



## Adsorption of Cu (II) and Ni (II) Ions from Solution onto Calcium Alginate Beads

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**ABSTRACT:** The objective of this study was to investigate the biosorption of Cu (II) and Ni (II) ions from aqueous solution by calcium alginate beads. The effects of solution pH, contact time and initial metal ion concentration were evaluated. The results showed that maximum Cu (II) removal (93.10%) occurred at pH of 9.0, contact time of 120 minutes and initial ion concentration of 10 mg/L while that of Ni (II) was 94.6%, which was achieved at pH of 8.0, contact time of 120 minutes and initial ion concentration of 10 mg/L. The equilibrium data fitted well to the Langmuir Isotherm indicating that the process is a monolayer adsorption. The coefficients of determination,  $R^2$ , values for the Langmuir Isotherm were 0.9799 and 0.9822 respectively for Cu (II) and Ni (II) ions. The values of the maximum biosorption capacity,  $Q^e$ , were 10.79 and 6.25  $\text{mgg}^{-1}$  respectively. The kinetic data also revealed that the sorption process could best be described by the pseudo – second order kinetic model. The  $R^2$  values for the pseudo – second order kinetic plots for Cu (II) and Ni (II) were 0.9988 and 0.9969 respectively. These values were higher than those for the pseudo – first order plots. The values of the biosorption capacity  $q_e$  obtained from the pseudo – second order plots were very close to the experimental values of  $q_e$  indicating that the biosorption process follows the second order kinetics. This study has therefore shown that calcium alginate beads can be used for the removal of Cu (II) and Ni (II) ions from wastewaters.

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Environmental pollution by toxic metals is a worldwide problem due to increased industrialisation. The metal ions are particularly problematic due to their accumulation in the food chain and their persistence (Bueno *et al.*, 2008). Cu (II) and Ni (II) are among the metals of concern. Nickel is regarded as one of the essential trace elements for humans, plants and animals but it causes toxicity to aquatic life at higher concentrations. Copper is also an essential element for plants, animals and humans but it is also toxic at higher concentrations (Franke *et al.*, 2003).

There are several methods for removing heavy metals from wastewater. Some of these methods include chemical precipitation, ion exchange, electrochemical treatment, membrane technologies, adsorption on activated carbon etc. (Mathieckal and Yu, 1999). However these methods are expensive and may produce harmful by-products (Zvinowanda *et al.*, 2010). Numerous studies have demonstrated that microorganisms have the ability to remove heavy metals from wastewater with better performance and lower cost compared with conventional technologies (Kapoor *et al.*, 1999; Liu *et al.*, 2004; Moon *et al.*, 2006)

Biopolymers such as alginates can uptake metal ions from aqueous solutions. They possess all of the biosorbent advantages and compete with other traditional methods such as ion exchange and activated carbon. Alginates are linear polysaccharides found in many algal species especially in brown algae and are also produced by certain bacteria (Arica *et al.*, 2001). The objective of this study was therefore to determine the adsorption capacity of calcium alginate beads for Cu (II) and Ni (II) ions in solution.

### MATERIALS AND METHODS

100 ml of 4 % (w/v) sodium alginate was prepared in a volumetric flask and was shaken until it became properly dissolved. The sodium alginate slurry was dropped through a 10 ml syringe into 2% (w/v)  $\text{CaCl}_2$  solution. Durable spherical beads of the alginates were formed immediately. The beads were washed with distilled water and stored at 4°C in distilled water until further use. The studies were carried out using a batch technique. The contact experiments were done in replicates in 100 ml conical flasks containing 50 ml of solution. The flask contents were mechanically agitated on a conical flask shaker at 150 rpm and a temperature of 29 °C. To determine the optimum

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conditions for biosorption, the pH of the solutions were varied from 3.0 – 9.0, contact time from 10 – 150 minutes and initial metal ion concentrations were varied from 10 – 100 mg/L. At the end of the reaction, the contents of the flask were separately filtered into polypropylene bottles using Whatman No 1 filter paper. Atomic Absorption Spectrometer (AAS) was used to determine Cu (II) and Ni (II) ion concentrations in the solution before and after contact with the adsorbent. The percentage metal removal (%) was calculated using the following equation:

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

The amount of each ion adsorbed was calculated from the difference between the added and equilibrium concentration by using the equation 2:

$$q_e = \frac{V(C_o - C_e)}{M} \quad (2)$$

Where  $q_e$  is the amount adsorbed in mg/g of the adsorbent at equilibrium,  $C_o$  and  $C_e$  are the initial and the equilibrium concentrations in mg/L, respectively,  $V$  is the volume in litres of the solution used during the experiment and  $M$  is the mass of the adsorbent in grams.

The experimental results were fitted to the Langmuir isotherm model as given by the equation

$$\frac{C_e}{q_e} = \frac{1}{K_L Q^o} + \frac{C_e}{Q^o} \quad (3)$$

Where  $K_L$  (L/g) is a constant related to the adsorption / desorption energy and  $Q^o$  (mg/g) is the maximum sorption upon complete saturation of the adsorption of the adsorbent (biosorbent) surface (Akgerman and Zardkoohi, 1996). A graph of  $C_e/q_e$  against  $C_e$  will have  $K_L$  (L/g) as the slope and  $Q^o$  (mg/g) as the intercept.

The experimental data for the adsorption process were fitted to the Pseudo – first order (Equation 4) and Pseudo – second order (Equation 5) kinetic models.

$$\text{Log}(q_e - q_t) = \text{Log } q_e - \frac{k_1}{2.303} t \quad (4)$$

Where  $q_e$  (mg/L) and  $q_t$  (mg/L) are the adsorption capacities at equilibrium and at time  $t$  respectively.  $k_1$  (L/min) is the rate constant for a pseudo – first order adsorption. A plot of  $\log (q_e - q_t)$  against  $t$  gave a straight line from which  $k_1$  (L/min) and  $q_e$  (mg/L) were determined from the slope and intercept of the plot respectively.

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

Where  $q_e$  (mg/L) and  $q_t$  (mg/L) are the adsorption capacities at equilibrium and at time  $t$  respectively and  $k_2$  (g/mgmin) is the rate constant for a pseudo – second order adsorption. A plot of  $t/q_t$  against  $t$  gave a linear plot from which  $q_e$  and  $k_2$  were determined from the slope and intercept respectively.

## RESULTS AND DISCUSSION

**Effect of Solution pH:** The effect of the solution pH on the removal of Cu (II) and Ni (II) ions from solution is presented in Fig 1. The removal percentage of both ions increased with an increase in solution pH. The removal percentage for Cu (II) increased from 7.5% at pH 3.0 to 93.10% at pH 9.0. The maximum adsorption of Ni (II) was 94.86% at pH 8.0 while the lowest was 1.42% at pH 3.0. The increase in metal ion removal with increase in pH is due to a decrease in competition between protons and the metal cations for the surface sites and by the decrease in positive surface charge which results in a lower coulombic repulsion of the sorbing metal cation (Ghorbani *et al.*, 2008). Ozer and Ozer, (2003) and Ghorbani *et al.* (2008) have reported similar results.

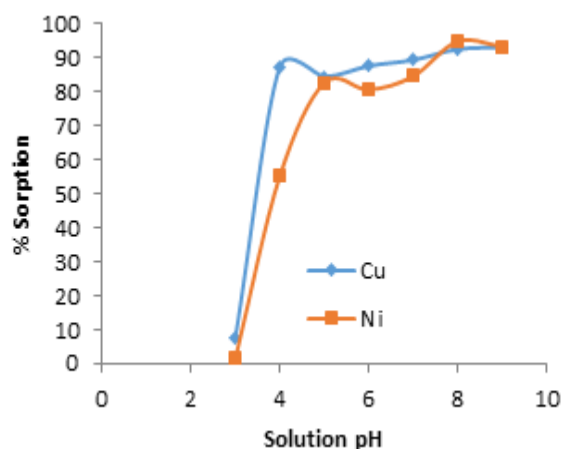


Fig 1. Effect of solution PH on adsorption of Cu (II) and Ni (II) onto calcium alginate beads

**Effect of contact time on adsorption of Cu (II) and Ni (II) ions:** The effect of the contact time on the removal of Cu (II) and Ni (II) ions from solution is presented in Fig 2. The removal percentage of the Cu (II) ions increased from 77.57% at 10 minutes to the maximum of 91.04% at 120 minutes. The removal percentage of Ni (II) ions by the biosorbent increased from 61.18% at 10 minutes contact time to 81.21% at 120 minutes. There was a general increase in removal percentage from the beginning which later became stable with

time. As the adsorption process proceeded, the adsorbate reached the saturation state and then the adsorbate tended to desorb back into the solution. Eventually the rates of adsorption and desorption became equal at equilibrium (Sari and Tuzen, 2008).

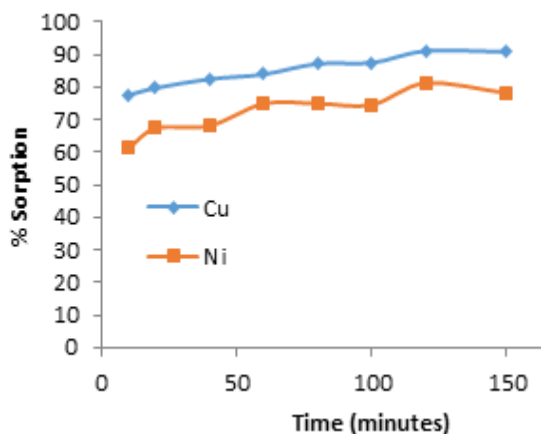


Fig 2 Effect of contact time on adsorption of Cu (II) and Ni (II) onto calcium alginate beads

**Effect of initial metal ion concentration:** The effect of initial metal ion concentration on the removal of Cu (II) and Ni (II) ions from solution is shown in the Fig 3. The removal percentage of Cu (II) ions decreased from 87.50% at 10 mg/L to 29.66% at 100 mg/L. For Ni (II) the removal percentage decreased from 79.49% at 10 mg/L to 17.89% at 100 mg/L metal ion concentration. Occurrence of more unoccupied surface binding sites on the adsorbent at low concentration of metal ions could possibly be responsible for higher removal efficiency at low concentration. But as the concentration increased, the number of ions competing for available binding sites on the adsorbent increased and hence the adsorption of metal ions decreased (Shoab *et al.*, 2013).

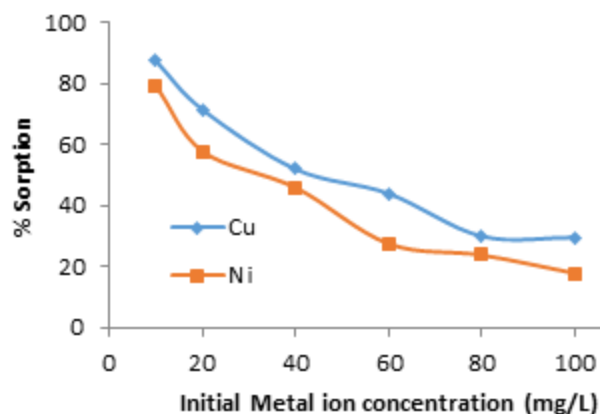


Fig 3 Effect of initial ion concentrations on adsorption of Cu (II) and Ni (II) onto calcium alginate beads

**Langmuir Isotherm:** The Langmuir isotherm for the biosorption of Cu (II) and Ni (II) by calcium alginate

beads is presented in Fig 4. The values of the coefficient of determination,  $R^2$ , for Langmuir equations for Cu (II) and Ni (II) were 0.9799 and 0.9822 respectively. Both exhibited high  $R^2$  values. Both ions therefore, exhibited a good fit of their equilibrium data for the Langmuir model which indicates a monolayer adsorption. Maximum biosorption capacity  $Q^0$  ( $\text{mg g}^{-1}$ ) for Cu (II) and Ni (II) were calculated to be 10.79 and 6.25  $\text{mg g}^{-1}$  respectively.

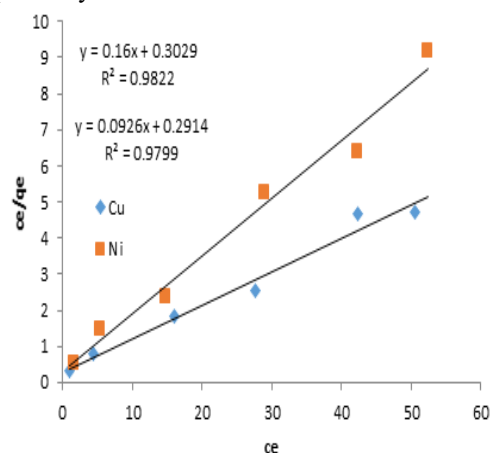


Fig 4 Langmuir Isotherm for the adsorption of Cu (II) and Ni (II) ions onto calcium alginate beads

#### Adsorption Kinetics

**Pseudo – first order kinetics:** The pseudo – first order kinetic plots for the adsorption of Cu (II) and Ni (II) onto calcium alginate beads is shown in Fig 5. The correlation coefficient,  $R^2$ , for the pseudo – first order kinetic plot for the ions were 0.9468 and 0.9146 respectively. The values of  $q_e$  and  $k_1$  obtained from the plots are shown in Table 1. From the table it can be seen that the calculated values of  $q_e$  were not in agreement with the experimental values. These results suggest that the biosorption of Cu (II) and Ni (II) onto the biosorbent can not be described by the pseudo – first order kinetic model.

**Pseudo – second order kinetics:** The pseudo – second order kinetic plots for the adsorption process is presented Figure 6. The pseudo – second order kinetic plot shows the  $R^2$  values for the Cu (II) and Ni (II) ions to be 0.9988 and 0.9969 respectively. The values of  $q_e$  and  $k_2$  obtained from the plots are shown in Table 1. The  $R^2$  values were high and very close to unity. Also the value of the theoretical and experimental  $q_e$  were the same for Ni (II) but the values for Cu (II) were slightly different as shown in the table. These results indicate that the biosorption reaction follows the pseudo – second order kinetic model and that chemisorption is the rate controlling mechanism (Mata *et al.*, 2008).

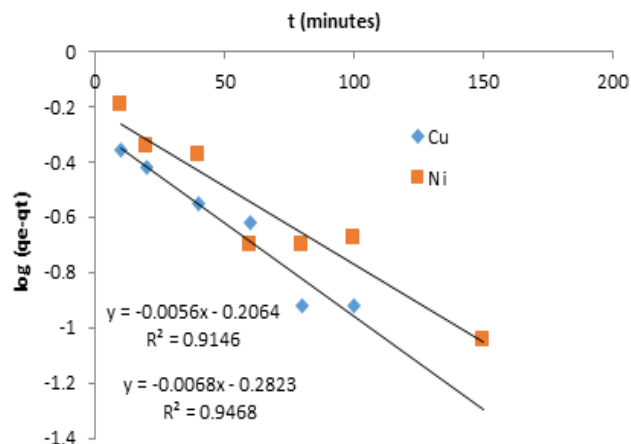


Fig 5 Pseudo – first order kinetic plot for the adsorption of Cu (II) and Ni (II) ions onto calcium alginate beads

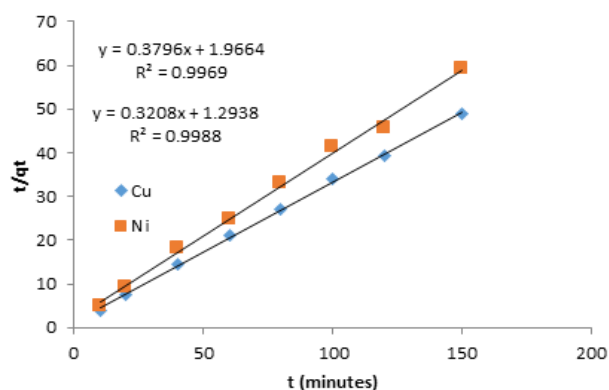


Fig 6 Pseudo – second order kinetic plot for the adsorption of Cu (II) and Ni (II) ions onto calcium alginate beads

Table 2 Pseudo – first and second order constants for the adsorption of Cu (II) and Ni (II) ions onto calcium alginate beads

	qe (experimental)	Pseudo – first order constants			Pseudo – second order constants		
		R <sup>2</sup>	k <sub>1</sub>	qe(calculated)	R <sup>2</sup>	k <sub>2</sub>	qe(calculated)
Cu(II)	1.53	0.9464	0.016	0.52	0.9988	0.079	3.12
Ni (II)	2.63	0.9146	0.013	0.62	0.9969	0.074	2.63

**Conclusion:** The results of this study have shown that calcium alginate beads can be utilized for the removal of Cu (II) and Ni (II) ions from solution. The removal efficiency of both ions by the adsorbent increased with increase in pH. The experimental data fitted the Langmuir Isotherm well for both ions indicating a monolayer adsorption. The kinetic modeling shows that the pseudo – second order model had a better fit than the pseudo – first order model.

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