



## ADSORPTION OF LEAD AND COPPER IONS FROM AQUEOUS SOLUTIONS USING MULTI-WALL CARBON NANOTUBE/KAOLINITE COMPOSITE BEADS

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### ABSTRACT

*In this study, adsorption of lead (Pb) and copper (Cu) ions from aqueous solution by kaolinite clay composite beads was investigated in batch systems. Alginate (crosslinker), kaolin and Multiwall carbon nanotube (MCNT) were used in the preparation of the composite beads. The composite beads were characterized using the following techniques, SEM, TGA and XRD. The adsorption parameters such as pH, metal concentration, adsorbent dose and shaking time were also studied. The Langmuir and Freundlich isotherm models were applied to describe the adsorption equilibrium process. The Langmuir model fitted well with experimental data based on correlation coefficients with maximum adsorption capacity ( $q_{max}$ ) of 83.33 mg/g and 76.92 mg/g for lead and copper ions, respectively. It was observed that the equilibrium time for both metal ions were attained in 60 minutes. Reusability studies revealed that the composite beads maintained good adsorption capacity after being used repeatedly. The composite beads could be used in the treatment of metal-bearing effluents.*

**Keywords:** Kaolin, alginate, carbon nanotube, beads, effluents

### INTRODUCTION

The preservation of the environment has become increasingly important in view of the ecological problems brought about by industrialization and urbanization (Kumar *et al.*, 2017). Lakes and rivers are particularly vulnerable to contamination as a result of the discharge of large quantities of effluents from industries and municipalities. The presence of heavy metals such as cadmium, chromium, cobalt, copper, lead, mercury, nickel, chromium, tin and zinc in rivers and waterways may result to serious public health problems and threaten many aquatic organisms (Alloway and Ayers, 1996, Wase and Foster, 1997). Conventional toxic heavy metals wastewater treatment techniques include chemical precipitation, ion-exchange, electrochemical processes, membrane filtration and adsorption. In this content, a cost-effective treatment of wastewater contaminated with heavy metals is required as environmental laws become more stringent (Kadirvelu *et al.*, 2002). Great deals of low cost materials are available in large quantities such as natural materials, agricultural waste or industrial by-products that can be utilized as adsorbents (Lu and Gibb, 2008; Javed *et al.*, 2007). Some of these materials can be used as adsorbents with little processing or by simple chemical modification. Biopolymer such as cellulose,

starch, chitin and alginate are the most abundant, cheap, renewable and possess many functional groups (Crini, 2006). Alginic acid or its salts called alginate are among the polysaccharides that occur in the cell walls of large number of algae species. Alginate (polysaccharide) is a copolymer which consist of two residues i.e  $\beta$ -1, 4-linked-D-mannuronic acid (M-block) and  $\alpha$ -1, 4-linked-L-guluronic acid (G-block) (Hauget *et al.*, 1966). Alginate form egg-box structure in dilute aqueous solutions of  $BaCl_2$  and  $CaCl_2$  due to presence of carboxyl (COOH) and hydroxyl (OH) functional groups acting as ligands (Holan *et al.*, 1993). Carbon nanotubes have been extensively researched for the removal of metal ions from aqueous solutions due to their highly porous and hollow structure, relatively large specific surface area and easily modified surfaces (Iijimi, 1991; Xiong *et al.*, 2006; Xuet *et al.*, 2006). Clay is another low-cost mineral that has a high cation exchange capacity in solution. Many clays have been studied for detoxification of metals from wastewaters e.g. montmorillonite (Sdiri *et al.*, 2011, Zhu *et al.*, 2015), bentonite (Chen *et al.*, 2012, Ye *et al.*, 2015) and kaolinite (Jiang *et al.*, 2010). In the present study, composite beads was developed using alginate (as cross linker), multiwall carbon nanotubes (MWCNT) and kaolinite for the removal of  $Pb^{2+}$  and  $Cu^{2+}$  ions from aqueous solutions.

## MATERIALS AND METHODS

Sodium alginate, multi wall carbon nanotubes were purchased from Sigma-Aldrich. Kaolin clay was collected from Dutsin-Ma L.G.A. Katsina State.  $Pb(NO_3)_2$  and  $Cu(NO_3)_2 \cdot 3H_2O$  salts were purchased from Loba Chemie (England). Stock solutions of  $Pb^{+2}$  and  $Cu^{+2}$  ions (1000 mg/L) were prepared by dissolving 3.880 g of  $Cu(NO_3)_2 \cdot 3H_2O$  and 1.599g of  $Pb(NO_3)_2$  salts in separate beakers (250 cm<sup>3</sup>) with deionized water respectively and the solutions were transferred to a 1.0litre volumetric flasks each was followed by the addition of 100 mL of 0.1M  $HNO_3$  and they were made to mark. Desired concentrations of the metal solutions were prepared by serial dilution of the stock solutions using deionized water. Other chemical reagents were of analytical grade and used as received.

### Preparation of the Adsorbent

The kaolin 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), kaolin clay (6.00 g) and MCNT (3.00 g) in 200cm<sup>3</sup> of deionized water and mechanically stirred. The resultant colloidal solution obtained was added drop-wise into a stirred 200cm<sup>3</sup> of  $CaCl_2$  (0.1 M) solution using a syringe. Solid gel beads were immediately formed. The beads were allowed to stay in the  $CaCl_2$  solution for 24 hours to stabilize. Subsequently, the beads were thoroughly washed with excess deionized water to removed  $CaCl_2$  from the surfaces. Thereafter, the gel beads were dried in the oven until constant weight (Wayne and Fong, 2012).

### Characterization

Thermogravimetric analyses (TGA) were carried out using Q500 TGA Thermal analyzer (USA). The analysis was conducted in an inert atmosphere from 30°C to 800°C at a heating rate of 20°C min<sup>-1</sup> (Ahmedy *et al.*, 2013).

The scanning electron microscope (SEM) micrograph of the beads and its surface morphology were examined using JEOL JSM 6390LV (Japan). Before SEM observation, all samples were fixed on aluminum stubs and coated with gold using auto fine coater (model JFC-1600). (Salisu *et al.*, 2015)

Powder X-ray diffraction patterns were recorded on ARL X'TRAX-ray Diffractometer S/N: 197492086 (Thermoscientific, Switzerland) using graphite monochromatic  $CuK\alpha_1$  (1.5406 Å) and  $K\alpha_2$  operated at 40 kV and 30 mA (Gupta, *et al.*, 2013)

### Batch Adsorption Experiments

The adsorption experiments were performed by batch equilibrium according to the method described by Pathania *et al.*, 2013 with some modifications. The experiments were carried out in 250cm<sup>3</sup> conical flasks by mixing 0.4g of the adsorbent with 50cm<sup>3</sup> of each metal ion solutions of concentrations, 50, 100, 150, 200, 250, and 300mg/L and pH= 4.0 at room temperature using a shaker operating at 300rpm. The samples were taken out from the conical flask on the shaker at specified time intervals and the remaining metal ions in the solutions were separated from the adsorbent by filtration and the filtrates were analyzed by using flame atomic absorption spectrophotometer (Shimadzu, 6800, Japan, 210) to determine the equilibrium metal ion concentrations. All the experiments were conducted in duplicate and averages of duplicate readings were presented. The percentage removal of metal ions and the amount of metal ions adsorbed on the composite beads at equilibrium ( $q_e$ ) were calculated using equations (1) and (2) respectively:

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

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

where  $C_0$  is the initial metal ions concentration (mg/L),  $C_e$  is the equilibrium concentration of 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). The equilibrium data obtained were tested using the linear forms of Langmuir and Freundlich isotherm models, as shown in equation (3) and (4), respectively;

### Langmuir isotherm

The general formula of the Langmuir isotherm for adsorption can be expressed as

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

Where  $q_m$  is the maximum adsorption capacity and  $Q_L$  Langmuir constant To validate this model, a plot of  $C_e/q_e$  vs  $C_e$  must be linear. The value of parameters,  $q_m$  and  $Q_L$  can be obtained from calculation of the slope and the intercept (Langmuir, 1916; Langmuir, 1918). The essential feature of the model can be stated in a dimensionless constant, referred to as separation factor or equilibrium parameter ( $R_L$ ) which can be calculated using equation (4), (Ho and Wang, 2008).

$$R_L = \frac{1}{1 + Q_L C_0} \quad (4)$$

### Freundlich Isotherm.

The Freundlich adsorption isotherm can be expressed using equation below

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

Where  $q_e$  is the amount of metal ion adsorbed at equilibrium time,  $C_e$  is the equilibrium concentration of metal ion in solution.  $K_F$  and  $n$  are isotherm constants which indicate the capacity and the intensity of the adsorption, respectively (Freundlich, 1906).

## RESULTS AND DISCUSSION

### Characterization

#### XRD Studies of the kaolinite clay

The single crystal X-ray crystallographic technique is the most accurate source of information regarding the structure of a material (Sanghavi *et al.*, 2013). Thus, XRD of the Kaolin was scanned in the range of 3 - 60° at a wavelength of 1.54Å to ascertain the level of crystallinity. The material exhibited sharp crystalline peaks, and its pattern accounts for six

reflections in a range of 8 - 65° ( $2\theta$ ), depicted in Fig. 1. Besides the XRD of the material showed a prominent reflection at  $2\theta$  values of roughly 13° and 25°, corresponding to the  $d$  values of 6.5139 and 3.6115, respectively. Those are the typical characteristic peaks of kaolinite (Moore and Reynolds, 1997). Again the other peaks corresponding to the  $2\theta$  value in the range of 15-24° and 26-65° are also characteristic of kaolinite, quartz, illite + quartz, goethite, gibbsite, and dickite (Moore and Reynolds, 1997; Jiang *et al.*, 2010; Emam, *et al.*, 2016).

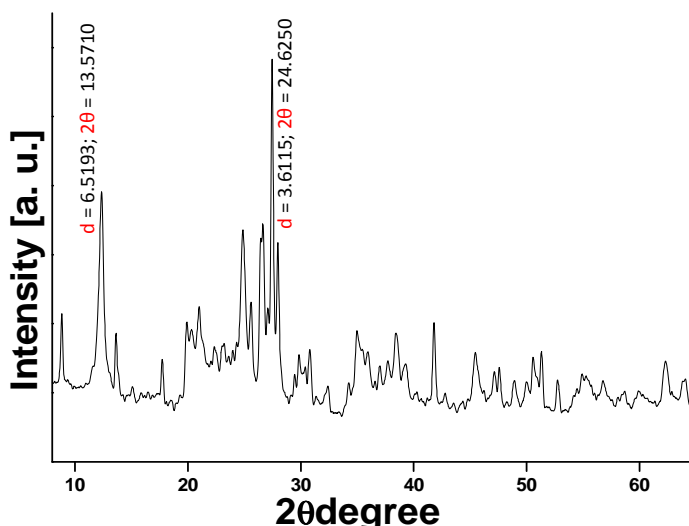


Figure 1: XRPD pattern of the kaolinite clay.

Peaks	$2\theta$ [°]	$\theta$ [°]	$\sin\theta$ [°]	$\sin^2(\theta)$	$1000\sin^2(\theta)$	$\frac{1000\sin 2\theta}{CF \cdot h^2+k^2+l^2}$	hkl	d-spacing [Å]		a in Å
								obs	cal	
1	8.759	4.379	0.07636	0.00583	5.8300	1.00 (1)	100	10.08778	10.0877	10.0877
2	13.571	6.786	0.11816	0.0140	13.9600	2.39 (2)	110	6.51933	6.51919	6.5193
3	18.959	9.479	0.16469	0.0271	27.1200	4.65 (5)	210	4.67713	4.67706	4.6771
4	24.629	12.314	0.21327	0.0455	45.4900	7.80 (8)	220	3.61179	3.61169	3.6117
5	26.588	13.294	0.22995	0.0529	52.8700	9.07 (9)	300	3.34992	3.34987	3.3499
6	27.494	13.747	0.23763	0.0565	56.4700	9.69 (10)	310	3.24153	3.24145	1.6207

### Thermogravimetric Analysis

The thermal stability of the beads was investigated by TGA. Thermogram of calcium alginate and the composite beads were presented in Fig. 2. Three major steps of weight loss were observed in Fig.2a. The initial

weight loss at 30-125°C was due to evaporation of moisture. The second weight loss at 200-300°C was due to breakage of C-O-C glycosidic bond and release of gases such methane carbon (IV) oxide as reported (Nuran and Fatma, 2013).

However, in the case of the composite beads (Fig. 2b), four major steps of weight loss were observed. It can be seen that degradation of the alginate backbone and release of the gases

occurred at 400°C which indicates that the thermal stability of the composite beads was higher due to the inclusion of carbon nanotube and kaolinite greater than alginate alone.

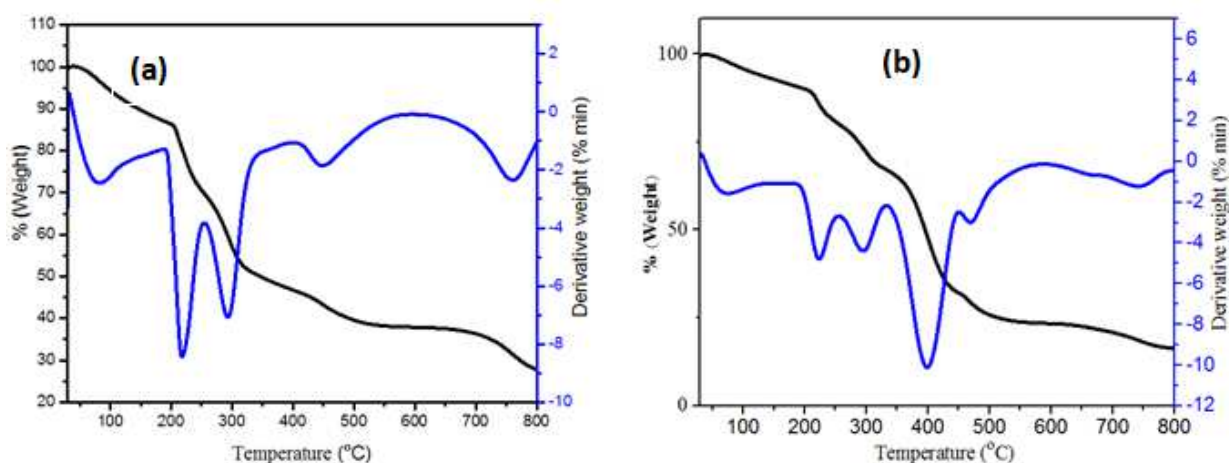


Figure 2: TGA thermogram of (a) calcium alginate and (b) composite bead

### Scanning Electron Microscope (SEM)

Scanning electron microscopy (SEM) is a useful tool to evaluate the surface morphology of materials. The micrograph images of the composite bead and its surface morphology is shown in Figure 3. It is obvious that the surface morphology of the bead is spherical in shape with rough surfaces and porous. The SEM micrographs of the composite beads illustrate

the surface texture and porosity of beads with holes and small openings on the surface, thereby increasing the contact area, which facilitates the pore diffusion during adsorption. The porous nature is clearly evident from these micrographs. The diameter of the bead was found to be 1 mm ±2 as measured by the SEM machine.

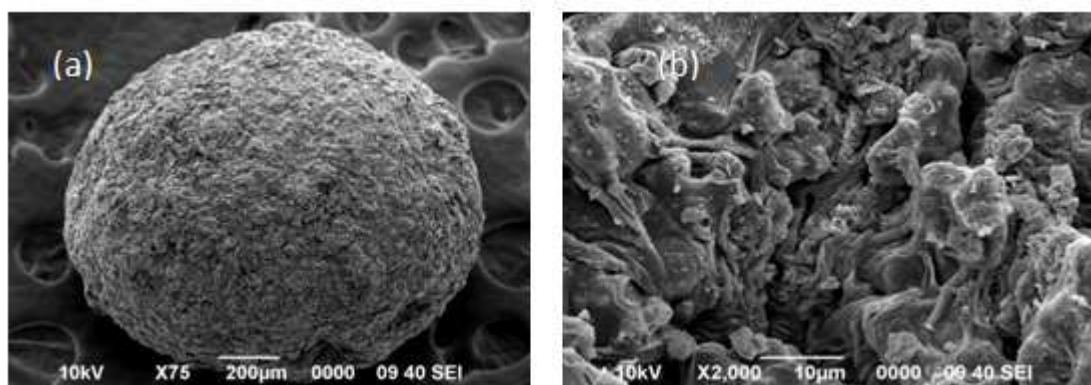


Figure 3: SEM image of the (a) composite bead and (b) surface morphology

### Adsorption Studies

#### Effects of Initial pH

Heavy metal adsorption is highly dependent on pH solution. The pH value affects the solubility of the metal ions in solution. The effect of pH change on adsorption of lead and copper was investigated in the range of 2-8 as shown in Fig. 4. It was observed that the maximum removal percentage (94.88 and 91.54 %) for  $Pb^{2+}$  and  $Cu^{2+}$  respectively took place at an optimum of pH 4. It has been established that alginate has pK value in the range of 3.4 to 4.5, therefore electrostatic attraction exists between

negatively charged carboxyl groups and the metal ions (Salisu *et al.*, 2015b). The optimum pH obtained are in agreement with the data reported by other authors (Chen and Lim 2007; Lim *et al.*, 2009). However, the variation of metal uptake by the adsorbent between lead and copper ions can be explained based on the metal ion charge density ionic radii, consequently the increase metal-binding affinity of  $Pb^{2+}$  over that of  $Cu^{2+}$  can be attributed to the preference of  $Pb^{2+}$  for binding with the carboxylate ions both in the mannuronic and guluronic residues of alginate.

This behaviour has also been reported by other authors (Haug, 1961; Haug and Smidstrod, 1965). The authors reported that the affinity of alginate to metal ions follows the order  $Pb^{2+} > Cu^{2+} > Cd^{2+} > Ba^{2+} > Ca^{2+} > Co^{2+} > Ni^{2+}$ . The decreased of percentage removal at lower pH may be due to the competition between

protons and metal ions in the solutions as a result of repulsion between adsorbent surface (positively charged) and incoming metal ions, thus lowering the rate of adsorption (Ahmed *et al.*, 1998). However, at higher pH beyond 8, precipitation may takes place instead of adsorption.

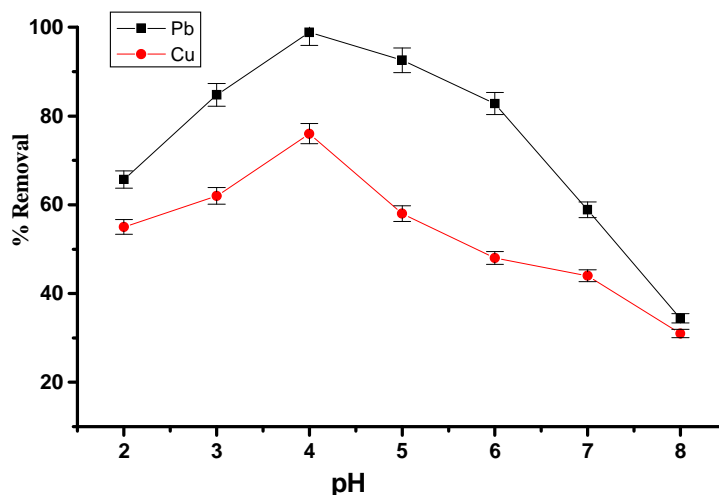


Figure 4: Effect of pH on the adsorption of metal ions by composite beads

#### Effects of Contact Time

In order to determine the effect of the contact time, 0.4g of the adsorbent was stirred with a 50cm<sup>3</sup> solution of initial metal concentration (100mg/L) for a time interval between 10 to 90 minutes at pH= 4. The data obtained was presented in Figure 5. The increases in contact time at 300 rpm stirring rate increased the rate

at which the metal ions were adsorbed. It was observed that 86% and 69% removal took place within 70 minutes for both  $Pb^{2+}$  and  $Cu^{2+}$ , respectively. This could be attributed to the high affinity and interaction between adsorbent and metal ions in the solution due to the sufficient equilibrium time.

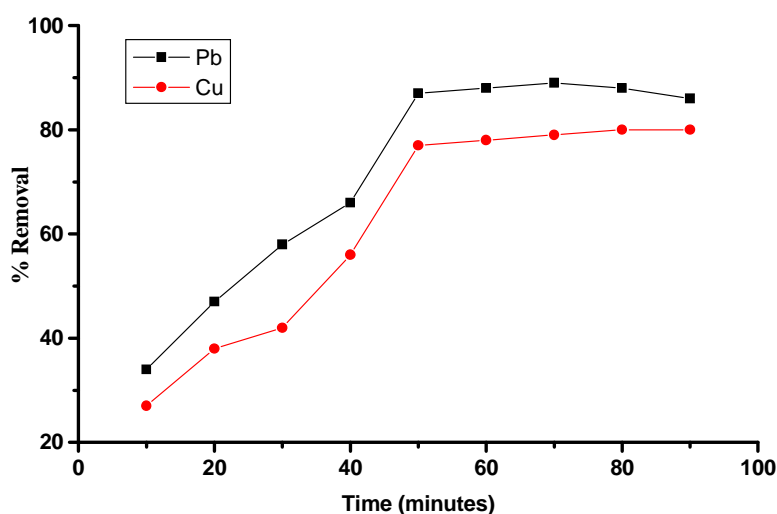


Figure 5: Effect of contact time on adsorption of metal ions by composite beads

### Effects of Initial Metal ions Concentration

The effect of initial concentration of  $Pb^{2+}$  and  $Cu^{2+}$  metal ions on the percentage removal by the composite beads was investigated in the range of 50-300 mg/L and the results were shown in Fig. 6. The removal percentage was found to be high at lower concentration of the

metal ions, but eventually decrease with the increased in the initial concentration. This can be attributed to the exhaustion of available active sites on the adsorbent required for the high initial concentration of the metal ions adsorption (Salisu *et al.*, 2016).

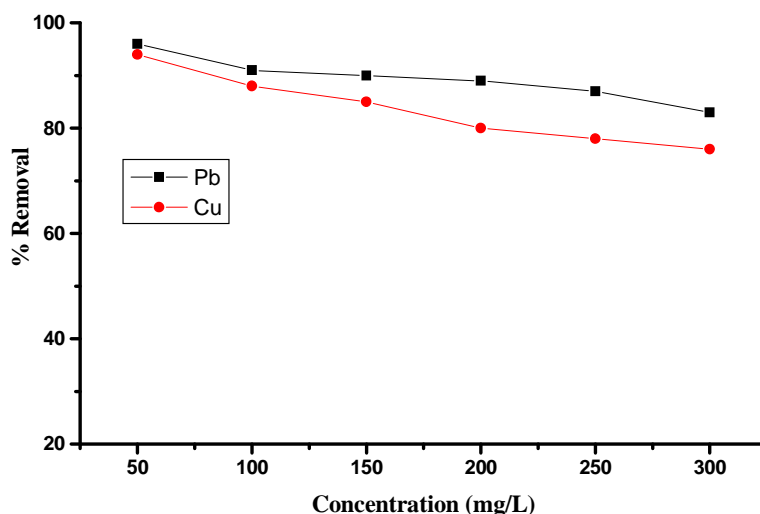


Figure 6: Effect of concentration of metal ions on adsorption by composite beads

### Effects of Adsorbent Dose

The effect of adsorbent dosage (0.1-0.5g) on percentage removal of  $Pb^{2+}$  and  $Cu^{2+}$  was shown in Figure 4. It was observed that the percentage removal increased with an increase in adsorbent dose up to 0.4 g, thereafter percentage removal was found to be decreasing, which may be attributed to saturation of the adsorbent which will not

allowed more adsorption. Furthermore, the observed reduction of metal ions uptake at higher dosage may be attributed to crowding effects, so that the active sites on the adsorbent become obscured for metal binding. Other researchers have also reported the crowding effects in the adsorption of heavy metals (Kandah and Meunier, 2007).

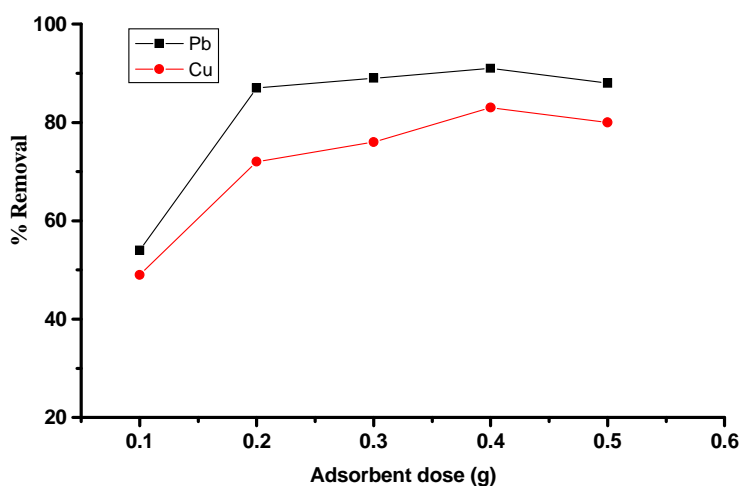


Figure 7: Effect of adsorbent dose on adsorption of metal ions by composite beads

### Equilibrium Studies

Adsorption isotherms are very useful tools for theoretical evaluation and modelling of adsorption process and performance. The Langmuir and Freundlich isotherms are the most common model for describing adsorption equilibrium in solid-liquid interface. The Langmuir model assumes a homogeneous surface coverage with respect to the energy of adsorption, which is constant and independent on the degree of occupation of an adsorbent's active centres (Langmuir, 1916).

The value describes the isotherm type: unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favourable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ). (Langmuir, 1916).

In general, the data obtained from the adsorption equilibrium studies revealed that Langmuir isotherm showed a better fitting (Table 1) as compared with Freundlich isotherm

equation based on higher correlation coefficients and adsorption capacity for both metal ions. The separation factor,  $R_L$  has been found to be less than unity in both cases which indicated that the adsorption was favourable. Although, the adsorption process revealed that it is a monolayer adsorption which implies that there is formation of covalent bond between the adsorbate and the adsorbent surface, notwithstanding there may be also other weak forces attraction (Van der Waals interactions) that could occurred during the adsorption process.

Thus, it can be generally concluded that the adsorption process assumed a monolayer adsorption process. The maximum adsorption capacity of the composite beads,  $q_{max}$ , constants and correlation coefficients were represented in Table 1.

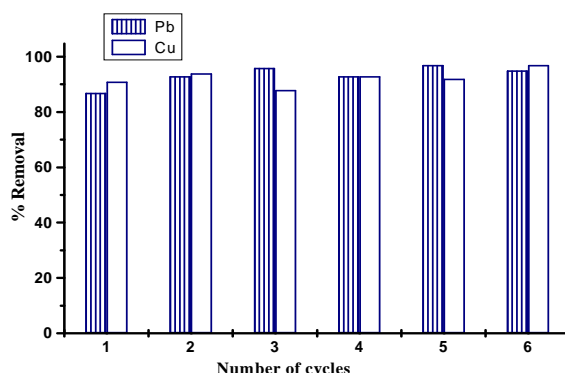
**Table 1:** Langmuir and Freundlich isotherms constants and correlation coefficients

Metal ion	Freundlich isotherm			Langmuir isotherm			
	( $K_F$ ) (mg/g)	( $n$ ) (g/L)	( $R^2$ )	( $Q_L$ ) (L/mg)	( $q_e$ ) (mg/g)	$R_L$	( $R^2$ )
Pb	72.25	2.32	0.930	0.015	83.33	0.6	0.999
Cu	66.75	1.43	0.918	0.044	76.92	0.3	0.996

### Reusability Studies

Adsorbent substances can be restored to original conditions by desorption process that usually involve the application of heat or by using a suitable solvents (usually mineral acids) (Wilson, 1994). Desorption experiments were performed to evaluate the possibility of reusability and regeneration of the alginate composite beads as an adsorbent. Adsorption-desorption cycles were repeated for five consecutive times using metal ion concentration of 100 mg/L, HCl (0.1 M, 10 mL) as adsorption solvent and 0.2 g of the adsorbent. The adsorbent was thoroughly

washed with deionized water before the next cycle. It was observed that in the first cycle, the percentage removal was 79% for lead and 82% for copper, but in the subsequent cycles, percentage removal was found to be greater than 95% for both lead and copper. This could be attributed to increase the surface porosity of the adsorbent as a result of interaction with the acid. A similar trend was reported on the adsorption and desorption of alginate beads using HCl (Salisu *et al.*, 2016). The result showed that the alginate composite beads maintained good adsorption capacity for several cycles.



**Figure 8:** Adsorption-desorption cycles of the adsorbent [ Extraction conditions: metal ion concentrations, 100 mg/L, adsorbent dose 0.4g, batch volume 50cm<sup>3</sup>, desorption solution, 0.1 M HNO<sub>3</sub> (10cm<sup>3</sup>), contact time 1 h ]

## CONCLUSION

A composite alginate adsorbent was prepared and used for the removal of lead and copper ions from aqueous solutions. There are several factors affecting the adsorption of metal ions onto alginate composites, however, pH was the significant factor to be considered. The optimum conditions found were 4, 150mg/L and 0.4g for pH, metal ions concentrations and adsorbent dose, respectively. The equilibrium data fitted better with Langmuir isotherm equation, with maximum adsorption of 83.33mg/g and 76.92mg/g for lead and copper

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- ions respectively. The adsorption equilibrium was achieved within 1 hr. Furthermore, characterization of the kaolin by XRPD showed that it is kaolinite clay based on the pattern observed as reported previously. The composite beads could be used for the removal of heavy metal ions (Cu and Pb) in real wastewater.
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