



Sequestration of cadmium ions onto mango (*Mangifera indica*) seed biomass: Kinetics and equilibrium studies

Chijioke John Ajaelu* and Modupe O. Dawodu

Department of Chemistry and Industrial Chemistry, Bowen University, Iwo Nigeria

ABSTRACT

This study presents the removal of Cd^{2+} by *Mangifera indica* seed biomass. The adsorption process was studied as a function of pH, adsorbent dosage and contact time. Sorption kinetic models such as the pseudo-first order, pseudo-second order and the intraparticle diffusion were used to test for the adsorption process. Results showed that the adsorption kinetics followed the pseudo-second order rate equation. The adsorption process also showed an intra-particle diffusion mechanism. Langmuir and Freundlich models were used to describe the adsorption of Cd^{2+} on *Mangifera indica* seed. Biosorption equilibrium was better described by the Freundlich than Langmuir model for Cd^{2+} . The monolayer biosorption capacities of *Mangifera indica* for Cd^{2+} was 833.3 mg/g. The present investigation showed that *Mangifera indica* seed may be utilized as a novel low cost and easily sourced biosorbent for Cd^{2+} removal.

Keywords: Cadmium, Equilibrium, Biosorption, Kinetics, *Mangifera indica*

INTRODUCTION

Rapid industrialization and population growth have increased the demand for water. Many water bodies are polluted by heavy metals. The major sources of water pollution by heavy metals are domestic, industrial and agricultural, as well as solid waste pollution, thermal and nuclear waste pollution. Heavy metals pose significant threat to the environment and public health because of their toxicity, accumulation in the food chain and persistence in nature [1]. Several chemical methods have been devised for the treatment and removal of heavy metals. The commonly used methods are phytoremediation, chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction [2,3,4]. However the disadvantages like incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require careful disposal have made these methods expensive for removing heavy metals from aqueous effluents [5]. The search for new techniques involving the removal of toxic metals from waste waters has directed attention to biosorption, based on metal binding capacities of various biological materials. Biosorption is considered to be a fast physico-chemical process. The biosorption process involves a solid phase (sorbent or biosorbent, biological material) and a liquid phase (solvent, normally water) containing dissolved species to be sorbed (sorbate, metal ions) due to higher affinity of biosorbent for the sorbate species. This resulted in the attraction and the binding of the later by different mechanisms [6].

Cadmium ($^{112,114}Cd_{48}$), a group IIB transition element is a non-essential and toxic element, without any metabolic significance. Cadmium has been classified as a group I human carcinogen by the International Agency for Research on Cancer [7, 8]. [9] worked on the adsorption of SO_2 pollutant on *Mangifera indica* bark.

The aim of this study is to use *Mangifera indica* seed as an inexpensive and effective biosorbent that is easily available in large quantities and feasible economically for heavy metal removal from solution. The influence of pH, biomass concentration and contact time was evaluated. Kinetic models such as pseudo-first order, pseudo-second order and intraparticle diffusion were used to describe the biosorption process. The equilibrium process was explained using Langmuir and Freundlich models. Thermodynamic parameters were also evaluated with respect to the adsorption process.

EXPERIMENTAL SECTION

2.1 Biomass preparation

Mangifera indica seed obtained from Iwo town was used as a biosorbent. The *Mangifera indica* was chopped into small length. It was then dried in an oven at 60°C and finally powdered in an electric grinder. The grinded powder was sieved to obtain fine particles of 1mm size. It was then stored in a clean plastic bag and used as the biosorbent without any further treatment.

2.2 Solution preparation

Salt of Cd(NO₃)₂.6H₂O (analytical reagent grade) was dissolved in double-distilled water to obtain a stock solution of 1000 mg/L. From this solution, aliquots were taken and made up to the mark in a 250 mL volumetric flask to give a final solution of 50 mg/L, 100mg/L, 150 mg/L, 200 mg/L and 250 mg/L of cadmium. The initial pH was adjusted with 0.1 M HCl and 0.1 M NaOH solutions using a pH meter (TOAV pH meter (HM30P)) calibrated with standard buffer solutions.

2.3 Biosorption experiments

Batch biosorption experiments were carried out to determine the effect of pH, adsorbent dosage on cadmium removal capacity of the *Mangifera indica*. The pH experiment was conducted by agitating 0.1 g of *Mangifera indica* with 100 mL of cadmium solution of initial concentration 50 mgL⁻¹ at different solution pH ranging from 2.0 to 7.0. The initial metal concentration (50-250 mg/L) and the biomass dose (100-500 mg) were carried out using a conical flask on an orbital shaker for 5 h at 30 ± 1 °C. The concentration of cadmium in the solution before and after adsorption was determined using Perkin-Elmer (Analyst 300) atomic absorption spectrophotometer.

2.4 Adsorption kinetics and equilibrium studies

Kinetic experiments were carried out in 250 mL conical flasks containing 100mL each of 50-250 mg/L of cadmium solutions to which 0.1 g of the biosorbent was added. All the experiments were performed at pH 4.0 for 5 h. Samples were collected from the flasks at predetermined time intervals for analyzing the residual concentration of Cd²⁺ in the solutions. The residual amount of Cd²⁺ in each flask was investigated using atomic absorption spectrophotometer. Similarly, the equilibrium experiments were conducted by adding to the 0.1 g of *Mangifera indica* 100 mL of cadmium solution (50-250 mg/L) at 30°C for 5 h. The concentrations of cadmium in the solution before and after sorption were determined using AAS. The amount of Cd²⁺ ions sorption at equilibrium, q_e (mg/g), were calculated according to the following mass balance equation for the metal ion concentration

$$q_e = \frac{C_o - C_e}{m} V \quad (1)$$

where q_e (mg/g) is the adsorption capacity at equilibrium, C_o and C_e are respectively initial and equilibrium concentrations (mg/L) of cadmium (II), m is the mass of adsorbent in grams and V is the volume of the solution in liters.

RESULTS AND DISCUSSION

3.1. Effect of pH

The pH of the aqueous solution is one of the key parameters which affects the biosorption of heavy metals. The effect of pH on the biosorption of cadmium is shown in Fig. 1. From pH 2-3 there was little effect on the adsorption. At pH 3 there was a sharp rise in adsorption up to pH 4. The biomass becomes saturated and reaches equilibrium beyond pH 4. Thus the optimum pH at which *Mangifera indica* adsorb Cd²⁺ was 4.

3.2 Effect of biomass dose

The study on the effect of the biomass dose (*Mangifera indica*) on the biosorption of Cd^{2+} was determined at $30 \pm 1^\circ\text{C}$ as shown in Fig. 2. Fig. 2 showed an initial increase in adsorption of Cd^{2+} with respect to the increase in the biomass dose up to 0.14 g. A transient equilibrium was reached from 0.14 g to 2 g after which there was a slight decrease in adsorption. At biomass dose $>0.3\text{g}$, adsorption increased gradually. The biomass dose was also studied with respect to different concentrations ranging from 50 mg/L to 250 mg/L. Fig. 2 showed that adsorption of Cd^{2+} increased with increase in the initial metal concentration. At 50 and 250 mg/L, the highest amount of Cd^{2+} removed by the varying mass of adsorbent was 41.61 mg/g and 214.1 mg/g respectively.

3.4 Effect of Contact Time

The time course for the adsorption of Cd^{2+} on *Mangifera indica* was carried out (Figure not shown). The amount of metal biosorbed increased with contact time before it reached a plateau which was an indication of equilibrium. In 1.0 h large amount of the Cd^{2+} has bound to the adsorbent. The initial high amount of metal ions biosorbed was attributed to the availability of binding sites on the adsorbent. The rate of biosorption slowed as it approached equilibrium. The adsorption of Cd^{2+} increased gradually for concentrations of 50, 100, 150, 200 and 250 mg/L before equilibrium was reached. At 50 mg/L the maximum amount of cadmium biosorbed was 51.12 mg/g while at 250 mg/L the amount was 274.5 mg/g.

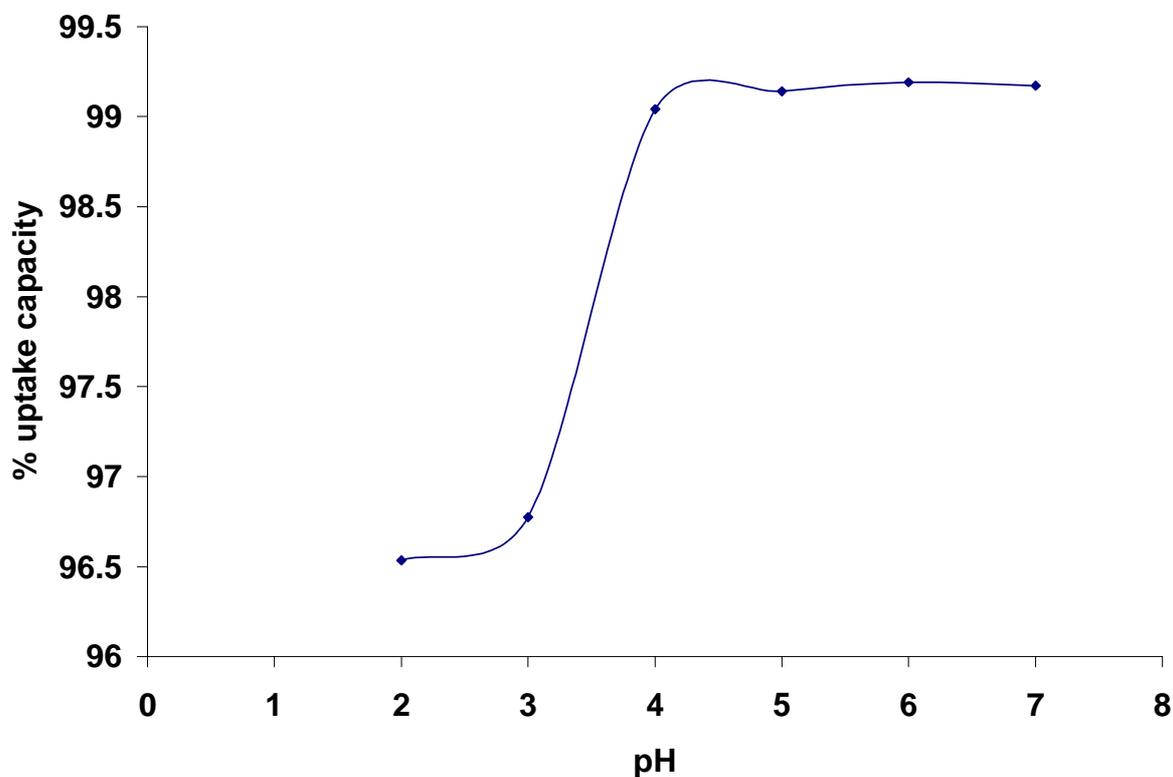


Fig.1. Effect of pH on the adsorption of Cd^{2+} on *Mangifera indica* seed at $30 \pm 1^\circ\text{C}$

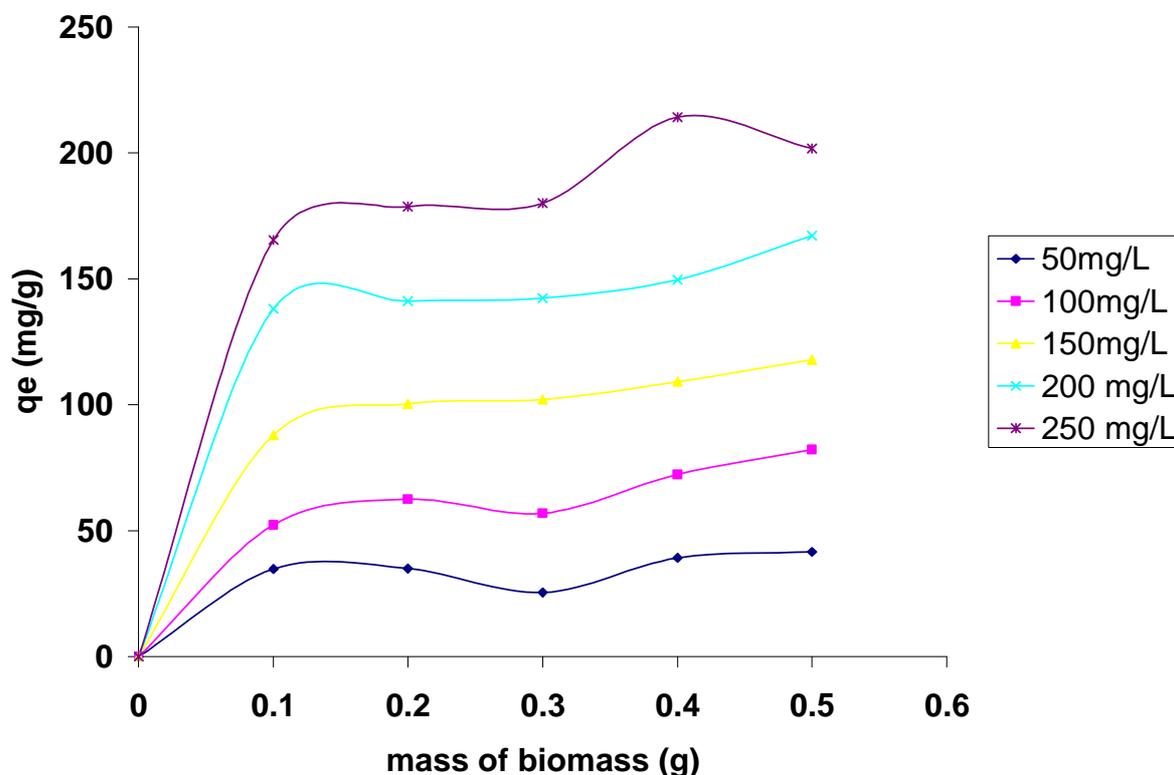


Fig. 2 Effect of biomass dose on the biosorption of Cadmium (II) ion on *Mangifera indica* seed. Experimental conditions: pH 4, temperature, $30 \pm 1^\circ\text{C}$

3.5 Kinetic modeling

In order to analyze the sorption kinetics of cadmium ions on *Mangifera indica*, the three kinetic models namely pseudo first order, pseudo second order and intra particle diffusion were applied to the data and the related parameters are shown in Table 1.

3.5.1 Langergren model

The linearized form of Langergren pseudo-first-order model is given by

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

Where q_e (mg/g) and q are the biosorption capacities of the biosorbent at equilibrium and at any time t , respectively; k_1 is the langergren rate constant of the first order biosorption (h^{-1}).

The plot of $\log(q_e - q)$ versus t (h) for different concentrations of cadmium gives straight lines. From the plot (not shown), k_1 and q_e are determined from the slope and intercept respectively as reflected in Table 1. From Table 1, $q_{(\text{calc})}$ is much lower than $q_{(\text{exp})}$. This indicates that the pseudo first order model is not suitable for describing the kinetics of adsorption of Cd^{2+} by *Mangifera indica* seed.

3.5.2 The pseudo second order model

The linearized form of the pseudo-second order chemisorptions of metal ions in solution is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where k_2 (g/mg h) is the pseudo second order rate constant. If second-order kinetics is applicable, the plot of t/q_t versus t should show a linear relationship. The values of q_e and k_2 can be determined from the slope and intercept of the plot. Table 1 also presents the rate parameters obtained from the straight line plots of t/q_t versus t for the pseudo-second-order model (Fig. 4). According to the values of the correlation factors, R^2 , in Table 1, the pseudo-second-order kinetic model showed satisfactory fits for Cd^{2+} . The experimental equilibrium sorption capacities, $q_{e(\text{exp})}$, obtained from the pseudo-second-order kinetic model were also in good agreement with the theoretical equilibrium sorption capacities ($q_{e(\text{calc})}$) at all concentrations studied for Cd^{2+} ions. Similar results were reported by [9]. These findings indicated that the pseudo-second-order kinetic model was more suitable to describe the Cd^{2+} ions biosorption onto *Mangifera indica* seed.

3.5.3 Intraparticle diffusion

The diffusion mechanism of adsorption cannot be explained by pseudo first order and second order kinetic models, hence the need to develop a more suitable model. Weber and Morris [10] developed a widely accepted kinetic-based model that represents the time dependent intra-particle diffusion of components and showed that the sorption process is diffusion controlled if the rate is dependent upon the rate at which adsorbate and adsorbent diffuse towards one another. The time dependent intraparticle diffusion equation is given by

$$q_t = K_p t^{0.5} + c \quad (4)$$

where q_t is the amount of metal ion adsorbed (mg/g) at time t (min) and K_p ($\text{mg g}^{-1} \text{min}^{-0.5}$) is the rate constant of intra-particle diffusion and c is the intercept which gives information about the thickness of the boundary layers i.e., boundary effect increases with increase in the intercept. *Mangifera indica* adsorption obeys intraparticle diffusion pattern as evident by straight line passing through the origin (Figure not shown) which also indicated an enhancement in the rate of adsorption. Initial portions of the linear segments also revealed that linear effect was due to external mass transfer and remaining linear portion was due to intraparticle diffusion; k_p values illustrated a better adsorption mechanism, which was related to an improved binding between the cadmium and the adsorbent particles [11, 12].

Table 1 Comparison of pseudo-first order, pseudo-second order and intra-particle diffusion (Weber-Morris) kinetic models for the sorption of cadmium (II) ions on *Mangifera indica* seed.

First order kinetics				Second order kinetics			Weber-Morris model
Initial conc. (mg/L)	$q_{e(\text{exp})}$ (mg/g)	K_1 (h^{-1})	$q_{e(\text{calc})}$ (mg/g)	R^2	K_2 (g(mgh)^{-1})	$q_{e(\text{calc})}$ (mg/g)	K_p
50	49.9	0.05	19.9	1.000	20.0	50.0	2.35
100	99.8	0.12	12.8	1.000	5.01	100.0	4.71
150	149.9	0.14	3.88	1.000	55.6	149.3	7.07
200	197.6	1.08	2.07	1.000	-	200.0	9.42
250	249.9	0.33	2.68	1.000	320.1	250.0	11.8

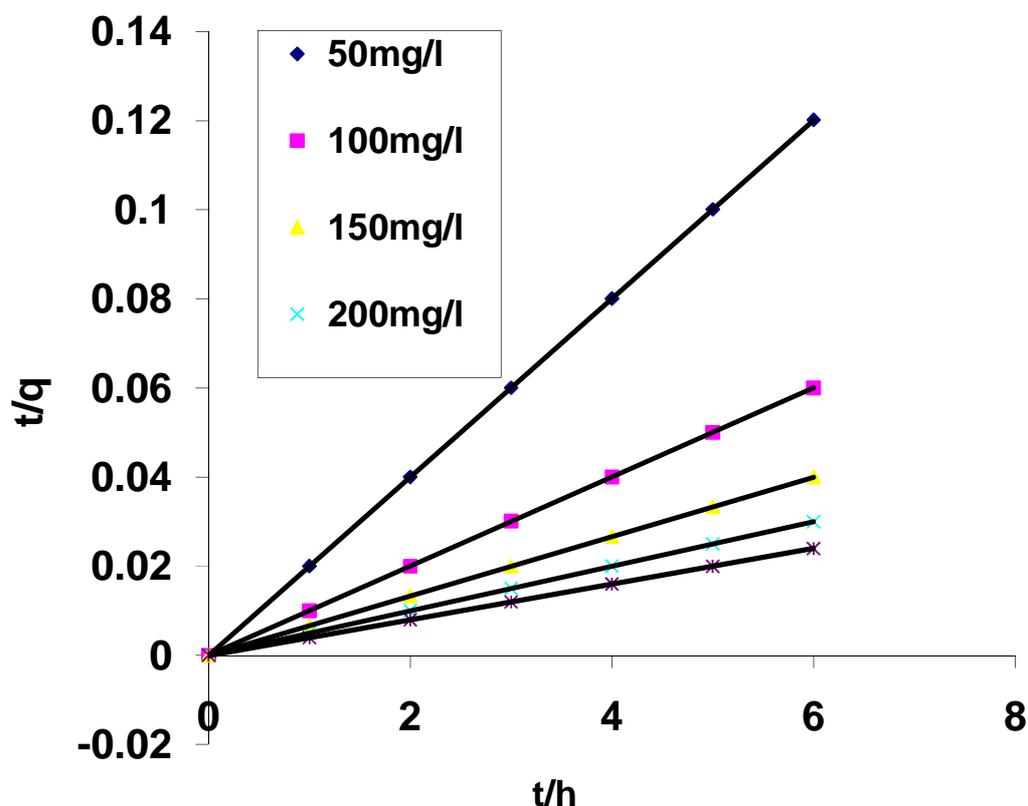


Fig.4 Pseudo-second-order kinetics for the biosorption of Cd²⁺ ions by *Mangifera indica* seed at 30 ± 1°C

3.6 Sorption isotherms

The sorption process was quantified from the equilibrium parameters obtained by fitting the experimental data to the two mathematical models usually employed in literature: Langmuir and Freundlich.

The Langmuir model assumes monolayer adsorption. The linear form of the Langmuir isotherm equation is given by the following:

$$\frac{C_e}{q_e} = \frac{1}{Q_o a} + \frac{C_e}{Q_o} \quad (5)$$

where q_e is the monolayer biosorption capacity of the biosorbent (mg/g); and a is the Langmuir constant (L/mol), and is related to the free energy of biosorption. A plot of C_e/q_e versus C_e for the biosorption of Cd²⁺ ions onto *Mangifera indica* (Fig. 5) showed a straight line of slope, $1/Q_o$, and intercept, $1/Q_o a$. The R^2 and Q_o values in Table 2 suggested that the Langmuir isotherm may be a suitable model and the maximum monolayer biosorption capacities was found to be 833.3 mg/g for Cd.

The essential characteristics of a separation factor, E_L , is defined by

$$E_L = \frac{1}{(1 + aC_o)} \quad (6)$$

In this expression C_o is the initial concentration of the adsorbent and the value obtained is related to the shape of the isotherm sorption [13], that can be unfavorable ($R_E > 1$), linear ($R_E = 1$), favorable ($0 < R_E < 1$) or irreversible ($R_E =$

0). Value of E_L was found to be 9.6×10^{-6} for Cd. This confirmed that *Mangifera indica* is favourable for the biosorption of Cd under conditions used in this study.

The Freundlich isotherms is an expression that deals with surface heterogeneity of adsorbent. The expression is given by

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

where q_e is the equilibrium metal concentration on the biomass (mg/g); C_e is the equilibrium metal concentration in the solution (mg/L); K_F (L/g) and n (dimensionless) are Freundlich isotherm constants that indicate the extent of the biosorption, and the degree of nonlinearity between solution concentration and biosorption, respectively. The Freundlich model plots for the biosorption of Cd^{2+} onto *Mangifera indica* biomass at 30°C is presented in Fig. 7. The numerical values of the Freundlich constant, n , for Cd^{2+} is 1.35. Since the values of n is greater than unity, it indicate that the metal is favorably biosorbed by *Mangifera indica* at the experimental temperature. Freundlich model fitted better for Cd ($R^2 = 0.97$) than for Langmuir model ($R^2 = 0.54$).

Table 2 Langmuir and Freundlich isotherm for cadmium (II) ion biosorption on *Mangifera indica* at $30 \pm 1^\circ\text{C}$

Langmuir				Freundlich		
R^2	$Q_0(\text{mg/g})$	$a(\text{L/mg})$	E_L	R^2	K_F	n
0.57	833.3	3.8×10^{-3}	9.6×10^{-6}	0.97	5.61	1.35

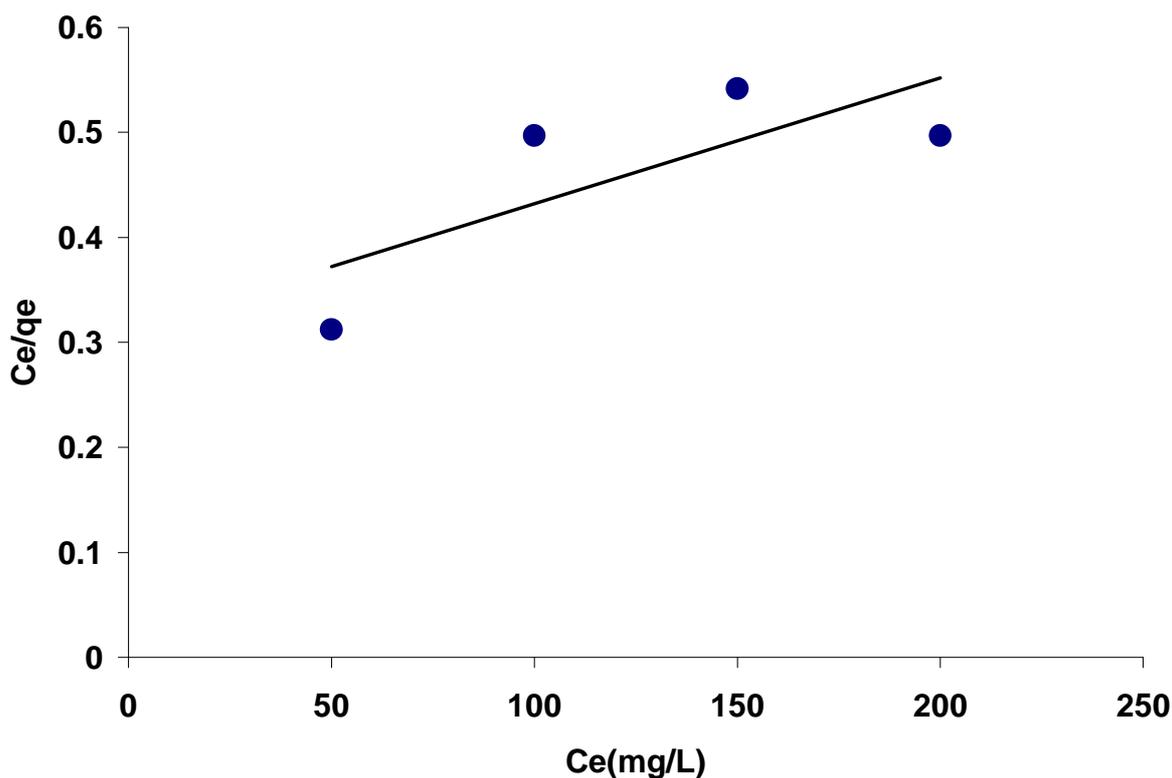


Fig. 5. Langmuir adsorption isotherm of cadmium (II) ion on *Mangifera indica* at $30 \pm 1^\circ\text{C}$

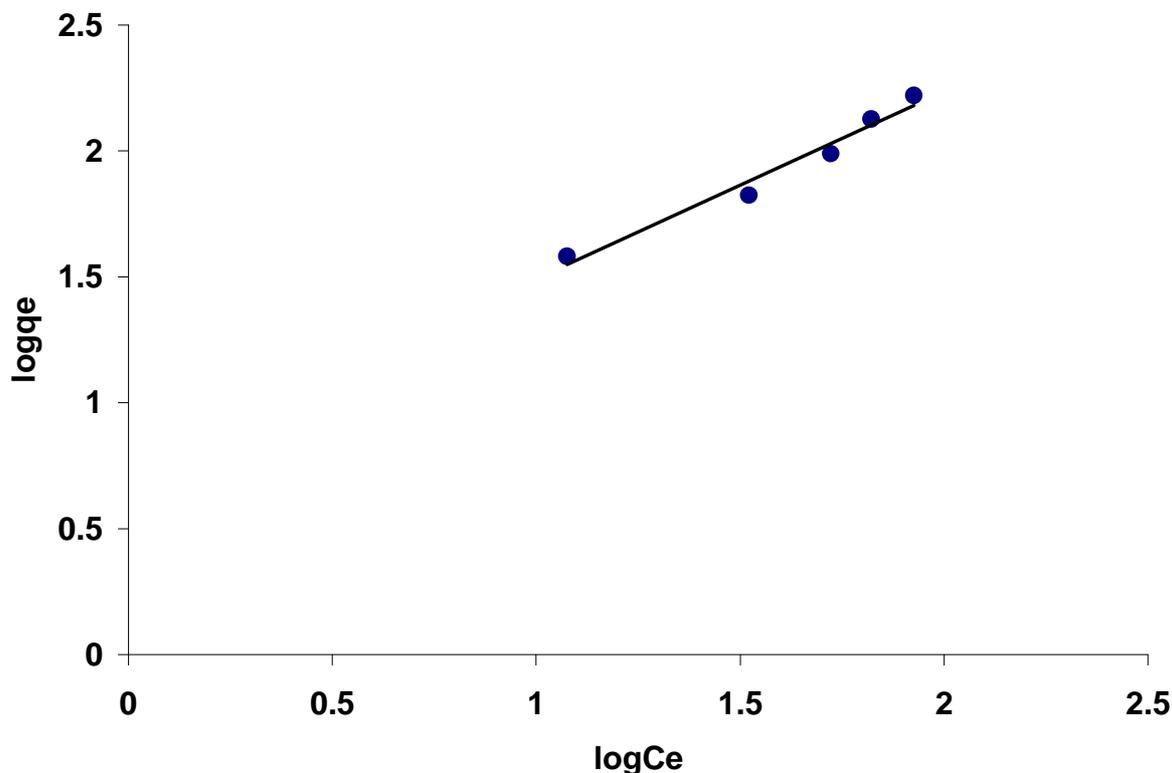


Fig. 6. Freundlich adsorption isotherm of cadmium (II) ions on *Mangifera indica* at $30 \pm 1^\circ\text{C}$

CONCLUSION

This study provided valuable information about the sorption behaviour of *Mangifera indica*. The pH, initial metal ion concentration, adsorbent dosage and contact time have effect on the extent of adsorption of Cd^{2+} ions on *Mangifera indica* seed. The maximum uptake of Cd^{2+} ions occurred at pH 4. Adsorption of Cd^{2+} increases with increase in the initial metal concentration. At 50 and 250 mg/L, the highest amount of Cd^{2+} removed by the varying mass of adsorbent were 41.61 mg/g and 214.1 mg/g respectively. The study also investigated the kinetics and the equilibrium of the uptake of Cd^{2+} on *Mangifera indica* seed. In 1.0 h a large amount of the Cd^{2+} has bound to the adsorbent. Pseudo –second order model best described the kinetics of the biosorption of Cd^{2+} ions. Biosorption equilibrium was better described by the Freundlich model than the Langmuir model. The maximum monolayer biosorption capacity of *Mangifera indica* for Cd^{2+} was 833.3 mg/g. *Mangifera indica* has proved from this study to be a low cost and easily sourced biosorbent for the removal of Cd^{2+} ions from industrial wastewater.

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