

# Removal of Cadmium (II) Ions from Synthetic Wastewaters by alginate – immobilized *Penicillium* sp biomass

## ABSTRACT

The objective of this investigation was to study the biosorption of Cd (II) from aqueous solution onto *Penicillium* sp immobilized in calcium alginate and to determine the isotherms and kinetics of the adsorption process. The capacity for Cd (II) biosorption was investigated as a function of pH, adsorbent dose, contact time and initial metal ion concentration. The results showed that the removal efficiency increased with increase in adsorbent dosage and solution pH. For adsorbent dosage, the highest removal efficiency was 93.45% (adsorbent dosage of 200 mg). In terms of pH, the highest removal percentage was 89.75% at pH of 9.0 and Cd (II) ion concentration of 2 mg/L. The experimental data fitted the Freundlich isotherm better than the Langmuir isotherm. Their  $R^2$  values were 0.9852 and 0.8053 respectively. The calculated maximum biosorption capacity  $Q^0$  was 7.12 mg  $g^{-1}$ . The values of  $R^2$  for the pseudo – first and pseudo – second order kinetics are 0.9007 and 0.9960 respectively. The experimental value of  $q_e$ , the biosorption capacity at equilibrium, for the pseudo second order model was closer to the theoretical value than that of the pseudo – first order indicating that chemisorption is the probable mechanism of the process. These results show that the investigated biosorbent is a good low cost adsorbent for the removal of Cd (II) from wastewaters.

*Keywords: Biosorption, Penicillium sp, Alginate, Isotherm, Langmuir, Freundlich*

## 1. INTRODUCTION

Heavy metal ions can be discharged into the environment from a variety of industrial activities. The presence of these heavy metals in the environment can be detrimental to a variety of living species, including man. Industrial wastewaters are considered the most important source of heavy metal pollution [1]. Many conventional methods have been used to remove heavy metals from solution, including chemical precipitation and filtration, electrochemical treatments, solvent extraction, application of membrane technology, ion exchange and activated carbon adsorption. However, some disadvantages such as high cost, incomplete removal, high energy consumption and generation of toxic wastes accompany these technologies [2]. Biosorption, which involves the use of microorganisms (i.e. fungi, bacteria, algae and yeasts) as adsorbents to remove metal ions from wastewaters offers a potential alternative to existing methods. 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 [3-5]. This study was therefore carried out to investigate the removal capacity of *Penicillium* sp, immobilized in calcium alginate, for Cd (II) ions from aqueous solution.

## **2. MATERIALS AND METHODS**

### **2.1 Generation and Immobilization of Biomass**

The fungal mycelium of *Penicillium* sp was obtained from National Institute for Leather Science and Technology (NILEST), Zaria. There were cultured over Potato Dextrose Agar (PDA) plates. The PDA plates of the stock culture were maintained by subculturing at 4°C. The fungal biomass were cultivated in composition (g/L): K<sub>2</sub>HPO<sub>4</sub>, 0.5; NaCl, 0.5; MgSO<sub>4</sub>, 0.5; NH<sub>4</sub>NO<sub>3</sub>, 0.5; yeast extract, 0.5, peptone, 10.0, glucose, 20. The pH of the media was adjusted to 5.0. The flask was autoclaved at 121°C for 15 minutes and then incubated in a rotary orbital shaker at 180 rpm and 30°C. The cells were dried at overnight at 80°C [6]. 100ml of 4 % (w/v) sodium alginate was mixed until homogenous with 2% (w/v) solution of the fungal biomass. The mixture was stirred for 1 hour at 30°C and then the slurry was dropped through a 10 ml syringe into 2% (w/v) CaCl<sub>2</sub> solution [7]. Durable spherical beads containing the biomass were formed immediately. The beads were washed with distilled water and stored at 4°C in distilled water until further use.

### **2.2 Adsorption Experiments**

The studies were carried out using a batch technique. The reactions were carried out in 100 ml corked conical flasks containing 50 ml of the solution. The pH of the solutions were adjusted with 0.1 mol dm<sup>-3</sup> NaOH and 0.1 mol dm<sup>-3</sup> HNO<sub>3</sub>. The flask contents were mechanically agitated

in a conical flask shaker at 150 rpm. The contact experiments were done in replicates and at the end of the adsorption process, 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 Cd (II) ion concentration in the solution before and after contact with the adsorbent. The percentage metal removal (%) was calculated using the following equation:

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

The amount of each ion adsorbed was calculated from the difference between the added and equilibrium concentration by using the equation below [8]:

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

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.

**2.2.1 Effect of Solution pH**

The Effect of pH on the adsorption of metal ions from aqueous solution was studied by varying the pH of the solution from 3.0 – 9.0 in 100 ml conical flasks containing 50 ml of solution of 2 mm/L Cd (II) ions. 100 mg of the adsorbent was added into each of the conical flasks containing the solutions. The samples were agitated in a conical flask shaker for 120 minutes at 29 °C. After equilibrium was attained, the samples were filtered into polypropylene bottles. The percentage removal of the ions adsorbed was calculated from the difference between the added and equilibrium concentration by using equation (1).

### **2.2.2 Effect of Adsorbent Dosage**

The effect of adsorbent dosage on the adsorption of metal ions from aqueous solutions was studied by varying the adsorbent weight from 10 – 200 mg while keeping the other parameters constant (i.e. pH of 5.0, contact time of 120 minutes and Cd (II) ion concentration of 2 mg/L). After equilibrium was attained, the samples were filtered into polypropylene bottles.

### **2.2.3 Effect of Contact Time**

To determine the effect of contact time on the removal of metal ions from the solution, 100 mg each of the adsorbent was added into different 100 ml conical flasks containing 50 ml of metal solution, initial concentration being 2 mg/L. The pH value was adjusted to 5.0. The samples were agitated in the conical flask shaker for 10, 20, 40, 60, 80, 100, 120 and 150 minutes. After equilibrium was attained the samples were filtered into polypropylene bottles.

### **2.2.4 Effect of Initial Metal Ion Concentration**

Different metal ion concentration ranging from 1 mg/L to 10 mg/L solutions by diluting appropriate amounts from the stock solution. The studies were conducted using a batch technique at 29 °C in different conical flasks of 100 ml containing 50 ml of metal solution of known concentration and initial pH adjusted to 5.0. 100 mg of the biosorbent was added to the each of the reaction vessels and after agitation for 120 minutes, the samples were filtered into polypropylene bottles.

### **2.2.5 Langmuir Adsorption Isotherm**

This isotherm is often used to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. It is expressed by the equation below.

$$\frac{C_e}{q_e} = \frac{1}{K_L Q^0} + \frac{C_e}{Q^0} \dots\dots\dots (3)$$

Where  $K_L$  (L/g) is a constant related to the adsorption / desorption energy and  $Q^0$  (mg/g) is the maximum sorption upon complete saturation of the adsorption of the adsorbent (biosorbent) surface [9]. A graph of  $C_e/q_e$  against  $C_e$  will have  $K_L$  (L/g) as the slope and  $Q^0$  (mg/g) as the intercept.

### 2.2.6 Freundlich Adsorption Isotherm

The Freundlich isotherm was also be used to correlate the adsorption equilibrium data in this work. The linearized form of the Freundlich equation is

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \dots\dots\dots (4)$$

Where  $q_e$  (mg/g) is the adsorption density,  $C_e$  is the concentration of metal ion in solution at equilibrium (mg/L),  $K_f$  and  $n$  are the Freundlich constants which determine the curvature and steepness of the isotherm [10]. Also the value of  $1/n$  indicates the affinity of the adsorbate towards the biomass. A plot of  $\log C_e$  against  $\log q_e$  gave the value of  $1/n$  and  $\log K_f$  from the slope and the intercept respectively.

### 2.2.7 Pseudo–First Order Kinetic Equation

The integrated form of the pseudo first order kinetic equation is given as follows:

$$\text{Log}(q_e - q_t) = \text{Log } q_e - \frac{k_1}{2.303} t \dots\dots\dots (5)$$

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.

### 2.2.8 Pseudo–Second Order Kinetic Equation

Pseudo – second order kinetic equation is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \dots\dots\dots (6)$$

On linearizing this equation we obtain

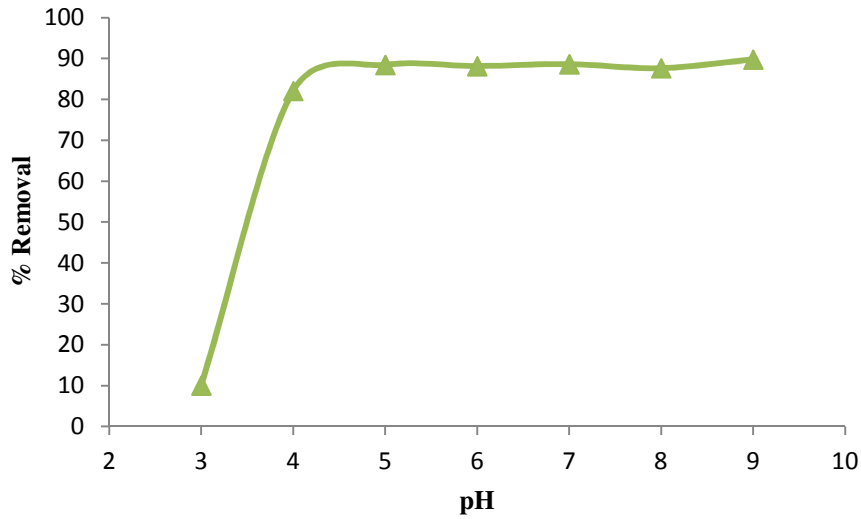
$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \dots\dots\dots (7)$$

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.

### 3. RESULTS AND DISCUSSION

#### 3.1 Effect of Solution pH on the Removal of Cd (II) Ions

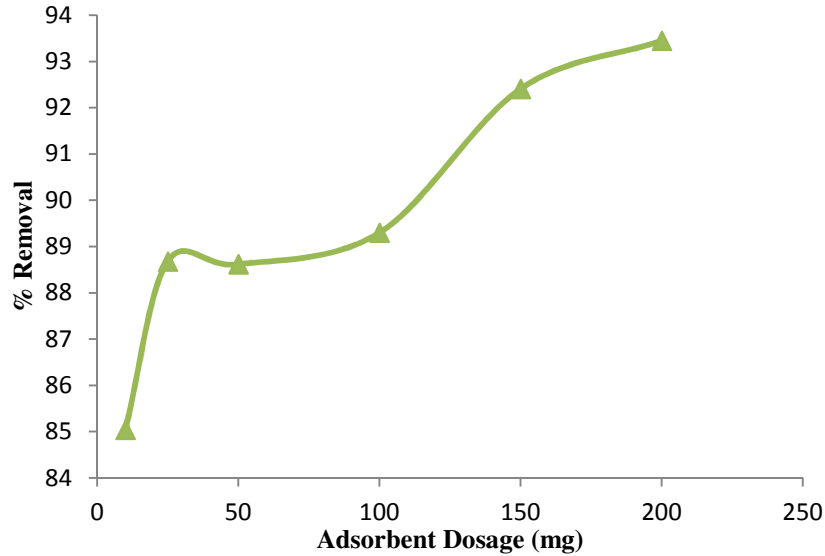
The effect of the pH on the removal of Cd (II) ions from solution is presented in Fig 1. As the figure shows, the removal percentage of Cd (II) by immobilized *Penicillium* sp increased from 10.07% at pH 3.0 to 88.43% at pH 5.0. The increase in Cd (II) removal with an increase in pH can be explained on the basis of 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 [11].



**Fig 1: Effect of solution pH on Cd (II) removal by alginate – immobilised *Penicillium* sp biomass**

### 3.2 Effect of Adsorbent Dosage

The effect of adsorbent dosage on the biosorption of cadmium ions from solution is presented in Fig 2. As the figure shows, the removal efficiency increased from 85.04% (at 10 mg dosage) to 93.45% at 200 mg dosage which was the highest. This suggests that the increase in percentage removal with increase in adsorbent dosage is due to the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent [12].



**Fig 2: Effect of adsorbent dosage on Cd (II) removal by alginate – immobilised *Penicillium* sp biomass**

### **3.3 Effect of Contact Time on Adsorption of Cd (II) Ions Removal**

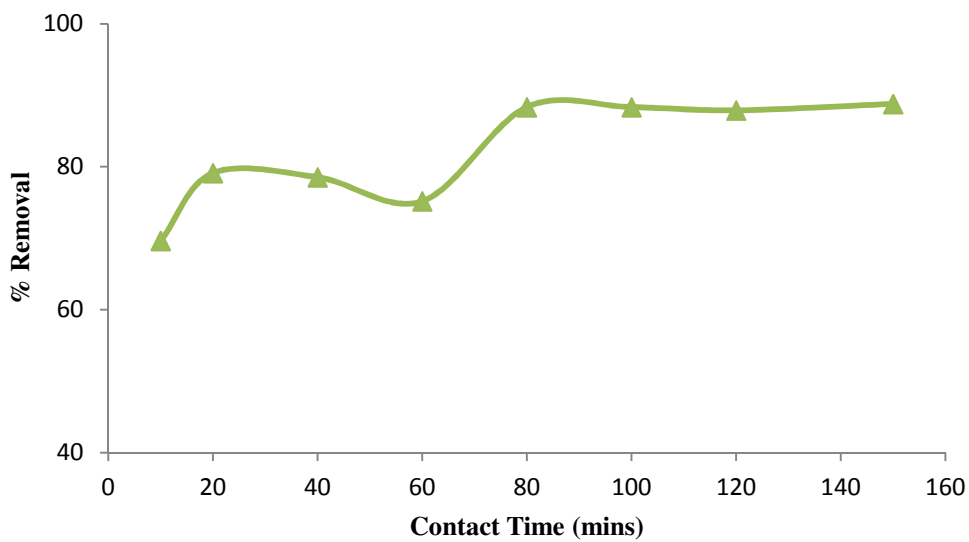
The effect of the contact time on the removal of Cd (II) ions from solution is presented in Fig 3. From the figure it can be seen that the removal percentage of Cd (II) ions by *Penicillium* sp increased from 69.65% at 10 minutes contact time to 88.78% at 150 minutes which was the maximum removal percentage. As the adsorption process proceeds, the adsorbate reaches the saturation state and then the adsorbate tends to desorb back into the solution. Eventually the rates of adsorption and desorption will be equal at equilibrium [13]

### **3.4 Effect of Initial Cd (II) Ion Concentration**

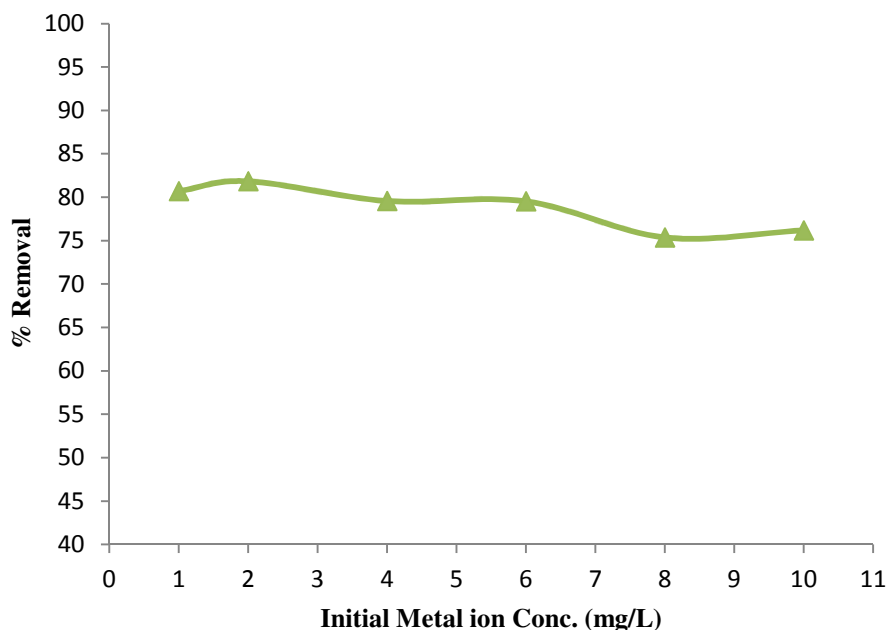
The effect of initial metal ion concentration on the removal of Cd (II) ions from solution is shown in Fig 4. From the figure it can be seen that the removal percentage of Cd (II) ions by



*Penicillium* sp increased slightly from 80.72% at 1 mg/L to 81.86% at 2 mg/L after which the graph levels off. 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. On the other hand, on increasing metal concentration, equilibrium between metal ions and the adsorbent's active sites were probably established very soon thus efficiency decreased due to the competitive effect of the metal ions for adsorptive site [14].



**Fig 3: Effect of contact time on Cd (II) removal by alginate – immobilised *Penicillium* sp biomass**

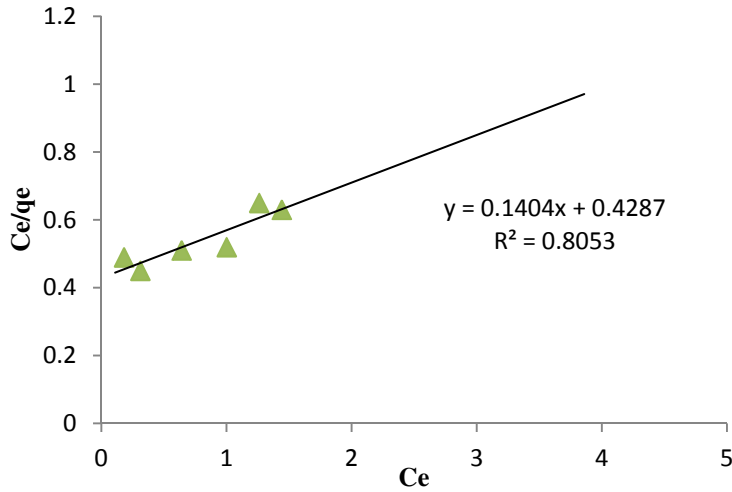


**Fig 4: Effect of initial metal ion concentration on Cd (II) removal by alginate – immobilized *Penicillium sp* biomass**

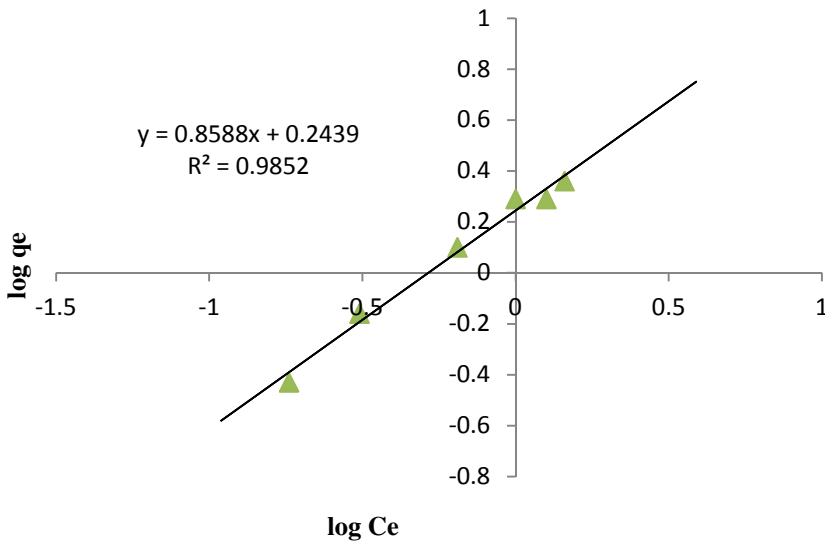
### 3.5 Adsorption Isotherms

The Langmuir isotherm for the biosorption of Cd (II) by the alginate – immobilized *Penicillium sp* is shown in Fig 5. The value of the coefficient of determination,  $R^2$ , for the Langmuir plot was found to be 0.8053. Maximum biosorption capacity  $Q^0$  was calculated as  $7.12 \text{ mgg}^{-1}$ .

The Freundlich isotherm plot for the *Penicillium sp* is presented in Fig 6. The value of the determination coefficient,  $R^2$ , was found to be 0.9852 which shows that the biosorption of Cd (II) ions onto the biosorbent had a good fit for the Freundlich isotherm. The values of  $K_f$  and  $n$  were calculated from slope and intercept of the Freundlich plot between  $\text{Log } q_e$  and  $\text{Log } C_e$ . The values were  $1.75 \text{ mgg}^{-1}$  and  $1.16 \text{ Lmg}^{-1}$  for  $K_f$  and  $n$  respectively. The value of  $n$  lies between 1 and 10 and according to Treybal [15] this indicates a beneficial adsorption.



**Fig 5: Langmuir isotherm for the biosorption of Cd (II) by alginate – immobilized *Penicillium* sp biomass**

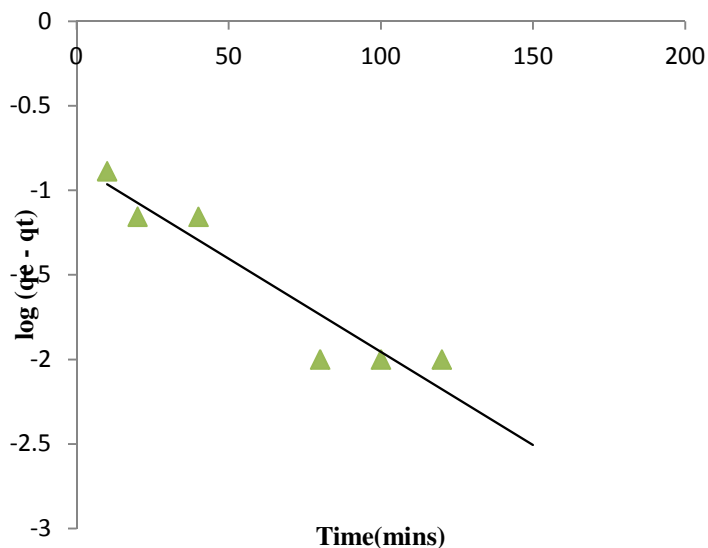


**Fig 6: Freundlich isotherm for the biosorption of Cd (II) by alginate – immobilized *Penicillium* sp biomass**

### 3.6 Adsorption Kinetics

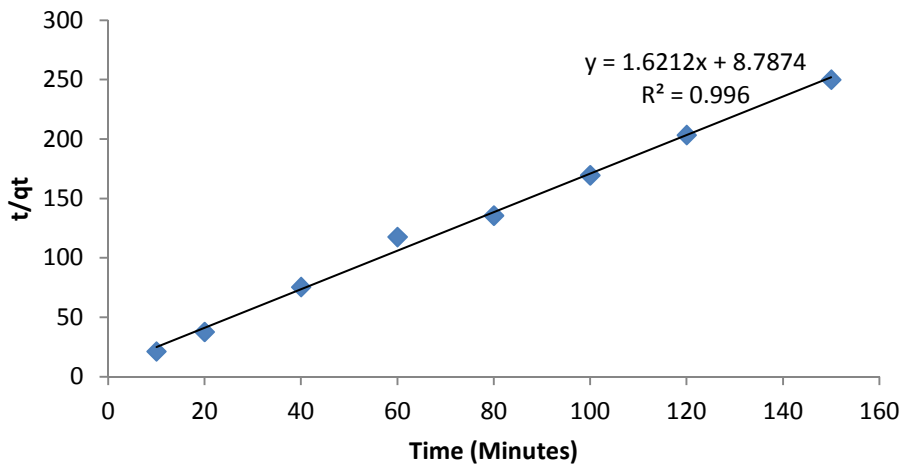
The pseudo – first order kinetic plot for the adsorption of Cd (II) onto *Penicillium* sp is shown in Fig 7. As the figure shows, the correlation coefficient,  $R^2$ , for the pseudo – first order kinetic plot

was 0.9007. The value of  $q_e$  obtained from the plots was  $0.140 \text{ mg g}^{-1}$ . Although the plot showed linearity, with  $R^2$  values close to unity, the calculated  $q_e$  value was not in agreement with the experimental  $q_e$  value of  $0.60 \text{ mg g}^{-1}$ . These results suggest that the biosorption of Cd (II) onto the biosorbents is not a unimolecular reaction and does not follow the pseudo – first order kinetic model.



**Fig 7: Pseudo – first order kinetic plot for the biosorption of Cd (II) onto alginate – immobilized *Penicillium* sp biomass**

The pseudo – second order kinetic plots for the adsorption of Cd (II) onto alginate - immobilized *Penicillium* sp is shown in Fig 8. The pseudo – second order kinetic plot shows the  $R^2$  value to be 0.9960. The adsorption capacity at equilibrium,  $q_e$ , is  $0.616 \text{ mg g}^{-1}$ . The value of the theoretical  $q_e$  was in good agreement with that obtained experimentally. This indicates that chemisorption is the rate controlling mechanism. The model is based on the assumption that the adsorption process involves the sharing or exchange of valence electrons between the adsorbent and the adsorbate [16]. Megat Hanafiah et al.[17] have suggested that the pseudo – second order model excellently describes biosorption process.



**Fig 8. Pseudo – second order kinetic plot for the biosorption of Cd (II) onto alginate – immobilised fungal biomass**

#### 4. CONCLUSION

The results of the batch adsorption processes undertaken in this study showed that the removal efficiency of the Cd (II) from aqueous solution by the biosorbent increased with an increase in adsorbent dose. The results obtained also showed that there was an increase in biosorption capacity with increase in pH. The adsorption isotherms plotted for the results showed that the experimental data fitted the Freundlich isotherm better than the Langmuir isotherm. The results also show that the adsorption process follows the pseudo – second order kinetics which describes a chemisorption process. These results indicate that Cd (II) ions removal by biomass of *Penicillium* sp immobilized in alginate is a low cost wastewater treatment option and can be effectively used in small scale treatment plants.

#### COMPETING INTERESTS

The authors declare that no competing interests exist.

## AUTHORS' CONTRIBUTIONS

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

## REFERENCES

1. Sun YM, Horng CY, Chang FL, Cheng LC, Tian WX. Biosorption of Lead, Mercury and cadmium ions by *Aspergillus terreus* immobilized in a natural matrix. *Polish J. Microbiol.* 2010; 59(1): 37 - 44
2. Ahalya N, Ramchanra TV, Kanamodi RD. Biosorption of heavy metals. *Res. J.Chem.EnvIRON.* 2003; 7: 71- 78
3. Kapoor A, Viraraghavan T, Cullimore DR. Removal of heavy metals using the fungus *Aspergillus niger*. *Bioresour. Technol.* 1999; 70: 95 – 104
4. Liu HL, Chen BY, Lan YW, Cheng WC. Biosorption of Zn (II) and Cu (II) by the indigenous *Thiobacillus thiooxidans*. *Chem. Eng. J.* 2004; 97: 195 – 201
5. Moon SH, Park CS, Kim YJ, Park YI. Biosorption isotherms of Pb (II) and Zn (II) on Pestan, an extracellular polysaccharide of *Pestalotiopsis* sp. KCTC8637. *Process Biochemistry.* 2006; 41: 312 - 316
6. Pundir R, Dastidar MG. Recovery of Cu and Ni ions from metal – loaded fungal biomass using acidic eluent. *Int. J. Chem. Environ. Eng.* 2010; 1(1): 63-66
7. Dong X. A comparative study of Cu (II) biosorption on Ca – alginate and immobilized live and inactivated *Cladosporium* sp. *J. Env. Biol.* 2004; 25:337-341
8. Babel S, Opiso EM. Removal of chromium from synthetic wastewater by sorption onto volcanic ash soil. *Int. J. Eng. Sci. Technol.* 2007; 4(1): 99-107
9. Horsfall M, Spiff AI, Abia AA. Studies on the influence of mercaptoacetic acid (MAA) modification of cassava (*Manihot esculenta*) waste biomass on the adsorption of Cu<sup>2+</sup> and Cd<sup>2+</sup> from aqueous solution. *Bull. Korr. Chem. Soc.* 2004; 25(7): 969-976
10. Akgerman A, Zardkoohi M. Adsorption of phenolic compounds on fly ash. *J. Chem. Eng. Data.* 1996; 41: 185 – 191
11. Dianati-Tilaki R A, Mahvi AH, Shariat M, Nasserli S. Study of cadmium removal from

- environmental water by biofilm covered granular activated carbon. *Iranian J. Public Health*. 2004; 33(4): 43 - 52
12. Garg VK, Gupta R, Kumar R, Gupta RK. Adsorption of chromium from aqueous solution on treated sawdust. *Bioresour. Technol*. 2004; 92: 79 - 81.
  13. Sari A, Tuzen M. Biosorption of cadmium (II) from aqueous solution by red algae (*Ceramium virgatum*): equilibrium, kinetic and thermodynamic studies. *J.Hazard. Mater.* 2008; 157(2-3): 448 - 454
  14. Zvinowanda CM, Okonkwo JO, Shabalala PN, Agyei NM. (2009). A novel adsorbent for heavy metal remediation in aqueous environments. *Int. J. Environ. Sci. Technol*. 2009; 6(3): 425 - 434
  15. Treybal RE. Mass transfer operations, 3rd edition. New York, McGraw Hill. 1980; 447-522.
  16. Mata YN, Blazquez ML, Ballester A, Gonzalez F, Munoz JA. Characterization of the biosorption of cadmium, lead and copper with brown algae *Fucus vesiculosus*. *J.Hazard. Mater.* 2008; 158: 316 - 323
  17. Megat Hanafiah, M A K, Ibrahim SC, Yahya MZA. Equilibrium adsorption study of lead ions onto sodium hydroxide modified lalang (*Imperata cylindrica*) leaf powder. *J. Applied Sci. Res.* 2006; 2(12): 1169 - 1174