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Performance of Plantain Pseudo Stem for Pb^{+2} Adsorption in Aqueous Solution

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ABSTRACT

Plantain pseudo stem is practically considered as waste material, but could be useful as adsorbent. Therefore, this study investigated the performance of plantain pseudo stem (PPS) for the adsorption of lead (II) ion (Pb^{2+}) from aqueous solution. The performance of PPS was studied at different initial concentrations of Pb^{2+} in solution, contact time and temperature. Further, the Langmuir and Freundlich isotherms were applied to study the adsorption of Pb^{2+} in solution, while the Pseudo first and second order kinetics were used to determine the mechanism of the adsorption process. It was shown that the concentration of Pb^{2+} ion in solution affects the performance of PPS particles as the percentage of Pb^{2+} ion adsorbed onto PPS particles decreased with increase in concentration of Pb^{2+} in the solution. The adsorption reached equilibrium at about 60 minutes, and the percentage of Pb^{2+} adsorbed at equilibrium was 85.89, 90.97 and 97.81% with 10mg/L initial Pb^{2+} concentration in solution, but decreased to 47.83, 49.89 and 52.31% with 50mg/L initial Pb^{2+} concentration at 28.8ºC, 40ºC and 50ºC respectively. Also, the percentage Pb^{2+} ion increased with contact time and temperature. Thus, the percentage of Pb^{2+} ion adsorbed within 30 minutes was 54.25, 59.03 and 76.42%, but increased to 87.58, 90.96 and 98.79% after 150 minutes at 28.8ºC, 40ºC and 50ºC respectively. The maximum adsorption capacity Q_e obtained with Langmuir isotherm was 6.6534mg/g, 6.6979mg/g and 6.7568mg/g at 28.8ºC, 40ºC and 50ºC, while the maximum adsorption capacity K_F in Freundlich isotherm was 1.9975mg/g, 3.4137mg/g and 2.4784mg/g at same temperatures. However, the Langmuir isotherm explained the adsorption process better than Freundlich isotherm. Also, the adsorption mechanism is both diffusion and chemisorption. The pseudo second order explained the adsorption kinetics better, and it is therefore the rate controlling step. The thermodynamic analysis revealed that adsorption of Pb^{2+} ion onto PPS is an endothermic process. Conclusively, the performance of PPS in adsorption of Pb^{2+} from aqueous solution showed it can be useful as adsorbent.

Key words: Plantain Pseudo Stem, Lead Ion, Adsorption Isotherm, Kinetics, Thermodynamics

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INTRODUCTION

Water, whether surface or groundwater, is a useful resources to man and its environment. In the industry and homes, water is used in many purposes. Unfortunately, most sources of water have been polluted due to human activities, which pose diverse of health challenges. One of such water pollutants is heavy metals. Heavy metals are useful materials to the construction and other industries, but can be potential cause of most diseases to humans if present above a certain limit. Thus, accumulation of heavy metals in human body can cause severe health disorder [1]. Therefore, it is imperative to remove any impurity present before consumption.

This study focused on lead ion (Pb^{2+}) as one of the heavy metals that is toxic to human body, which is often consumed through water. Children between 0 and 6 years, as well as pregnant women are most susceptible to health effects of lead. High concentration of lead in the body up to 0.01mg/l, can cause central and peripheral nervous systems disorder, cancer, interference with vitamin D metabolism, mental development in infants and behavioural effects [2,3].

Several studies have been devoted on finding alternative treatment for water contaminants that is environmentally friendly, yet cost effective [4]. Notable techniques employed for the removal of heavy metals from aqueous solution include, membrane technology, ion exchange, adsorption amongst others [5]. Among the methods, adsorption has been

reported to be one of the effective techniques for heavy metal removal due to high surface area to volume ratio, high efficiency and the use of wide range of adsorbents [5,6]. Varieties of plants and animal sources investigated in previous studies showed high removal efficiency of metallic ions in aqueous solution [7,8,9]. The use of plants or animal particles for adsorption of heavy metals is advantageous on the fact that it is locally available, eco-friendly and cost effective [10,11].

In this paper, the pseudo stem of plantain is used as adsorbent. Plantain pseudo stem is practically considered as waste material, and almost every household own a piece of land for growing of plantain. This over the years has become a concern on how to reduce and converting the waste to useful material. It is on this premise we investigated the efficacy of plantain pseudo stem for adsorption lead ion in aqueous solution. Additionally, the Langmuir and Freundlich adsorption isotherm models were applied in the study. Also, adsorption kinetics and thermodynamics for adsorption of Pb^{2+} from water were investigated.

MATERIALS AND METHODS

Sample Collection and preparation

The plantain pseudo stem (PPS) was collected from local plantation in Enito II community, Ahoada-West Local Government Area of Rivers State, Nigeria. The adsorbents were prepared according to the method described by Sharma *et al*. [12]. The plantain pseudo stems were first washed with distilled water to remove soil particles and other debris. Upon washing, they were sun-dried for about 48 hours and then, further dried with oven at temperature of 70-100°C for another 4 hours to dispel moisture content. The dried stems were crushed to fine powdered particles and sieved through 0.2mm mesh size. The sieved particles were soaked in 0.1N NaOH for about 10 hours, washed again with distilled water to remove lignin and then dried. Upon drying, the particles were further soaked into 0.1N H_2SO_4 for another 9 hours and washed with distilled water to remove traces of alkalinity. The washed stems were sun-dried and stored in desiccator.

Adsorbent experiment

$Pb(NO_3)_2$ was purchased from a chemical retail shop at City of Port Harcourt, Rivers State, Nigeria. Other chemical reagents were used without further purification. The adsorption of Pb^{2+} ion onto PPS particles was studied in a batch system. 1000 mg/L of $Pb(NO_3)_2$ was dissolving in distilled water, and the respective concentrations of Pb^{2+} ion (10 – 50mg/L) were obtained by slowly diluting the prepared solution to the desired concentrations. In order to minimize error, the adsorption Pb^{2+} ion onto PPS particles was performed at pH 5.5.

0.1g of the treated PPS particles was weighed into a test tube used as reactor and 25ml of distilled water was added into it, followed by the respective initial concentrations of the Pb^{2+} ion at separate times at room temperature of 28.8ºC. The solution in the reactor was stirred vigorously and allowed to settle for about 60 minutes. Upon attaining equilibrium, the solution was filtered through filter paper. The obtained filtrate was then analysed using Atomic Absorption Spectrophotometer to determine the equilibrium concentration. The steps were repeated when the solution was heat and maintained at temperatures of 40ºC and 50ºC respectively.

For effect of contact time, the adsorption of Pb^{2+} ion onto PPS particles was studied at 0.1g weight of adsorbent and initial concentration of 10mg/L Pb^{2+} ion at the respective temperatures. The total contact time was 150 minutes, but at every 30 minute intervals, sample was collected, filtered through filter paper, and the filtrate analysed as in above.

The percentage of Pb^{2+} ion adsorbed by the PPS particles was calculated using the expression:

$$Pb^{2+}\text{ ion adsorbed}(\%) = \frac{C_i - C_f}{C_i} \times 100\% \quad (1)$$

The adsorption capacity at equilibrium was calculated using the expression:

$$Q_e = (C_i - C_e)\frac{V}{w} \quad (2)$$

Also, the adsorption capacity at any time was calculated using the expression:

$$Q_t = (C_i - C_t)\frac{V}{w} \quad (3)$$

where: $Q_e =$ Adsorption capacity at equilibrium (mg/g), $Q_t =$ Adsorption capacity at time, t (mg/g), $C_f =$ Concentration of Pb^{2+} ion in the liquid mixture (mg/L), $C_i =$ Initial concentration of metal ion in the aqueous solution (mg/L), $C_e =$ Concentration of Pb^{2+} ion in the aqueous solution at equilibrium (mg/L), $V =$ Volume of solution (L), $w =$ Weight of adsorbent (g).

Adsorption isotherm

The Langmuir and Freundlich isotherm models were used to study the adsorption of Pb^{2+} ion onto PPS particles.

Langmuir isotherm model

The Langmuir isotherm model as expressed in previous work [13] is given as:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \quad (4)$$

A plot of $\frac{C_e}{Q_e}$ versus C_e gives a straight line graph with slope equivalent to $\frac{1}{Q_m}$ and the intercept as $\frac{1}{K_L Q_m}$.

Where: $Q_m =$ Maximum adsorption capacity (mg/g) and $K_L =$ Langmuir constants at relating to energy of the adsorption (L/mg).

Freundlich isotherm

The Freundlich isotherm model as expressed as expressed in previous work [12] is given as:

$$Q_e = K_F C_e^{1/n} \quad (5)$$

Taking the logarithm of both sides of equation (5) gives:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

A plot of $\log Q_e$ versus $\log C_e$ gives a slope equivalent to $\frac{1}{n}$ and intercept equivalent to $\log K_F$.

where: $n =$ Heterogeneity of the adsorption energy across the adsorbent surface and K_F = Freundlich constant relating to maximum adsorption capacity (mg/g)

Adsorption kinetics

Like adsorption isotherm, the pseudo first and second order kinetic as well as the intra-particle diffusion models were applied to study adsorption of heavy metals onto garlic and ginger particles.

Pseudo first order kinetics

The Lagergren's pseudo first order equation is expressed as [14]:

$$\frac{dQ_t}{dt} = k_1 (Q_e - Q_t) \quad (7)$$

Where: $k_1 =$ pseudo first order adsorption rate constant (min^{-1}), $Q_e =$ concentration of Pb^{2+} adsorbed at equilibrium (mg/g), $Q_t =$ concentration of Pb^{2+} adsorbed with time (mg/g), $t =$ contact time (min).

Rearranging equation (7) gives:

$$\log (Q_e - Q_t) = \log Q_e - k_1 t \quad (8)$$

The plot of $\log (Q_e - Q_t)$ versus t gives slope equivalent to k_1 and intercept equivalent to $\log Q_e$.

Pseudo second order kinetics

The pseudo second order model is expressed as [14].

$$\frac{dQ_t}{dt} = k_2 (Q_e - Q_t)^2 \quad (9)$$

Where: $k_2 =$ Pseudo second order rate constant (g/gm.min). Every other variable has the same definition as above. The solution to equation (9) is given as:

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{Q_e^2 k_2} \quad (10)$$

The plot of $\frac{t}{Q_t}$ against t gives slope equivalent to $\frac{1}{Q_e}$ and intercept equivalent to $\frac{1}{Q_e^2 k_2}$.

Thermodynamic analysis

The effect of temperature on the adsorption of Pb^{2+} ion in solution was studied at 28.8, 40, and 50°C. To determine the thermodynamic parameters, the Van't Hoff equation was used [7]:

$$\ln K_e = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \quad (11)$$

Where: ΔH^o is the change in enthalpy (kJ/mol), ΔS^o is the change in entropy (kJ/mol.K), R is gas constant (8.314 J/mol.K), T the absolute temperature (K) and K_e is equilibrium constant, which from the Langmuir isotherm (L/mol).

The plot of $\ln K_e$ versus $\frac{1}{T}$ will give the slope as $\frac{\Delta H^o}{R}$ and the intercept as $\frac{\Delta S^o}{R}$, where upon ΔH^o and ΔS^o are determined.

Similarly, the Gibbs free energy change, ΔG^o of the adsorption is obtained from the equation:

$$\Delta G^o = -RT \ln K_e \quad (12)$$

RESULTS AND DISCUSSION

The results obtained from the experiment as well as the analysis of the adsorption isotherm, kinetics and thermodynamics are presented as follows.

Effect of initial concentration on adsorption capacity

Increasing the concentration of Pb^{2+} ion in the solution at constant volume affects the overall performance of the adsorbent. This is demonstrated in Figure 1. Thus, there was decrease in the concentration of Pb^{2+} removed when the initial concentration in the solution was increased. However, increase in temperature of the process favoured the removal of Pb^{2+}. The percentage of Pb^{2+} adsorbed by PPS particles at equilibrium were 85.89, 90.97 and 97.81% at 28.8ºC, 40ºC and 50ºC when the initial lead concentration was 10mg/L. But when initial lead concentration was increased to 50mg/L, the percentage of Pb^{2+} adsorbed decreased to 47.83, 49.89 and 52.31% at 28.8ºC, 40ºC and 50ºC respectively. This suggested thus, that to achieve high removing efficiency of Pb^{2+} in the solution, there should be balance on both the initial concentration and the volume of the solution in the system. The decrease in Pb^{2+} adsorbed when its concentration is increased in the solution was due to limited surface area of the adsorbent available to take up the Pb^{2+} [12, 13].

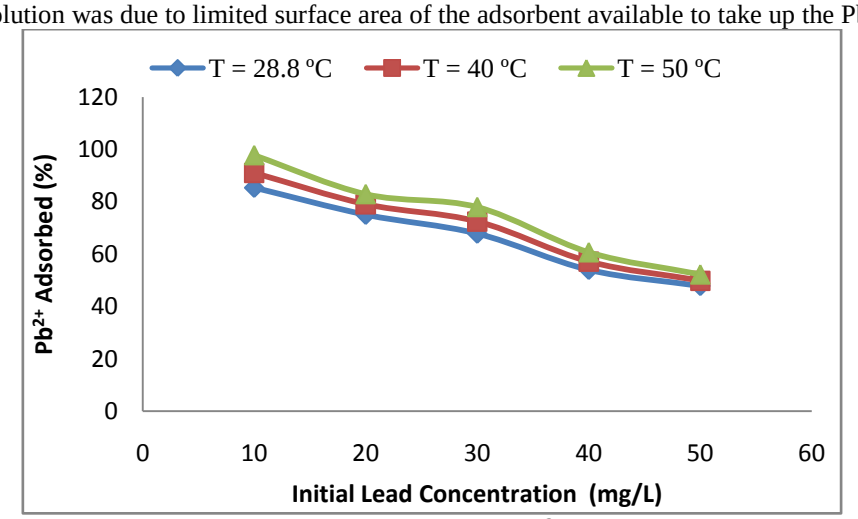

Fig. 1 Effect of temperature on Pb^{2+} adsorption

Effect of contact time on Pb^{2+} adsorption

Figure 2 showed the percentage of Pb^{2+} ion removed by the adsorbent with time. As the profiles in the figure indicated, the percentage of Pb^{2+} ion adsorbed tends to attained equilibrium at about 60 minutes. Nevertheless, the percentage of Pb^{2+} ion adsorbed increased with time, and within the first 30 minutes, 54.25, 59.03 and 76.42% was adsorbed, which then increased to 87.58, 90.96 and 98.79% at contact time of 150 minutes when the system temperature were 28.8ºC, 40ºC and 50ºC respectively.

The adsorption of lead (II) ion onto plantain pseudo stem attained equilibrium at lesser time compared to some previous works, which reported 175 minutes for the removal of chromium ion [15] and 3 hours for the removal of manganese [16], though, with different adsorbents.

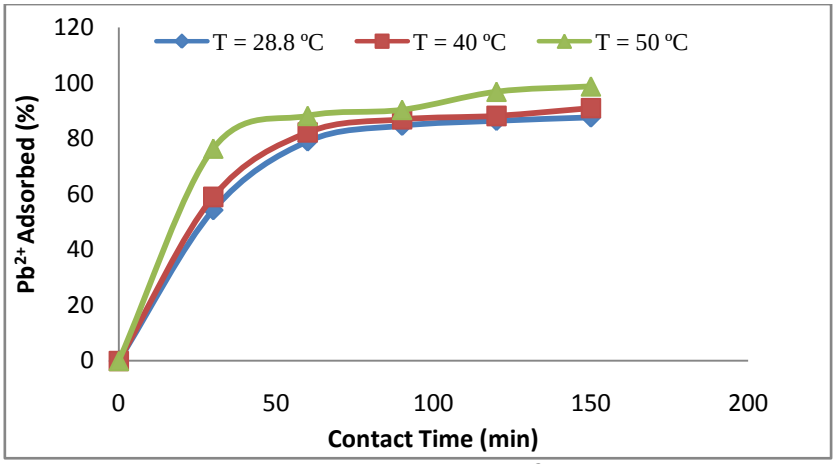

Fig. 2 Effect of contact time on Pb^{2+} adsorption

Adsorption isotherm

The Langmuir and Freundlich isotherms were applied to study the adsorption of Pb^{2+} ion onto PPS particles. Figures 3, 4 and 5 showed the plots for Langmuir isotherm at adsorption temperatures of 28.8ºC, 40ºC and 50ºC respectively. The linearity of the plots at equilibrium is an indication that the Langmuir isotherm model fits the adsorption of Pb^{2+} ion onto PPS adsorbent. The maximum adsorption capacity Q_e and the Langmuir constant K_L are obtained as 6.6534mg/g and 0.2913L/g; 6.6979mg/g and 0.4391L/g; and 6.7568mg/g and 0.8186L/g at adsorption temperatures of 28.8ºC, 40ºC and 50ºC respectively. Also, the R-squared values at equilibrium for the investigated adsorption temperatures are 99.64, 99.64 and 99.45%.

Similarly, Figures 6, 7 and 8 showed the plots for Freundlich isotherm at the investigated adsorption temperatures. Thus, the Freundlich constant, which is synonymous to maximum adsorption capacity K_F and the heterogeneity of the adsorption energy across the adsorbent surface n are obtained as 1.9975mg/g and 2.8035; 3.4137mg/g and 0.8145; and 2.4784mg/g and 3.2510 at adsorption temperatures of 28.8ºC, 40ºC and 50ºC respectively. Also, the R-squared values at equilibrium for the investigated adsorption temperatures are 99.64, 99.64 and 99.45%. The adsorption parameters of Pb^{2+} ion onto plantain pseudo stem particles are shown in Table 1.

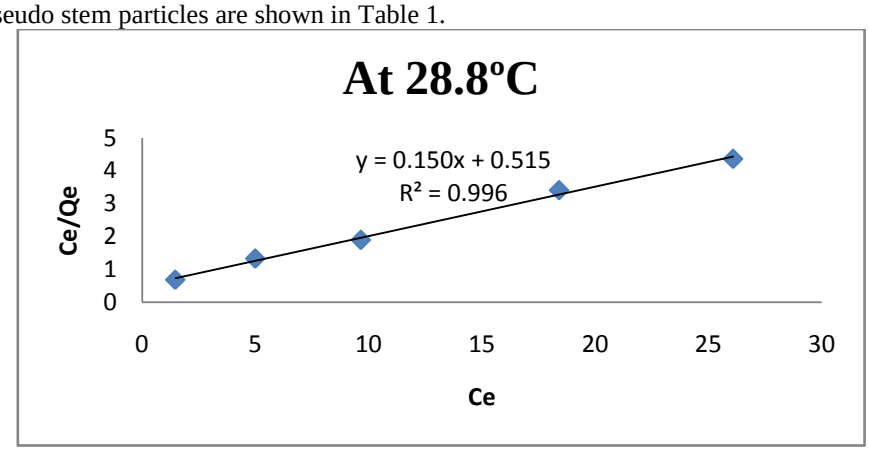

Fig. 3 Langmuir isotherm at 28.8ºC

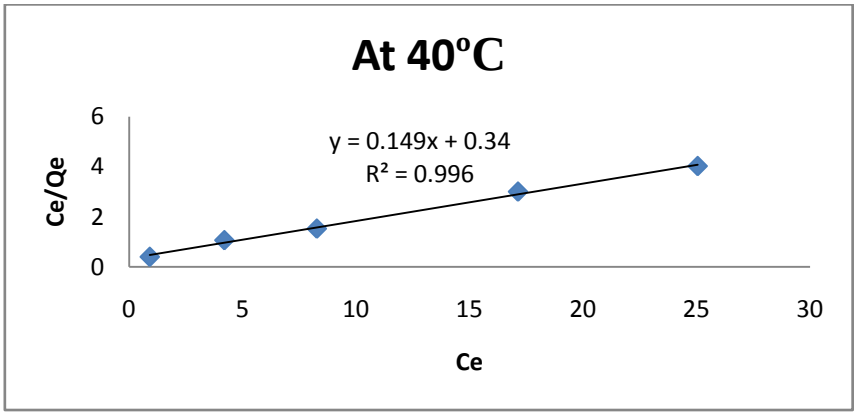

Fig. 4 Langmuir isotherm at 40ºC

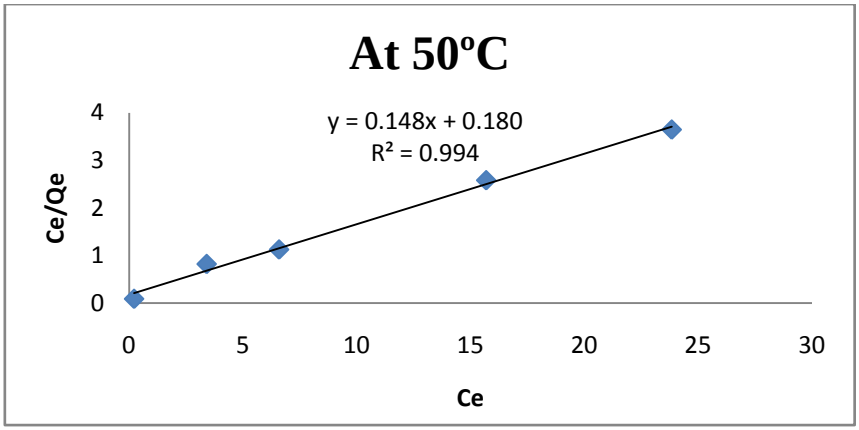

Fig. 5 Langmuir isotherm at 50°C

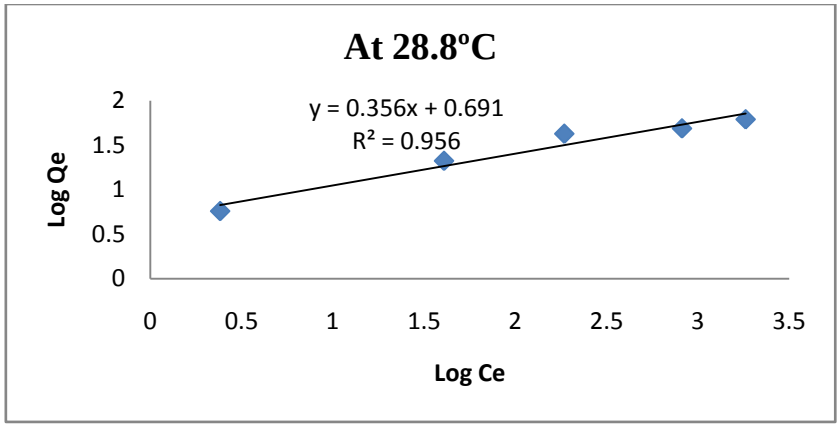

Fig. 6 Freundlich isotherm at 28.8°C

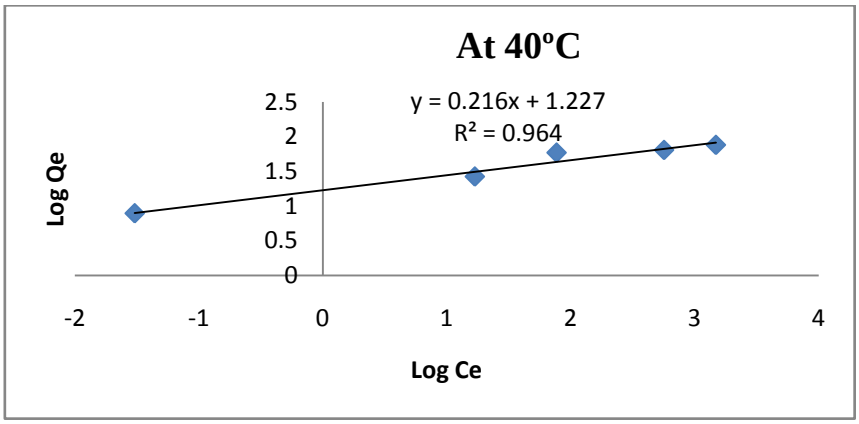

Fig. 7 Freundlich isotherm at 40°C

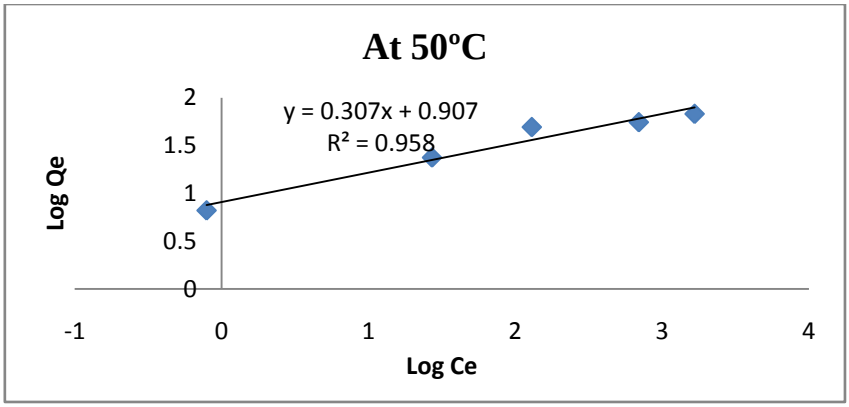

Fig. 8 Freundlich isotherm at 50°C

Table 1: Adsorption isotherm parameters for adsorption of Pb^{2+}

	Langmuir isotherm			Freundlich isotherm		
Temp. (ºC)	**Q_m (mg/g)**	**K_L (L/g)**	***R^2***	***K_F* (mg/g)**	***n***	***R^2***
28.8	6.6534	0.2913	0.9964	1.9975	2.8035	0.9563
40	6.6979	0.4391	0.9964	3.4137	0.8145	0.9642
50	6.7568	0.8186	0.9945	2.4784	3.2510	0.9589

Adsorption kinetics

The kinetic study of Pb^{2+} ion adsorption in solution onto plantain pseudo stem particles has been carried out, while the analyses are shown in Figures 9 and 10. The Pseudo First and Second Order Kinetics were applied to determine the mechanism and rate controlling step of adsorption process [13]. In this study, however, the linear lines for the two kinetic orders did not pass through the origin. This means that the adsorption of Pb^{2+} ion onto PPS particles occurred on the surface of the adsorbent, and the mechanism of adsorption process is chemisorption and diffusion.

The predicted equilibrium adsorption capacity at 28.8ºC, 40ºC and 50ºC are 1.708, 1.675 and 4.538mg/g for the Pseudo First Order kinetics; and 2.445, 2.456 and 2.477mg/g for the Pseudo Second Order. From the predicted equilibrium adsorption capacity, the Pseudo Second Order kinetics explained the experimental results better than the Pseudo First Order kinetics. Also, the R-squared values are higher for the Pseudo Second Order kinetics. The comparison of the kinetic parameters is shown in Table 2. The results obtained in this work also agreed with previously reported on comparison of First and Second Order Pseudo Kinetics [5,12,17].

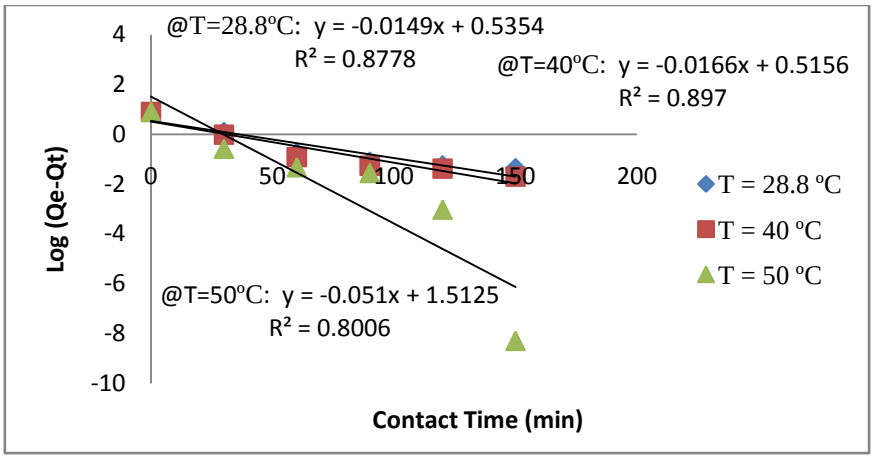

Fig. 9 Pseudo 1st order kinetics

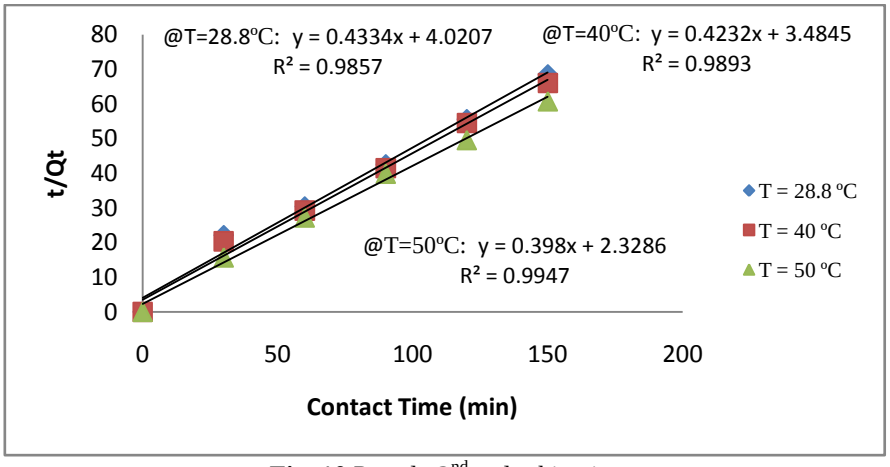

Fig. 10 Pseudo 2nd order kinetics

Table 2: kinetic parameters for adsorption of Pb^{2+}

Temp. (ºC)	**Q_e (mg/g)**			**Rate Constant**		***R^2***	
	Expt.	**Pseudo 1st Order**	**Pseudo 2nd Order**	***k_1* (min^{-1})**	***K_2* (g/mg/min)**	**Pseudo 1st Order**	**Pseudo 2nd Order**
28.8	2.134	1.708	2.445	0.0149	0.1878	0.8778	0.9857
40	2.274	1.675	2.456	0.0166	0.1791	0.8970	0.9893
50	2.445	4.538	2.477	0.0510	0.1584	0.8006	0.9947

Thermodynamics of the adsorption

Table 3 showed the thermodynamic parameters determined from the plot in Figure 11. Thus, the change in enthalpy ΔH^o and entropy ΔS^o for the adsorption of Pb^{2+} onto PPS particles are given as 40.8284kJ/mol and 0.14022kJ/mol.K. The value of ΔH^o is positive, which is an indication that the adsorption process is endothermic. Also, the value of ΔS^o is positive, suggesting that the adsorption process is possible and there was increase in randomness on the solid-liquid interface in the solution. Alternatively, the corresponding negative values obtained for the Gibbs free energy ΔG^o as presented in Table 3, showed that the adsorption process was spontaneous, causing a decrease in ΔG^o as adsorption temperature was increased, thereby making the reaction favourable [18].

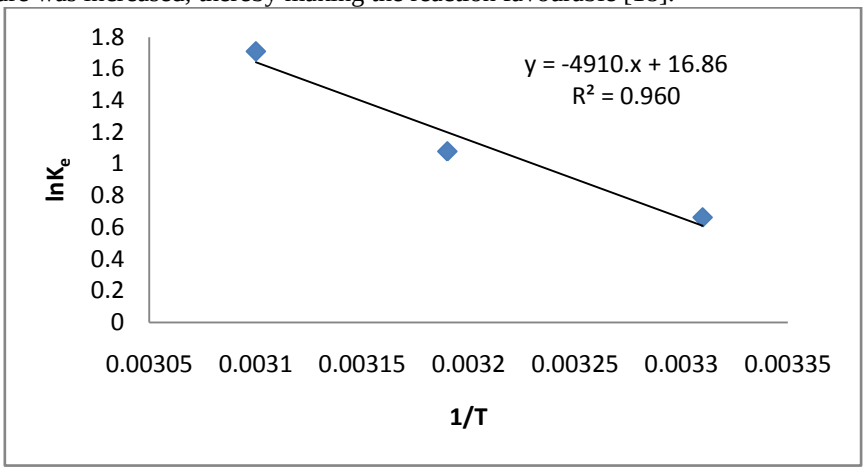

Fig. 11 Plot for thermodynamic analysis

Table 3: Thermodynamic parameters for Pb^{2+} adsorption

T (°C)	ΔG^o (KJ/mol)	ΔH^o (KJ/mol)	ΔS^o (KJ/mol.K)
28.8	-1.6607	40.8284	0.14022
40	-2.8074		
50	-4.593		

CONCLUSION

The use of particles of biomaterials for the removal of toxic substances such as heavy metals from aqueous solution has proved to be effective. This is also true for plantain pseudo stem (PPS) used in this study. Like in previous studies, this study showed that the concentration of Pb^{2+} ion affects the performance of the adsorbent. Thus, the amount of Pb^{2+} ion removed in the solution depends on the balance between the concentration of contaminant in solution and the volume of the solution. Also, the adsorption process was better explained by the Langmuir isotherm than the Freundlich isotherm. Again, the adsorption mechanism can be described as both diffusion and chemisorptions, though, the Pseudo-Second-order kinetics followed the adsorption process than the Pseudo First Order kinetics, and it is therefore the rate controlling step. Finally, the thermodynamic analysis revealed that adsorption of Pb^{2+} ion onto PPS particles is an endothermic process.

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