

Evaluation of Kinetic Models of Copper and Lead Uptake from Dye Wastewater by Activated Pride of Barbados Shell

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Abstract Pride of Barbados shell was effectively used as a raw materials for the production of activated carbon with HNO₃ as an activating agent using twostep process. Batch adsorption was used in interacting the dye wastewater with activated carbon within 30-150 minutes contact time. The maximum adsorption of Cu and Pb were 96.63% and 85.55% at 150 minutes and 30 minute contact time respectively. The result was found to match well with pseudo second-order compared to pseudo first-order, Natarajan and khalaf first order and Elovich model tested. Therefore, activated pride of barbados shell could be employed as an adsorbent in removing Cu and Pb from similar wastewater and aqueous solution.

Keywords Activated Carbon, Pseudo Second-Order, Copper, Lead, Elovich Model

1. Introduction

Activated carbon is the common term used for a group of adsorption substances with large internal structures that make the carbon more adsorbent. Activated carbon is made from a variety of raw materials that are heated and further treated, during this treatment some part turn to gas and leave pores behind. The effectiveness of activated carbon depends on its ability to adsorb a carbon substance or substances depending on the chemical and physical properties that carbon possesses (Jason, 2010). Activated carbon remains a best available technology for water treatment as it removes many organic compounds effectively. Specifically, activated carbon is commonly used for removal of organic taste and odor-causing compounds. Activated carbon is also apply in drinking water treatment to remove natural organic compounds that produce carcinogenic chlorinated by-products during chlorine disinfection of water.

In wastewater treatment, activated carbon is usually used as a filter medium in tertiary treatment processes. In these applications, carbon filters are usually quite effective in removing low concentration of organic compounds as well as some inorganic metals. In addition to its drinking water and wastewater treatment application, activated carbon is used today for many other purposes. Some other common uses are corn and cane sugar refining, gas adsorption, dry

cleaning recovery processes, pharmaceuticals, fat and oil removal, alcoholic beverage production.

The aim of this work is to develop an adsorbent with appropriate porosity from pride of barbados shell by HNO₃ activation and to investigate its adsorption kinetic using pseudo first-order model, pseudo second-order model, Natarajan and khalaf first order equation, Elovich model and to test the adsorption mechanism using intraparticle diffusion model.

2. Material and Methods

The pride of barbados shell was collected from the premises of Government secondary school (GSS) Minna, Niger State, Nigeria. The dye wastewater was obtained from local dye industry, Jafaru Mairiga street F-layout Minna, Niger State, Nigeria in the month of June, 2010. It was stored at room temperature without further purification.

The pride of barbados shell was dried and ground then sieved with a 2 mm mesh size sieve. The less than 2 mm samples were stored in air tight container. Ash content was determined according to the methods of AOAC (1990). Method described by Udo and Ogunwale (1986) was used to digest the dye wastewater. 10 cm³ of dye wastewater was measured into a beaker, 5cm³ of conc. HNO₃ and 2 cm³ of HCl was added and covered with a watch glass. It was digested in a fume cupboard; 15 cm³ of deionized water was added and filtered using what man filtered paper No. 42. The final solution (i.e filtrate) was made to 100cm³ with deionized water.

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2.1. Preparation of Activated Carbon

Activation involving two steps activation process was adopted. Firstly, 5g of grounded raw sample was weighed into clean and weighed crucibles. They were introduced into a muffle furnace at 600°C for 5 minutes after which they were poured from the crucible into a bath of ice water. The excess water was drained off. The carbonized sample was washed using 0.1M HCl to remove surface ash, followed by hot water wash and further washing with distilled water to remove residual acid. The sample was then sun dried and further dried in the oven at 100°C for one hour. This process was repeated until a substantial amount of carbonated sample was obtained.

Thereafter, 5g of carbonized sample was mixed with 5 cm³ of activation agent (1M HNO₃). The sample was allowed to stand for 2 hours, after which it was introduced into a furnace and heated at 800°C for 5 minutes. The activated sample was cooled with ice-cold water, excess water was drained off and the sample dried at room temperature. The above procedure was repeated for different dwell time (10 min and 15min) until substantial amount of the activated carbon was obtained. Washing of the activated sample was done with 0.1M HCl to remove surface ash, followed by hot water wash and rinsing with distilled water to remove residual acid. Washing was completed until the pH of the supernatant fell within 6-7, then the sample was dried in an oven at 110°C overnight and stored in an airtight container (Rahman *et al.*, 2005; Fan *et al.*, 2005; Ahmedna *et al.*, 2005).

2.2. Activated Carbon Characteristics

Apparent (bulk) density (gcm⁻³) =

$$\frac{\text{weight of activated carbon (g)}}{\text{Volume of packed dry material (cm}^3\text{)}} \quad (1)$$

(Apipreeya *et al.*, 2006)

$$\% \text{ Burn off} = \frac{W_0 - W_1}{W_0} \quad (2)$$

W₀ = Weight of char after pyrolysis, washing and drying

W₁ = Weight of carbon after activation, washing and drying (Ioamidou and Zabaniotou, 2006).

$$\% \text{ Yield} = \frac{W_1}{W_0} \times 100 \quad (3)$$

W₀ = Original mass of precursor on a dry basis

W₁ = Weight of carbon after activation, washing and drying. (Apipreeya *et al.*, 2006)

pH was determined using a pH meter and the conductivity was taken using a conductivity meter at room temperature (Okiemen *et al.*, 2004).

2.3. Batch Adsorption

Adsorption was performed in batch where 2g of activated carbon was interacted with 40cm³ of dye wastewater and allowed to stand for 30 minutes. It was then filtered using Whatman filter paper (No. 42). The process was repeated at pre-set times (60, 90, 120 and 150 minutes). The concentra-

tion of copper and lead in the dye wastewater was determined before and after interaction with the activated carbon by a bulk scientific atomic absorption spectrophotometer (MODEL 210VGP) (Apipreeya *et al.*, 2006).

2.3.1. Determination of the Adsorption Capacity

$$q_t = \frac{C_i - C_t}{W} \quad (4)$$

Where q_t = Adsorption capacity at time t (mg/g)

C_i = Concentration of Cu/Pb before interaction with activated carbon (mg/l).

C_t = Concentration of Cu/Pb after interaction with the activated carbon (mg/l)

V = Volume of the dye wastewater (L)

W = Weight of the activated carbon (g). (Hameed, 2009).

2.4. Adsorption Kinetics

In order to describe the adsorption kinetics for copper and lead on activated carbon, pseudo first-order (Lagergren, 1898), pseudo second-order (Ho *et al.*, 2000), Natarajan and Khalaf first order (Raji *et al.*, 1986) and Elovich Model (Chien and Clayton, 1980; Sparks, 1986) were applied to the experimental data.

Pseudo first-order equation:

$$\text{Log}(q_e - q_t) = \text{Log } q_e - \frac{k_1 t}{2.303} \quad (5)$$

Pseudo second-order equation:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (6)$$

Natarajan and Khalaf first order equation

$$\text{Log}(C_i/C_t) = K_1/2.303 t \quad (7)$$

Elovich model equation:

$$q_t = 1/\beta \ln(\alpha \beta) + 1/\beta \ln(t) \quad (8)$$

Where q_e = amount of adsorbate adsorbed at equilibrium (mg/g).

K₁ = Adsorption rate constant for first-order (min⁻¹).

K₂ = Adsorption rate constant for second-order (g.mg⁻¹ min⁻¹).

α = Initial adsorption rate (mg.g⁻¹min⁻¹).

β = desorption constant (g.mg⁻¹) during any experiment.

2.5. Test of Kinetics Model

The applicability of pseudo first-order and pseudo second-order kinetic models are verified through the sum of error squares (SSE, %) given by:

$$\% \text{ SSE} = \frac{\sqrt{\sum (q_{e(\text{exp})} - q_{e(\text{cal})})^2}}{N} \quad (9)$$

q_{e(exp)} = adsorption capacity at equilibrium experimental (mg/g)

q_{e(cal)} = adsorption capacity at equilibrium calculated (mg/g)

N = number of data point (Hameed *et al.*, 2007)

In order to investigate the mechanism of the copper and lead adsorption onto pride of Barbados shell, intraparticle diffusion mechanism was used.

$$q_t = K_p t^{1/2} + C \quad (10)$$

where C = Intercept.

K_p = Intraparticle diffusion rate constant ($\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1/2}$) (Crank, 1933).

3. Results and Discussion

3.1. Characteristic of Activated Carbon

The percentage ash content was low which is an indication of high carbon content. The pH of the activated carbon fall within the range of 6.48 ± 0.02 to 6.65 ± 0.01 . This is in agreement with Ahmedna *et al.* (1997) that activated carbons produced from precursors with low ash content have been found to have low pH. The percentages yield of activated carbon was found to decrease with increase activation burn off because at longer residual time more volatiles are released from the char resulting to a higher burn off and a corresponding lower yield. Similar result was reported by Martinez *et al.* (2006). The result revealed that the apparent (bulk) density increase with increasing activation residual time which is an indication that at higher activation residual time, the hardness of activated carbon is high with a resultant high tendency for regeneration.

Table 1. Characteristics of Activated Carbon

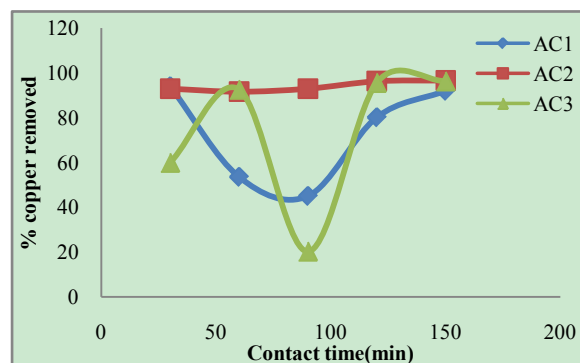
Parameter	PBS/ HNO ₃ /5	PBS/ HNO ₃ /10	PBS/ HNO ₃ /15
Activation burn off	34.10 ± 0.01	40.01 ± 0.03	42.11 ± 0.02
Yield (%)	66.30 ± 0.03	60.12 ± 0.01	58.07 ± 0.02
Apparent density(g/cm^3)	0.54 ± 0.01	0.58 ± 0.05	0.60 ± 0.02
pH	6.54 ± 0.01	6.65 ± 0.01	6.48 ± 0.02
Conductivity ($\mu\text{S}/\text{cm}$)	560.20 ± 0.03	600.15 ± 0.01	600.25 ± 0.05

3.2. Effect of Contact Time

The activated carbon (PBS/HNO₃/5) indicated the maximum percentage of Cu removal at shorter contact time of 30 minutes, that is, 93.94% removed, thereafter desorption occur at contact time of 60 minutes which can be due to the decreased or lesser number of active sites. The adsorbent (PBS/HNO₃/10) and (PBS/HNO₃/15) showed optimum percentage Cu adsorption at longer contact time of 150 minutes, that is, 96.63% and 96.30% removed. The desorptions that occur at the short contact time give rises to more active site development which increases the adsorption efficiency (Fig.1).

The findings show that the percentage Pb adsorption by adsorbent (PBS/HNO₃/10) increased from 36.42% to 65.32% in the first 90 minute while the percentage Pb removed by activated carbon (PBS/HNO₃/15) increased from 50.87% to 65.32% in first 60 minutes and after a decrease in the efficiency was observed. This may be due to the complete clogging of available adsorption sites on adsorbent material and unavailability of the free sites. The results further revealed the highest percentage Pb uptakes by the adsorbent

(PBS/HNO₃/15) of 30 minutes and 90 minutes that is, 85.55% adsorbed. Therefore, the slight desorption may be due exhausted binding sites of the adsorbent (Fig.2). Similar process was reported for the removal of chromium (vi) from aqueous solutions (Sucharita and Nandini, 2009).



AC1 = PBS/HNO₃/5 AC2 = PBS/HNO₃/10 AC3 = PBS/HNO₃/15

Figure 1. Effect of contact time on the removal of copper by activated pride of Barbados shell

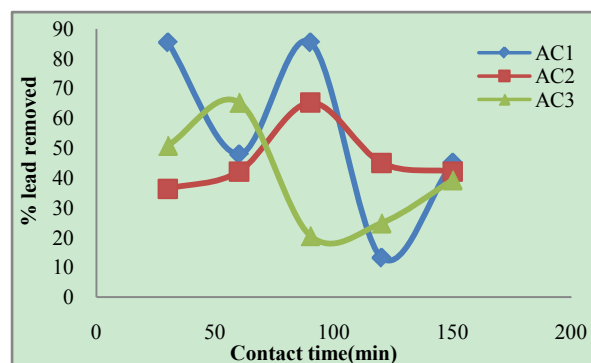


Figure 2. Effect of contact time on the removal of lead by activated pride of Barbados shell

3.3. Kinetic of Adsorption

The pseudo first-order, pseudo second-order, Natarajan and Khalaf first order and Elovich model equations and were applied to the adsorption data. The results of kinetic parameters are shown in table 2-7. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients R^2 (R^2 values close or equal to 1). A relatively high R^2 value indicates that the model successfully describe the adsorption kinetics. The R^2 value of pseudo second-order is higher compared to R^2 values of other kinetic models tested (table2-table7), Fig.3 and 4.

Table 2 Kinetics parameters of the pseudo first-order for the Cu adsorption

Sample	R^2	K_1 (min^{-1})	$q_{e(\text{exp})}$ (mg/g)	$q_{e(\text{cal})}$ (mg/g)	%SSE
PBS/HNO ₃ /5	0.485	-0.027	0.55	0.01	0.2388
PBS/HNO ₃ /10	0.122	-0.016	0.57	0.01	0.2536
PBS/HNO ₃ /15	0.008	-0.005	0.57	0.06	0.2276

Pseudo second-order kinetics models shown that the values of adsorption capacity at equilibrium calculated $q_{e(\text{cal})}$ were closer to the experimental $q_{e(\text{exp})}$ values (table 2-5). These findings revealed that the pseudo second-order kinetic

model provided a good correlation for the adsorption of Cu and Pb onto activated pride of barbados shell compared to other kinetic model used. Bulut and Aydin (2006) reported pseudo second-order kinetics for adsorption of methylene blue on wheat shell.

Table 3 kinetic parameters of the pseudo first-order for the Pb adsorption

Sample	R ²	K ₁ (Min ⁻¹)	q _{e(exp)} (mg/g)	q _{e(cal)} (mg/g)	% SSE
PBS/HNO ₃ /5	0.298	-0.016	0.31	0.05	0.1189
PBS/HNO ₃ /10	0.049	-0.009	0.29	0.28	0.0957
PBS/HNO ₃ /15	0.503	-0.015	0.27	0.05	0.0979

Table 4 kinetic parameters of the pseudo second-order for the Cu adsorption

Sample	R ²	K ₂ (gmg ⁻¹ min ⁻¹)	q _{e(exp)} (mg/g)	q _{e(cal)} (mg/g)	% SSE
PBS/HNO ₃ /5	0.992	0.001	0.55	0.54	0.0004
PBS/HNO ₃ /10	0.999	0.512	0.57	0.58	0.0004
PBS/HNO ₃ /15	0.996	-0.016	0.57	0.59	0.0089

Table 5 kinetic parameters of the pseudo second-order for the Pb adsorption

Sample	R ²	K ₂ (gmg ⁻¹ min ⁻¹)	q _{e(exp)} (mg/g)	q _{e(cal)} (mg/g)	% SSE
PBS/HNO ₃ /5	0.990	-0.271	0.31	0.33	0.0089
PBS/HNO ₃ /10	0.906	-1.698	0.29	0.31	0.0089
PBS/HNO ₃ /15	0.962	0.061	0.27	0.25	0.0089

Table 6 kinetic parameters of the Elovich model for the Cu and Pb adsorption

Sample	Cu R ²	β(g mg)	α(mg ⁻¹ min ⁻¹)	Pb R ²	β(g/ mg)	α(mg.g ⁻¹ min ⁻¹)
PBS/H NO ₃ /5	0.008	-30.30	-3.60x10 ⁻⁹	0.371	-4.95	-0.0004
PBS/H NO ₃ /10	0.543	66.67	2.47x10 ¹²	0.126	23.26	0.9261
PBS/H NO ₃ /15	0.085	10.64	0.1226	0.239	-8.06	0.0002

Table 7 kinetic parameters of the Natarajan and Khalaf First order for the Cu and Pb adsorption

Sample	Cu R ²	K ₁ (min ⁻¹)	Pb R ²	K ₁ (min ⁻¹)
BS/HNO ₃ /5	0.001	0.000	0.368	-0.009
PBS/HNO ₃ /10	0.754	0.007	0.025	0.000
PBS/HNO ₃ /15	0.378	0.016	0.236	-0.002

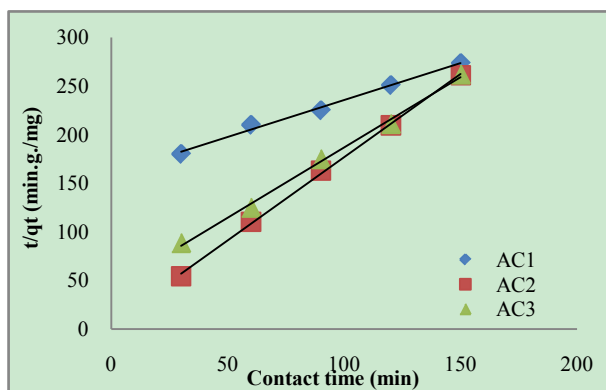


Figure 3. Pseudo second-order model for copper adsorption by activated pride of Barbados shell

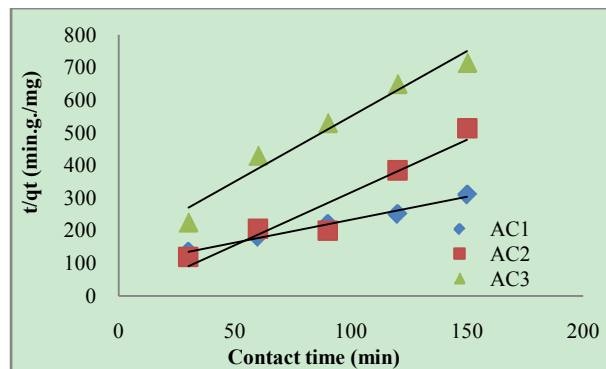


Figure 4. Pseudo second-order model for lead adsorption by activated pride of Barbados shell

3.4. Test of Kinetic Models

Percentage sum of error squares (%SSE) was used to test the applicability of pseudo first-order and pseudo second-order kinetic models. The higher the value of R² and the lower the values of % SSE, the better will be the goodness of fit. Also sample with least % SSE is accepted for a given model. The % SSE value for pseudo second order is lower compared to that of pseudo first-order (Table 2-Table 5). The result further confirm that the adsorption of Cu and Pb on the adsorbent could be best described by the pseudo second-order kinetic models. Similar process was reported by Malik (2004) on the removal of dye one activated carbon prepared from sawdust.

Table 8 show the intraparticle diffusion parameters for Cu and Pb adsorption. R² value is low for all the adsorbent except 0.641 obtained for PBS /HNO₃/10 for the Cu adsorption which implies that Cu adsorption by the adsorbent is intraparticle diffusion controlled.

Table 8. Intraparticle diffusion parameters for Cu and Pb adsorption

Sample	Cu R ²	Kp(mg.g ⁻¹ m ^{-1/2})	C	Pb R ²	Kp(mg.g ⁻¹ m ^{-1/2})	C
PBS/HN O ₃ /5	4x10 ⁻⁶	0.000	0.380	0.367	-0.048	0.826
PBS/HN O ₃ /10	0.641	0.004	0.521	0.080	0.008	0.244
PBS/HN O ₃ /15	0.100	0.024	0.212	0.216	-0.028	0.516

4. Conclusions

Removal of Cu and Pb from dye effluent was carried out using activated carbon prepared from pride of barbados as an adsorbent. Contact time for the interaction of the adsorbent with dye effluent is within 30-150 minutes. Maximum Cu adsorption of 96.63% was obtained at 150 minutes contact time and the maximum Pb removal of 85.55% was indicated at contact time of 30 minutes. Four kinetic model which include pseudo first-order, pseudo second-order, Natarajan and n Khalaf first order and Elovich model were used to test the adsorption. The kinetic of Cu and Pb adsorption on the different adsorbent was found to follow a pseudo second-order model. The findings revealed that the activation dwell

time and contact time are also determining factors.

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