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EVALUATION OF DUM PALM KERNEL ACTIVATED CARBON IN CHROMIUM AND LEAD ADSORPTION FROM SYNTHETIC WASTE WATER

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Abstract

This study aimed at the co-current removal of chromium and lead ions from synthetic waste water using dum palm kernel activated carbon. The adsorption experiment was conducted by varying time, pH and concentrations of the simulated solution. The data obtained were analyzed, and the best conditions for the uptake were at pH of 6, equilibrium time of 40 minutes. The two best isotherms models for the adsorption system were Sip, and Dubinin–Radushkevich, models respectively. Based on the Temkin adsorption energy calculated as 9.5793 and 0.4997 J/mol, the uptake of lead and chromium were chemisorption and physico-sorption, respectively. The maximum uptake calculated from Dubinin–Radushkevich plots were 14.1696 and 7.7191 mg/g, for lead and chromium, respectively.

Key words*:* Dum palm kernel, activated carbon, surface functional groups, surface area, Sip model, Dubinin–Radushkevich model

Introduction

Studies have shown that Lead and chromium are the major heavy metals that pollutes water body as a results of manufacturing activities by industries (Qaiser *et al*., 2009). “Lead is one of the largest environmental medicine problems in terms of numbers of people exposed and public health toll it takes” (http1). Zamafara and Niger State in Nigeria have witnessed this, where score of people died from lead poisoning. It has been reported that globally, exposure to lead causes 0.6 of disability and 0.2% of all deaths. (http1, 2015). Small concentration of lead in drinking water causes anemia, kidney and liver problems (Bohli *et al*., 2013). Hexavalent chromium has been reported to be carcinogenic and mutagenic to animals species include man (Attia *et al.*, 2010).

Performance evaluation and utilization of activated carbon from various sources for industrial effluent treatment have been reported by many authors. Performance of activated carbon from rice husk and waste wood in removal of lead, cadmium ions and acetic acid have been evaluated (Goodhead, and Dagde, 2011). Performance of rice husk activated carbon in co-current adsorption of lead, zinc and nickel ions have been studied (Taha *et al*., 2011). Utilization of orange peel activated carbon from orange peel in removal of lead, iron, copper, and, zinc ions from electroplating waste-water have been investigated (Bernard and Jimoh, 2013). In a separate studies, Bernard *et al*. (2013) have used coconut shell activated carbon in removal of lead, iron, copper, and, zinc ions from electroplating waste water. Chaouch *et al*. (2014) have used date stone activated carbon in removal of lead ions. Moreno- Barbosa *et al*. (2013) have investigated the adsorption of lead and zinc ions from aqueous solutions onto watermelon shell and walnut shell activated carbon. Shamungavalli *et al*. (n.d) have studied the adsorption of chromium (VI) onto silk cotton hull carbon. Attia *et al*. (2010) have studied the removal of hexavalent chromium using olive acid activated carbon. Qaiser *et al*. (2009) have investigated the uptake of lead and chromium onto groundnut hull. Based on the available literature, there is need to evaluate the performance activated carbon prepared from dum palm kernel in adsorption of lead and chromium which has similar appearance to that of date stone.

The aim of this research is to evaluate the performance of dum palm kernel activated carbon in chromium and lead removal from aqueous solution. The objectives are to:

i. investigate the effect of time, initial concentration and pH on co-current removal of lead and chromium onto dum palm kernel activated carbon;
ii. determine the suitable adsorption isotherm for the system. e

Methodology

Preparation of Synthetic Waste water

A synthetic waste water containing lead and chromium of concentration 1000 mg/l was prepared by adding, 2.827 g of potassium dichromate and 1.6 g of lead nitrate to distilled water in a volumetric flask and shake water was added until it was exactly one litre.

Adsorption Experiment

In the batch experiment process, Das and Mondal (2011), methods was adopted. The prpared synthetic waste water was divided into five (5), and their pH was varied using NaOH and HCl, to 5, 6, 7, 8 and 9. The concentration was diluted to 20, 40, 60, 80, 100 mg/L. 100 ml, 20mg/l of each of the five samples were measured out, and one gram of the dum palm kernel activated carbon (DPK AC) obtained from University of Maiduguri, Chemical Engineering Laboratory was added and stirred using magnetic stirrer at 80 rpm. The sample is withdrawn at an interval of 20 minutes using syringe and concentration is measured using AAS, up to the time when there was no change in concentration, and that is the equilibrium point. To develop the equilibrium model, effect of concentration was considered, the equilibrium concentration were determined for each initial concentration between 20 to 100 mg/L at interval of twenty.

Adsorption experiment

In the batch experiment process, Das and Mondal, (2011) methods was adopted. The prepared synthetic waste water was divided into three (3), and their pH was varied using NaOH and HCl, to 6, 7, and 8. The solution was diluted to 50 mg/L. Six samples of 100 ml, of each of the three samples were measured out, and one gram of the DPK AC prepared was added and stirred using magnetic stirrer. The sample was withdrawn at an interval of 20 minutes using syringe and concentration is measured using Atomic Absorption Spectrophotometer (AAS), up to the time when there was no change in concentration, and that is the equilibrium point. To develop the equilibrium model, effect of concentration was considered, the equilibrium concentration were determined for each initial concentration between 20 to 100 mg/L at interval of twenty.

Data analysis

The adsorbates uptakes at every time, t, were calculated using equation one:

$$q_t = \frac{(C_o - C_e)V}{1000w} \qquad (eqn. 1)$$

Where q_t = metal ion uptake in mg/g at time, t

C_o =initial concentration mg/l

C_e =concentration at equilibrium, in mg/l

V =olume in ml

W =mass of adsorbent in g

The data obtained from the experiment were analyzed, the isotherm of the adsorption process were modeled by performing linear and non-linear regression on the data obtained from the adsorption experiments using the existing models with the aid of Microsoft excel.

Equilibrium modeling

The analysis of the adsorptive uptake of lead and chromium metals from aqueous phase at different initial concentration, was conducted to fit the isotherm models. The equilibrium models were grouped in to: two parameter models and three parameters models. The two parameters models include Langmuir, Freudlinch, Dubinin-Radushkevich, and Temkin models (Shahbeig *et al*., 2013). The two parameters models were fitted to model the equilibrium of lead and chromium adsorption onto dum palm kernel activated carbon. The original and the linear forms of the equations are presented in equations 2 to 4.

Freundlich isotherm is mostly conforms to adsorption of polar substances on molecular sieves and activated carbon (Foo and Hameed, 2010). The exponent, *n* ranges between 0 and 1, and is a measure of binding intensity of the adsorbates to the adsorbent. A value below unity implies chemisorptions process where 1/n above one is an indicative of cooperative adsorption. Recently, Freundlich isotherm is censured for its inability to explain the underlying thermodynamic principle at lower concentration (Foo and Hameed, 2010).

$$q_e = K_F C_e^{1/n} \qquad (eqn. 2)$$

$$log q_e = log K_F + \frac{1}{n}\log C_e \qquad (eqn. 2\ a)$$

Temkin isotherm was used firstly used to describe the uptake of hydrogen onto platinum electrodes in an acidic medium. The isotherm contains a parameter that explain the thermodynamics principle of adsorbent–adsorbate interactions.

$$q_e = \frac{RT}{b_T}\ln(A_T C_e) \qquad (eqn. 3)$$

$$q_e = \frac{RT}{b_T}\ln(A_T) + \frac{RT}{b_T}\ln(C_e) \qquad (eqn. 3\ a)$$

$\frac{RT}{b_T}$ =heat of adsorption,

$A_T =$ is the maximum binding energy of the adsorbate to the activated carbon,

b_T = Temkin constant

Dubinin–Radushkevich isotherm is an empirical model first used to describe the adsorption of subcritical vapors onto adsorbent. (Foo and Hameed, 2010). The uptake of species onto solids adsorbent conforms to a pore filling mechanism (Foo and Hameed, 2010).

$$q_e = q_s \exp(-k_{ad}\mathcal{E}^2) \qquad (eqn. 4)$$

$$\ln(q_e) = \ln(q_s) - k_{ad}\mathcal{E}^2 \qquad (eqn. 4\ a)$$

Where $\mathcal{E} = \mathrm{RTln}(\ 1 + 1/\mathrm{Ce})$

The most applicable three parameters isotherm models to liquid adsorption system include, Redlich-Peterson, and Sip’s models (Shahbeig *et al.*, 2013), and are presented in equations 5 to 6.

Redlich–Peterson isotherm is a hybrid isotherm featuring Freundlich and Langmuir isotherms, which incorporate three constants into an empirical equation (Foo and Hameed, 2010).The model is linear in the numerator and an exponential function in the denominator. (Foo and Hameed, 2010; Shahbeig *et al.*, 2013).

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g} \qquad (eqn. 5)$$

Sips isotherm is a hybrid of Freundlich and Langmuir models. It predicts adsorption both at higher concentration and very low concentrion. (Foo and Hameed, 2010).

$$q_e = \frac{Q_{SH} C_e^{\beta S}}{1 + a_S C_e^{\beta S}} \qquad (eqn. 6)$$

Results and discussion

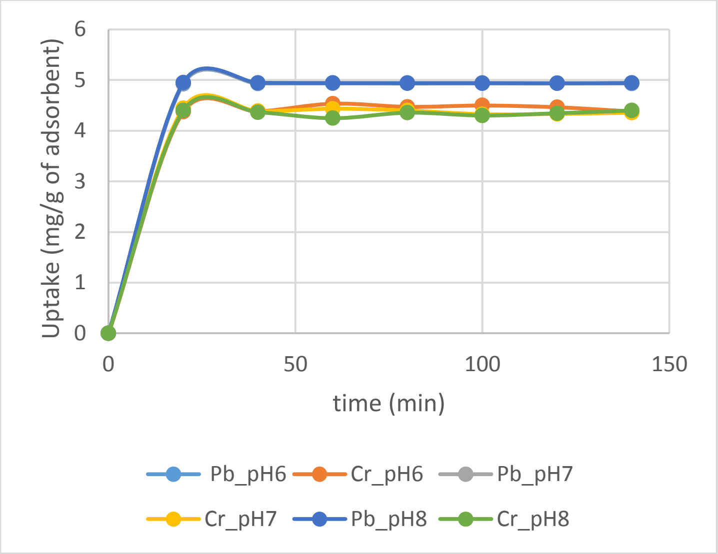

Fig. 2: Uptakes of Lead and Chromium at Various pH

The co-current uptake of lead and chromium onto DPK AC was studied for 120 min at an interval of 20 minutes. The uptakes as time dependent at various pH is represented in Fig. 2. As observed in Fig. 2, the equilibrium contact time was between 20 to 40 minutes at all pH conditions studied. The contact time above 40 minutes shows no significant increase in uptake rather constant fluctuation, which exhibit dynamic equilibrium.

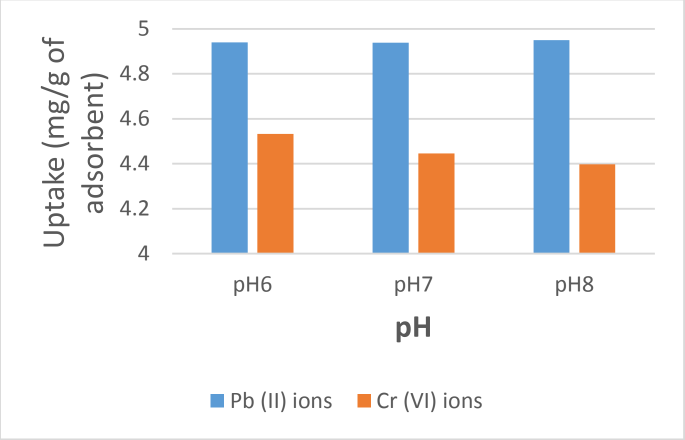

Fig. 3: Effect of Initial pH on Uptake of Lead and Chromium

The pH of the aqueous solution is among the factors influencing adsorption processes, as it dictates the interactions between the adsorbate and adsorbent. In this study, the initial pH was varied from 6 to 8. The uptakes of the lead and chromium as related to pH is presented in Fig. 3. The uptake for lead is almost the same for all the pH studied, however, there is variation of chromium uptake, and the chromium is better adsorbed at pH of 6, about 0.5 and 0.7 mg/g above that of 7 and 8 respectively. The trend is in agreement with the finding of Das and Mondal, where he observed that the maximum uptake of lead is at pH of 6, Bernard and Jimoh (2013), also found that pH of 6 is the optimum condition for co-current adsorption of lead, iron, copper, and zinc. This trend is observed because, the pH variation was adjusted using NaOH and HCl, the solution is dominated by H^+. Despite this domination, the uptakes is higher in both the adsorbates. This is due to the fact that both lead and chromium are above hydrogen in electrochemical series (ECS), the competition favours lead most, which is above them in ECS, therefore makes the uptake to be higher, Qaiser *et al*. also observed the higher uptake of lead in co-current adsorption of lead and chromium using ground nut hull (Qaiser *et al*., 2009).

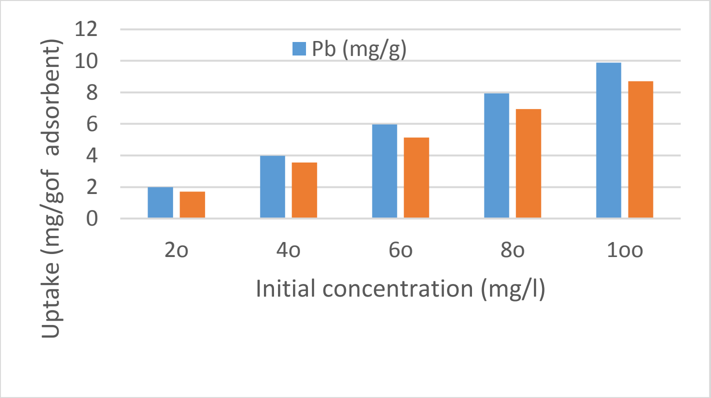

Fig. 4: Effect of initial concentration of solution on uptakes

The effect of initial concentration of lead and chromium in solution on sorption capacity is presented in Fig. 4. The initial concentration between 20 to 100 mg/l at an interval of twenty were studied. It can be observed in Figure. 4 that the uptakes of the adsorbates increases with an increase in initial concentration from 20 to 100 mg/l. This is may be due to the fact that, at higher initial concentration, the population of the species are so large that there is higher frequency of interaction between the adsorbent and the adsorbates, which leads to adsorption. This trend was also observed by Onundi *et al*., 2010.

Table 2: Constants of Two Parameters Models for Lead and Chromium Adsorption onto DPK AC

Models	Parameters	Lead (ii) ions	Chromium (vi) ions
Freudlinch			
	K	11.2898	0.6616
	1/n	0.8584	0.9944
	R^2	0.9102	0.9683
Dubinin-Radushkevich			
	K_d (mol/J)	$8x10^{-8}$	$3x10^{-6}$
	q_s (mg/g)	14.1696	7.7191
	R^2	0.9996	0.9377
Temkin			
	A_T (J/mol)	9.5793	0.4997
	b_T (l/g)	568.6093	602.4065
	R^2	0.9713	0.9356

The regression results are presented in Table 5, and 6 showing models constants, their coefficients of determination, (R^2), and non-linear chi-square, (χ^2) values, respectively. As it appears in Table 5, it was observed that the Dubinin-Radushkevich isotherm has R^2 of 0.9996 and 0.9377 for lead and chromium, closer to 1 than the other models, this shows better fit to the experimental adsorption data than the Freundlich, and Temkin isotherm equations for both Pb (II) and Cr (VI) sorption. It was also observed from Table 5 that the Dubinin-Radushkevich maximum adsorption capacity, for lead and chromium of 14.1696 and 7.7191 mg/g respectively. Similarly, in Table 6, Sip's model showed better fit to the experimental adsorption data than the Redlich-Peterson. The non-linear regression chi-square value are 0.0113 and 0.1817 for lead and chromium respectively, closer to zero than any other models. The value of Sip's exponents are 1.9134 and 0.9993 for the lead and chromium, respectively.

The value for lead lies between 1 and 10 indicating favorable adsorption (McCabe *et al*., 1993). That is, high adsorbent uptake can be achieved for lean adsorbates solution. While for chromium is an unfavourable adsorption. The linearity indicates concentration dependency (McCabe *et al*., 1993). From Temkin isotherm model, the value of the adsorption binding energy, b_T was estimated at 9.5793 and 0.4997 J/mol for lead and chromium, respectively. The estimated value of b_T for the present study was found in the range of chemical adsorption, for lead, while chromium is in the range of physical adsorption.

Table 3: Constants of Three Parameters Models for Lead and Chromium Adsorption onto DPK AC

Models	Parameters	Lead	Chromium
Redlich-Peterson			
	g	0.0000	0.0019
	a_R (l/mg)	22.0458	19.5270
	K_R (g/mg.l)	332.8930	13.4635
	χ^2	3.7358	0.1816
Sips			
	K_S	76.2832	0.6540
	a_s	6.9295	0.0000
	β_S	1.9134	0.9993
	χ^2	0.0113	0.1817

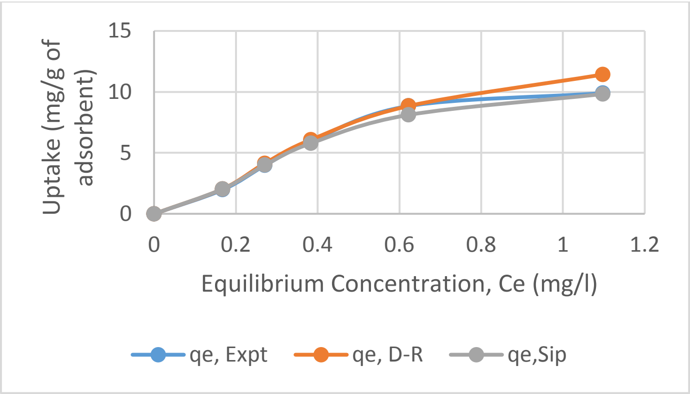

Fig. 6: Comparison of D-R, and Sip's models with Experimental Data for Lead

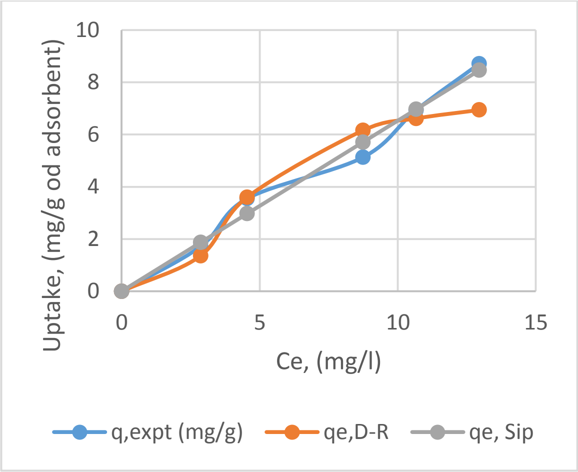

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Fig. 7: Comparison of D-R, and Sip's models with Experimental Data for Chromium

The best candidates from the two and three parameters models are Dubinin-Radushkevich and Sip models, respectively. The experimental trend is compared with the two models in Fig. 6 and 7, the Dubinin-Radushkevich predicts slightly above, while Sip's model predicts below, it is therefore safer to predicts the uptakes and equilibrium concentration using the Sip model.

Table 4: A Comparisons of Calculated Maximum Uptakes for Lead and Chromium by Activated Carbon from Different Sources

Adsorbent	q_{max} (mg/g)		Reference
	Pb	Cr	
palm shell activated carbon	1.58	-	Onundi *et al.* (2010)
Typha latifolia activated carbon	-	12.987	Jayasantha *et al.* (2015)
Rice husk activated carbon	6.16	-	Taha *et al. (*2011)
palmyra palm nut activated carbon	140		Nwabanne and Igbokwe (2012)
Olive stone activated carbon	-	71	Attia *et al* (2010)
Marine green algae activated carbon	22.93	-	Suresh Jeyakumar and Chandrasekaran (2014)
Dum palm kernel activated carbon	14.17	7.72	Present study

Maximum uptake by different adsorbents is compared in Table 4.6. Palmyra palm nut activated carbon has higher lead adsorption capacity, while olive stone activated carbon has higher chromium adsorption capacity. The dum palm kernel activated carbon even as it co-currently adsorbed lead and chromium, it has higher adsorption capacity than palm shell, and rice husk activated carbon. This implies that the activated carbon from from DPK is comparably good activated carbon for removal of lead and chromium from aqueous phase.

Conclusion

The co-current adsorption of lead (II) and hexavalent chromium from aqueous solutions onto DPK AC have investigated. Time, pH, and initial concentration dependence on uptake were also investigated.

The results lead to the following conclusions:

1. The parameters for co-current adsorption of lead and chromium onto DPK AC are: the initial pH of 6, the equilibrium contact time is established around 40 minutes. The uptake step up from 1.9 to 9.8 mg/g for lead, and for chromium, from 1.7 to 8 mg/g, with change in initial concentration from 20 to 100 mg/l
2. The adsorption experimental data are better conforms to Sip’s model. The maximum uptake of the DPK AC for lead and chromium are 14.1696 and 7.7191 mg/g respectively. The adsorption type is chemisorption for lead and physic-sorption for chromium, based on the Temkin’s constant calculated as 9.5793 and 0.4997 J/mol for lead and chromium, respectively.

Nomenclature

Symbol/abbreviation	Nomenclature
a_R	Redlich-Peterson denominator co-efficient (l/mg)
a_s	Sip’s constant (denominator coefficient) (l/g)
A_T	Tempkin model binding constant (l/g)
b_T	Temkin constant (J/mol)
ε	Dubinin–Radushkevich isotherm constant
D-R	Dubinin–Radushkevich
G	Redlich-Peterson exponent
K_d	Dubinin–Radushkevich isotherm constant (mol/J)
K_F	Freudlinch constant
K_R	Redlich-Peterson constant, (numerator co-efficient) (g/mg.l)
K_S	Sip’s isotherm constant (numerator coefficient) (l/g)
N	Freudlinch adsorption intensity

Qe	Calculated equilibrium uptake (mg/g)
q_s	Dubinin–Radushkevich isotherm maximum adsorption capacity (mg/g)
Q_{sH}	Hill’s model maximum capacity (mg/g)
R	Universal gas constant
R^2	Regression correlation coefficient
T	Temperature
β_S	Sip’s adsorbate fluid concentration exponent
$\chi 2$	Non-linear regression chi-square

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