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Equilibrium, Thermodynamic and Kinetics Studies on the Adsorption of Lead (II) and Cadmium (II) from Aqueous Solution by Oil Palm Flower

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ABSTRACT: The feasibility of using oil palm flower as a low-cost absorbent for the removal of Pb(II) and Cd(II) from aqueous solution was studied. The % adsorption of the metal ions was found to be pH, initial metal concentration, contact time, adsorbent dose and temperature dependent. The optimum pH was found to be pH 5 for Pb(II) and pH 7 for Cd (II). About 97-100% removal of the metal ions was observed with an adsorbent dose range of 1-3g per 100ml of 50mg/L solution. The optimum temperature for the removal of both metal ions was found to be 40^{o}C. The values of ΔH^{o} and ΔG^{o} indicated that the adsorption of Pb(II) and Cd(II) onto oil palm flower was exothermic and spontaneous. The equilibrium adsorption data were better fitted to the Langmuir adsorption isotherm than the Freundlich. The maximum adsorption capacity q_{max} was 12.987mg/g for Pb(II) and 13.514mg/g for Cd(II). The rate of Pb(II) and Cd(II) adsorption onto oil palm flower followed the pseudo-second order kinetics. The result of the study showed that oil palm flower holds good potential as a low-cost adsorbent in the removal of heavy metals from aqueous solution.
KEY WORDS: Adsorbent, Adsorption kinetics, aqueous solution, metal ions**,** oil palm

1. INTRODUCTION

Rapid technological advancement, industrialization and urbanization as feature of modern societies have led to the release of heavy metals into the environment through activities such as mining, electroplating, tanning, metallurgical operations, manufacturing and the use of chemicals for agricultural purposes. The discharge of wastewater containing heavy metals from municipalities and communities has contributed to environmental and water bodies' pollution [1, 2].

The resultant effect is the accumulation of these metals in the soil and in the aquatic environment [3]. Plants, soil microorganism, aquatic organism and human being which ultimately depend on the plants and some aquatic organism are consequently affected. The metal bioaccumulation in living tissues via food chain at high concentrations can cause serious diseases and physiological disorders [2].

The contamination of an aquatic environment with heavy metals is a complex problem and their removal requires much attention. Different methods have been developed to remove heavy metals from industrial wastewater before discharge into water bodies, such methods are solvent extraction, membrane filtration, ion exchange, chemical precipitation, electrochemical deposition, chemical oxidation and reduction, reverse osmosis, dialysis carbon sorption, electrolysis and adsorption [4, 5]. The high energy, high cost and other drawbacks associated with the aforementioned techniques and processes have led to the search for low-cost techniques and locally available materials which can be efficient as the other techniques [6]. Adsorption has been found to be most successful due to its relative low maintenance cost high efficiency and ease of operation [7].

Therefore, the focus of recent researches has been on the use of the principle of adsorption and biomaterials as natural adsorbents for the removal of heavy metals from aqueous streams due to their availability and low-cost [8].

Thus, this study is aimed at utilizing oil palm flower as a low-cost adsorbent in the removal of lead and cadmium from aqueous solution. Experimental conditions such as pH, temperature, metal ion concentration, contact time and adsorbent dose were varied and the equilibrium data were examined using Langmuir and Freundlich isotherm models. The mechanism was investigated in terms of thermodynamics and kinetics.

2. MATERIALS AND METHODS

2.1 Absorbent and Adsorbate Preparation

The flower of oil palm (*Elaesis guineensis*) was collected from Rayfield in Jos, Plateau State. The strands of the flower were removed from the comb using a knife and washed thoroughly in hot deionized water. The washed flower strands were dried to a constant weight in an electric oven at 100.5^{0}C. The dried flower strands were ground using mortar and pestle and sieved to fine particles size of ≤ 0.5mm in diameter. The fine particles were then stored in an air-tight polythene bag and were subsequently used as adsorbent in adsorption tests.

The absorbate Pb(II) and Cd(II) ions were prepared by separately dissolving appropriate quantity of analytical grade of $Pb(NO_3)_2$ and $CdCl_2$ in deionized water in order to obtain 1000mg/L stock solutions of the metal ions. Several standard solutions of concentrations 20,30,40,50 and 60mg/L were prepared from the stock solutions. The pH of each solution was adjusted to the required value by dropwise addition of 0.1M NaOH or 0.1M HNO_3 using a pH meter. Freshly prepared solution was used for each experiment.

2.2 Biosorption Experiment

The effect of pH, initial metal ion concentration, contact time and temperature on the adsorption of Pb(II) and Cd(II) on oil palm flower were studied using batch technique at temperature of 25±2^{o}C. This was done at pH 1, 3, 5, 7 and 9, initial concentration 20-60mg/L, contact time 30-150min, adsorbent dose 1.00g-3.00g and temperature 30^{0}C-70^{0}C. The experiment was performed by contacting 0.5g of the adsorbent with 100ml of a given concentration of Pb(II) and Cd(II) in a thermostatic water bath for temperature control.

For a particular study, a parameter was varied while the others were kept constant. At the end of the contact time, the solution was filtered and filtrate was analyzed for the concentration of Pb(II) and Cd(II) ions remaining in solution using AAS. Each experiment was done in duplicate and the mean value was calculated to ensure quality assurance. The amount of Pb(II) and Cd(II) absorbed by the oil palm flower was calculated from a mass balance equation as given in (1):

$$q_e = \frac{C_o - C_e}{M} \times V \qquad (1)$$

The percentage adsorbed by the oil palm flower was calculated from

$$\%R = \frac{C_o - C_e}{C_o} \times 100 \qquad (2)$$

Where q_e (mg/g) is the equilibrium adsorption capacity, C_o (mg/L) is the initial Pb(II) and Cd(II) ion concentration in solution, C_e (mg/g) is the concentration of Pb(II) and Cd(II) in solution remaining after adsorption, M (mg) is the mass of oil palm flower used and V (litres) is the volume of solution

3. RESULTS AND DISCUSSION

3.1 Effect of Contact Time

The influence of time is an important factor to be considered on the adsorption of metal ions by an adsorbent. The adsorption of Pb (II) and Cd(II) on oil palm flower as a function of time is shown in Fig 1. It can be seen that adsorption by both ions increased with increase in contact time from 30-120 minutes and decreased afterwards. With increase in time from 30-120 minutes, the adsorption of Pb(II) increased gradually from 98.65-99.38% and decreased with further increase in time. The rate of adsorption decreased as the process tended to approach equilibrium at 120minutes. In the case of Cd (II), adsorption increased from 96.24-98.31% as the contact time increased from 30minutes to equilibrium time of 120minutes. Further increase in contact time led to decrease in the adsorption of Cd(II).

The decrease in the amount of metal ions removed after equilibrium time could be due to desorption of the metal ions from the surface of the adsorbent into the solution. At equilibrium time, the surface of the adsorbent is already saturated with the ions and further agitation led to removal of some of the ions from the adsorption sites [3, 9].

3.2 Effect of Initial Metal Concentration

The adsorption of metal ions by an adsorbent is strongly dependent on the initial concentration of metal ions in solution. This makes it an important parameter to be determined in adsorption studies. The results of the effect of initial Pb(II) and Cd(II) concentrations on their adsorption by oil palm flower is shown in Fig 2. At an initial concentration of 20mg/L, the adsorption of Pb^{2+} by oil palm

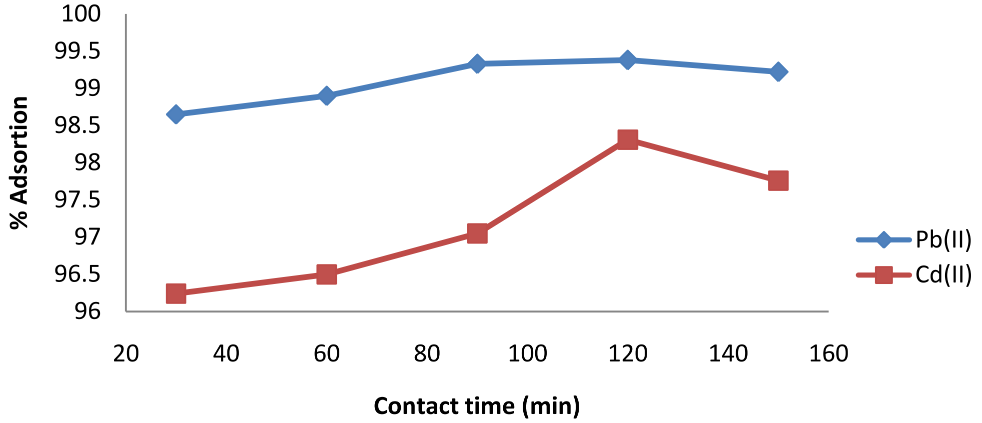

Fig 1. Effect of contact time on adsorption of Pb(II) and Cd(II) onto oil palm flower (Mass = 0.5g, conc. = 50mg/L, volume = 100ml)

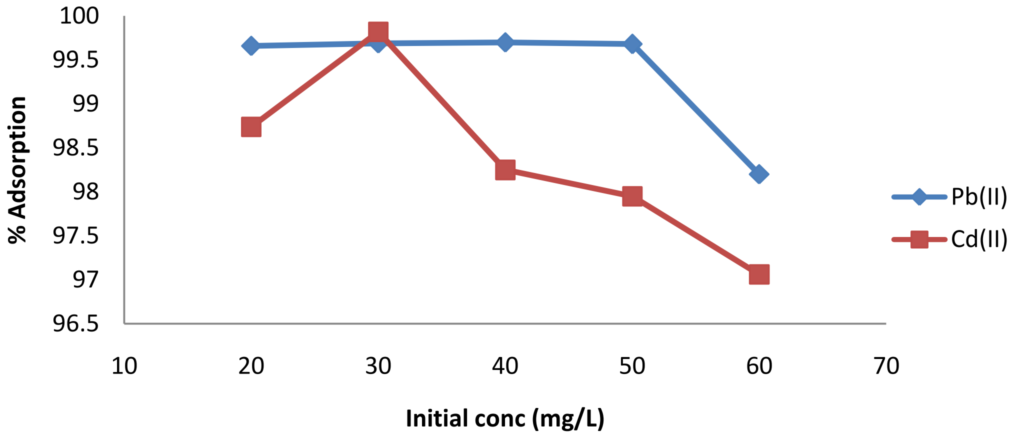

Fig 2. Effect of initial concentration on adsorption of P(II) and Cd(II) onto oil palm flower (Mass = 0.5g, volume = 100ml, time = 120min)

flower was up to 99.66%. Percentage adsorption increased to 99.70% as the initial concentration increased up to 40mg/L. Further increase in initial concentration led to decrease in the percentage adsorption. In the case of Cd^{2+}, the percentage adsorption was 98.74% at an initial concentration of 20mg/L. The percentage adsorption increased sharply to an optimum of 99.82% with increase in initial concentration to 30mg/L and gradually decreased afterwards. This is similar to the findings of [10]. However, the amount in mg/g of metal ions removed was found to increase with increase in initial metal ion concentration. This observation has been reported by [7] and [11].
The initial increase in the adsorption of the metal ions is plausibly due to the large number of vacant sites available on the adsorbent. As the concentration of metal ions increased, the number of vacant sites reduced, leading to decrease in the ratio of number of adsorbed ions to the initial number of ions, $(C_o\text{-}C_e)/C_o$, hence the reduction in the percentage of ions removed.

3.3 Effect of pH

The initial pH of a solution is a very significant factor in the adsorption of heavy metals as it has a major effect on the protonation and deprotonation of the active sites and functional groups of an adsorbent. The effect of pH on the adsorption Pb(II) and Cd(II) by oil palm flower is shown in Fig 3. There was an initial sharp increase in the adsorption of Pb(II) from 75.37%-99.33%, as the pH increased from 1-5. Further increase beyond pH 5 led to decrease in adsorption of Pb(II). However, the adsorption of Cd(II) increased gradually as the pH increased from 1-7. Further increase in pH beyond 7 led to decrease in adsorption of Cd(II).

These observations agree with observations of [7, 12, 13]. The initial rise in the amount of metal ions adsorbed as the pH of solution increased could be due to the reduction in the number of hydrogen ions (H^+). At highly acidic pH, there are many

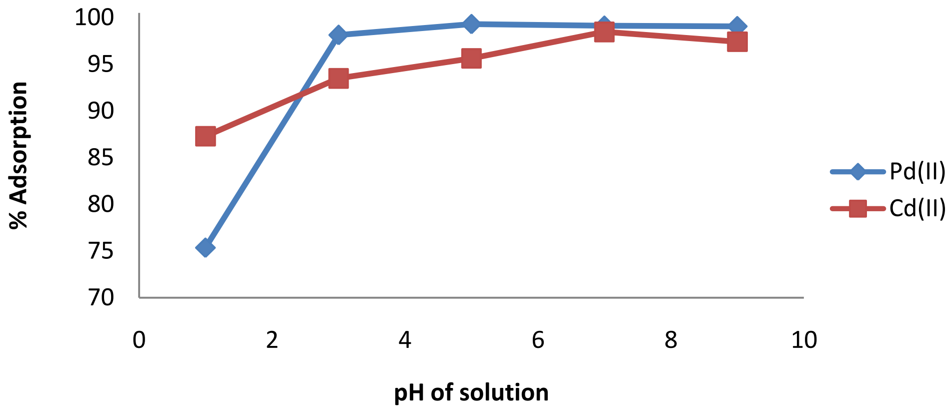

Fig 3. Effect of pH on adsorption of Pb(II) and Cd(II) onto oil palm flower (Mass = 0.5g, conc. = 50mg/L, volume = 100ml, time =120min)

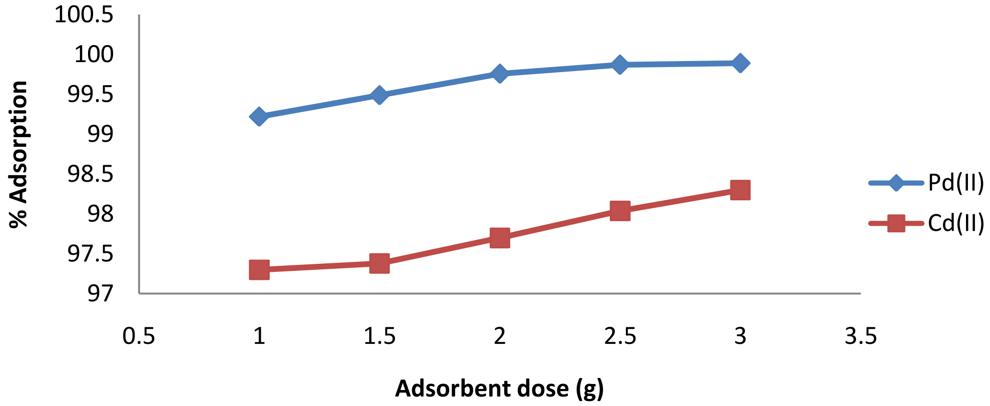

Fig 4. Effect of adsorbent dose on adsorption of Pb(II) and Cd(II) onto oil palm flower (Conc. = 50mg/L, volume = 100ml, time = 120min)

hydrogen ions competing with the metal ions for the available vacant sites on the adsorbent.

3.4 Effect of Adsorbent Dose

Adsorbent dose is another important parameter in adsorption studies because it determines the capacity of an adsorbent for a given initial concentration of the metal ion at the operating condition [14]. The variation in the adsorption of Pb(II) and Cd(II) with adsorbent dose is shown in Fig 4. It is observed that the adsorption of lead and cadmium ions increased with increase in the adsorbent dose. With increase in the mass of adsorbent from 1.0g-3.0g the percentage adsorption increase from 99.22%-99.89% and 97.30%-98.23% for Pb(II) and Cd(II) respectively. This increase in adsorption with increase adsorbent dosage may be due to increase in the number of available adsorption sites. This is similar to results obtained by [4, 15, 16].

3.5 Effect of Solution Temperature

The result on the effect of temperature of solution on the adsorption of Pb(II) and Cd(II) ions by oil palm flower is presented in Fig 5. An increase in adsorption with increase in temperature from 30^0C-40^0C was observed for both Pb(II) and Cd(II). However, further increase in temperature led to decrease in adsorption. Similar observations have been reported by [17, 18]. This decrease in adsorption at higher temperatures may be due to an exothermic adsorption process. It also suggests that the mechanism involve in the removal of the Pb(II) and Cd(II) ions by the oil palm flower is chemisorption. It is restricted to just one layer of molecules on the surface but may be followed by an additional layer of physically adsorbed metal ions [19, 20].

A good literature search has revealed different types of results on the effects of temperature on the adsorption of heavy metals. A decrease in adsorption potential with increase in temperature has been observed [21]. Temperature-independent effect on adsorption has also been recorded [22].

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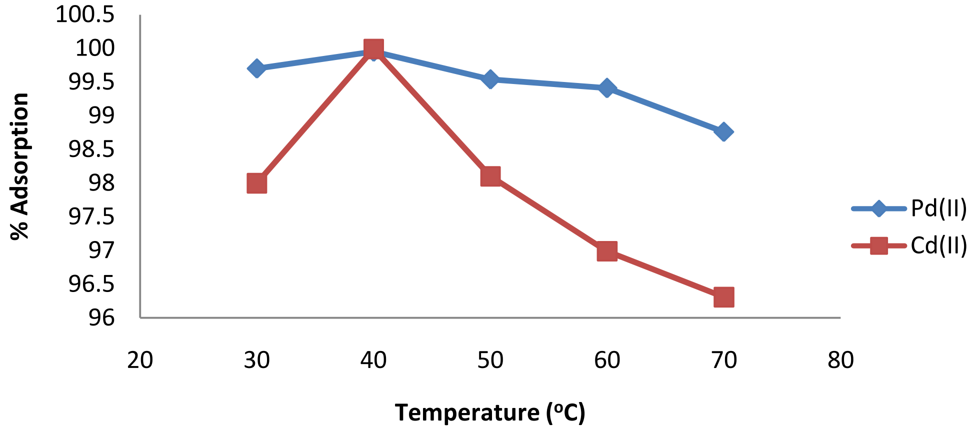

Fig 5. Effect of temperature on adsorption of Pb(II) and Cd(II) onto oil palm flower (Mass = 0.5g, conc. = 50mg/L, volume = 100ml, time = 120min)

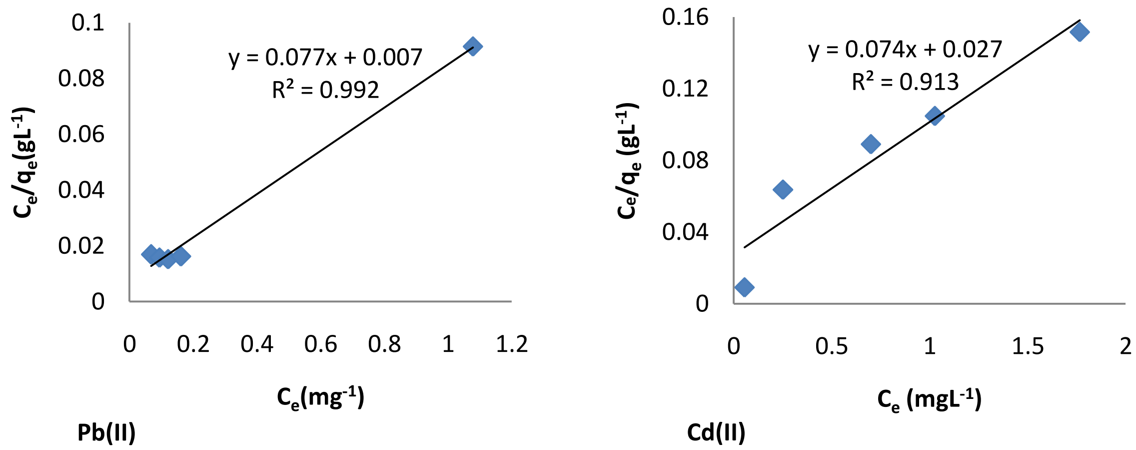

Fig 6. Langmuir Isotherms for adsorption of Pb(II) and Cd(II) on oil palm flower (Mass = 0.5g, conc.= 50mg/L, volume = 100ml, time = 120min)

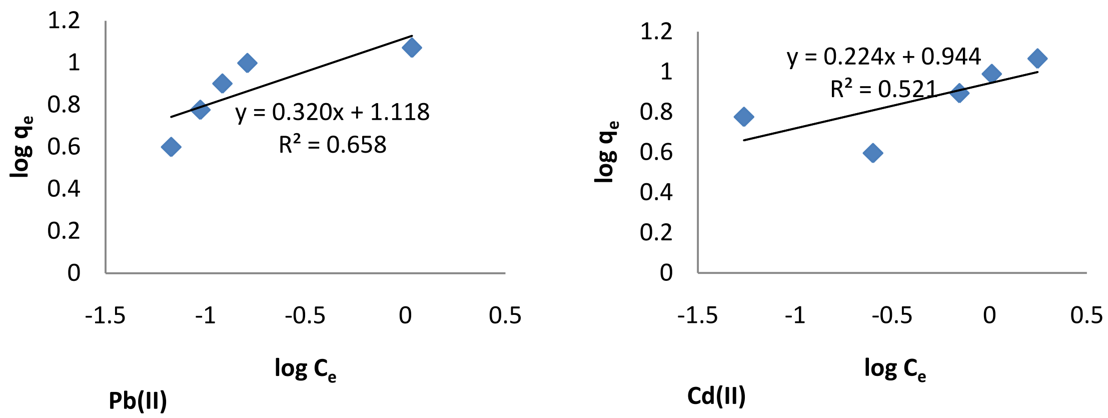

Fig 7: Freundlich isotherms for adsorption of Pb(II) and Cd(II) on oil palm flower (Mass = 0.5g, conc. = 50mg/L, volume = 100ml, time = 120min)

3.6 Equilibrium Modeling

Equilibrium adsorption isotherms help to provide important information on the adsorption mechanism, the surface properties and affinities of the adsorbent. The equilibrium of adsorption process is often described by fitting the experimental points with models which are used to represent the equilibrium adsorption isotherm. The simplest forms of these isotherms are Langmuir and Freundlich isotherms.

3.6.1 Langmuir isotherm model

The Langmuir isotherm essentially describes monolayer adsorption on a uniform surface with a finite number of adsorption sites [23]. Its advantage depends on the availability of interpretable parameters. Langmuir isotherm is represented by the expression:

$$\frac{q_e}{q_{max}} = \frac{K_L C_e}{1 + K_L C_e} \qquad (3)$$

where, C_e is the equilibrium solute concentration in the fluid (mg/L); K_L represents Langmuir equilibrium adsorption constant (L/mg); q_{max} is the maximum metal uptake in (mg/g).
The linearized form of the equation is:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}} C_e \qquad (4)$$

The linear plot of C_e/q_e against C_e in Fig 6 has $1/q_{max}$ as slope and $1/K_L q_{max}$ as intercept.
The values of linear correlation coefficients R^2 and Langmuir parameters are given in Table 1. These results indicate that the adsorption of the metal ions onto oil palm flower fitted well with the Langmuir model. The maximum adsorption capacity (q_{max}) was found to be 12.987mg/g and 13.514mg/g for Pb(II) and Cd(II) respectively.

3.6.2 Freundlich isotherm model

Freundlich isotherm model applies to adsorption on heterogeneous surfaces with interaction between adsorbed molecules [24]. It is an empirical equation used to estimate the adsorption intensity of adsorbent towards the adsorbate and is given by the equation:

$$q_e = K_F {C_e}^{1/n} \qquad (5)$$

Where q_e is metal uptake (mg/g); C_e is the equilibrium solute concentration in the fluid (mg/L); n represents Freundlich constant (dimensionless) related to adsorption intensity; K_F is Freundlich adsorption constant related to adsorption capacity.
On Linearizing, the equation becomes:

$$log q_e = log K_F + \frac{1}{n} log C_e \qquad (6)$$

The linear plot of log q_e against log C_e in Fig 7 has 1/n as slope and Log K_F as intercept.
The corresponding constants and coefficients of correlation, R^2, associated with Langmuir and Freundlich adsorption isotherms at 25±2°C for the adsorption of Pb(II) and Cd(II) ions by oil palm flower are presented in Table 1.

The values of R^2 which are much higher and closer to 1 for both Pb(II) and Cd(II) in the Langmuir isotherm than in the Freundlich isotherm shows that Langmuir isotherm is more fitted to the adsorption of the metal ions by oil palm flower.

Table 1: Langmuir and Freundlich isotherm constants for adsorption of Pb(II) and Cd(II) onto oil palm flower.

Metal ion	Langmuir Isotherm			Freundlich Isotherm			
	q_{max} (mg/g)	K_L	R^2	K_F (mg/g)	1/n	n	R^2
Pb(II)	12.987	11.000	0.992	13.122	0.320	3.125	0.658
Cb(II)	13.514	2.741	0.913	8.790	0.224	4.464	0.521

Table 2: Thermodynamic parameters for adsorption of Pb(II) and Cd(II) onto oil palm flower

Metal ion	ΔG°(kJ/mol)		ΔS°(kJ/mol)	ΔH°(kJ/mol)
	303K	343K		
Pb(II)	-14.848	-13.128	-0.043	-27.877
Cd(II)	-9.999	-9.519	-0.012	-13.635

3.7 Thermodynamics Studies

The thermodynamics parameters for the adsorption of Pb (II) and Cd (II) by oil palm flower were determined from the data obtained from the effect of temperature. The thermodynamics parameters include changes in Gibbs free energy, ΔG°, enthalpy change, ΔH° and entropy change, ΔS°. These parameters were determined using

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (7)$$

$$\Delta G^o = -RTlnK_c \quad (8)$$

$$lnK_c = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} \quad (9)$$

where K_c is the ratio C_s/C_e, C_s(mg/g) is the solid phase concentration at equilibrium, C_e(mg/L) is the equilibrium concentration in solution, T(K) is temperature and R ($8.314 JK^{-1}mol^{-1}$) is gas constant.

The values of ΔH° and ΔS° are calculated from the slope and intercept of the linear plots of lnK_c versus 1/T from which the slope and intercept are equal to -ΔH°/R and ΔS°/R respectively. Values of the thermodynamic parameters ΔH°, ΔG° and ΔS° are given in Table 2. The negative value of ΔG° obtained at all temperatures showed that the adsorption process was feasible and spontaneous and the degree of spontaneity decreased with increasing temperature. The negative values of ΔH° and ΔS° confirmed the exothermic nature of adsorption and decreased randomness at the solid/solute interface during the adsorption of lead and cadmium ions.

3.8 Kinetics Studies

In order to evaluate the kinetics of the adsorption process, the data from the experiment on contact time were fitted into the pseudo-first order and pseudo-second order models. Kinetics of adsorption of heavy metals from wastewater has been studied using mostly pseudo-first order [25] and pseudo-second order [26] models.

3.8.1 Pseudo-First Order Model

The rate law is given by

$$\frac{dq_t}{d_t} = K_1(q_e - q_t) \quad (10)$$

where q_e and q_t represent adsorption in mg/g at equilibrium and time t, respectively. Integrating this equation between the boundary conditions t=0, t=t and q_t=0, q_t=q_e gives the linearized form:

$$\log(q_e - q_t) = logq_e - \frac{k_1}{2.303}t \quad (11)$$

where K_1 is the rate constant of pseudo-first order adsorption, q_e is the metal uptake in mg/g at equilibrium and

q_t is the metal uptake in mg/g at time t. The values of K_1 and q_e were respectively obtained from the slope and intercept of the plot of log (q_e-q_t) against t in Fig 8.

3.8.2 Pseudo-Second Order Model

The rate law is given below:

$$\frac{dq_t}{d_t} = K_2(q_e - q_t)^2 \qquad (12)$$

where K_2, is the rate constant of pseudo-second order adsorption. Integrating between the boundary conditions t=0, t=t and q_t=0, q_t= q_e, the equation becomes

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + K_2 t \qquad (13)$$

This can be rearranged to give

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t \qquad (14)$$

A plot of t/q_t against t shown in Fig. 9 gives 1/q_e as slope and 1/$K_2{q_e}^2$ as intercept from which K_2 and q_e are calculated.

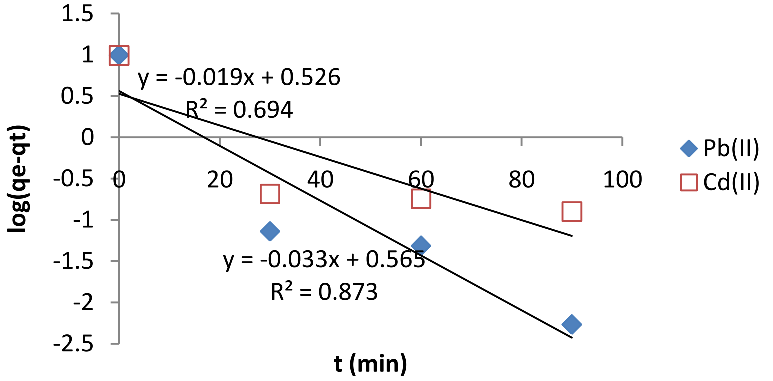

Fig 8. Pseudo-first order kinetics for Pb(II) and Cd(II) adsorption on oil palm flower (Mass = 0.5g, conc. = 50mg/L, volume = 100ml)

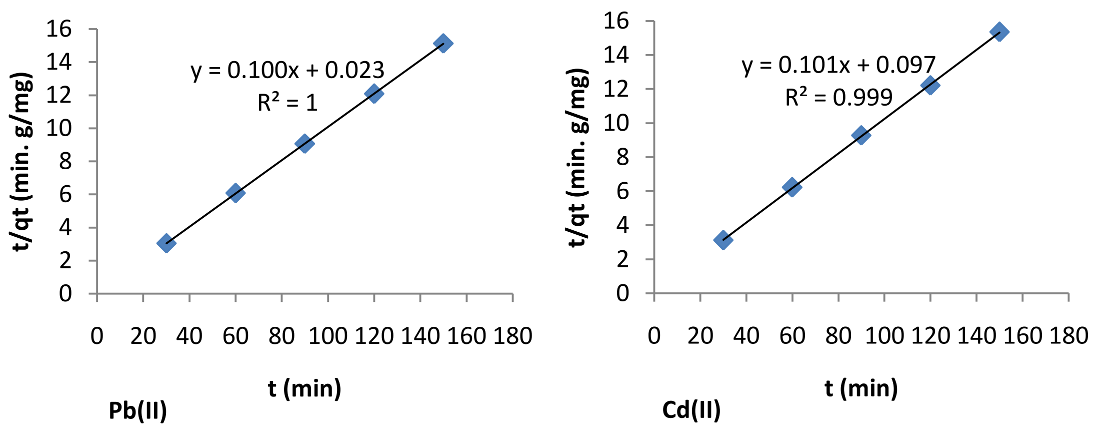

Fig 9: Pseudo-second order kinetics for Pb(II) and Cd(II) adsorption onto oil palm flower (Mass = 0.5g, conc = 50ppm volume = 100ml)

Table 3: Kinetics constants for adsorption of Pb(II) and Cd(II) onto oil palm flower

Metal ion	q_e(exp) (mg/g)	Pseudo-first order			Pseudo-second order		
		k_1(min^{-1})	R^2	q_e(cal) (mg/g)	K_2(min^{-1})	R^2	q_e(cal) (mg/g)
Pb(II)	9.9380	0.0760	0.873	3.6728	0.4348	1	10.000
Cd(II)	9.8306	0.0438	0.694	3.3574	0.0108	0.999	9.901

The pseudo-first and pseudo second-order kinetics models are tested for suitability using their linear correlation coefficient, R^2 (Ho and Mckay, 2000). The values of q_e and the constants K_1 and K_2 obtained for both models are presented in Table 3.

The values of the linear correlation coefficients for Pb^{2+} and Cd^{2+} which were 1 and 0.999 respectively in the pseudo-second kinetics model were indications of very good fit. Also, for both metal ions, the difference between the q(cal) values and the q(exp) values were very small. The reverse is the case in the pseudo-first order kinetics. These showed that the adsorption process for both metal ions was better fitted to the pseudo-second order kinetics model.

4. CONCLUSION

The results of this study showed that the removal of lead and cadmium ions from aqueous solution by oil palm flower is dependent on pH of solution, initial concentration of the metal ions, contact time, adsorbent dose and temperature of the solution. An appreciable removal of the metal ions from aqueous solution was observed with a minimal mass of the adsorbent. Thermodynamic parameters indicated that the adsorption of Pb(II) and Cd(II) onto oil palm flower was exothermic and spontaneous. The equilibrium adsorption data were better fitted to the Langmuir adsorption isotherm than the Freundlich. The kinetics of Pb(II) and Cd(II) adsorption onto oil palm flower was well described by pseudo-second order rate equation. The result of this research shows that oil palm flower holds good potential for use as a low cost adsorbent in removal of heavy metals from aqueous solution.

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