



Adsorption Kinetics of Cr (III) and Pb (II) ions by Chemically Modified Palm Kernel Shell

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ABSTRACT

The demand for cheap but efficient adsorbent to meet the need for water treatment has been on the increase. This study explores the suitability of palm kernel shell activated carbon prepared using H₂PO₄ and KOH as activating agents in the adsorption of Cr (III) and Pb (II) ions from wastewater using the batch adsorption method at different interaction periods. Natarajan and Khalaf first order, pseudo first-order, pseudo second-order and Elovich models were used to study adsorption kinetics. Pseudo second order kinetics was found to give a good fit for the adsorption of Cr (III) and Pb (II) ions with high correlation value (> 0.96) and low SSE (≤ 0.002) for both acid (PSH) and base (KSH) treated activated carbons. These results indicated that palm kernel shell activated carbon could be used for removal of heavy metal ions from aqueous solutions.

Keywords: Activated carbon, heavy metals, adsorption, adsorption kinetics, palm kernel shell

INTRODUCTION

In recent years, the use of metals and their products have continued to find applications in the industrial, agricultural and technological development the modern society (Badmus *et al.*, 2007). With this rapid increase in industrial activities, pollution arising from the improper disposal of heavy metal wastes into the environment has also continued to increase, affecting soil, surface and ground water. Heavy metals are known to have adverse effects on biological system when ingested above tolerable level, and can enter the human through food chain. The annual toxicity resulting from heavy metals discharged into the environment as at 2007 is believed to exceed the combined toxicity of organic and radioactive wastes (Badmus *et al.*, 2007). This would have increased, as at date the level of heavy metals released from industrial activities into the environment which have become a real threat to human and animal health (Azizi *et al.*, 2016; Orjuela and Gonzalez, 2011). Recently, activated carbon is considered to be effective adsorbent for the adsorption of heavy metals ions at trace quantities and their use for removal of toxic heavy metals from wastewater have been reported (Erdem *et al.*, 2004).

METHODOLOGY

Palm kernel shell used for preparation of the activated carbon was sourced from a local oil mills in Minna, Nigeria. The samples were washed with plenty of water to remove sand and other impurities then sundried. The dried samples were then ground into powder and stored for carbonization.

Preparation of activated carbon

The two steps process was used for preparation of activated carbon. This process involves carbonization of pre-treated raw material in a furnace at a temperature of 400°C for ten minutes, quenched in iced water then washed with 0.1M HCl to remove ash and distilled water, then dried in oven at 105 °C (Rahman *et al.*, 2014). 5 g of the carbonized sample was macerated in 5 cm³ H₃PO₄ for 2 hours and subsequently activated in an oven at 600 °C for twenty minutes (Musah *et al.*, 2016). The process was repeated using KOH.

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Analysis

Batch experiments with the activated carbons were used to study the effect of contact time on adsorption of lead (II) and chromium (III) ions. Lead and Chromium solutions were prepared by dissolving known quantities of AR grade $Pb(NO_3)_2$ and $Cr(NO_3)_3 \cdot 9H_2O$ in distilled water. The stock solutions were diluted to desired concentrations using the dilution factor. Solution of each metal (20 cm^3) was interacted with 0.2 g of the adsorbent in a beaker at 200 rpm and $28 \pm 2\text{ }^\circ\text{C}$ for 60, 120, 180, 240 and 300 mins. Concentrations of Pb(II) and Cr(III) ions in the solutions were determined before and after interaction with activated carbon using Atomic Absorption Spectrophotometer (Buck Scientific model 210 VGP). Removal efficiency (%) is as follows:

$$RE(\%) = ((C_o - C_f)/C_o) \times 100 \quad (1)$$

Where

C_o is the concentration of heavy, metal ion before interaction.

C_f is the concentration of heavy metal, ion after interaction.

The amount of ions adsorbed at time t (q_t) was calculated using the formula below:

$$q_t = ((C_o - C_f)/m) \times v \quad (2)$$

Where

v is the volume of aqueous solution used for interaction

m is the mass of adsorbent used

Adsorption Kinetics

Pseudo first order, Pseudo second order, Natarajan and Khalaf first order and Elovich models were tested to fit the kinetics of the adsorption process.

Pseudo first order equation

The adsorption kinetic equation for pseudo first order is expressed as:

$$\log(q_e - q_t) = \log(q_e) - (k_1/2.303)t \quad (3)$$

Where:

q_e and q_t are adsorption capacities at equilibrium and time t , respectively ($\text{mg} \cdot \text{g}^{-1}$).

k_1 is the rate constant for Pseudo first order (min^{-1}) reaction.

When values of $\log(q_e - q_t)$ were correlated linearly with t . The plot of $\log(q_e - q_t)$ versus t gives a relationship that is linear from which k_1 and q_e can be determined from the slope and intercept of the plot (Bernard *et al.*, 2013).

Pseudo second order equation

The expression for pseudo second order model is presented in equation (4):

$$(t/q_t) = 1/k_2q_e^2 + (1/q_e)t \quad (4)$$

Where:

k_2 is the rate constant for Pseudo second order ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) reaction.

A plot of (t/q_t) against t is expected to give a linear relationship from where q_e and k_2 can be determined from the intercept and slope of the plot (Santuraki and Muazu, 2015).

Test of Kinetic model of Pseudo first-order and Pseudo second-order Reactions

The suitability of pseudo first and second order kinetic models in describing the sorption process was verified by Sum of Squares Error (SSE, %):

$$SSE(\%) = \sqrt{(q_e(\text{exp}) - q_e(\text{cal}))^2/N} \quad (5)$$

Where:

N is the number of data points.

$q_{e(\text{cal})}$ is the calculated adsorption capacity at equilibrium (mg/g)

$q_{e(\text{exp})}$ is the experimental adsorption capacity at equilibrium (mg/g) (Musah and Birnin-Yauri, 2011).

Natarajan and Khalaf first order kinetic equation

$$\log(C_o/C_t) = (k/2.303)t \quad (6)$$

Where

C_o and C_t are concentrations (mg l^{-1}) at time zero and time t respectively.

k = first order adsorption rate constant (min^{-1}) which was calculated from slope of the plot $\log(C_o/C_t)$ against t (Meera and Ganesan, 2015).

The Elovich equation

The Elovich model equation is expressed as:

$$q_t = (1/\beta)\ln(\alpha\beta) + (1/\beta)\ln t \quad (7)$$

α is adsorption rate ($\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$)

β is the extent of surface coverage

Plot of q_t versus $\ln(t)$ yields a linear relationship with a slope of $(1/\beta)$ and an intercept $(1/\beta)\ln(\alpha\beta)$ (Farouk and Yousef, 2015).

RESULTS AND DISCUSSION

The results of the various experiments carried out are presented in the tables below:

Table 1: Pseudo first order parameters for adsorption of Pb (II) and Cr (III)

Ions	PSH					PSK				
	R^2	k_1	$q_e(\text{cal})$	$q_e(\text{exp})$	SSE (%)	R^2	k_1	$q_e(\text{cal})$	$q_e(\text{exp})$	SSE (%)
Cr (III)	0.020	-0.004	0.010	0.183	0.078	0.299	-0.015	0.005	0.164	0.071
Pb (II)	0.013	-0.004	0.008	0.182	0.078	0.031	-0.006	0.005	0.0173	0.075

PSH = palm kernel shell activated carbon modified with H_3PO_4 ; PSK = palm kernel shell activated carbon modified with KOH

Table 2: Pseudo second order parameters for adsorption of Pb (II) and Cr (III)

Ions	PSH					PSK				
	R^2	k_2	$q_e(\text{cal})$	$q_e(\text{exp})$	SSE(%)	R^2	K_2	$q_e(\text{cal})$	$q_e(\text{exp})$	SSE(%)
Cr (III)	0.974	0.314	0.189	0.183	0.002	0.966	0.289	0.172	0.164	0.004
Pb (II)	0.996	0.335	0.189	0.182	0.003	0.989	0.532	0.179	0.117	0.002

PSH = palm kernel shell activated carbon modified with H_3PO_4 ; PSK = palm kernel shell activated carbon modified with KOH

Table 3: Natarajan and Khalaf first order parameters for adsorption of Pb (II) and Cr (III)

Sample	PSH		PSK	
	R^2	k_1	R^2	k_1
Cr (III)	0.781	0.005	0.833	0.004
Pb (II)	0.771	0.006	0.770	0.004

PSH = palm kernel shell activated carbon modified with H_3PO_4 ; PSK = palm kernel shell activated carbon modified with KOH

Table 4: Elovich model parameter for adsorption of Pb (II) and Cr (III)

Sample	PSH			PSK		
	β	α	R^2	β	α	R^2
Cr (III)	25.71	0.017	0.903	25.97	0.011	0.901
Pb (II)	25.55	0.021	0.888	40.65	0.113	0.878

Pseudo first-order, pseudo second-order, Natarajan and Khalaf first order and elovich models were used to test the data obtained from the study. Samples with correlation coefficient (R^2) values close or equal to one (1) is considered acceptable for a given kinetic model. A high R^2 value indicates that the model successfully describes the adsorption kinetics. The highest correlation coefficient (R^2) for

pseudo first-order reaction was experienced when PSH used as adsorbent at 0.484 which is higher than the 0.403 obtained when PSK was used. These values are lower than the 0.944 reported for adsorption of Cd (II) from aqueous solution (Meera and Ganesan, 2015). The first order rate constants (k_1) relatively were low. Maximum of -0.004 was obtained for PSH and -0.015 for PSK which are also lower than -

0.027 and - 0.028 obtained for the adsorption of Cu (II) and Pb (II) ions from simulated wastewater (Ejikeme *et al.*, 2011). Wide difference also existed between $q_{e(cal)}$ and $q_{e(exp)}$ for the first order reaction. These low values indicate that the adsorption of the heavy metal ions does not follow pseudo first order kinetics; the smaller the difference between $q_{e(cal)}$ and $q_{e(exp)}$ the better the fit of the model.

Correlation coefficient (R^2) values for pseudo second-order were higher than those of pseudo first order and Natarajan and Khalaf kinetics; R^2 values obtained were greater than 0.966 and $q_{e(cal)}$ and $q_{e(exp)}$ values were close than when compared with pseudo first-order-kinetic model. The high R^2 values of pseudo second-order kinetic model indicate a good fit of the model for the sorption process. From the study, it can therefore be inferred that the adsorption of Pb (II) and Cr (III) ions followed pseudo second-order kinetic model.

The applicability of pseudo first-order and pseudo second-order reaction kinetic models was verified using the sum of error squares (% SSE). The higher the value of R^2 and the lower the values of %SSE obtained, the better will be the fit of the model; sample with least % SSE is usually accepted for a given model. The findings indicate that %SSE for pseudo second-order is lower than that of pseudo first-order which further showed that the adsorption process followed pseudo second-order model. Similar processes were reported for the adsorption of Cd (II) Pb (II) onto activated carbon and prepared from agricultural wastes (Meera and Ganesan, 2015; Ejikeme *et al.*, 2011). The parameter α in the Elovic model represent chemisorptions and β is related to the extent of surface coverage and activation energy of chemisorptions (Badmus *et al.*, 2007). The results obtained suggest adsorption is a chemisorptions process (Senthilkumaar *et al.*, 2010).

Conclusion

The study revealed the suitability of chemically modified palm kernel in the removal of heavy metal ions from aqueous solutions. Results of the study indicate that the palm kernel shell activated carbon can be used as adsorbent for the adsorption of Pb (II) and Cr (III) from aqueous solution and the process followed a pseudo second adsorption kinetic model.

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