

Sorptive Removal of Lead from Aqueous Solution using Bark Powder of *Bridelia ferruginea* Plant

Adetunmbi Abdulafeez Adekunle¹

¹Department of Chemistry, Federal University of Technology, Akure, Nigeria.

Correspondence E-mail Id: editor@eurekajournals.com

Abstract

The potentials of *Bridelia ferruginea* plant bark powder for adsorption of Pb²⁺ under different experimental conditions was investigated. Effects of various parameters such as solution pH, sorbent-sorbate resident time and ratio, concentration and temperature were investigated. The sorption of lead followed pseudo-second-order rate kinetics. Thermodynamic studies revealed that the sorption of lead endothermic and spontaneous, with good affinity toward the sorbent. The isotherm models used were Langmuir and Freundlich. These models were used to analyze the equilibrium data at different temperatures. The Freundlich, and Langmuir models were found to be in good agreement with experimental data with high R². The results show that the sorption capacity increases with an increase in solution temperature from 25 to 65°C. The maximum sorption capacity calculated from Langmuir isotherm was 22.98mg/g at optimum condition of pH 3 and contact time of 30 min.

Keywords: Lead, Adsorption, *Bidelia ferruginea*, Kienetics, Isotherm uptake.

Introduction

Heavy metals enter into the environment mainly via three routes, which are through deposition of atmospheric particulates, disposal of metal enriched sewage sludge as well as sewage effluents and by-products from metal mining processes. Heavy metals can be released into the environment by both natural and anthropogenic sources. The major causes of introduction of these metals are the anthropogenic sources, specifically mining operations [1]. The released metals are likely to persist in the environment even longer after mining activities have ceased. Through mining activities, water bodies are most polluted, as these metals may leach to sloppy areas and they are carried by acidic water downstream. Certain heavy metals such as Iron (Fe), Copper (Cu), Zinc (Zn), and Manganese (Mn) are required by humans for normal biological functioning. However, heavy metals such as Mercury (Hg), Lead (Pb), Cadmium (Cd), Cobalt (Co) are toxic to organisms[8].

The destruction of aquatic life by heavy metals such as Lead (Pb) has generated a lot of researches tailored towards evaluating removal strategies to mitigate this effect. Lead is categorized under heavy metals which are metals. Pb and their related compounds are amongst the 129 so-called 'black-list' substances in the dangerous substances directive 76/464/EEC [2]. Effluents from production of batteries, gasoline additives, pigments, alloys and sheets etc. contain often high concentrations of lead ions [9].

These metals are also recognized by the World Health Organization (WHO) as metals of most immediate concern (WHO 1984). This is because both metals show acute toxicity and are capable of bioaccumulation and biomagnifications in biological tissues. When ingested, they cause accumulative poisoning, cancer, brain damage and other related health disorders [2]. Lead is a general metabolic poison and enzyme inhibitor. It can cause mental retardation and semi-permanent damage in young children. Cd and Pb have the potential to replace Zn and calcium (Ca), respectively, in biological processes and hence interfere with the natural workings of the body system.

Furthermore, several technologies are presently been utilized for the removal of these metals from industrial wastewater in order to prevent their release into the environment. Conventional technologies used include: chemical precipitation, coagulation, chemical/electrochemical reduction, solvent extraction, and electrolysis [4]. These methods of treatment suffer several limitations based on their technical and/or economical viability. Some of these methods do not possess removal efficiencies which are sufficient for meeting the ever increasing environmental requirements been set by regulatory bodies. Also, the possibility of secondary contamination from concentrated sludge and other secondary pollutants is a subject of concern when utilizing these conventional techniques.

However, Adsorption is the process of collecting soluble substances (adsorbate) that are in solution, on a suitable interface (with adsorbent). The interface can be between the liquid and a gas, a solid, or another liquid. This process is categorized into three distinct steps [5], these are: the transferring of the adsorbate molecules through the film that surrounds the adsorbent, diffusion through the pores of adsorbent which is porous and uptake of the adsorbate molecules by the active surface, including formation of the bond between the adsorbate and the adsorbent. The rate of the adsorption process depends on the rate at which the molecules move by diffusion in solution or the rate at which the molecules can reach available surface by diffusing through the film and the pores. Generally, adsorption process can be classified as either Physical adsorption (physisorption) or Chemical adsorption (chemisorption).

Materials and Method

Materials

➤ Apparatus

In the determination of the efficiency of the *Bridelia ferruginea* plant bark in removing lead from aqueous solution, the following apparatus were used in the study; Thermostatically controlled oven (model: OV-160), Multiflix Rotary shaker (model: CF-158), Electrical Analytical Balance (model: DR-169FT), Digital pH meter (EUTECH pH 510), Flame atomic absorption spectrophotometer (FAAS) (Buck Scientific, Model: 200), Electrical steam water bath (model: M-80), Manual Hand Sieve (Pore Size: 250µm). While the chemical used for the research are of analytical grade.

Methods

➤ Sample Collection and Preparation

Bridelia ferruginea plant bark was collected from a farm in Akoko, present day Ondo state and was authenticated by Crop scientists from the Crop, Soil and Pest department of the Federal University of Technology Akure. The samples were sundried for a period of 7 days and ground into powder using grinding mill. The dried bark powder was then sieved using a manual hand sieve. The sieved powder was then stored in plastic containers for use as adsorbent.

➤ Preparation of Lead Nitrate stock solution

The aqueous solution was prepared by dissolving an appropriate weight of the metal salt in 1000 mL standard volumetric flask containing 500 mL distilled water and then made up to the mark on the flask using distilled water to prepare 1000 ppm of the stock solution. The lead salt used in the adsorption study is Lead (ii) Nitrate ($\text{Pb}(\text{NO}_3)_2$). Serial dilutions of different concentrations (10, 25, 50, 100 and 200) were prepared from the 1000mg/L stock solution. In determination of the mass of salt to be dissolved the equation used is:

$$\text{Mass of salt to be dissolved} = \frac{\text{MW Of Lead Nitrate} \times 100}{\text{AW of Lead} \times \text{Purity}} \quad (1)$$

Where;

MW = molecular weight

AW = atomic weight.

The appropriate mass of lead nitrate to be dissolved was calculated to be 1.6146g.

➤ Preparation of 0.1 M HCl and NaOH Solution

8.3 mL of 37.2 % concentrated HCl was measured into 500 mL of distilled water in 1000 mL Standard flask and then made up to the mark to prepare 1000 mL of 0.1 M HCl solution. While for NaOH, 4.0 g of the compound was weighed accurately and dissolved into 500 mL distilled water in a 1000 mL. Standard flask and then made up to the mark with distilled water.

Batch Adsorption Experiment

Adsorption studies were carried out to investigate the effect of pH, initial concentration of the metal ions, contact time, adsorbent dosage and temperature. Adsorption studies were done using 50 mL of the lead ion solution and the pH of the lead ion solution was adjusted using 0.1 M HCl and 0.1 M NaOH solution. At the end of each experiment, the content of each bottle was filtered using a whatman NO. 42 filter paper into different sample bottle. The concentration of the residual metal ions of individual filtrate was determined by Flame atomic absorption spectrophotometer (FAAS), model:

pH Study

Batch adsorption was carried out using initial metal ion concentration of 50 mg/L. 0.5g of the adsorbent was measured into beakers. The adsorption mixture was agitated intermittently at intervals for a total of 360 minutes. The values of pH studied are pH 1,2,3,4,5 and 6. The content of each bottle was filtered into clean sample bottles. The concentration of the residual metal ion in the filtrate was determined by AAS.

Contact Time study

The effect of contact time on adsorption was carried out by varying contact time of 5,15 30, 60, 90,120, 180,240 and 360 minutes for the aqueous solution of lead. 0.5g of the adsorbent was weighed into beakers and 50 mg/L of the metal ion solution was added. The adsorption mixture was agitated intermittently until the expiration of each time investigated. The content of each bottle was filtered into clean sample bottles. The concentration of the residual metal ion in the filtrate was determined by AAS.

Initial Concentration of Metal Ion study

Batch adsorption was carried out using initial metal ion concentrations of 10, 25, 50, 100 and 200 mg/L. 0.5g of the adsorbent was weighed into beakers and 50mL of each metal concentration was added. The adsorption mixture was agitated intermittently for 30 minutes. The content of each bottle was filtered into clean sample bottles. The concentration of the residual metal ion in the filtrate was determined by AAS.

Temperature Study

The effect of temperature was carried out using the bark powder at different temperature ranges of 28, 35, 45, 55 and 65 at pH 3. 0.5g of the adsorbent was weighed into different beakers and various concentrations of 10, 25, 5,100 and 200 mg/L were added to the beakers. They were then placed in a steam water bath which was adjusted according to the temperature to be studied and allowed to heat for a 30 minutes period. The content of each beaker was filtered into clean sample bottles after cooling. The concentration of the residual metal ion in the filtrate was determined by AAS.

Adsorbent dosage study

The effect of adsorbent dosage on adsorption of metal ion was carried out by varying the dosage of the adsorbent for 50mg/L of the metal ion solution. The adsorbent of different mass were weighed into 50ml beakers. The mass of adsorbent weighed are 0.1g, 0.2g, 0.3g, 0.5g and 0.75g. The adsorption mixtures were shaken intermittently for a 30 minutes period. The content of each bottle was filtered into clean sample bottles. The concentration of the residual metal ion in the filtrate was determined by AAS.

Metal Analysis

The metal analysis was performed using flame atomic absorption spectrophotometer (FAAS) model: Buck Scientific; 200. The analysis by AAS of each sample was carried out in duplicates and the mean value was calculated for each sample.

Data Analysis

The percentage (%) removal of the metal ion was computed using the equation below;

$$\% \text{ Removal} = \frac{C_b}{C_o} \times 100 \quad (2)$$

Where C_o = Initial Concentration

C_b = Concentration Bound

$$C_b = C_o - C_f \quad (3)$$

Where C_f = Final Concentration

Adsorption Isotherms

Adsorption isotherm expresses the relationship between the amounts of adsorbate removed from the liquid phase by unit mass of adsorbent at a constant temperature. Adsorption isotherms are basic requirements for the design of adsorption systems. In this study, two isotherm models (Langmuir, Freundlich) were tested to analyze the equilibrium concentration between adsorbed metal ion (Pb^{2+}) and the bark powder of the *Bridelia ferruginea* plant.

Langmuir Adsorption Isotherm: The Langmuir isotherm is used to describe adsorption phenomena and is based on the assumption that uptake occurs on a homogenous surface by monolayer sorption without interaction between adsorbed molecules. The linear form of the

Langmuir isotherm equation can be expressed as:

$$\frac{C_e}{q_e} = \frac{1}{K_a \cdot q_{max}} + \frac{C_e}{q_{max}} \quad (4)$$

Where q_{max} = the maximum monolayer adsorption capacity of adsorbent (mg/g)

K_a = the Langmuir adsorption constant (L/mg) related to the energy of adsorption, which quantitatively reflects the affinity between the adsorbent and adsorbate.

C_e = the metal ion concentration in the solution at equilibrium (mg/L)

q_e = the monolayer adsorption capacity of the adsorbent (mg/g)

The q_{max} and K_a are determined from the slope ($1/q_{max}$) and the Intercept ($\frac{1}{K_a \cdot q_{max}}$) by plotting a graph of C_e/q_e against C_e . While the Freundlich isotherm model on the other hand, was used to describe the amount of substance adsorbed per unit gram of the adsorbent (q_e) is related to the equilibrium concentration (C_e) of the metal ion. This is applied to non-ideal sorption on heterogeneous surfaces and the linear form of the equation is given as;

$$\text{Log } q_e = \text{Log } K_f + 1/n \text{Log } C_e \quad (5)$$

Where;

K_f = the constant indicative of the relative adsorption capacity of the adsorbent (mg/g)

n = the constant indicative of the intensity of the adsorption

Freundlich isotherm is drawn by plotting the graph between $\log q_e$ and $\log C_e$ to obtain the slope ($1/n$) in order to compute for K_f . When the value of n lies between 1 and 10, it indicates a favourable adsorption.

Adsorption Kinetics

In order to determine the order and rate of adsorption, four kinetic models were used to describe the order of adsorbate-adsorbent interactions in the adsorption. The metal uptake q_t at time t was determined by mass balance as follows;

$$q_t = C_b \times VM \quad (6)$$

Where C_o and C_t are metal ion concentrations at time 0 and at time t respectively (mg/L).

q_t = the uptake capacity of the metal ion at time t (mg/g)

V = volume of solution used (L)

M = mass of adsorbent used (g)

(a) Pseudo-first order kinetic model: The pseudo first-order kinetic model also known as Lagergren equation was applied.

$$\log(q_e - qt) = \log q_e - \frac{K_1}{2.303t} \quad (7)$$

The plot of $\log (q_e - qt)$ versus t were used to determine the rate constant (K_1) from the slope and the intercept $\log q_e$ of the plot and the values are recorded.

Where qt and q_e are the amounts of metal ions adsorbed at time t and at equilibrium in (mg/g) respectively. K_1 is the pseudo-first order adsorption constant (min^{-1}).

The Pseudo second-order kinetic model is based on the assumption that chemisorptions is the rate determining step and is given as:

$$\frac{t}{q_t} = 1/k_2(q_e)^2 + \frac{1}{q_e} t \quad (8)$$

Where;

$$h = K_2 q_e^2 \quad (9)$$

t = contact time (min)

qt and q_e are the amounts of metal ions adsorbed at time and at equilibrium in (mg/g). K^2 is the equilibrium rate constant of pseudo-second order adsorption (g/mgmin). h is the initial sorption rate, h (mg/gmin),

The values of q_e and K^2 were calculated from the slope and intercept of the linear plot of t/q_t versus t and values are recorded.

Thermodynamic Studies

The Van't-Hoff plot was used in studying the thermodynamic model of the adsorption. The Van't-Hoff equation is given below;

$$\ln K_{eq} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (10)$$

Where;

$$\Delta G^\circ = -RT \ln K \quad (11)$$

The Van't-Hoff plot is a graph of $\ln K_{eq}$ against $1/T$. In literary terms; ΔG° is the change in Gibbs free energy ΔH° is the change in Enthalpy ΔS° is the change in Entropy R is the molar gas constant T is the temperature in Kelvin.

Results and Discussion

Parameters affecting adsorption of the Pb^{2+} by *Bridelia ferruginea* bark powder.

Effect of pH

One of the most important factors controlling the adsorption of heavy metals onto adsorbent particles is the pH of the aqueous solution which affect the surface charge of the adsorbent. The effect of the pH of the aqueous solution on the adsorption of lead ion using the bark powder was investigated at different pH values ranging from 1 to 6 in Figure 1. The percentage removal was found to increase with a corresponding pH increase from 1 to 3 and attained a maximum adsorption capacity at pH 3. There was a decline in the adsorption efficiency from pH 4 to 6. Thus, the optimum pH is found to be pH 3 and this was used in subsequent study of other parameters in the batch adsorption study. The reduced adsorption efficiency of Lead ion removal at very low pH could be attributed to the presence of H^+ ions in the mixture, which compete with Lead (II) ions for the binding sites on the adsorbent. Similar observation have also been reported by some researchers [7] where the leaves of the plant *Zea mays* were used as biosorbent.

Effect of Contact Time

The adsorption time curve is shown in Figure 2, at the initial concentration of 50 mg/L and at room temperature. The adsorption rate was rapid within the first 15 minutes and equilibrium was attained at 30 minutes. The effect of contact time on the adsorption of lead ion on the bark powder was investigated in order to determine the minimum time necessary to achieve maximum adsorption. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system. This result is consistent with what was reported by Ghasemi and Gholami, where Myrtaceae Sawdust was used as the biosorbent [6]. Adebowale *et al.*, (2006) also observed that Pb ion on maize plant leave reached equilibrium in 30 minutes. Considering the time importance at adsorption process, the optimum contact time of lead, 30 minutes was determined [7].

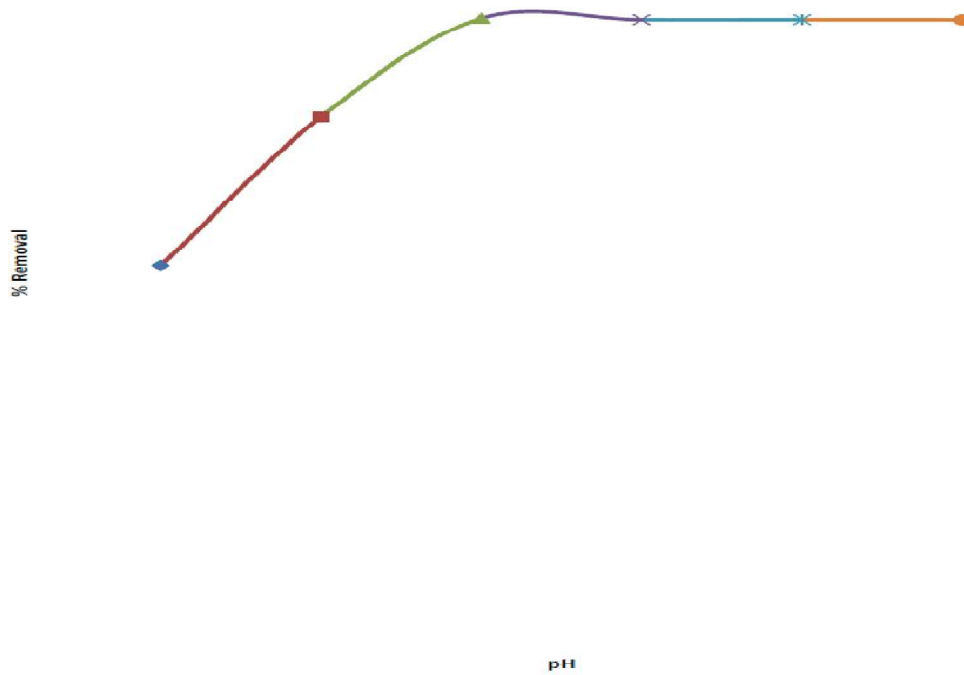


Figure 1. Effect of pH on the adsorption of Pb(II)
 (CO =50mg/L, Cdosage = 0.5g, T = 25°C, t= 6hours)

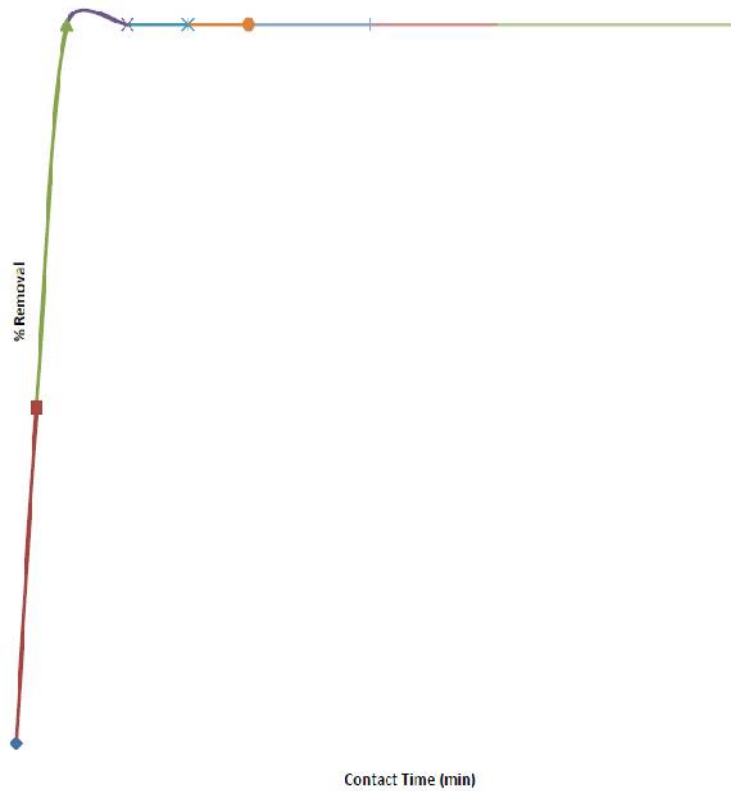


Figure 2. Effect of contact time on the adsorption of Pb(II)
 (Co = 50mg/L, Cdosage= 0.5g, T= 25°C, pH =3)

Effect of Initial Metal Ion Concentration and Temperature

The graphical illustration of the result shown in Figure 3, for the effect of initial metal ion and concentration of lead ion for maximum uptake within the concentration ranges of 10mg/L to 200mg/L. These studies were carried out at different temperature ranging from room temperature to 65°C. As the concentration of Pb ion was increased from 10mg/L to 200mg/L, the percentage adsorption increased. The same observation was observed at different temperature ranges studied. It can be deduced that there is an increase in adsorption as temperature is increased. The reason for this is that, an increase in temperature causes an increase in the kinetic energy of the ions, making it more possible for more particles of the adsorbate to be bonded onto the adsorbent. The decrease in adsorption at higher concentration of metal ions is due to the fact that all adsorbents have a fixed number of active sites and at higher concentration the active sites become saturated. The optimum initial metal ion concentration was found to be 10ppm while the optimum temperature was deduced to be 65°C. These claims are consistent with what was reported by Hafiza *et al.*, where rice straw was used as the biosorbent [10]. Similar trend was reported by Yakot and El-Sherif, 2010 [11].

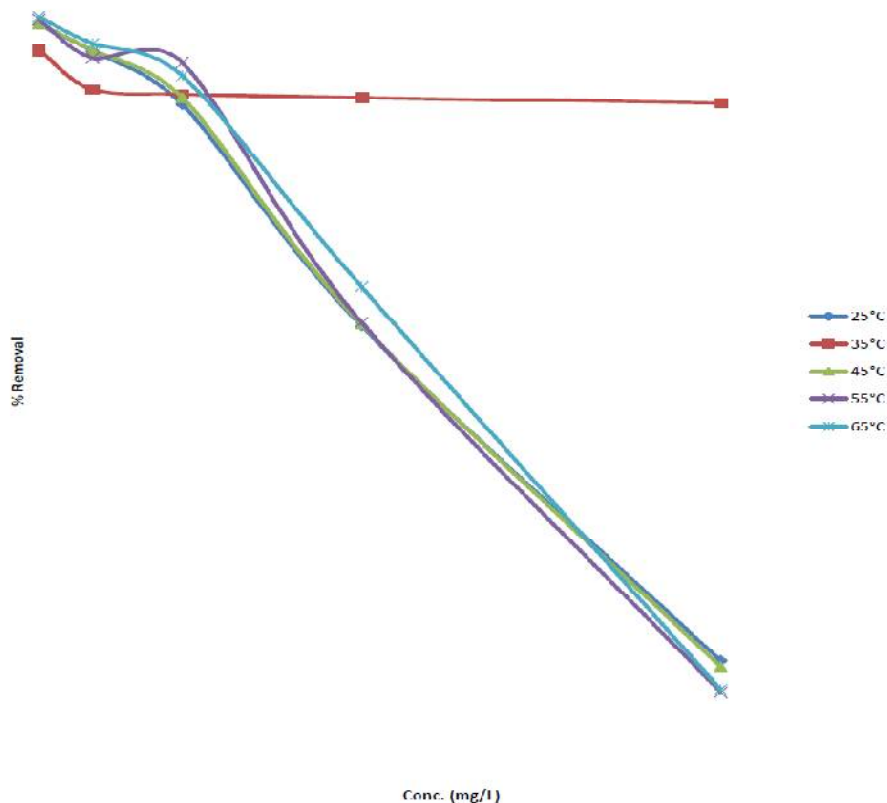


Figure 3. Effect of Initial Metal ion Concentration and Temperature On adsorption of Pb(II) ion
 ($C_0 = 10\text{mg/L}$ to 200mg/L , $C_{\text{dosage}} = 0.5\text{g}$, $T = 25^\circ\text{C}$ to 65°C , $\text{pH} = 3$, $t = 30$ minutes)

Effect of Adsorbent Dosage

The effect of adsorbent dose on the percentage removal of the metal ion Pb(II) is shown in Figure 4. It can be seen that there was an initial increase in percentage removal up to a maximum at 0.2g. This is mainly due to an increase in the sorptive surface area and the availability of more active binding sites on the surface of the adsorbent with increase in adsorbent dose. There was then a dip to the minimum point at 0.3g. An increase was then noted from the lowest point to the last weighed adsorption dosage.

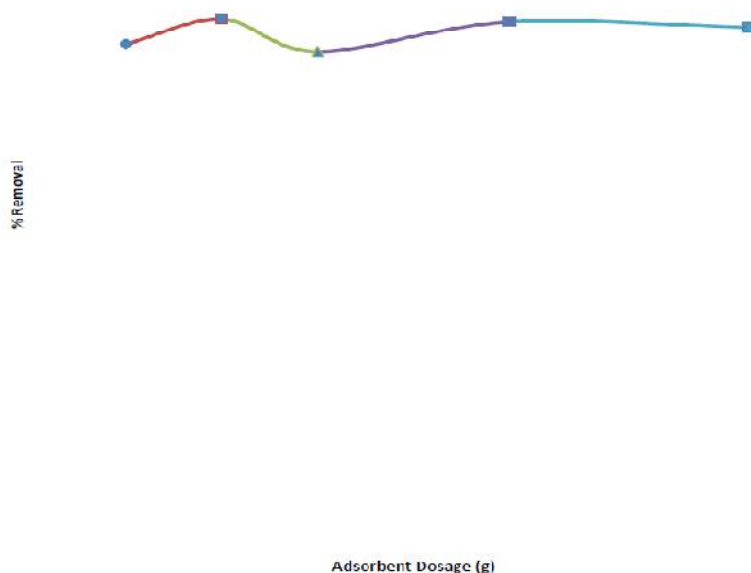


Figure 4. Effect of Adsorbent Dosage on Pb(II) adsorption
 (Co= 50mg/L , Cdosage = 0.1g to 0.75g, pH= 3, T= 25°C , t= 30 minutes)

Adsorption Isotherms

Adsorption isotherm models are commonly used to describe a relationship between concentration of lead in solution and the amount of lead adsorbed on adsorbent when both the phases are in equilibrium. An appropriate model can help in understanding process mechanism, analyze experimental data, predict answer to operational conditions, and optimize processes. Hence , two isotherm models – Langmuir and Freundlich were used to analyze the experimental data by varying initial metal ion concentrations (10mg/L, 25mg/L , 50mg/L , 100mg/L and 200mg/L) at different temperatures (25°C , 35°C , 45°C , 55°C and 65°C). The constant parameters of each isotherm model were calculated, in addition to this, the better fit model was checked by correlation coefficient R^2 , values which are summarized in Table 1.

Table 1. Isotherm constants of different isotherm models

Parameters		Temperature				
		25°C	35°C	45°C	55°C	65°C
Langmuir	q_{\max} (mg/g)	22.73	22.84	22.86	22.93	22.98
	K_L (L/mg)	0.5788	0.5524	0.6165	0.6493	0.6681
	R_L	0.0086-	0.0089-	0.0085-	0.0076-	0.0074-
		0.1473	0.1529	0.1313	0.1355	0.1302
	R^2	0.963	0.927	0.963	0.965	0.974
Freundlich	K_F (mg/g)L/mg ^{1/n}	6.28	6.29	6.30	6.43	6.55
	n	1.1173	1.0040	1.0173	1.0267	1.020
	$1/n$	0.859	0.837	0.819	0.808	0.806
	R^2	0.959	0.996	0.983	0.974	0.980

Langmuir Isotherm Model

The Langmuir isotherm model assumes that the activity of every site on the sorbent's surface is identical and equivalent, and the sorbate is adsorbed homogeneously without interaction. The graph is a plot of C_e/Q_e against C_e for the adsorption of Pb ion and it is shown in Figure 5a: The isotherm was found to be linear over the entire concentration range with good correlation coefficients (average of $R^2 = 0.958$). The maximum adsorption capacities q_{\max} improved with an increase in temperature, which indicates an endothermic process. The values of K_L (L/mg) parameter of the model is the constant representing the affinity of sorbate to sorbent. Higher K_L values mean more affinity for the sorption of Pb onto the bark powder. The implication of the K_L value as shown in Table 1 is that at higher temperature, there will be swelling of the internal structure of the adsorbent materials to increase the monolayer adsorption capacity value (q_{\max}) and adsorb more Pb molecules on its surface. The values of R_L for this isotherm ($1 > R_L > 0$) from the Table 1, shows that the process favourable.

Freundlich isotherm model

The empirical Freundlich equation on sorption onto heterogeneous surface is given by equation 5. The constant n is the Freundlich exponent and should have a value lying in the range of 1 to 10 for classification as favorable adsorption. The adsorbent indicated that the adsorption was favorable as shown in Table 1. The plot is presented in figure 5b. The Freundlich model presented a better fit to the adsorption data compared to the Langmuir

model. This is because of the correlation coefficient R^2 closer to 1. Mechanism of chemisorptions is confirmed if $1/n < 1$ and it was evident that $1/n$ decreased as the temperature increased. This is an indication that the surface becomes more heterogeneous and the possibility of swelling of the adsorption sites at higher temperature. The Freundlich constant, K_f , which is related to adsorption capacity increased with temperature, indicating an endothermic process.

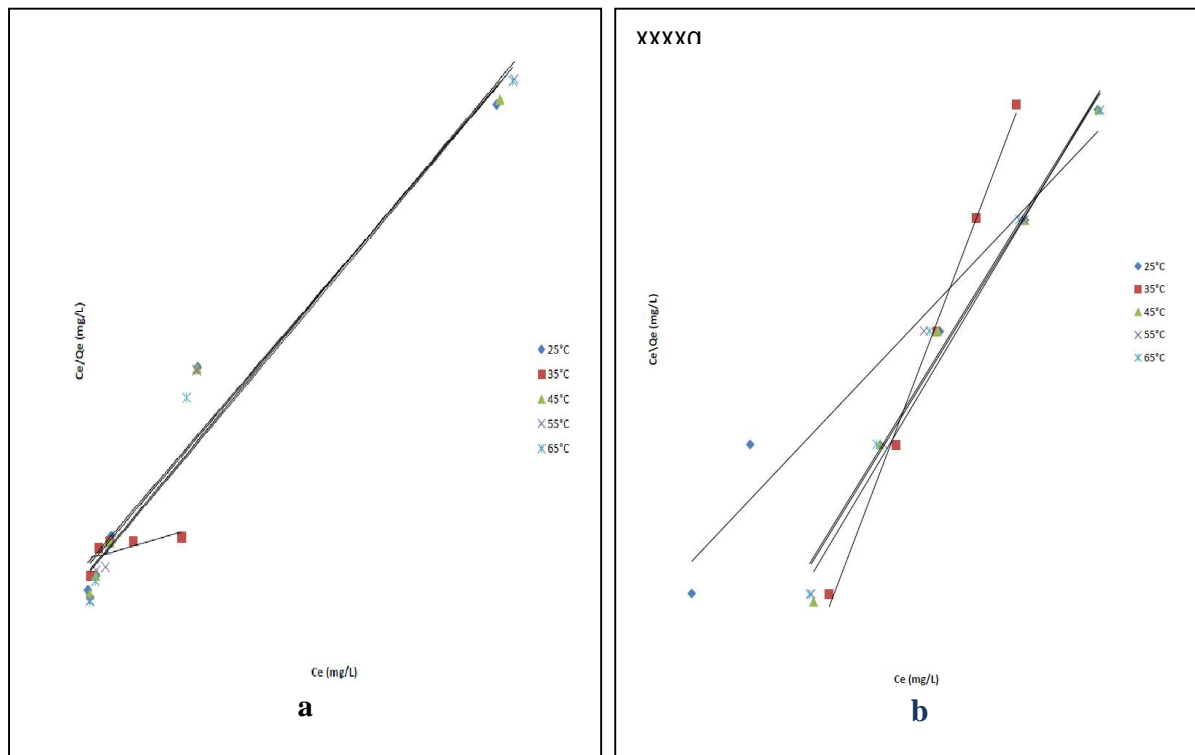


Figure 5.(a) Langmuir Isotherm Plot for adsorption of Pb(II) Onto *Bridelia ferruginea* Plant Bark Powder ($C_0 = 10-200\text{mg/L}$, $C_{\text{dosage}} = 0.5\text{g}$, $T = 25-65^\circ\text{C}$, $\text{pH} = 3$, $t = 30\text{mins}$). (b) Freundlich Isotherm Plot for adsorption of Pb(II) Onto *Bridelia ferruginea* Plant Bark Powder ($C_0 = 10-200\text{mg/L}$, $C_{\text{dosage}} = 0.5\text{g}$, $T = 25-65^\circ\text{C}$, $\text{pH} = 3$, $t = 30\text{mins}$)

Pseudo-first-order kinetic

The rate constant of adsorption was determined from pseudo-first-order rate expression given in equation 7, where q_e and q_t are the amount of lead adsorbed at equilibrium and at time (t) (mg/g) respectively and k_1 (min^{-1}) is the rate constant of adsorption. The values of the k_1 and q_e cal were evaluated from the slope and intercept of the plot $\log(q_e - q_t)$ versus t as shown in Figure 6a and reported in Table 2. The table shows that there is a large difference in the value of q_e , cal and q_e , exp and R^2 is not close to unity for the adsorbent. This concluded that the pseudo-first-order model was not suitable to describe the kinetic profile of the adsorption.

Pseudo-second-Order kinetic

The pseudo-second-order kinetic model is given in equation 8 considers the rate-limiting step as the formation of a chemisorptive bond involving sharing or exchange of electrons between the sorbate and the sorbent. In contrast to other kinetic model used, it predicts the behavior over the whole range of studies supporting a pseudo-second-order equation and is in agreement with chemisorption being the rate controlling step. For pseudo-second-order parameters, q_e , cal , K^2 and h were calculated from the linear plot of t/qt versus t (Figure 6b). These results are presented in Table 2. The calculated q_e values agreed well with the experimental values. This indicates that the uptake of Pb ions onto the bark powder is rapid and favorable. In addition, the initial sorption rate (h) calculated by using equation 9 is given as $0.495 \text{ mg g}^{-1} \text{ min}^{-1}$. This is an indication that the initial sorption rate is fast. Furthermore, the correlation coefficient R^2 for the pseudo-second-order adsorption mechanism was closer to unity compared to that obtained for the pseudo-first order model as shown in Table 2. These suggest that the pseudo-second-order adsorption mechanism is more operative and that the overall rate of the Pb ion adsorption process appears to be predominantly controlled by the chemisorption process, which may involve valence forces through sharing or exchange of electrons between sorbent and sorbate and also by the interaction between polar functional groups on the adsorbent surface and the metals.

Table 2. Kinetic parameters for adsorption on lead ions onto bark powder of *Bridelia ferruginea* plant

Parameters	
Pseudo-first-order	
$q_{e,exp} \text{ (mg/g)}$	6.94
$q_{e,cal} \text{ (mg/g)}$	4.39
$K_1 \text{ (min}^{-1}\text{)}$	0.02303
R^2	0.575
Pseudo-second-order	
$q_{e,cal} \text{ (mg/g)}$	7.32
$k_2 \text{ (g mg}^{-1} \text{ min}^{-1}\text{)}$	0.0202
$h \text{ (mg g}^{-1} \text{ min}^{-1}\text{)}$	0.495
R^2	0.908

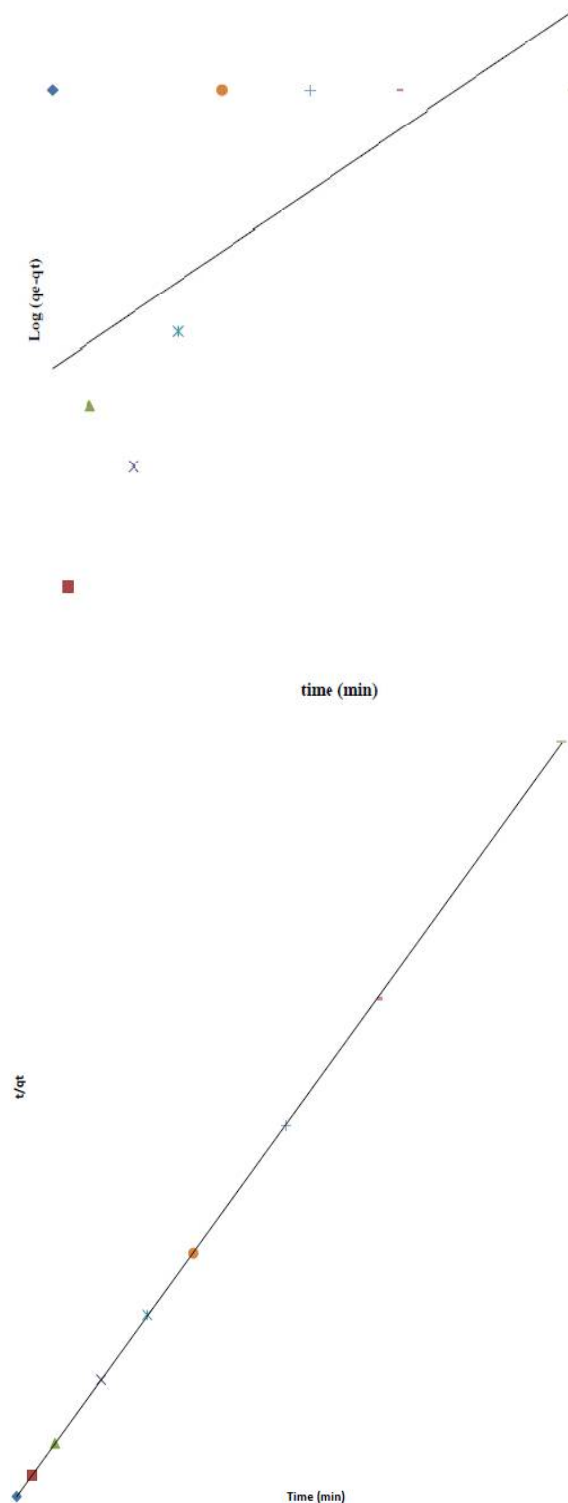


Figure 6.(a) Pseudo first order plot for adsorption of Pb(II) onto Bridelia ferruginea plant Bark Powder ($C_o = 10-200\text{mg/L}$, $C_{\text{dosage}} = 0.5\text{g}$, $T = 25-65^\circ\text{C}$, $\text{pH} = 3$, $t = 30\text{mins}$).
(b) Pseudo second order plot for adsorption of Pb(II) onto Bridelia ferruginea plant Bark Powder ($C_o = 10-200\text{mg/L}$, $C_{\text{dosage}} = 0.5\text{g}$, $T = 25-65^\circ\text{C}$, $\text{pH} = 3$, $t = 30\text{mins}$)

Thermodynamic Studies

From the result of the thermodynamic studies, the Table 3, the positive values of ΔH° suggest the endothermic nature of the adsorption. One possible interpretation of endothermicity of adsorption was that the metal ions were highly solvated in water, in order for these ions to be adsorbed, the hydration sphere must be removed and the process requires energy intake. The energy of dehydration supersedes that required for getting the ions attached to the surface of the adsorbent.

The positive value of ΔS° shows increased randomness at the adsorbent-solution interface during the adsorption of metal ions on the bark powder. The adsorbed water molecules, which are displaced by adsorbate species, gain more translational entropy than is lost by the adsorbate molecules, thus allowing the prevalence of randomness in the system.

The negative values of ΔG° decreased with an increase in temperature, suggesting that a better adsorption is actually obtained at higher temperature. This is because at higher temperature, ions are easily desolvated and therefore their adsorption become more favorable. The negative values of ΔG° indicate the spontaneous nature and feasibility of the adsorption process at the range of temperature studied.

Table 3. Thermodynamic parameters for adsorption of lead ions onto *Bridelia ferruginea* Plant Bark powder

C_0 (mg/L)	ΔG° (KJ/mol)					ΔH°	ΔS°
	298K	308K	318K	328K	338K	(KJ/mol)	(J/mol/K)
10	-5.88	-6.68	-3.62	-7.48	-9.08	17.90	79.81
25	-0.64	-1.18	-1.73	-2.27	-2.81	15.56	54.36
50	-0.85	-0.3	-0.91	-0.50	-0.79	16.39	52.15
100	-0.33	-0.63	-0.95	-1.44	-1.55	13.48	49.38
200	-0.54	-0.93	-1.35	-1.63	-1.89	10.57	33.95

Conclusion

In this study, the ability of the bark powder to adsorb lead ions from aqueous solution has been explored. The adsorption mechanism was dependent on the pH of the solution, temperature and contact times. The maximum adsorption capacity occurred at pH 3 and a contact time of 30 minutes. The kinetic studies revealed that the adsorption process best fit the pseudo-second-order kinetic model for the adsorbent. The adsorption isotherms at different temperatures could be well described by the two isotherm models; Langmuir and Freundlich. The adsorption data fitted best for the Freundlich Isotherm with the highest

R² value. Thermodynamic studies revealed that the adsorption process was endothermic, feasible and spontaneous in nature, with good affinity toward the sorbent. Based on all results from this study, it can be concluded that the adsorption mechanism of the adsorbent could be explained as primary chemical adsorption and secondary physical adsorption, i.e. physico-chemical adsorption process rather than a pure physical or chemical adsorption process.

References

1. Fourest, E., and Roux, J. C. (1992). Heavy metal biosorption by fungal mycelial byproducts: mechanism and influence of pH. *Applied Microbiology Biotechnology*, 3: 399-403.
2. Choy, K.K.H., and McKay, G. (2005). Sorption of Metal ions from Aqueous Solution using bone Char. *Environment International*. 31: 845-854.
3. Qasim J. M. S, Cecilia K. H. and Yossor R. A., (2010). Removal of heavy metals ions from aqueous solutions using biosorption onto bamboo; *Iraqi Journal of Chemical and Petroleum Engineering*; 11 (.3): 23-32.
4. Dewayanto, N., Husin, M.H., Yonk, L.k. and Nordin, M.R. (2010). "Waste to valuable by-product: Kinetic and thermodynamic studies of Cd, Cu and Pb ion by decanter cake," *J.Eng. Technol.* 1(1), 85-89.
5. Metcalf and Eddy, (1991). *Waste water engineering, treatment disposal and reuse*, 3rd Edition. McGraw-Hill, NY.
6. Gimba, C.E., Oholi, O. and Nok, A.J. (2002). Preparation of Activated Carbons from Agricultural Wastes I: Cyanide Binding With Activated Carbon Matrix from Coconut Shell. *Paper Presented at The International Conference of the Chemical Society of Nigeria*, Calabar, Nigeria.
7. Adebowale, K.O. I.E. Unuabonah, B.I. Olu-Owolabi, Adsorption of some heavy metal ions on sulphate and phosphate-modified kaolin, *Appl. Clay Sci.* 29 (2) (2005) 145-1488.
8. Zouboulis A.I, Lazaridis N. K, Karapantsios .T D. and Matis K. A., (2008). Metal ions biosorption from dilute aqueous solution, special issue; application of biosorbents on waste water treatment. *International Journal of Environmental pollution*; 34: 231-245.
9. Tunali S.O, Tare, V, Jawed, M and Iyengar, L. (1988). Application of xanthates in heavy metal removal. *Indian Association Water Pollution Control Technology Annual*, 15: 88-94.
10. Hafizah, M.A.K.M., Ngah, W.S.W., Ibrahim, S.C., Zakaria, H., and Ilias, W.A.H.W., (2006). Kinetics and thermodynamic study of lead adsorption from aqueous solution onto rubber (*Hevea brasiliensis*) leaf powder. *Journal of Applied Sciences*, 6(13): 2762-2767.
11. Yakout, S. M., Elsherif, E. (2010). Batch kinetics, isotherm and thermodynamic studies of adsorption of strontium from aqueous solutions onto low cost rice-straw based carbons. *Carbon-Sci. Tech.* 1, 144-153.