

Another research also attributed this to overlapping and over-crowding of the adsorbent molecules (Low *et al.*, 2008).

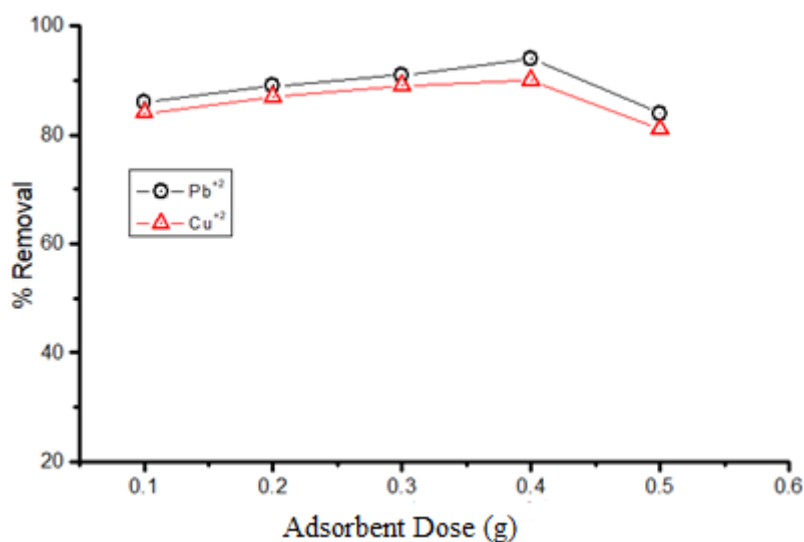


Figure 4 Effect of adsorbent dose on adsorption of metal ions by alginate composite beads

Equilibrium isotherm studies

To determine the nature of the adsorption process, two isotherm models (i.e. Langmuir and Freundlich) models were employed. Adsorption isotherm describes the relationship between the amount of adsorbate that is adsorbed on the adsorbent and the concentration of the dissolved adsorbate in the liquid at equilibrium.

Langmuir isotherm model

This model assumes a homogeneous surface with respect to the energy of adsorption, which is constant and independent on the degree of occupation of an adsorbent's active centers (Ahmed *et al.*, 2016). The essential feature of the model can be stated in a dimensionless constant, called separation factor or equilibrium parameter (R_L), which can be calculated using equation (5).

$$R_L = \frac{1}{1 + Q_L C_0} \quad (5)$$

Where C_0 (mg/L) is initial concentration of metal ions in solution and Q_L (L/g) is the Langmuir constant related to the energy of adsorption.

Freundlich Isotherm Model

The equilibrium data fitted well to the Langmuir isotherm due to the high correlation coefficient (R^2) of 0.997 and 0.999 for Pb^{2+} and Cu^{2+} respectively, as compared to Freundlich model with (R^2) value of 0.9576 and 0.914 for Pb^{2+} Cu^{2+} respectively. The R^2 values of Freundlich isotherm are greater than 0.9 but lower than 0.999, indicating that the model cannot adequately describe the relationship between the amount of metals adsorbed by the adsorbent and its equilibrium concentration in the solution. The Langmuir isotherm gave R^2 values close to unity,

which suggested that the adsorption of metal ions on the alginate composite beads is best described by Langmuir model. The results indicated surface homogeneity of the adsorbent and monolayer adsorption. From Langmuir model, the maximum monolayer adsorption capacity (q_{max}) was found as 73.2 mg/g and 35 mg/g for Pb^{2+} and Cu^{2+} respectively. The adsorbent has good adsorption capacity to remove Pb^{2+} ions better than Cu^{2+} . Furthermore, separation factors (R_L) were less than unity and thus adsorption was favourable. The value describes the isotherm type: unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$), the adsorption is favourable (Chantawong *et al.*, 2003). Other parameters were summarized in Table 1.

Table 1: Langmuir and Freundlich isotherms Constants for Pb²⁺ and Cu²⁺ metal ions adsorption on alginate composite beads.

Metal ion	Freundlich isotherm			Langmuir isotherm		
	(K _F) (mg/g)	(n) (g/L)	(R ²)	(b) (L/mg)	(q _e) (mg/g)	(R ²)
Pb ²⁺	111	1.82	0.957	1.049	73.20	0.997
Cu ²⁺	197	3.23	0.914	1.97	35.00	0.999

Kinetic studies

The kinetics of the adsorption of metal ions was studied to analyse two kinetic models. The parameters for these models were shown in Table 2. It was noted that the adsorption of the metal ions adequately follows pseudo second order kinetic model based on the correlation coefficients. The pseudo-first order model fits the experimental data poorly. Because the first order equation of Lagergren does not fit well to the whole range of

contact time and therefore is generally applicable over initial stage of the adsorption processes (Febrianto *et al.*, 2009). On the other hand pseudo-second order model gave good correlation coefficient R²=0.999. This model assumes that the rate-limiting step may involve chemical adsorption. Since the adsorbent consist of kaolinite and alginate that have ion-exchange sites, it is more likely to predict that the adsorption behaviour may predominantly involve ion-exchange.

Table 2: Rate constants and correlation coefficient for Pb²⁺ and Cu²⁺ metal ions adsorption on alginate composite beads.

Metal ion	Pseudo-first-order model				Pseudo-second-order model			
	q _{max exp.} (mg/g)	q _{max cal.} (mg/g)	k ₁ (min ⁻¹)	(R ²)	q _{max exp.} (mg/g)	q _{max cal.} (mg/g)	k ₂ (g/mg/min)	(R ²)
Pb ²⁺	47.76	34.22	0.0245	0.606	48.13	47.22	0.0066	0.999
Cu ²⁺	43.41	27.12	0.0105	0.435	27.32	28.42	0.0045	0.999

CONCLUSION

The results of this study demonstrate that, alginate composite beads have ability to remove lead and copper ions from aqueous solutions. The adsorption process depend on the initial pH, metal concentration and amount of adsorbent. The optimum conditions were 6, 200 mg/L and 0.4 g for the pH, metal ions concentrations and adsorbent dose, respectively. The equilibrium data fitted more with Langmuir isotherm model, with maximum adsorption of 73.2mg/g and 35 mg/g for lead and copper ions respectively. The adsorption kinetics data was best described by the pseudo-second order model. The kinetic study indicated that the equilibrium time can be achieved within 1 hr. Therefore, alginate composite beads could be used to remove trace amounts of heavy metals from aqueous solutions.

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