

STUDIES ON EQUILIBRIUM ADSORPTION, ISOTHERMS AND KINETICS OF LEAD (II) ONTO ACTIVATED CARBON PRODUCED FROM *ANNOGEISSUS LEIOCARPUS* STEM

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ABSTRACT

The adsorption potential of Activated carbon (AC) prepared from Annogeissus leiocarpus stem on the removal of Lead (II) ion from aqueous solution has been studied using batch adsorption techniques, adsorption isotherms and kinetics models. The parameters that were varied for equilibrium adsorption were initial concentration, adsorbent dose and contact time. Langmuir and Freundlich isotherms models were chosen, while Pseudo-First order and Pseudo second order were chosen as the kinetics models. The correlation coefficient (R^2) was observed to be 0.996 and dimensionless separation factor (R_L) at 0.0099 confirmed that the best fitted model that described the adsorption process of Lead (II) ion was Langmuir Adsorption isotherm similarly, the kinetic model that best fitted the adsorption process was Pseudo-second order kinetics. Base on the research findings, Annogeissus leiocarpus stem Activated Carbon possessed the potential for removal of lead (II) ions from aqueous solution. Therefore, it can be utilized for the removal of heavy metals for the treatments of wastewater.

Key words; Activated Carbon, Isotherm, Kinetics, Adsorption and Equilibrium.

1. Introduction

Heavy metal contamination in surface and groundwater has been a major concern due to its non biodegradability and acute toxicity effects on public health and the environment. The presence of heavy metals in waste effluents is generated by several anthropogenic sources such as agricultural use of pesticide and fungicide, paper and pulp industry, mining activities, smelting processes, battery manufacturing, and oil refining (Gupta and Bhattacharyya, 2008). Conventional methods used in removing heavy metal from industrial effluents are chemical precipitation, ion exchange, electrode position, evaporation, and membrane separation (Dinu and Dragon, 2010). These technologies have certain drawbacks such as being costly and ineffective in removing heavy metals at dilute concentration. In addition, chemical methods generate sludge, which requires proper confinement and disposal (Amuda *et al.*, 2007). Among the physicochemical treatments, adsorption using activated carbon in the removal of heavy metals and dyes has been employed. Materials of biological origin have been considered as an alternative to the conventional treatment of wastewater containing heavy metals. Natural adsorbents, such as clay materials, coconut shell, chitin, and chitosan are industrially attractive due to their low cost, availability, and capacity of lowering the heavy metal concentration to parts per billion (Wan and Fatinathan, 2010).

Many methods have been developed to make sea water and waste water from different industries into fresh water. Some methods include Reverse Osmosis (RO), Electro Dialysis (ED), and Capacitive deionization (CDI) (Min and Boff, 2002). Adsorption by activated carbons method is an environmentally friendly method because it does not generate waste that pollutes the environment. Activated carbons having high specific porosity, high surface areas are extremely versatile adsorbents of major industrial significance. It has wide range of applications, principally for the removal of species (contaminants) by adsorption from the liquid or gas phase. Activated Carbon can be produced from a number of precursor materials including wood, agricultural wastes, coal and synthetic resins. These precursors are normally exposed to a number of different activation method such as physical or chemical in an effort to achieve- carbon with the high adsorption capacity for a particular application. For the past few decades, attention has been shifted towards adsorption technique, which emerged as one of the widely accepted methods for the removal of contaminants from wastewater (USEP).

The study is designed to evaluate the adsorption potentials of *Annogeissus leiocarpus* stem Activated Carbon for removal of Pb^{2+} ion from aqueous solution by analysing equilibrium adsorption, adsorption isotherms and adsorption kinetics for adsorption process.

2. Material and Methods

2.1 Preparation of adsorbent

The carbonized sample (5 g) of *Annogeissus leiocarpus* was mixed with 5cm³ of 1M ZnCl₂ solution. The sample was introduced in to the furnace at 800°C for 5 minutes, after which the activated sample was cooled with cold water. Excess water was drained and the activated carbon allowed to dry at room temperature (Gimba *et al.*, 2002; Itodo, 2010). It was then washed with 10%HCl acid to remove surface ash, followed by hot water and then with distilled water to remove the residual acid until the pH of 6- 8 is attained (Rahman *et al.*, 2002; Itodo 2010). The generated activated carbon was placed in an oven at 110°C overnight and stored in an air tight container.

2.2 Lead stock solution

The Pb^{2+} stock solution (500mg/L) was prepared by dissolving 1.5991g of $\text{Pb}(\text{NO}_3)_2$ in 500cm^3 of deionized water,

2.3 Batch Adsorption Study

2.3.1 Effect of initial adsorbate concentration

The effect of initial adsorbate concentration was investigated by adjusting the initial concentration of adsorbate through dilution of working solution to the desired concentration. This was started by diluting the stock solution to 10, 20, 30, 40, 50 to 60mg/l. Adjustment of pH solution of Pb^{2+} to 6.8 was carried out using 1.0M NaOH and/or 1.0M H_2SO_4 . Agitation of the system under investigation was carried out on a rotary shaker the residual concentration of the metal ions was analyzed by Atomic absorption spectroscopy (AAS).

2.3.2 Effect of adsorbent dose

Adsorbent dosages of 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2g were used for the investigation by adding them to separate beakers containing 50mg/L of adsorbate solutions and stirred at 150 rpm using magnetic stirrer for 30 minutes and kept for 12 hours. The beakers were removed and the adsorbate solution filtered. The filtrate was separately analyzed to determine the residual concentrations of Pb^{2+} were determined. The graph of q_e against adsorbent dose was plotted.

2.3.3 Effect of Contact Time

50ml of Pb^{2+} solutions with concentration of 20mg/L each was prepared. 1g of AC was added and stirred continuously using magnetic stirrer at 150rpm for different contact time from 10, 30, 90, 180, 300, 480, 600 minutes. The residual metal ions concentrations were analyzed using AAS. The graph of equilibrium adsorption against time was plotted.

2.4 Adsorption Isotherms

2.4.1 Langmuir adsorption isotherm

Langmuir Adsorption Isotherm is the simplest of the types of isotherms that describes quantitatively the formation of a monolayer of adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Therefore, Langmuir adsorption isotherm represents the equilibrium adsorption of the sorbate molecules or ions between the solid and liquid phases (Langmuir, 1918). The Langmuir adsorption isotherm is based on the view that every adsorption site is identical and energetically equivalent (thermodynamically, each site can hold one adsorbate molecule). The Langmuir adsorption isotherm is an empirical model based on the following assumptions (Langmuir, 1916 and Langmuir, 1918);

- Intermolecular forces decrease rapidly with distance and consequently predict the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent
- Adsorption takes place at specific homogeneous sites within the adsorbent,
- Once an adsorbate molecule occupies a site, no further adsorption can take place at that site and
- The Langmuir equation is based on the assumption of a structurally homogeneous adsorbent where all sorption sites are identical and energetically equivalent (Wong *et al.*, 2004).

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{1}{Q_0} C_e \dots\dots\dots(1)$$

where C_e is the equilibrium metal ion concentration (mg/l), q_e the amount of metal ion adsorbed at equilibrium (mg/g) and Q_0 (mg/g) and K_L (l/mg) are Langmuir constants related to adsorption capacity and energy of adsorption, respectively (Goel *et al.*, 2005).

In order to know the feasibility of the isotherm, the essential features of Langmuir model can be expressed in terms of separation factor or equilibrium parameter RL, which is defined by

$$RL = \frac{1}{1 + K_L C_i} \dots\dots\dots(2)$$

C_i = Highest initial concentration of the adsorbent

K_L = Langmuir constant

The values of RL indicate the shapes of isotherms as shown in the table below;

Table 1: Condition of Langmuir isotherms according to separation factor values.

Separation Factor (RL)	Characteristics
$RL > 1$	Unfavourable
$RL = 1$	Linear
$0 < RL < 1$	Favourable
$RL = 0$	Irreversible

(Jain *et al.*, 2015).

2.4.2 Freundlich adsorption isotherm

The Freundlich adsorption model is used for heterogeneous surfaces, it is also used to describe non ideal and reversible adsorption, which can be applied to multilayer adsorption on assumption that the surface is energetically heterogeneous (Ng *et al.*, 2002). The nonlinear expression of Freundlich isotherm model can be illustrated in the equation below (Freundlich, 1906 and Xunjun, 2015).

$$q_e = K_f C_e^{1/n} \text{ (where } n > 1\text{)} \dots\dots\dots(3)$$

Where K_f = Freundlich constant related to maximum adsorption capacity (mg/g) and it is a temperature dependent.

n = Freundlich constant related to surface homogeneity (dimensionless) and it gives an indication of how favourable the adsorption processes is.

$$q_e = K_f \times C_e \dots\dots\dots(4)$$

The plot of q_e versus C_e yield non regression line, which permits the determination of $1/n$ and K_f Values of $1/n$ ranges from 0 to 1, the closer the values of $1/n$ to zero the more heterogeneous the adsorption surface. These values can be linearized by obtaining by plotting $\ln q_e$ versus $\ln C_e$ as represented by equation (6)

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \dots\dots\dots(5)$$

Where the slope is $1/n$ and the intercept is $\ln k_f$

2.5 Adsorption Kinetic Models

2.5.1 Lagergren pseudo first order kinetic

The Lagergren first-order kinetic equation is based on adsorbent capacity (Lagergren, 1928 and Adda *et al.*, 2019) and is written as:

$$\frac{dq_t}{dt} = K_{1,ads} (q_e - q_t) \dots \dots \dots (6)$$

where $k_{1,ads}$ (1/min) is the first-order sorption rate constant, q_e is the equilibrium uptake and q_t is the uptake at time t . Equation 7 can be integrated using the boundary condition $q_t = 0$ at $t = 0$ to give:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \dots \dots \dots (7)$$

Thus, if the adsorption kinetics obey the Lagergren first-order kinetic equation, a plot of $\ln(q_e - q_t)$ versus t should result in a straight line. However, in many cases, the Lagergren first-order equation only fits the sorption kinetics over the first 20–30 min of the sorption process (Aksu and Yener, 2001).

2.5.2 Pseudo-second-order kinetic model

The pseudo-second-order kinetic equation, suggested by Ho and McKay (2000), is also based on the sorption capacity of the sorbent and is given by:

$$\frac{dq_t}{dt} = K_{2,ads} (q_e - q_t)^2 \dots \dots \dots (8)$$

where $k_{2,ads}$ (g/mg min) is the rate constant for pseudo-second-order sorption. Integrating equation (8) with the boundary condition $q_t = 0$ at $t = 0$ gives:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_{2,ads} q_e^2} \dots \dots \dots (9)$$

Where, k_2 ($\text{mol L}^{-1} \text{min}^{-1}$) is the pseudo-second-order adsorption rate constant q_e the amount adsorbed at equilibrium, and q_t is the amount of adsorbed at time 't'. The product $k_2 q_e^2$ actually represents the initial sorption rate ($\text{Rate} = k_2 q_e^2$). Thus, for pseudo-second-order kinetics, a plot of t/q_t versus t should result in a straight line.

3.0 Results and Discussion

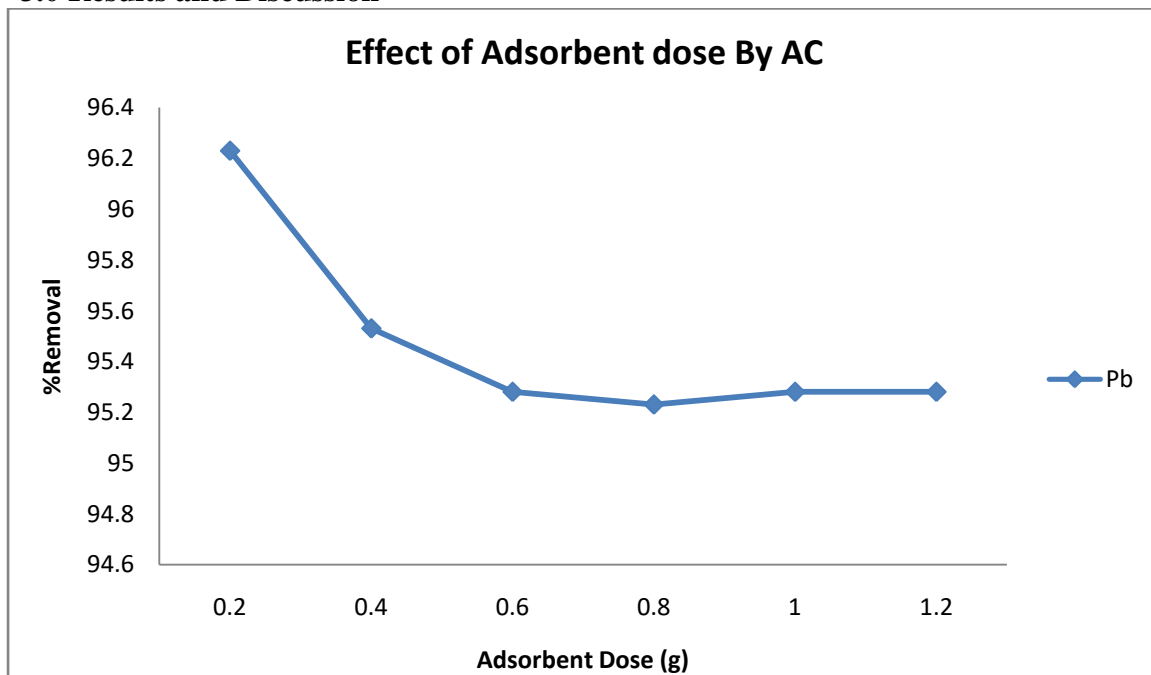


Figure1. Effect of Adsorbent dose on the percentage removal of heavy metal by AC

The result of this study indicated that rapid % adsorption capacity was recorded at adsorbent dose of 0.2g which gave the optimum percentage removal of Pb^{2+} on AC, (96%). It has been found that Pb^{2+} adsorption happen so rapid at the beginning slightly decrease with increase in adsorbent dose. But any addition over 1.0g made only little or no increment in the adsorption of heavy metal ion. This is due to increase in number of exchangeable sites with limited number of metal ions, after equilibrium is reach. This result is in line with findings of Mutasim and Yusuf (2015). The optimum values obtained in this work also agreed with the Monika *et al.*, (2010).

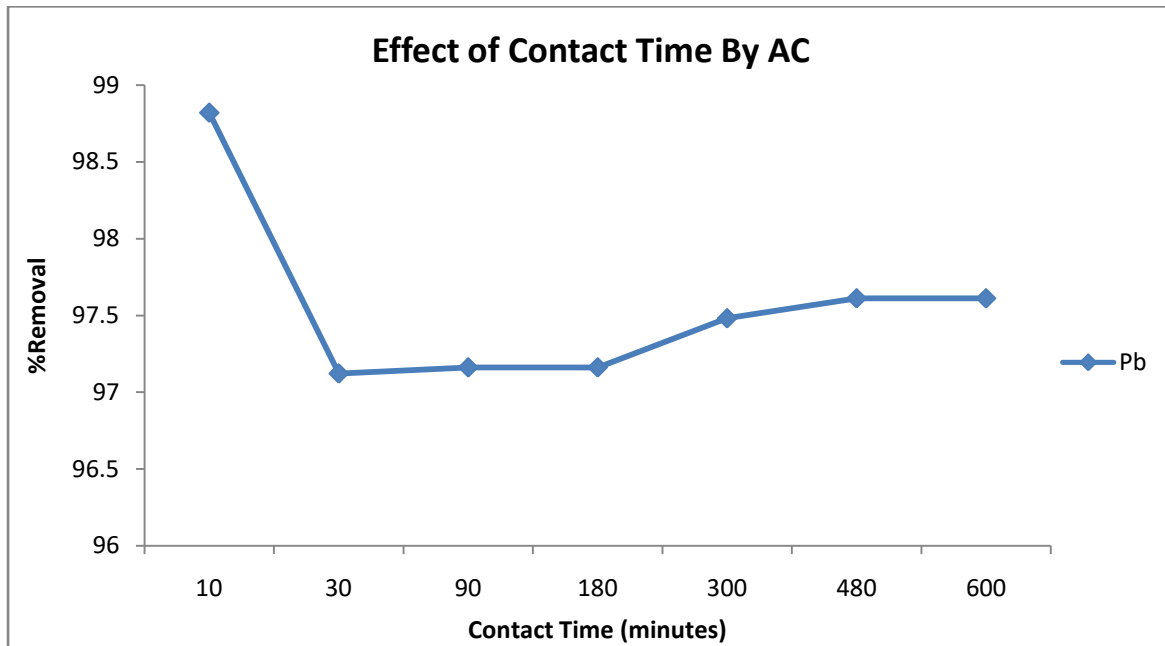


Figure 2. Effect of contact time on the percentage removal of heavy metal by AC

The effect of contact time on the removal of Pb^{2+} on AC was investigated and the results have shown that the adsorption of metal ions is very fast at the beginning. In the first ten minutes (10), the % removal of Pb^{2+} was 98.8% which gave the optimum value. This is because of the availability of the adsorption sites at the initial stage of the process (Mutasim and Yusuf, 2015). The slight decrease in the percentage removal on AC was due to desorption after equilibrium was reached. The Maximum percentage removal obtained in this work is in agreement with findings of Badalmoole, *et al.*, (2018).

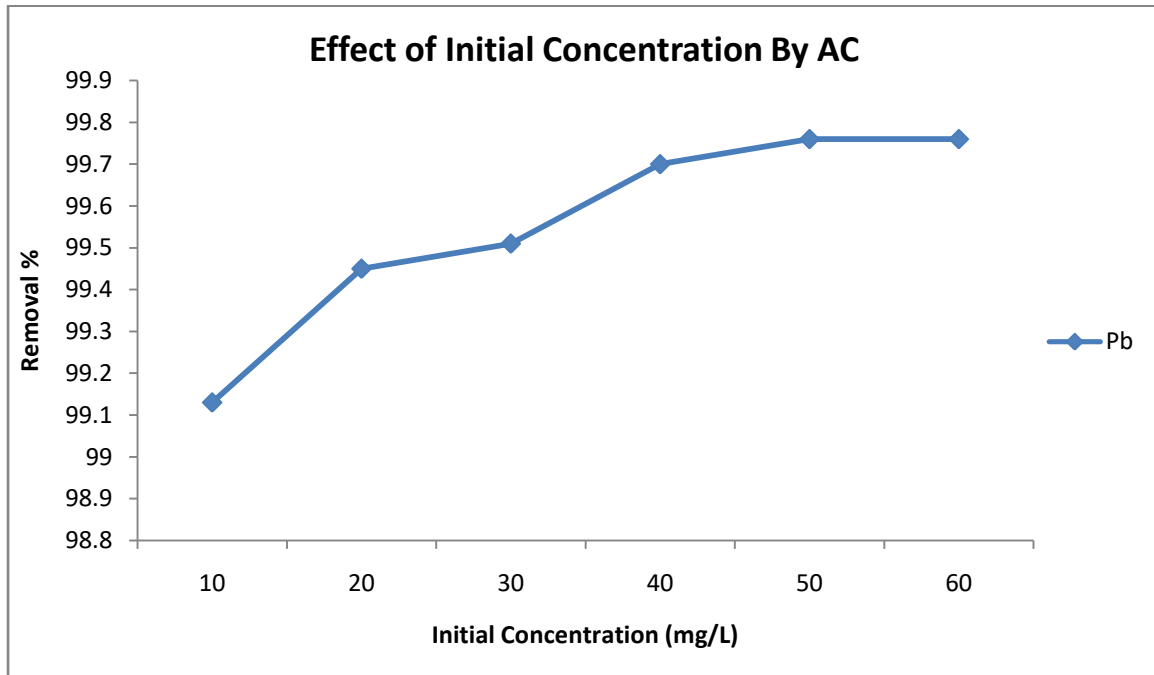


Figure 3. Effect of Initial Concentration on the percentage removal of heavy metal by AC

The effect of initial concentration on the percentage removal of Pb^{2+} is shown in figure 3 and the result revealed that there was general increase in percentage removal of Pb^{2+} from 10mg/L to 60mg/L. This is due to increase in metal ion concentration for the available adsorption sites. It can be seen that the percentage removal of Pb^{2+} increases from 92.96 at 10mg/L to 99.05% at 60mg/. Therefore the percentage removal of Pb^{2+} increases with increase in metal ion concentration. At low concentration of metal ions, sufficient adsorption sites are available for adsorption. Therefore, the fraction of adsorption is dependant on the initial concentration of metal ion. However at high concentration, there was sufficient number of heavy metal ions that can match the available adsorptive sites which in turns increased percentage removal. This is also what was observed by Dinu and Dragon, (2010).

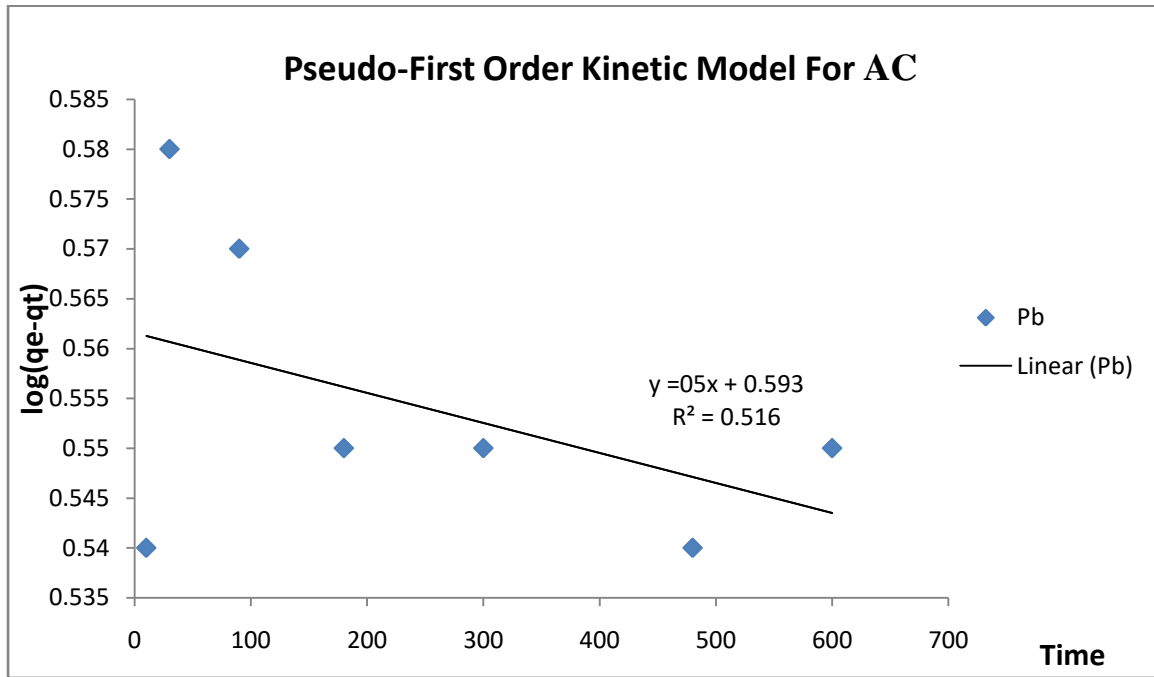


Figure.4: Pseudo-First Order Kinetic Model For AC

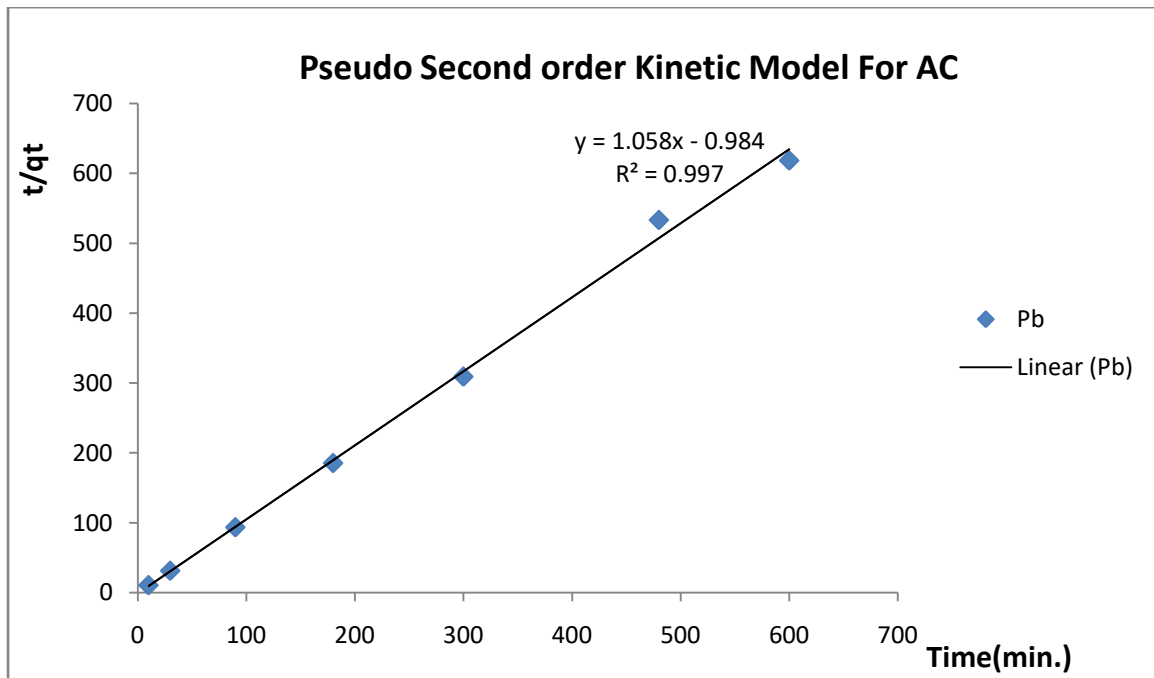


Figure 5: Pseudo Second order Kinetic Model For AC

Table 2: Kinetic Parameters for the Adsorption of Heavy metal by Activated carbon produced from *Annogeissus leiocarpus*

Adsorbent	Heavy metal	Pseudo First Order			Pseudo-second order		
		$\ln(q_e - qt) = \ln q_e - k_1 t$			$\frac{t}{dt} = \frac{t}{q_e} + \frac{1}{K_{2,ads} q_e^2}$		
		q_e	K_1	R^2	q_e	K_2	R^2
AC	Pb	1.75	0.5×10^{-6}	0.207	1.02	9.3×10^{-1}	0.997

The adsorption parameters on kinetic study for pseudo first order and pseudo second order have been carefully investigated and recorded. The pseudo-first-order showed that the correlation coefficient (R^2) for AC, (0.207). This low R^2 value (0.207) that pseudo-first-order kinetic model does not adequately describe the adsorption process for the selected heavy metal Pb^{2+} . While the R^2 values for pseudo-second-order kinetic model showed a better fit to the experimental data $R^2 = 0.997$ compared to the first-order kinetics and also had a better fit at all parameters studied. The pseudo-second-order model assumes that each metal ion is adsorbed onto two adsorption sites which allows a stable binuclear bond to form (Karaca *et al.*, 2004). Furthermore, values for quantity of metal ion adsorbed (q_e) obtained at equilibrium for the study were found to be more consistent with those calculated for pseudo second order kinetics. (Meena *et al.*, 2005; Arshad *et al.*, 2008; Boulaiche *et al.*, 2019), they worked independently and reported that pseudo second order kinetic is more appropriate in explaining adsorption of metal ions.

Table 3: Isotherm constants for the Adsorption of Heavy metal by Activated carbon produced from *Annogeissus leiocarpus*

Adsorbent	Heavy metal	Langmuir Isotherm				Freundlich Isotherm			
		$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{1}{Q_0} C_e$				$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e$			
		K_L	q_0	R_L	R^2	K_f	$1/n$	N	R^2
AC	Pb	0.091	50.00	0.729	0.999	2.654	0.670	1.493	0.948

Based on the R^2 values, Langmuir isotherm provided the best fit for adsorption of Pb^{2+} . Meanwhile, the adsorption of Pb^{2+} onto AC correlated very well with $R^2 = 0.999$. This result is in line with Moore *et al.*, (2013). The q_0 value obtained can be seen at 0.729 for Pb^{2+} and it exhibits a very good adsorption capacity. The Langmuir constant, b is related to the affinity of metal ions to the binding sites, where Pb^{2+} provided high value. The high value obtained for Pb^{2+} implies high affinity to the adsorbent. The value of the equilibrium parameter R_L would indicate if the adsorption system would be: unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The obtained R_L values are found in the range of (0.011–0.79), which confirmed that removal of Pb^{2+} using AC is favourable. For the

Freundlich model, the value of n would give an indication on the favourability of adsorption. If the adsorption intensity $n < 1$, it would imply that adsorption is favourable over the whole concentration range studied. Meanwhile, a value of $n > 1$ would indicate the adsorption intensity is favourable only for high concentration range (Shokat *et al.*, 2019). Based on the n values, adsorption of Pb^{2+} onto AC implies that adsorption intensity is favourable at high concentration range. The obtained KF values, which indicate the relative sorption capacity is good for adsorption of Pb^{2+} on AC.

Conclusion

The Removal of Pb^{2+} ions from aqueous solution by adsorption techniques using *Annogeissus leiocarpus* stem activated carbon has been the focus of this research work. The following conclusion was drawn. It has been observed that the %removal increase with the increase of the processed parameters.

- The optimum adsorbent dose attained 1.2 g with the %removal of 95.53, The optimum Contact time 10min with the % removal of 98.82 and optimum initial concentration is 10mg/L with the % removal of 99.76.
- Adsorption Isotherms such as Langmuir and Freundlich were tested and Langmuir adsorption isotherm happened to be the best fitted model for the adsorption process.
- Kinetics of the adsorption was investigated and pseudo second order described the adsorption process very well. Therefore the adsorption of Pb^{2+} obeys pseudo-second order Kinetics.

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