

ADSORPTION OF Cd (II) FROM AQUEOUS SOLUTION USING TERMITE MOUND

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ABSTRACT

The adsorption characteristics of cadmium (II) ion onto termite mound from aqueous solution was investigated with respect to changes in initial Cd²⁺ concentration and contact time of the solution. The elemental compositions as well as the physicochemical properties of the termite mound were also determined. It was observed that the termite mound used in this study contained higher amount of silicon (57.1%) followed by Iron (33.41%) and Aluminium (16.6%). The adsorbent sample had pH 7.2, porosity 0.96mm and moisture content 11.6%. The maximum removal efficiency of Cd²⁺ was 98.9% at 120mins. For the adsorption pattern, the Langmuir isotherm model fitted into the equilibrium data was better than the Freundlich isotherm model. Experimental data were also evaluated in terms of kinetic characteristics of adsorption and it was found that the adsorption process followed pseudo-second-order kinetics. The results showed that the adsorption of Cd (II) ion onto termite mound is feasible.

Keywords: Termite mound, Adsorption, Cadmium, Kinetics, Aqueous solution, Pseudo-second Order kinetics.

INTRODUCTION

Environmental contamination by heavy metals is of growing concern because of its health risks on humans and animals. Among the heavy metals of public concern, cadmium has received attention, probably because of its toxicity. The adverse effects of cadmium have been reported by various researchers (Wang *et al.*, 2011). Cadmium has also been classified as a potent neurotoxic metal (Steven *et al.*, 2014). The heavy metal ions are stable and persistent with environmental contaminants since they cannot be degraded and destroyed (Luter *et al.*, 2012).

Various treatment options used to remove heavy metals from aqueous solution include chemical precipitation, electrochemical reduction, ion exchange, reverse osmosis, membrane separation and adsorption. Compared with other treatment methods, adsorption appears to be an attractive process due to its simplicity and effectiveness in the removal of heavy metals from aqueous solution (Udeh and Agunwamba, 2017). The efficiency of adsorption relies on the capability of the adsorbent to concentrate or adsorb metal ions from solution on its surface and the rate of removing ions from the solution (Olayinka *et al.*, 2009). Different adsorbents such as tea waste, zeolite, resins, bio-sorbent, hydrogels, activated carbon and egg shell-magnetite powder, etc, have been used for the removal of heavy metal ions from

aqueous solutions. There is still the need for the development of new adsorbents with superior adsorption capacity, facile adsorption-desorption kinetic, high stability and easiness of operation (Emadi *et al.*, 2012).

Termites are social insects that build nests in soil or wood. The mounds are features built from subsoil taken from a depth as low as 3 meters below the earth surface. Thus, the composition of mound soil is closely related to the nature of adjacent subsoil (Abdus-Salam and Bello, 2015). The use of termite mound as an adsorbent for the removal of Pb (II) ion from aqueous solution, has been reported (Abdus-Salam and Itiola, 2012). There is still the need to investigate the effect of termite mound on other metal ions and also to see if the soil topography and different weather conditions, will have impact on the adsorption process.

The aim of this research is to investigate the adsorption potential of termite mound for the removal of Cd (II) ion from aqueous solution within various experimental conditions such as the initial Cd (II) ion concentration and contact time. The specific objectives is to carry out batch adsorption study, investigate the best kinetic and isotherm models suitable for the adsorption of cadmium (II) ions onto termite mound.

The Freundlich and Langmuir adsorption isotherms were used to investigate the adsorption

process. Kinetic study was also carried out to evaluate the order of adsorption.

MATERIALS AND METHODS

The termite mound samples were obtained from The Federal Polytechnic, Idah, Kogi State. The termite mound was used without any chemical treatment for the sorption study. The sample was air-dried for three days in the laboratory at room temperature and crushed in a porcelain mortar using pestle, and was sieved into fine particles (2mm mesh size) and kept in a clean container for analysis. The chemical composition of the termite mound as determined by XRF is given in Table 1. The porosity, pH and moisture content were determined using the method adopted by Adie *et al.* (2013). Cadmium solutions were prepared by using analytical grade cadmium chloride (CdCl₂.H₂O). Varying solutions of Cd (II) ion were prepared from stock, a solution containing 1000mg/L of Cd (II) ion. All the solutions in this study were prepared using deionized water.

Table 1: Chemical Composition of Termite Mound

Constituents	Percentage (wt. %)
Al	16.6
Si	57.1
K	6.26
Ca	4.36
Ti	3.83
V	0.29
Cr	0.014
Mn	0.28
Fe	33.41
Ni	0.055
Cu	0.099
Zn	0.05
Mo	0.90
Eu	0.56
Yb	0.03
R	0.2

Adsorption experiments were carried out at the desired initial Cd (II) ion concentrations and contact time using 0.5g weight of the adsorbent in 100mL conical flasks containing 30mL of the Cd (II) ion solutions. The initial concentrations of Cd (II) ion, were 25, 50, 70, 100 and 150mg/L. Samples were collected at 30, 60, 90, 120 and 180mins to determine optimal shaking time. During the adsorption process, the flasks were agitated on a Gallenhemp shaker. The mixture in each case was filtered using filter paper (Whatman 11cm filter paper) and the filtrate was analyzed for residual Cd (II) ion using Bulk Scientific 210 VGP Atomic Absorption Spectrophotometer (AAS). The quantity adsorbed per unit mass of the adsorbent and % removal, was evaluated using equations 1 and 2 respectively. These equations are shown below:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

$$\% \text{ adsorption} = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{2}$$

Where C₀ (mg/L) and C_e (mg/L) are the initial concentration and concentration at equilibrium respectively, V(L) is the volume of the solution, q_e(mg/g) is the amount of metal ion adsorbed at equilibrium and W(g) is the weight of the adsorbent used (Jimoh *et al.*, 2012).

RESULTS AND DISCUSSION

The Physiochemical Properties of Termite Mound

The physical properties of the termite mound are summarized in Table 2. The termite mound was brownish in colour and it was within the variable colour of termite mound (brownish and blackish) depending on the soil morphology of the environment. The pH of the termite mound sample was slightly higher than the neutral (7.2). This pH value indicates that the adsorbent pH was in the range of 6-8, which is the acceptable pH for most adsorption application in aqueous phase media. The porosity of an adsorbent is the measure of the void in the adsorbent and the greater the porosity of a given adsorbent, the greater the relative size of the molecules it can adsorb onto its crystal structure. In this study, the termite mound has a porosity of 0.94, which showed that the adsorbent is suitable for adsorption purpose. The amount of moisture present in the termite mound, was determined to be 11.6%

(a value far lower than 50% upper limit for adsorbent). This implies that the termite mound can be stored for long period without significant microbial activities being observed (Adie *et al.*, 2013).

Table 2: Physiochemical Properties of Termite Mound

Parameters	Values
Color	brown
Texture	fine
pH	7.2
Porosity (mm)	0.96
Moisture content (%)	11.6

Effect of Initial Cd²⁺ Concentration

Figure 1, represents a two-step process an initial linear rise in the uptake of Cd²⁺ which is followed by a steep curve. As the initial concentration increased, the amount adsorbed increased proportionally until a plateau was reached where there was no corresponding rise in the amount adsorbed. The favorable site with lower adsorption energies have been filled thus making the unfavorable sites more difficult to fill. This is an indication of surface saturation or a monolayer adsorption. The second rise is a continuation of monolayer adsorption given a two-step Langmuir curve (Abdus-salam and Itiola, 2012). The initial faster rate of removal of metal ion could be due to the availability of the uncovered surface area of the adsorbent. This could also be explained in terms of the progressive increase in the electrostatic interaction between the metal and the adsorbent active sites. More adsorption sites were being covered as the metal ion concentration increased, (Egila *et al.*, 2010). The intermediate flat region in the graph, which corresponds to monolayer formation, ends at 75mg/L and the multilayer portion starts from 100mg/L. The plot of percentage removal efficiency against initial Cd²⁺ concentration. is shown in Figure 2. The initial concentration 25, 50, 70, 100 and 150mg/L, gave removal efficiency of 97%, 99%, 92%, 94% and 67% respectively. Therefore, 150mg/L initial Cd²⁺ concentration was chosen for further experiments.

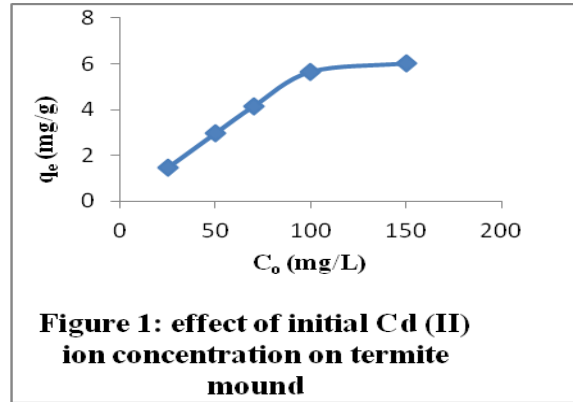


Figure 1: effect of initial Cd (II) ion concentration on termite mound

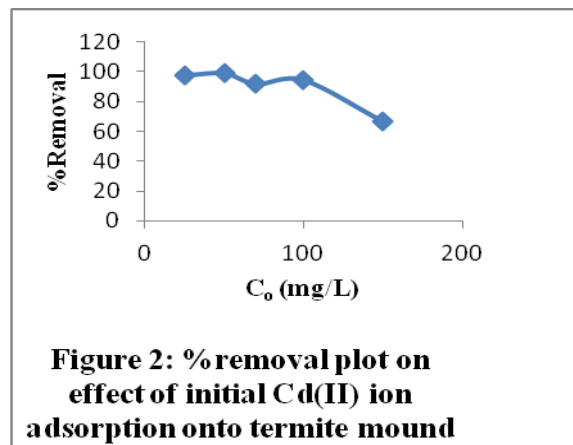


Figure 2: %removal plot on effect of initial Cd(II) ion adsorption onto termite mound

Effect of Contact Time

The effect of contact time on Cd²⁺ removal from aqueous solution is illustrated in Figures 3 and 4. The rate of metal uptake level was rapid within 120 minutes and further additional increase in time, resulted in a decrease in the amount of Cd²⁺ adsorbed. This implies that the binding site of the adsorbent was exhausted and further shaken resulting in desorption or the adsorption site becoming saturated to maximum uptake capacity.

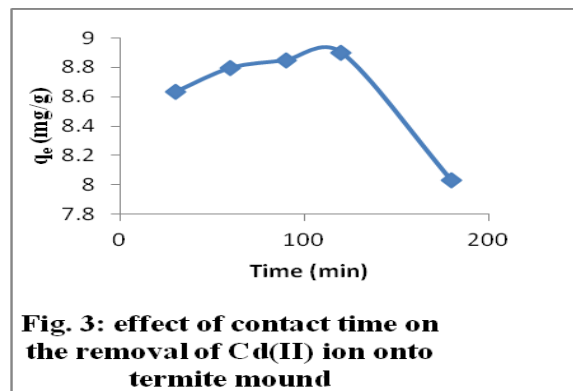


Fig. 3: effect of contact time on the removal of Cd(II) ion onto termite mound

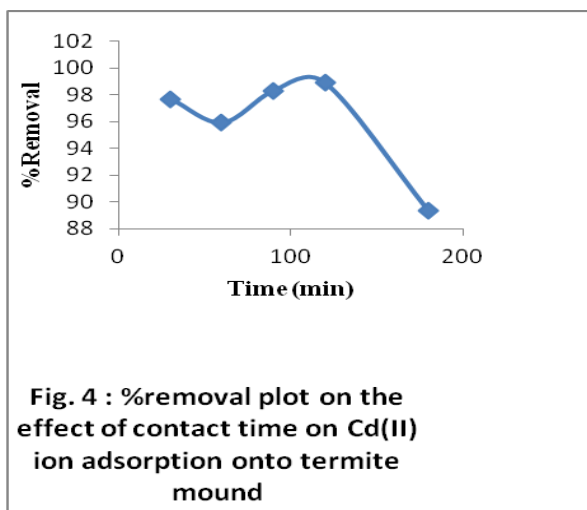


Fig. 4 : %removal plot on the effect of contact time on Cd(II) ion adsorption onto termite mound

Adsorption Isotherm Models

The equilibrium adsorption isotherm is of fundamental importance in the design of adsorption system. The Langmuir model, which is valid for monolayer adsorption onto surface containing a finite number of identical sites, is the model most frequently used to represent data on adsorption from solution. The exact shape of the adsorption isotherm for a heterogeneous adsorbent will depend on the distribution of the K_L values or, more specifically, on the frequency distribution of the adsorption energies of site on the adsorbent (Torab-Mostaedi *et al.*, 2010). This model can be expressed in equation 3 below:

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

Where q_m (mg/g), is the Langmuir maximum adsorption capacity, K_L (L/mg) is the Lang 17 adsorption equilibrium constant and q_e (mg/g) C_e (mg/L) are as described earlier.

This type of adsorption is valid when: (i) the adsorbent surface is homogeneous (ii) both surface and bulk phases exhibit ideal behaviour and (iii) the adsorption film is monomolecular.

The Freundlich model is an empirical equation and can be applied for non-ideal sorption on heterogeneous surfaces and multilayer sorption. The equation is commonly given as in equation 4 below:

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

Where K_F , is the Freundlich parameter relating to adsorption capacity, q_e (mg/g) and C_e (mg/L), are as described before, and $1/n$ is a

parameter relating to adsorption intensity (Ren *et al.*, 2012).

The Langmuir model constants, are presented in Table 3 and the plot in Figure 5. The correlation coefficient (R^2), is found to be 0.997 for the adsorption of Cd^{2+} , indicating that the Langmuir model was able to describe the adsorption of Cd^{2+} adequately. The value of the maximum capacity (q_m), was found to be 6.2mg/g. The K_L value, was found to be 0.6610(L/mg). The shape of the isotherm can also be considered when predicting whether an adsorption system is “favorable” or “unfavorable”. The essential characteristic of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor or equilibrium parameter R_L , which is defined by equation 5 below:

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

Where K_L is the Langmuir constant and C_0 is the initial concentration of cadmium (II) ion. The value of separation parameter R_L provides important information about the nature of the adsorption. The value of R_L , indicated the type of Langmuir isotherm to be irreversible ($R_L=0$), favourable ($0 < R_L < 1$), linear ($R_L=1$) or unfavourable ($R_L > 1$) (Awwad and Farhan, 2012). The R_L was found to be 0.00999 for cadmium ion concentration of 150mg/L, which indicates a favorable adsorption. Figure 6, shows the Freundlich isotherm plot, and Table 3 presents the results for the Freundlich isotherm model constants and correlation coefficient. The values K_f and $1/n$, were found to be 2.612 and 0.254 for Cd^{2+} respectively. The $1/n$ values were between 0 and 1, indicating that the adsorption of Cd^{2+} onto termite mound was favourable under selected operating conditions. The R^2 value was found to be 0.671. As can be seen from the R^2 values of both models, the adsorption results obtained were best described by the Langmuir isotherm model.

Table 3: Langmuir and Freundlich constants for adsorption of Cd^{2+} onto termite mound

Langmuir model				Freundlich model			
Metal ion	q_m (mg/g)	K_L (L/mg)	R^2	Metal ion	$1/n$	K_F	R^2
Cd(II)	6.2	0.6610	0.997	Cd(II)	0.254	2.612	0.671

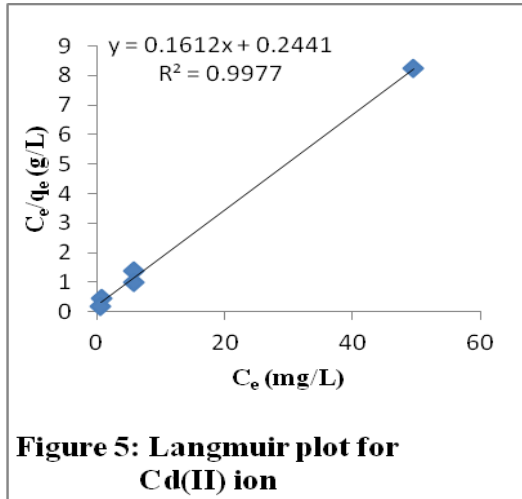


Figure 5: Langmuir plot for Cd(II) ion

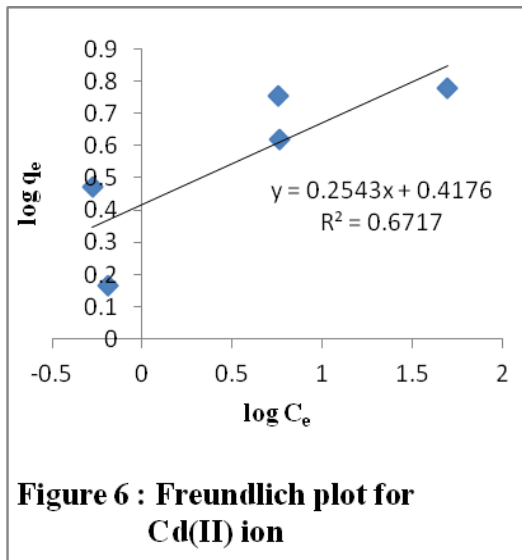


Figure 6 : Freundlich plot for Cd(II) ion

Adsorption Kinetics

In order to clarify the adsorption kinetics of Cd²⁺ onto termite mound, Lagergren pseudo-first order and pseudo-second-order kinetic models, were applied to the experimental data. Figure 7, shows pseudo-first-order plot for the kinetics of Cd²⁺ onto termite mound and the constants, are presented in Table 4. The Lagergren pseudo-first order rate equation used by researchers to study the kinetics of heavy metals adsorption, is given in equation 6 below:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{6}$$

Where q_e and q_t (mg g⁻¹), are the amount of Cd²⁺ ion adsorbed on the adsorbent at equilibrium and at time t, respectively. K₁ is the first order rate constant (min⁻¹) (Xu *et al.*, 2012). Figure 7, shows Lagergren pseudo-first-order plot.

Table 4: Pseudo-first-order rate equation constants and pseudo-second-order rate constants for adsorption of Cd²⁺ onto termite mound

Metal ion	Pseudo-first-order		Pseudo-second-order			
	K ₁ (min ⁻¹)	R ²	q _e (calc)(mg/g)	q _e (exp)(mg/g)	K ₂ (g/mgmin)	R ²
Cd(II)	-0.005	0.342	Cd(II) 8.0	8.901	-0.0205	0.993

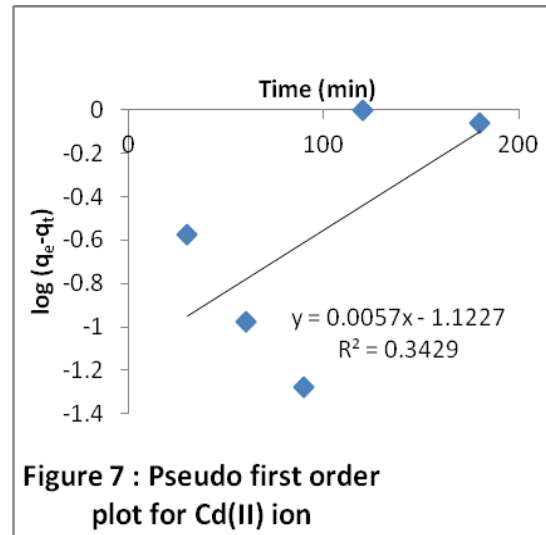


Figure 7 : Pseudo first order plot for Cd(II) ion

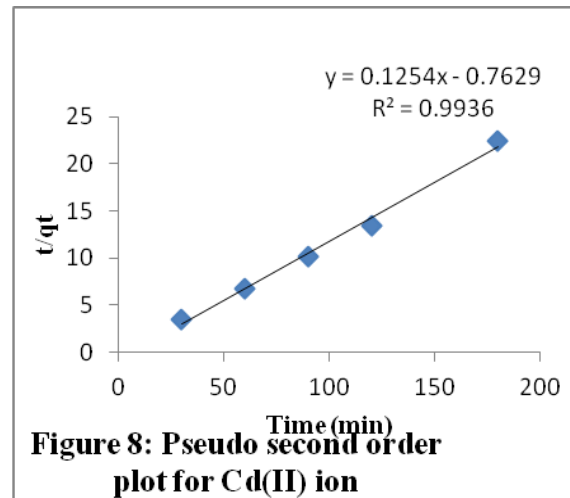


Figure 8: Pseudo second order plot for Cd(II) ion

The pseudo-second-order equation is given in equation 7 below:

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

Where q_t (mg g⁻¹) is the amount adsorbed at time t, q_e (mg g⁻¹) is the amount of ions adsorbed at

equilibrium, k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is the rate constant of pseudo-second-order (Ho and McKay, 1999).

The pseudo-second-order model constants are also given in Table 4. It is clear from the results that the adsorption of Cd^{2+} onto termite mound, follows well the pseudo-second-order kinetics. Figure 8, shows pseudo-second-order model plot for the kinetics of Cd^{2+} onto termite mound. The calculated q_e value obtained from the pseudo-second-order kinetics was close to the experimentally obtained q_e value thereby supporting the pseudo-second-order reaction kinetics. For Cd (II) ion, q_e calculated = 8.0mg/g, $q_{e\text{experimental}}$ = 8.901 mg/g. In general, when an adsorption process fits into the adsorption kinetics following the pseudo-second-order, then the reaction kinetics agrees with chemisorption process and the rate-limiting mechanism is through sharing or exchange of electrons between sorbent and sorbate. The low values of the rate constant k_2 , suggest that the adsorption rate decreased with the increase in time, and the adsorption rate was proportional to the number of unoccupied sites (Mohapatra *et al.*, 2009).

CONCLUSION

The removal of Cd (II) ion from aqueous solution was carried out in a batch adsorption mode using termite mound. The mineralogical detail of the adsorbent was reported using X-Ray fluorescence (XRF). The mineral composition and physiochemical properties suggest that termite mound is a promising adsorbent for Cd (II) ion removal. The adsorption process was found to be dependent on initial Cd^{2+} concentration and contact time. The rate of Cd^{2+} adsorption was rapid and attained equilibrium at 120 minutes. Isotherm analysis of the data showed that the adsorption process of Cd^{2+} onto termite mound, followed Langmuir model. Using the Langmuir model equation, the maximum capacity of termite mound was found to be 6.2 (mg/g). The pseudo-second-order reaction rate model, best described the kinetic data. It can be concluded that termite mound is a good adsorbent for the removal of Cd^{2+} from aqueous solution.

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