



# Thermodynamic and Kinetic Characterization of Lead (II) Ion Biosorption Using Plantain (*Musa paradisiaca*) Pseudo stem Biomass: Isotherm Modeling and Mechanistic Analysis"

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## Abstract

This study investigates the efficacy of plantain pseudo stem (PPS), an agricultural waste material, as a bio sorbent for lead ( $Pb^{2+}$ ) ion removal from contaminated aqueous solutions. The adsorption performance was systematically evaluated under varying operational parameters including initial  $Pb^{2+}$  concentration (10–50 mg/L), contact time (0–150 min), and temperature (28.8–50°C). Equilibrium studies revealed maximum  $Pb^{2+}$  removal efficiencies of 85.89–97.81% at 10 mg/L initial concentration, decreasing to 47.83–52.31% at 50 mg/L across the studied temperature range. Kinetic analysis demonstrated time-dependent adsorption progression, with removal rates increasing from 54.25–76.42% at 30 minutes to 87.58–98.79% after 150 minutes.

Isotherm modeling showed Langmuir maximum adsorption capacities ( $Q_e$ ) of 6.6534–6.7568 mg/g, outperforming Freundlich isotherm fits ( $K_F = 1.9975$ –3.4137 mg/g), indicating predominant monolayer adsorption. Kinetic studies revealed that the pseudo-second-order model ( $R^2 > 0.98$ ) better described the adsorption mechanism than pseudo-first-order kinetics, suggesting chemisorption as the rate-limiting step. Thermodynamic analysis confirmed the endothermic nature of the process ( $\Delta H > 0$ ), with increasing temperature enhancing adsorption capacity.

These findings demonstrate PPS as a viable, low-cost bio sorbent for  $Pb^{2+}$  remediation, with optimal performance at lower contaminant concentrations and elevated temperatures. The material's adsorption characteristics, coupled with its agricultural waste origin, position it as an environmentally sustainable alternative for heavy metal wastewater treatment.

**Keywords:** Plantain pseudo stem • Lead ion remediation • Adsorption isotherms • Biosorption kinetics • Thermodynamic analysis • Wastewater treatment

## INTRODUCTION

Water, whether surface or groundwater, is a useful resource 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 behavioral 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 28.8°C. 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 analyzed using Atomic Absorption Spectrophotometer to determine the equilibrium concentration. The steps were repeated when the solution was heat and maintained at temperatures of 40°C and 50°C 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 analyzed as in above. The percentage of  $Pb^{2+}$  ion adsorbed by the PPS particles was calculated using the expression:

### Adsorption isotherm

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

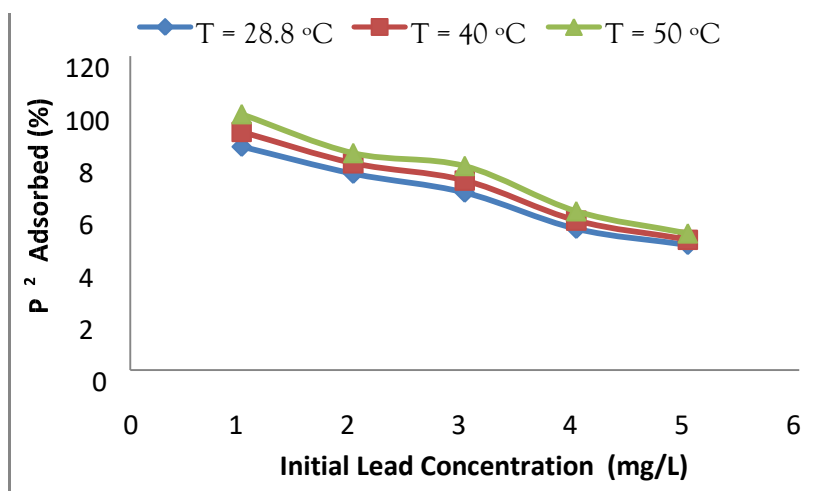
## RESULTS AND DISCUSSION

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 28.8°C, 40°C and 50°C 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 28.8°C, 40°C and 50°C respectively. This suggested thus, that to achieve high removing efficiency of  $\text{Pb}^{2+}$  in the solution, there should be balance on both the initial concentration and the volume of the solution in the system. The decrease in  $\text{Pb}^{2+}$  adsorbed when its concentration is increased in the solution was due to limited surface area of the adsorbent available to take up the  $\text{Pb}^{2+}$  [12, 13].

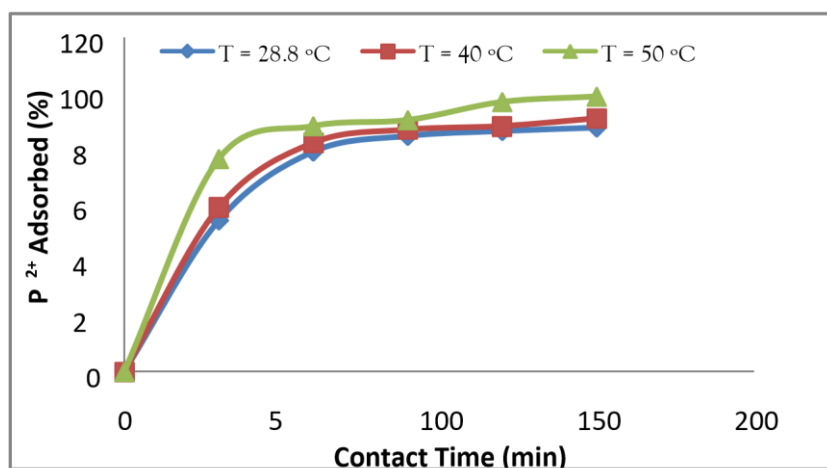


**Fig. 1** Effect of temperature on adsorption of  $\text{Pb}^{2+}$

#### Effect of contact time on $\text{Pb}^{2+}$ adsorption

Figure 2 showed the percentage of  $\text{Pb}^{2+}$  ion removed by the adsorbent with time. As the profiles in the figure indicated, the percentage of  $\text{Pb}^{2+}$  ion adsorbed tends to attained equilibrium at about 60 minutes. Nevertheless, the percentage of  $\text{Pb}^{2+}$  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 28.8°C, 40°C and 50°C 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.



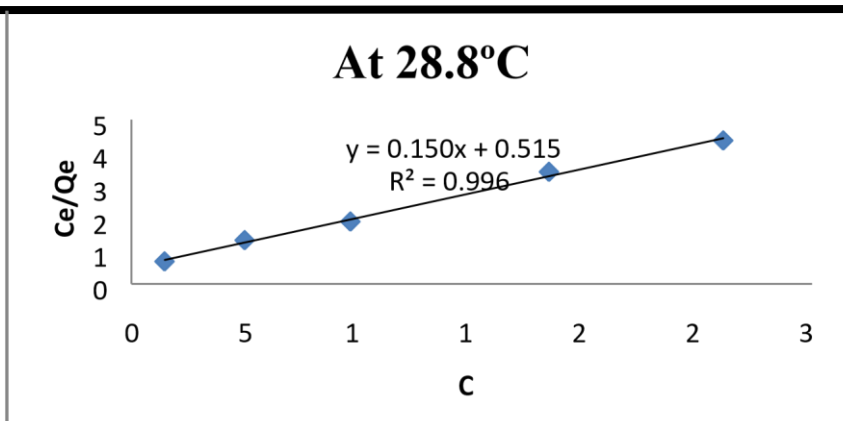
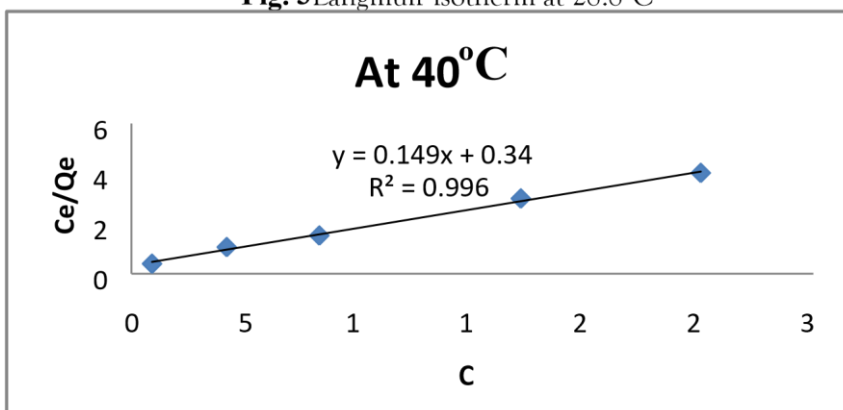
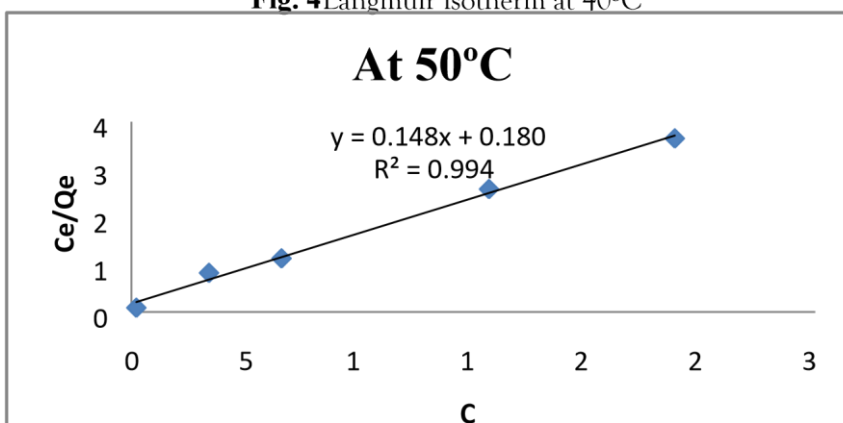
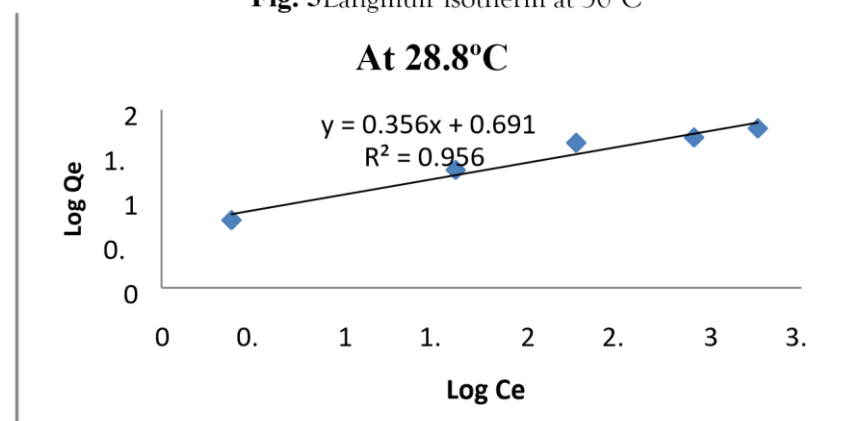
**Fig. 2** Effect of contact time on  $\text{Pb}^{2+}$  adsorption

#### Adsorption isotherm

The Langmuir and Freundlich isotherms were applied to study the adsorption of  $\text{Pb}^{2+}$  ion onto PPS particles. Figures 3, 4 and 5 showed the plots for Langmuir isotherm at adsorption temperatures of 28.8°C, 40°C and 50°C respectively. The linearity of the plots at equilibrium is an indication that the Langmuir isotherm model fits the adsorption of  $\text{Pb}^{2+}$  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 28.8°C, 40°C and 50°C 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

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temperatures of 28.8°C, 40°C and 50°C 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  $\text{Pb}^{2+}$  ion onto plantain pseudo stem particles are shown in Table 1.

**Fig. 3**Langmuir isotherm at 28.8°C**Fig. 4**Langmuir isotherm at 40°C**Fig. 5**Langmuir isotherm at 50°C**Fig. 6**Freundlich isotherm at 28.8°C

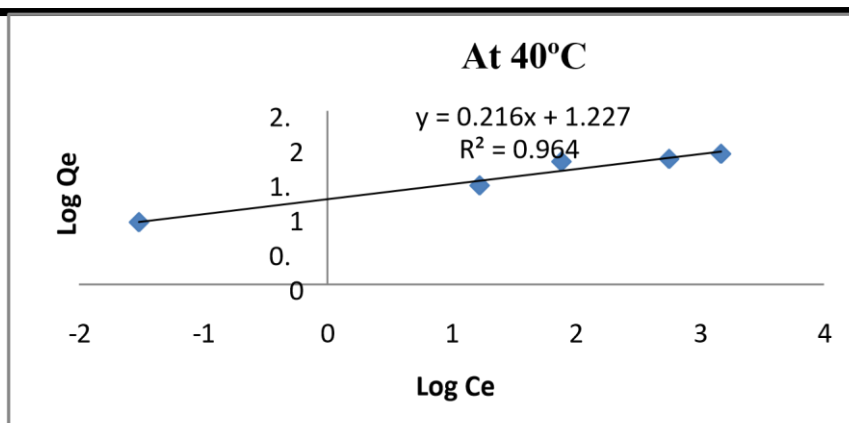


Fig. 7 Freundlich isotherm at 40°C

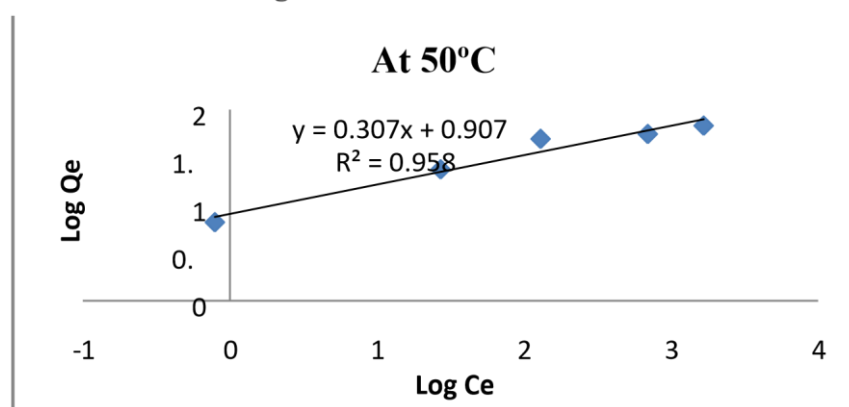


Fig. 8 Freundlich isotherm at 50°C

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

Temp. (°C)	Langmuir isotherm			Freundlich isotherm		
	$Q_m$ (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 28.8°C, 40°C and 50°C 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].

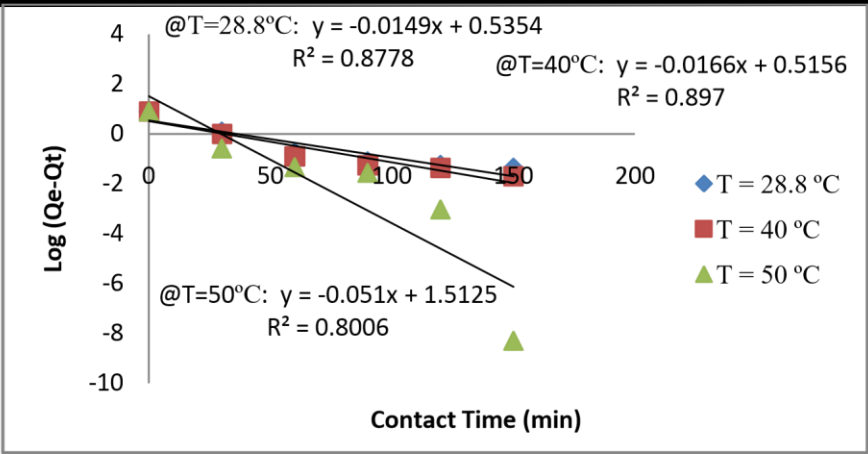


Fig. 9 Pseudo 1<sup>st</sup> order kinetics

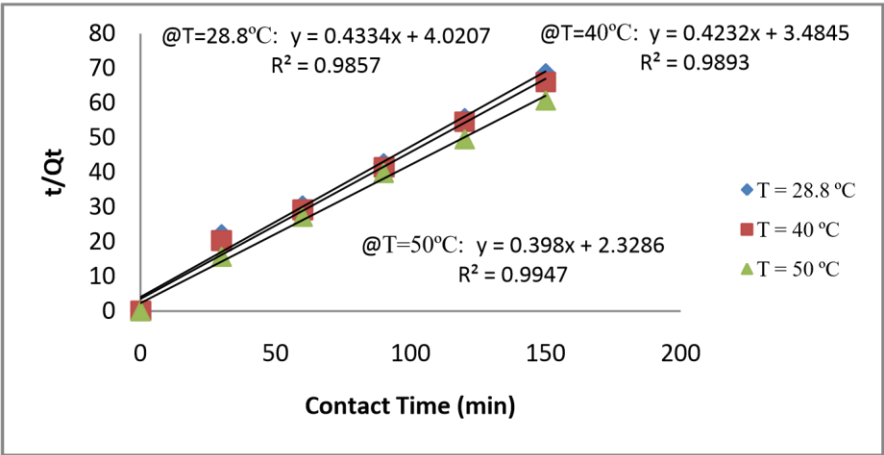


Fig. 10 Pseudo 2<sup>nd</sup> order kinetics

Table 2: kinetic parameters for adsorption of Pb<sup>2+</sup>

Temp. (°C)	Q <sub>e</sub> (mg/g)			Rate Constant		R <sup>2</sup>	
	Expt.	Pseudo 1 <sup>st</sup> Order	Pseudo 2 <sup>nd</sup> Order	k <sub>1</sub> (min <sup>-1</sup> )	K <sub>2</sub> (g/mg/min)	Pseudo 1 <sup>st</sup> Order	Pseudo 2 <sup>nd</sup> 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  $\Delta H^\circ$  and entropy  $\Delta S^\circ$  for the adsorption of Pb<sup>2+</sup> onto PPS particles are given as 40.8284kJ/mol and 0.14022kJ/mol.K.

The value of  $\Delta H^\circ$  is positive, which is an indication that the adsorption process is endothermic. Also, the value of  $\Delta S^\circ$  is positive, suggesting that the adsorption process is possible and there was increase in randomness on the solidliquid interface in the solution. Alternatively, the corresponding negative values obtained for the Gibbs free energy  $\Delta G^\circ$  as presented in Table 3, showed that the adsorption process was spontaneous, causing a decrease in  $\Delta G^\circ$  as adsorption temperature was increased, thereby making the reaction favourable [18].

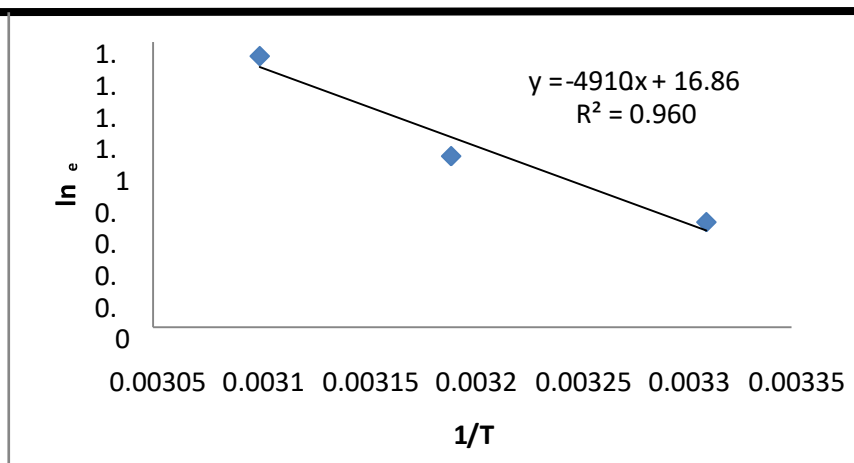


Fig. 11 Plot for thermodynamic analysis

Table 3: Thermodynamic parameters for Pb<sup>2+</sup> adsorption

T (°C)	$\Delta G$ (KJ/mol)	$\Delta H$ (KJ/mol)	$\Delta S$ (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<sup>2+</sup> ion affects the performance of the adsorbent. Thus, the amount of Pb<sup>2+</sup> 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-Secondorder 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<sup>2+</sup> ion onto PPS particles is an endothermic process.

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