Kinetic Study of the Adsorption of Pb^{2+} and Cr^{3+} ions on Palm Kernel Shell Activated Carbon

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Abstract: The production of activated carbon from palm kernel shells using H_3PO_4 and KOH as activating agents by means of a two step activation process was studied. Results of analysis indicate 30.22±0.15% yield, 69.78±0.15% burn off and 0.61±0.01g/cm^3 bulk density for activated carbon prepared using H_3PO_4 as activating agent (Ps/H_3PO_4). Those prepared using KOH as activating agent (Ps/KOH) gave slightly different results on analysis: yield, burn off and bulk density were 32.71±0.31%, 67.29±0.31% and 0.58±0.02g/cm^3 respectively. 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 be better fit for adsorption of Pb^{2+} and Cr^{3+} ions with good correlation and low SSE when Ps/H_3PO_4 or Ps/KOH was used. These results reveal that activated carbon made from palm kernel shell good properties required for adsorption of heavy metal ions from aqueous solution.
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Key words: Activated carbon, adsorption, palm kernel shell, kinetics, heavy metals

Introduction

Metals and their compounds are indispensable to the industrial, agricultural and technological development of any nation (Badmus *et al*., 2007). With rapid increase in industrial activities, pollution derived from heavy metals have been in waste streams from mining operations, tanneries, electronics, electroplating and petrochemicals industries (Kongsuwan *et al*., 2006). When ingested above tolerable level, heavy metals can have harmful effects on human biological system. It has been estimated that the annual toxicity resulting from heavy metal discharge into the environment exceeds the combined total toxicity of all radioactive and organic wastes (Badmus *et al*., 2007). In view of these, the use of activated carbon for adsorption of heavy metals has been emphasized recently, as it is considered to be a practically effective adsorbent for the removal of heavy metals at trace quantities (Erdem *et al*., 2004).

Locally generated low cost materials have been tested in the production of activated. Materials that are available in large quantities are wastes from agricultural operations (Abdel-Ghana *et al*., 2007). Studies show that these materials have high carbon content and are effective as adsorbent in removing heavy metal pollutants from soil, water and air has continued to increase over the years (Demirbas *et al*., 2004; Erdem *et al*., 2004). Some of the materials used to prepare activated carbons include coconut husk and goat skin, haze nut shells, rise husk and cashew nut shells (Babarinde, 2002; Khalkhali and Omidvari, 2005; Iyagba and Opete, 2009; Tangjuank *et al*., 2009).

This study investigated the properties of activated carbon generated using KOH and H_3PO_4 as activating agents, and their adsorption kinetics.

Materials and Methods

Material

The raw material (Palm kernel shell) used for preparation was obtained from a local oil mill in Minna, Nigeria. The sample was washed with plenty of water to remove surface impurities and then sundried. The dried sample was ground then sieved through a mesh sieve and stored.

Preparation of activated carbon

The two step process was used to activate the sample. This process involves carbonization of pre-treated raw material in a furnace at a temperature of 600^{o}C for five minutes, then cooled in ice block, washed with 0.1M HCl followed by hot water and distilled water, then dried (Gimba *et al*., 2004; Rhaman *et al* ., 2005). The carbonized sample was subsequently activated at 800^{o}C using H_3PO_4 as activating agent (Gimba *et al*., 2004; Turoti *et al*., 2007).

Analysis

Residual moisture content was determined by drying 5g of sample (trpplicate) in a Gellenkanp oven at 105^{o}C until constant weight was obtained (AOAC, 1990). Ash content was determined according to the method described by Ceirwyn (1998), which involves dry in a muffle furnace at 600^{o}C until grayish white ash was obtained. Bulk density was determined by packing 3g of the sample into a graduated cylinder and tapped on bench top until the volume of the

sample stop decreasing (Yoshiyuki and Yukata, 2003). pH was determined according to method of Okiemen *et al* (2004), and conductivity was measured using conductivity meter as described by Ahmedna *et al* (2000).

Carbon hardness (% attrition) was determined using the wet attrition test. Burn off was determined from the difference from the weight of the original char and activated sample divided by weight of original char with both weights on dry bases (Rao *et al*, 2003). Percentage yield of activated carbon was obtained by finding the ratio of weight of the resultant activated carbon to that of the precursor (Yulu *et al*., 2003).

Batch experiments with the generated activated carbon were conducted to investigate the effect of time on adsorption. Lead and Chromium samples were prepared by dissolving known quantities of AR grade $Pb(NO_3)_2$ and $Cr(NO_3)_3.9H_2O$ in distilled water. The stock solution was diluted to required concentration. Concentrations of Pb(II) and Cr(III) were determined from the aqueous solutions before after interaction with activated carbon using Atomic Absorption Spectrophotometer (Buck Scientific model 210 VGP). Removal efficiency (%) is as follows:

$$RE\ (\%) = \frac{(C_0 - C_t)}{C_o} \times 100 \quad \text{.....1}$$

Where

C_o = concentration of heavy metal ion before interaction with activated carbon

C_t = concentration of heavy metal ion after interaction with activated carbon

The amount of ions adsorbed at time *t* (*qt*) was calculated using the formula below (Badmus *et al*., 2007):

$$q_t = \frac{(C_o - C_t)\, v}{m} \quad \text{.....2}$$

v = volume of aqueous solution used for interaction

m = mass of adsorbent used.

Adsorption Dynamics

Models used to fit kinetic adsorption experiments in this research work are Natarajan and Khalaf first order, Pseudo first-order, Pseudo second-order and Elovich models.

Natarajan and Khalaf first order kinetic quation

$\text{Log}(C_o/C_t) = (k/2.303)t$ 3

Where

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

k = first order adsorption rate constant (min1) which was calculated from slope of the plot log (Co/Ct) against t,

Pseudo first-order equation

$\text{Log}(q_e-q_t) = \log(q_e) - (k_1/2.303)t$ 4

Where:

q_e and q_t are adsorption capacity at equilibrium and time *t*, respectively (mg.g^{-1}).

k_1 = the rate constant of Pseudo first-order (min^{-1}).

The values of log ($q_e - q_t$) were linearly correlated with *t*. The plot of log ($q_e - q_t$) versus *t* should give a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the plot (Demirbas *et al.*, 2004).

Pseudo-second order equation

$(t/q_t) = 1/k_2q_e^2 + (1/q_e)t$ 5

Where:

k_2 = rate constant of the Pseudo second-order (g.mg^{-1}.min^{-1}).

The plot of *(t/qt)* and *t* should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively (Zawani *et al*., 2009).

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

The applicability of these kinetic models is verified by Sum of Error Squares (SSE, %):

$\text{SSE}(\%) = \sqrt{(\text{qe(exp)} - \text{qe(cal)})^2/N}$ 6

Where:

N = number of data point (Hameed *et al*., 2006)

$q_{e(cal)}$= Adsorption capacity at equilibrium-calculated (mg/g)

$q_{e(exp)}$ =Adsorption capacity at equilibrium-experimental (mg/g)

The Elovich equation

The Elovich equation is generally expressed as (Demirbas *et al.,* 2004):

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

α is adsorption rate (mg.g^{-1}.min^{-1})

β is related to the extent of surface coverage (Badmus *et al*.,2007).

A plot of q_t versus In (t) should yield a linear relationship with a slope of (1/β) and an intercept of (1/β)In(αβ).

Results and Discussion

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

Table 1: Characteristics of adsorbent (activated carbon)

Parameter	Value	
	Ps/H_3PO_4	Ps/KOH
Residual moisture (%)	6.80±0.20	6.20±0.20
Ash (%)	4.67±0.29	6.17±0.29
pH	6.65±0.06	7.38±0.04
Attrition (%)	71.46±0.36	69.76±0.29
Yield (%)	30.22±0.15	32.71±0.31
Burn off (%)	69.78±0.15	67.29±0.31
Bulk density (g/cm^3)	0.61±0.01	0.58±0.02
Conductivity (μS)	35.67±0.58	39.33±0.58

Note:
Ps/H_3PO_4 = palm kernel shell activated carbon modified with H_3PO_4 (source: Musah *et al*., 2011)
Ps/KOH = palm kernel shell activated carbon modified with KOH

Table 2: Natarajan and Khalaf first order parameters

	Ps/H_3PO_4		Ps/KOH	
Sample	R^2	k_1	R^2	k_1
Pb^{2+}	0.7714	0.0058	0.7702	0.0037
Cr^{3+}	0.7806	0.0046	0.8326	0.0035

Table 3: Pseudo first order parameters

	Ps/H_3PO_4					Ps/KOH				
Sample	R^2	k_1	q_e(cal)	q_e(exp)	SSE(%)	R^2	k_1	q_e(cal)	q_e(exp)	SSE(%)
Pb^{2+}	0.0133	-0.0037	0.0084	0.1818	0.0776	0.0309	-0.0055	0.0053	0.1732	0.0751
Cr^{3+}	0.0196	-0.0042	0.0101	0.1834	0.0775	0.2987	-0.0152	0.0053	0.1638	0.0709

Table 4: Pseudo second order parameters

	Ps/H_3PO_4					Ps/KOH				
Sample	R^2	k_2	q_e(cal)	q_e(exp)	SSE(%)	R^2	k_2	q_e(cal)	q_e(exp)	SSE(%)
Pb^{2+}	0.9963	0.3346	0.1887	0.1818	0.0031	0.9887	0.5324	0.1786	0.1173	0.0024
Cr^{3+}	0.9742	0.3138	0.1887	0.1834	0.0024	0.9664	0.2893	0.1724	0.1638	0.0039

Table 5: Elovich model parameter

	Ps/H_3PO_4			Ps/KOH		
Sample	β	α	R^2	β	α	R^2
Pb^{2+}	25.548	0.0220	0.8884	40.650	0.1134	0.8783
Cr^{3+}	25.707	0.0171	0.9027	25.974	0.0107	0.9011

From table 1, it can be seen that palm kernel shell acid and base catalyzed activated carbons has moisture content of 6.80±0.20% for Ps/H_3PO_4 and lower in Ps/KOH (6.20±0.20%). These values are higher than 1.64%, 1.34% and 1.50% for *Recinius communis* Linn, *Carica papaya* Linn *and Morida pubescence* activated carbons(Kathikeyan and Ilango,2008) and lower than 7.18% and 7.21% obtained for apricot stone and almond shells activated carbon (Demirbas *et al*., 2004). Ash content was found to be 4.67±0.29% and 6.17±0.29% respectively. These values are higher than 2.08%, 2.21% and 2.14% obtained for activated carbons made from cornelian cherry, apricot stone and almond shell (Demirbas *et al*., 2004) but less than 9.26% for activated carbon from sugar cane bagasse (Qureshi *et al*., 2007). Ash content is the residue that remains when carbonaceous portion is burned off, and is considered an impurity. It is an indication of the quality of activated carbon (Qureshi *et al*., 2007).

pH value of Ps/H_3PO_4 was found to be 6.65±0.06, lower than 7.38±0.04 for Ps/KOH although higher than 5.35 and 6.25 obtained for thiolated coconut fibre and apricot stone activated carbons (Igwe *et al*., 2008; Demirbas *et al*., 2004) but still lower than 7.1, 6.9 and 6.7±0.32 for *Recinius comunis* Linn, *Carica papaya* Linn and maize cob activated carbons (Karthikeyan and Ilango, 2008; Akporhonor and Egwaikhide, 2007). Attrition, a measure of hardness was found to be 71.46±0.36% for Ps/H_3PO_4 and 69.76±0.29% for Ps/KOH indicating that Ps/H_3PO_4 is harder than Ps/KOH. These activated carbons are harder than those obtained from sugar cane bagasse and less hard when compared to thoseobtained from bituminous coal with attrition values of 40.26% and 82.80% respectively (Qureshi *et al*., 2007; Faulkner *et al*., 1987).

Percentage yield of 30.22±0.15% and 32.71±0.31% were obtained for Ps/H_3PO_4 and Ps/KOH after carbonization and activation. The yield for Ps/H_3PO_4 is lower than that of Ps/KOH and the 31.9% obtained for *Eucalyptus camaldulensis Dehn* Bark activated carbons (Kongsuwan *et al*., 2006) but higher than 23% in sugar cane bagasse carbon (Qureshi *et al*.,2007). The % yield of Ps/H_3PO_4 and Ps/KOH are both lower than 38% obtained for coconut activated carbon (Amuda and Ibrahim, 2006) but higher than 23% for sugar cane bagasse activated carbon (Qureshi *et al*., 2007). Very low burn offs are usually undesirable as they may lead to low adsorption of target molecules (Senthilkumaar *et al*., 2010; Karthikeyan and Ilango, 2008; Qureshi *et al*., 2007). Burn off of 69.78±0.15% and 67.29±0.31% were obtained for Ps/H_3PO_4 and Ps/KOH respectively. These values are higher than 61.28% for Jute fiber carbon and lower than 85.1% for activated carbon made from *Carica papaya* (Senthilkumaar *et al*., 2010; Karthikeyan and Ilango, 2008).

Bulk density determines the amount of carbon that can be contained in a filter of a given solid's capacity and the quality of liquid that is retained by the filter cake (Hutchin, 1988). It was to be 0.61±0.01g/cm^3 for Ps/H_3PO_4 and 0.58±0.02 g/cm^3 for Ps/KOH. These values are higher than *0.*56±0.09g/cm^3 reported for maize cobs and 0.13g/cm^3 for Algerian hoofs activated carbons (Akporhonor and Egwaikhide,2007; Souag *et al*., 2009) but less than 0.63g/cm^3 obtained for coconut shell activated carbon (Amuda and Ibrahim, 2006).

Conductivity test is important because it shows the presence of impurities on activated carbon (Qureshi *et al*., 2007). The samples showed conductivities of 35.67±0.58 μS for Ps/H_3PO_4 and 39.33±0.58 μS for Ps/KOH, which are less than 51.00±0.60 μS obtained for coconut shell activated carbon but higher than 6.10±0.22 for Calgon F-300 commercial carbon (Amuda and Ibrahim, 2006).

Evaluating the adsorption kinetics of heavy metal ions studied, the Natarajan and Khalaf first order, pseudo first-order, pseudo second-order and elovich models were employed to analyse the experimental data obtained. Sample with correlation coefficient (R^2) values close or equal to one is accepted for a given model and relatively high R^2 value indicates that the model successfully describes the adsorption kinetics. The optimum correlation coefficient (R^2) for pseudo first-order when Ps/H_3PO_4 is used as adsorbent is 0.4837 which was higher than the 0.4031 obtained when Ps/KOH was used. The first order rate constant (k_1) was low. Maximum of -0.010 was obtained for Ps/H_3PO_4 and -0.011 for Ps/KOH. A wide range of variation also exist between $q_{e(cal)}$ and $q_{e(exp)}$. These low values indicate that adsorption of the heavy metal ions does not follow pseudo first order kinetics.

Experimental data were further analyzed using pseudo second-order. Correlation coefficient (R^2) values for pseudo second-order was higher with the values greater than 0.9660 and the values $q_{e(cal)}$ were closer than $q_{e(exp)}$. When compared to pseudo first-order-kinetic model, the R^2 values of pseudo second-order kinetic model were higher. The study therefore revealed that the adsorption of these heavy metal ions followed pseudo second-order kinetic model. Hameed (2009), Kongsuwan *et a*l (2006) and, Ho and McKay (2002) also reported pseudo second-order adsorption kinetic model.

Beside the values of R^2, the applicability of pseudo first-order and pseudo second-order kinetic models are verified through the sum of error squares (SSE %). The higher the value of R^2 and the lower

the values of %SSE, the better will be the fit; sample with least %SSE is accepted for a given model. The findings indicate that %SSE for pseudo second-order is lower than that of pseudo first-order which further confirms that the adsorption of these heavy metal ions followed pseudo second-order model. Similar processes were reported for the adsorption of lead onto periwinkle shell activated carbon and adsorption of chromium (IV) onto cornelian cherry, apricot stone and almond shells activated carbons (Badmus *et al*., 2007; Demirbas *et al*., 2004). The parameter α represent chemisorptions and β is related to the extent of surface coverage and activation energy of chemisorptions (Badmus *et al*., 2007). From the results obtained, adsorption mechanism is probably chemisorptions process (Badmus *et al*., 2007; Senthilkumaar *et al*., 2010; Ho and McKay, 2002).

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