

Kinetics and Isotherm Studies of Cu^{2+} and Pb^{2+} Ions Removal from Simulated Waste Water by *Gambeya Albida* Seed Shell Activated Carbon

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The aim of this study was to investigate the ability or otherwise of using star apple (*Gambeya albida*, *G. albida*) seed shells as an alternative adsorbent for the removal of lead (II) and copper (II) ions from simulated waste water. Batch adsorption of copper (II) and lead (II) ions from simulated waste water was investigated using activated carbon produced from the seed shell. Pseudo-first order, pseudo-second order, Bhattacharya-Venkobachar, Elovich and intra-particle and film diffusion kinetic models were employed to carry out kinetic analysis of the adsorption processes. Langmuir, Freundlich and Temkin models were used for isotherm studies. Adsorption of both metal ions was found to increase with an increase in the initial metal concentration and contact time. The rates of the adsorption processes were controlled by film (boundary layer) diffusion. Langmuir isotherm best described the adsorption processes and the monolayer adsorption capacities were found to be 16.67 and 18.52 mg.g^{-1} for copper (II) and lead (II) ions, respectively.

1. Introduction

Water pollution by heavy metal ions has been on the increase due to increase industrialization. The presence of these heavy metal ion contaminants in the treated or untreated waste water from industries either producing or using these metal bearing products introduces the metal ions into water bodies [1]. These metal ions are toxic when present in significant quantities and the toxicity is owing to their ability to bind with protein molecules and prevent replication of DNA and thus subsequent cell division [2, 3]. A range of industries, which generate waste waters containing significant concentrations of lead, include the lead-acid battery industry, smelting, printed wiring board manufacture and paper mills [4, 5]. Copper is mainly employed in electrical and electroplating industries [6].

High concentrations of copper can lead to many important health conditions like fatigue, premenstrual syndrome, anorexia, depression, anxiety, migraine headaches, allergies (food and environmental allergies), and many others [7]. Lead poisoning causes severe damage to kidney, nervous system, reproductive system, liver, and brain [8]. As a result of the toxicity of these metal ions, it is therefore imperative to remove them from wastewater before disposing the water into the environment.

Various treatment technologies have been employed for the removal of heavy metal ions from wastewater and they include chemical precipitation, ion exchange, reverse osmosis, electro dialysis, and activated carbon adsorption [9]. Among these various technologies, activated carbon adsorption is commonly used because it has been shown to be economically favorable (compared with ion exchange, liquid extraction or electro-dialysis) and technically easy (compared with precipitation or reverse osmosis) [10]. Also, it can be produced from cheap and locally available materials [11-13].

In a report aimed to show the relevance of seed shell pericarp of *Chrysophyllum aibidum* in water and waste water treatment among other uses by Ewansiha et al. [14], they had concluded that *Chrysophyllum albidum* (*Gambeya Albida*) seeds can be an effective biomaterial in water and waste water treatment among many other uses. Oboh et al carried out sorption experiments with neither activation nor carbonization of the *G. albida* seed shells and concluded that the ability of *C. albidum* seeds to absorb metal ions could be used for the development of a cheap technology for effluent treatment [15]. *G. albida* was then activated with HNO_3 and was further treated with 1.0 M mercaptoacetic acid (HSCH_2COOH) solution (without carbonization), and then used for the removal of metal ions from solution by Onwu and Oga [16]. They reported varying degrees of

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removal for the metals studied and concluded that African star apple can be a good sorbent for heavy metals. In this work, activated carbon was produced from the seed shells of star apple (*Gambeya albida*) with combined activation and carbonization method, to enhance the pore size development [Elizalde-González et al. [17], and tested for the removal of Cu (II) and Pb (II) ions from simulated wastewater. Kinetic and isotherm modeling were carried out for the first time to the best knowledge of the authors. Further establishment of the process parameters that could enhance the use of this biomass could help reduce the expenditure on importation of activated carbon, which is the major material in use in industries in Nigeria for wastewater treatment.

2. Materials and Methods

2.1 Preparation of adsorbent

Activated carbon was produced from *Gambeya albida* seed shells by the method of Theivarasu and Mylsamy [18], with activation carried out using concentrated phosphoric acid and carbonization done at 600°C for 1 hour.

2.2 Preparation of adsorbate

Cu (II) solution of 1000mg/L was prepared from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and was used to prepare the desired concentrations by appropriate dilution with de-ionized water.

2.3 Adsorption study

This was carried out using the batch process. 2g of activated carbon was agitated with 400 ml of metal solutions of varying concentrations (50, 100, 150 and 200mg/L) until equilibrium was attained. Samples were withdrawn at fixed time intervals, filtered and analyzed for residual metal concentration by atomic absorption spectrometry, using Atomic Absorption Spectrophotometer, Model 210VGP, Buck Scientific, Connecticut, USA.

2.4 Isotherm study

Isotherm study was carried out by agitating 100ml of metal solutions of varying concentrations (50, 100, 150 and 200mg/L) with 0.5 g of adsorbent until equilibrium was achieved. The reaction mixture was then filtered and the filtrates analyzed for residual metal concentrations.

2.5 Kinetic modeling

Various kinetic models; pseudo-first order [19], pseudo-second order [20], Bhattacharya-Venkobachar [21], Elovich [22], and intra-particle and film diffusion kinetics [23] as described elsewhere [24], were tested using the experimental data. The linear equation for each of the above models is given in Table 1.

2.6 Isotherms

2.6.1 Langmuir isotherm

Patel and Suresh [25] used Langmuir isotherm

$$q_e = (q_{\max} C_e) / (K_L + C_e) \quad (1)$$

which, in the linearized form gives

$$C_e/q_e = (1/k_L \cdot q_{\max}) + (1/q_{\max}) \cdot C_e \quad (2)$$

in the analysis of data obtained from their studies.

A plot of C_e/q_e versus C_e yields a straight line graph with a slope and intercept that correspond to $(1/q_{\max})$ and $(1/k_L \cdot q_{\max})$, respectively, from which $q_{\max}$ and k_L can be calculated. The behavior of the Langmuir isotherm in relation to an adsorption process can also be determined by means of a dimensionless constant known as the separation factor, R_L , which is calculated [26] from Eqn.3;

$$R_L = 1/(1 + k_L \cdot C_o) \quad (3)$$

Where, C_o is the initial adsorbate concentration.

$R_L=0$ shows that the isotherm is irreversible, $0 < R_L < 1$ shows that it is favourable, $R_L = 1$ shows that it is linear, and $R_L > 1$ shows that it is unfavourable.

2.6.2 Freundlich isotherm

The Freundlich isotherm expressed as:

$$q_e = k_F \cdot C_e^{1/n} \quad (4)$$

Table 1: Linear equations for the kinetic models studied.

	Model	Linear Equations	Plots
1	Pseudo-first order [19]	$\log (q_e - q_t) = \log q_e - (k_1 t)/2.303$ q_t and q_e = adsorption capacity (mg.g^{-1}) at time t and at equilibrium; t = time (min); k_1 = rate constant of pseudo first order adsorption (min^{-1})	$\log (q_e - q_t)$ vs t
2	Pseudo-second order [20]	$t/q_t = 1/(k_2 q_e^2) + t/q_e$ q_t and q_e = adsorption capacity (mg.g^{-1}) at time t and at equilibrium; t = time (min); k_2 = rate constant of pseudo second order adsorption ($\text{g.mg}^{-1}.\text{min}^{-1}$)	t/q_t vs t
3	Bhattacharya-Venkobachar [21]	$\log [1 - (U)T] = (k_B/2.303) t$ $\{(U)T = (C_o - C_t) / (C_o - C_e)\}$ k_B = B-V constant (min^{-1}); C_o = initial concentration (mg/L); C_t and C_e = concentration (mg/L) at time t and at equilibrium.	$\log [1 - (U)T]$ vs t
4	Elovich [22]	$q_t = (1/\beta) \ln (\alpha\beta) + (1/\beta) \ln (t)$ α = initial adsorption rate ($\text{mg.g}^{-1}.\text{min}^{-1}$); β = desorption rate constant ($\text{mg.g}^{-1}.\text{min}^{-1}$); time (t).	q_t vs $\ln (t)$
5	Intra-particle and film diffusion [23]	$-\log q_t = \log k_{id} + 0.5 \log t$ q_t = amount of adsorbate adsorbed at time t (mg.g^{-1}); time t (min); k_{id} = intra-particle rate constant ($\text{mg.g}^{-1}.\text{min}^{-0.5}$) $-D_p = (0.03r_o^2)/t_{0.5}$ r_o (cm) = average radius of the adsorbent particle; $t_{0.5}$ (min) = time required to complete the half of the adsorption $-D_F = (0.23r_o\delta C_S)/(C_L t_{0.5})$ δ = film thickness (10^{-3}cm), C_S and C_L = concentrations of adsorbate at time t in the solid and the liquid phases, respectively.	$\log q_t$ vs $0.5 \log t$

And, in linearized form [27] as

$$\log q_e = \log k_F + 1/n \log C_e \quad (5)$$

A plot of $\log q_e$ versus $\log C_e$ yields a straight line graph with a slope and intercept that correspond to $(1/n)$ and $(\log k_F)$, respectively, from which n and k_F can be calculated if the adsorption process followed the model.

2.6.3 Temkin isotherm

The Temkin isotherm [28] is expressed as shown in Eqn.6.

$$q_e = (RT)/b_T \ln k_T + (RT)/b_T \ln C_e \quad (6)$$

Where, b_T indicates the adsorption potential of the adsorbent and k_T is the Temkin constant.

A plot of q_e versus $\ln C_e$ for a process that is described by the equation gives a straight line

graph with a slope and intercept that correspond to $((RT)/b_T)$ and $((RT)/b_T \ln k_T)$, respectively, from which b_T and k_T can be calculated.

3. Results and Discussion

The results obtained from the experiments are summarized in below.

3.1 Effects of contact time and initial metal concentration

The dependence of quantity of metal adsorbed on contact time and initial metal ion concentration is shown in Fig. 1. There was rapid adsorption during the first 30 minutes of agitation after which the rate of adsorption became slower. For the various concentrations of Pb (II) studied, equilibrium was attained after 210 minutes of agitation, while for Cu (II), equilibrium was attained faster (after 130 minutes for concentrations of 50 and 100mg/L and

170minutes for 150 and 200mg/L). This trend can be explained by the fact that within the first 30 minutes, the adsorbent still had a vast number of unoccupied sites unto which the adsorbate particles could adsorb. As a result, there was a high probability of adsorption for every migrating/diffusing molecule of adsorbate. As so many adsorbate particles adsorbed within this time, the number of unoccupied sites decreased and the adsorbent surface started approaching saturation [29-30]. The plots are single, smooth and continuous leading to saturation. Fig. 1 also show that the amount of metal adsorbed per unit weight of carbon increased with the increase in metal concentration. This is because an increase in the initial metal ion concentrations are effective to break the resistance originating from mass transfer, resulting in increased adsorption [31].

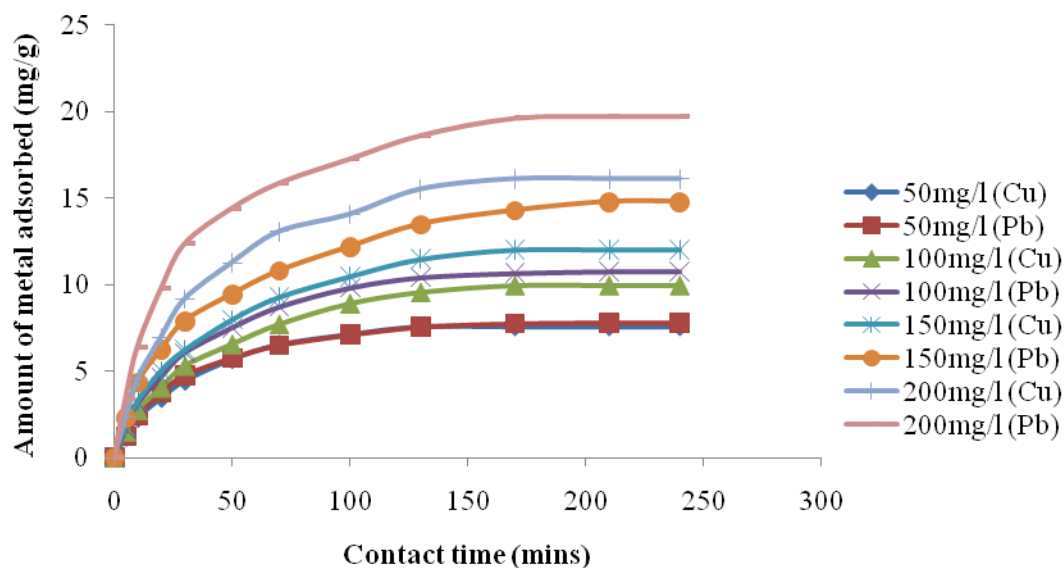


Fig.1: Effect of contact time and initial concentration of Cu (II) and Pb (II) ions on the adsorption process.

The parameters obtained from these various models, Bhattacharya-Venkobachar and Elovich plots (not shown), pseudo first order (Fig. 2) and

pseudo second order (Fig. 3) plots for Cu(II) and Pb(II), were compared in Tables 2 and 3.

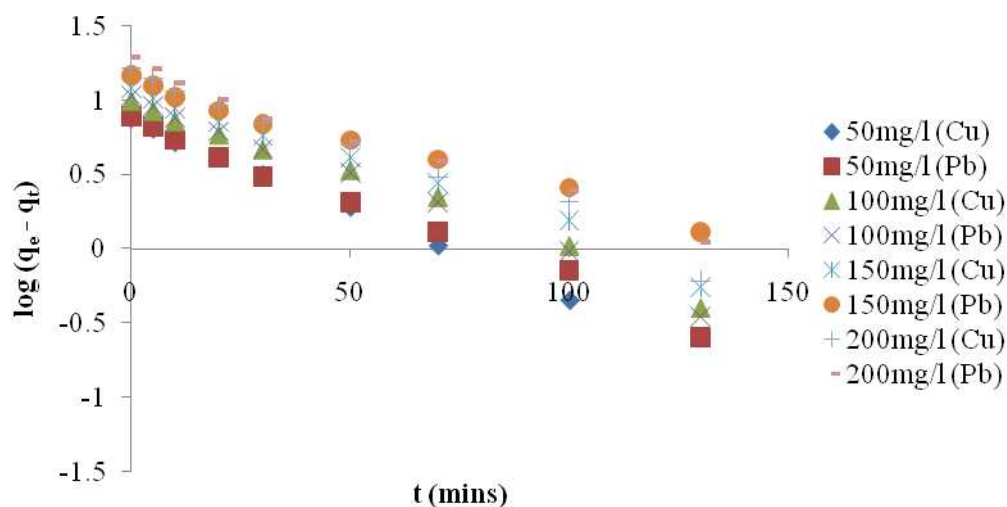


Fig.2: Pseudo first order plot for Cu (II) and Pb (II) ion adsorption on the adsorbent.

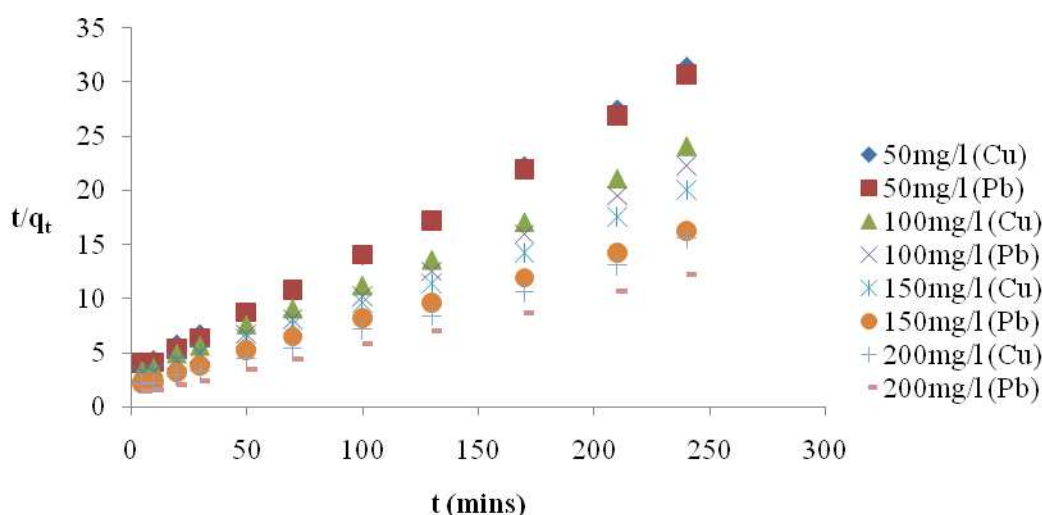


Fig.3: Pseudo second order plot for Cu (II) and Pb (II) ion adsorption on the adsorbent.

A comparison of these kinetic models based on the linear regression coefficient (R^2) values (Tables 2 and 3) shows that the pseudo second order model best describes all the adsorption processes ($R^2 > 0.994$), except at low concentration of Cu (II) ion (50mg/L), which was best described by the Bhattacharya-Venkobachar and the pseudo first order models. For the adsorption of 200mg/L of Cu (II), Elovich model gave a similar correlation as the

pseudo second order model. Confirmation of adsorption processes to pseudo second order kinetics have also been reported [32] for the removal of Pb (II) and Cr (VI) from aqueous solution, Pb (II) ion removal with fluted pumpkin seed shell activated carbon [24], and for Co (II) removal with lemon peel bio-sorbent [33].

Table 2: The kinetic parameters evaluated for Cu (II) ion adsorption.

Kinetic model	Parameter	Solute Concentration (mg/L)			
		50	100	150	200
Bhattacharya-Venkobachar	$K_B (\text{min}^{-1})$	-0.028	-0.023	-0.021	-0.023
	R^2	0.999	0.988	0.986	0.980
Pseudo-first order	$K_1 (\text{min}^{-1})$	-0.027	-0.023	-0.021	-0.023
	$q_e (\text{mg/g})$	7.345	9.840	11.588	15.240
	R^2	0.999	0.990	0.988	0.982
Elovich	$\alpha (\text{mg.g}^{-1}.\text{min}^{-1})$	0.649	0.759	0.909	1.301
	$\beta (\text{mg.g}^{-1}.\text{min}^{-1})$	0.489	0.396	0.331	0.246
	R^2	0.993	0.989	0.991	0.995
Pseudo-second order	$K_2 (\text{g.mg}^{-1}.\text{min}^{-1})$	0.0042	0.0025	0.0020	0.0019
	$q_e (\text{mg/g})$	8.772	11.628	14.085	18.182
	R^2	0.997	0.997	0.998	0.995

Table 3: The kinetic parameters evaluated for Pb (II) ion adsorption.

Kinetic model	Parameter	Solute Concentration (mg/L)			
		50	100	150	200
Bhattacharya-Venkobachar	$K_B (\text{min}^{-1})$	-0.028	-0.026	-0.018	-0.026
	R^2	0.985	0.992	0.990	0.933
Pseudo-first order	$K_1 (\text{min}^{-1})$	-0.028	-0.026	-0.018	-0.026
	$q_e (\text{mg/g})$	7.768	10.967	13.527	19.756
	R^2	0.986	0.993	0.990	0.940
Elovich	$\alpha (\text{mg.g}^{-1}.\text{min}^{-1})$	0.725	0.876	1.192	1.955
	$\beta (\text{mg.g}^{-1}.\text{min}^{-1})$	0.518	0.365	0.290	0.215
	R^2	0.996	0.993	0.995	0.998
Pseudo-second order	$K_2 (\text{g.mg}^{-1}.\text{min}^{-1})$	0.004	0.003	0.002	0.002
	$q_e (\text{mg/g})$	8.803	12.453	17.007	22.026
	R^2	0.999	0.998	0.998	0.999

3.2 Intra-particle and film diffusion kinetics

The Weber and Morris plots for the adsorption of various concentrations of both Cu (II) and Pb (II) ions (Fig. 4) are not completely linear, suggesting that intra-particle diffusion is not the rate determining step. The calculated intra-particle diffusion coefficient (D_p) values do not have orders in the range of 10^{-11} to $10^{-13} \text{ cm}^2.\text{s}^{-1}$ but are all of the order of 10^{-5} for both Cu (II) and Pb (II) ions (Table 4), confirming that intra-particle diffusion is not the rate determining step. Odoemelam et al. [34] reported a contrary result, where for the adsorption

of Copper (II), Cadmium (II) and Lead (II) ions from aqueous metal solutions using chemically modified and unmodified cocoa pod husk (*Theobroma cacao*) waste biomass, intra-particle diffusion was the rate determining step. The film diffusion co-efficient (D_F) values are of the order of $10^{-7} \text{ cm}^2.\text{s}^{-1}$ for Cu (II) and $10^{-6} \text{ cm}^2.\text{s}^{-1}$ for Pb (II) ions (Table 4). This is an indication that the rate limiting step for the adsorption of the various concentrations of both ions is controlled by film (boundary layer) diffusion.

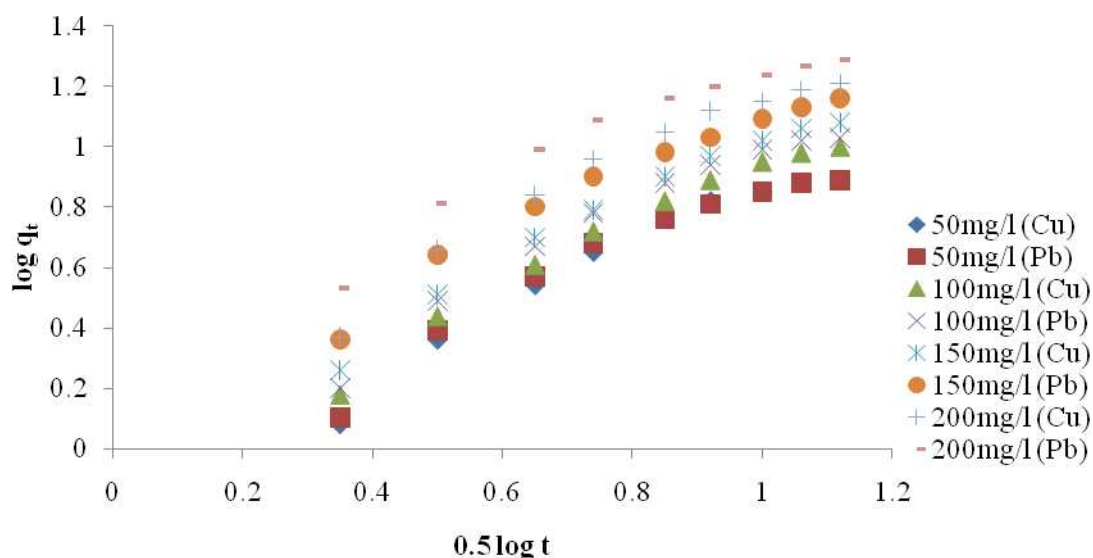


Fig.4: Weber and Morris plot for Cu (II) and Pb (II) ion adsorption on the adsorbent.

Table 4: Intra-particle and film diffusion parameters for Cu (II) and Pb (II) adsorption.

Parameter	Solute Concentration (mg/L)							
	50		100		150		200	
	Cu	Pb	Cu	Pb	Cu	Pb	Cu	Pb
$K_{id} (mg \cdot g^{-1} \cdot min^{0.5})$	0.601	0.745	0.785	0.868	0.938	1.297	0.780	2.090
$D_p (cm^2 \cdot s^{-1})$	3.53×10^{-5}	2.26×10^{-5}	2.72×10^{-5}	2.68×10^{-5}	2.56×10^{-5}	2.50×10^{-5}	2.53×10^{-5}	2.83×10^{-5}
$D_F (cm^2 \cdot s^{-1})$	6.32×10^{-7}	3.40×10^{-6}	8.61×10^{-7}	2.31×10^{-6}	6.19×10^{-7}	1.92×10^{-6}	5.68×10^{-7}	2.16×10^{-6}
R^2	0.961	0.936	0.970	0.952	0.971	0.961	0.951	0.932

3.3 Isotherm study

The Langmuir and Freundlich plots for the adsorption of Cu (II) are shown in Fig. 5 and Fig. 7, respectively, while for adsorption of Pb (II), the plots are shown in Fig. 6 and Fig.8, respectively.

Similar plots for the Temkin adsorption isotherm (not shown) were also made and the parameters compared for Cu (II) and Pb(II) adsorption in Table 5.

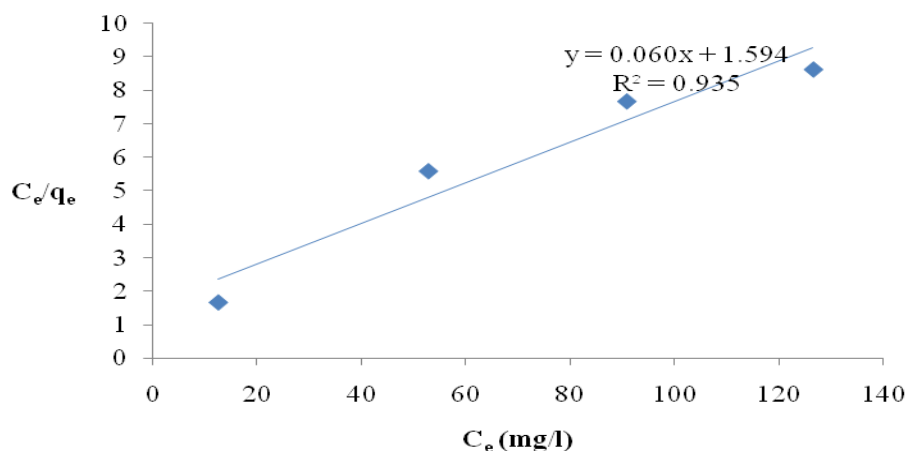


Fig.5: Langmuir isotherm for Cu (II) ion adsorption on the adsorbent.

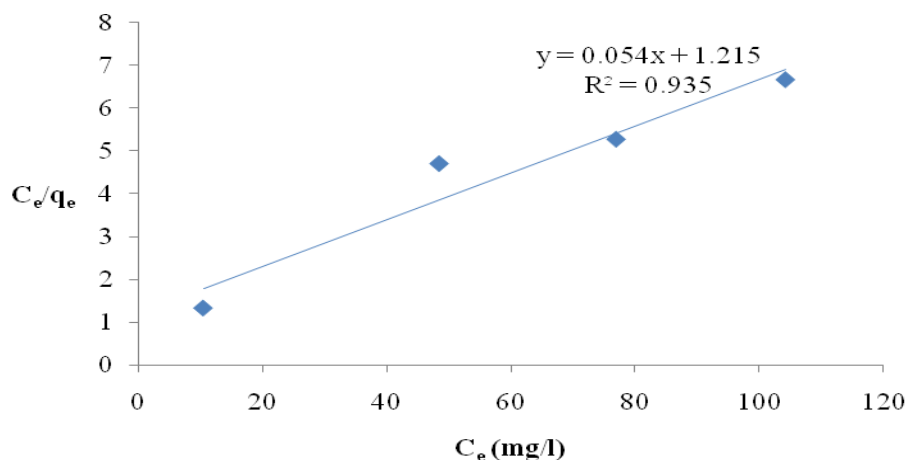


Fig.6: Langmuir isotherm for Pb(II) ion adsorption on the adsorbent.

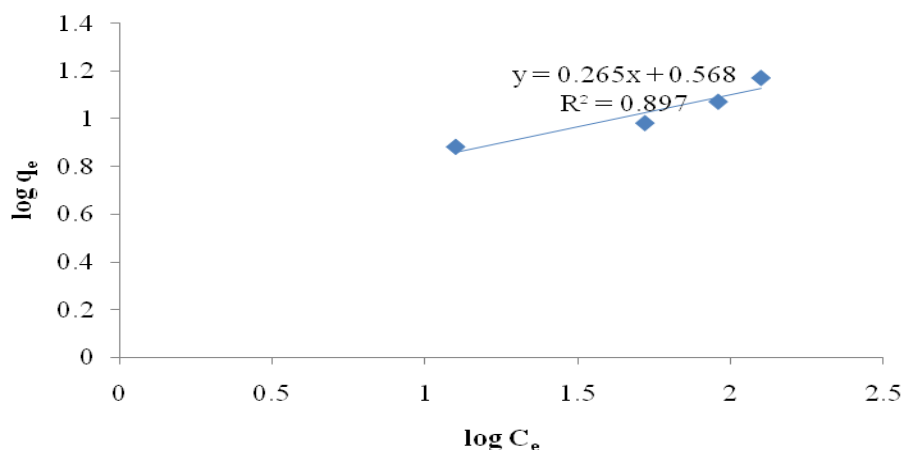


Fig.7: Freundlich isotherm for Cu (II) ion adsorption on the adsorbent.

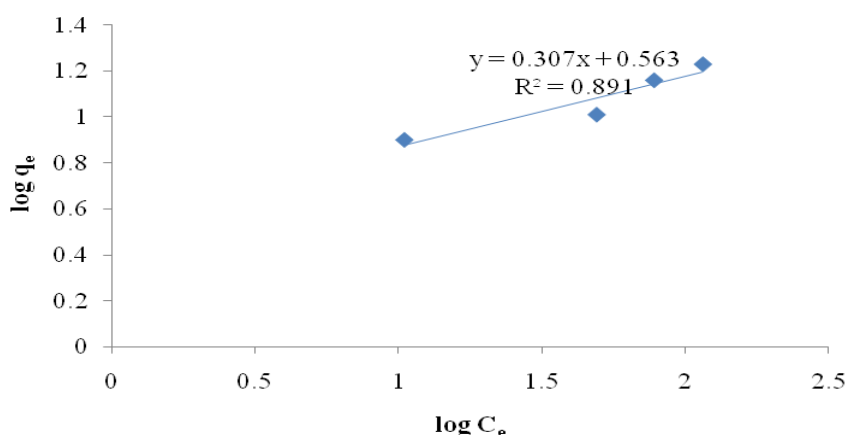


Fig.8: Freundlich isotherm for Pb(II) ion adsorption on the adsorbent.

A comparison of the various isotherms based on the linear regression coefficient (R^2) values (Table

5) shows that the Langmuir isotherm ($R^2 > 0.9$) best describes the adsorption of both metal ions.

Table 5: Evaluated isotherm parameters for Cu(II) and Pb(II) ions adsorption

Isotherm model	Parameter	Cu (II)	Pb (II)
Langmuir Isotherm	$K_L (\text{L.mg}^{-1})$	0.038	0.044
	$q_m (\text{mg.g}^{-1})$	16.67	18.52
	R_L	0.116	0.009
	R^2	0.935	0.935
Freundlich Isotherm	$K_F (\text{mg/g})$	3.698	3.656
	n	3.774	3.257
	R^2	0.897	0.891
Temkin Isotherm	K_T	-0.066	-0.749
	$b_T (\text{kJ.mol}^{-1})$	0.903	0.593
	R^2	0.838	0.765

The calculated R_L values are in between 0 and 1 (0.116 for Cu (II) and 0.009 for Pb (II)), showing that Langmuir isotherm is favourable for the description of adsorption of both metal ions [35]. The values of the Freundlich constants (K_F and n), which are constants incorporating the factors affecting the adsorption capacity and intensity of adsorption, respectively, are greater than unity for adsorption of both metal ions. This indicates that the adsorption of both Cu (II) and Pb (II) ions on the star apple seed shell activated carbon are very much favourable.

4. Conclusion

The present investigation shows that activated carbon made from star apple (*G. albida*) seed shells is an effective adsorbent for the removal of heavy metal ions, Cu (II) and Pb (II) from aqueous solution. Adsorption of both metal ions was found to increase with the increase in contact time and initial metal ion concentration. Pseudo second order kinetic model best described the adsorption of various concentrations of both ions except 50mg/L of Cu (II), which was best described by pseudo first order model. The rate of the adsorption processes was controlled by film (boundary layer) diffusion. Langmuir isotherm was found to be most

favourable for the description of the adsorption processes. *G. albida* seed shells are abundant agricultural wastes and are not utilized in any known industrial process to our knowledge. In most areas of South Eastern States of Nigeria and in some other West African countries, where it exists, the seeds are usually discarded, while in some other localities they are used for local games and plays as anklets in dancing indicating that there is little or no significant end use of the seeds [15] and its shells. The successful use therefore of this material in waste water treatment could help reduce the expenditure on importation of activated carbon, which is the major material in use in industries in Nigeria for wastewater treatment.

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