



## Adsorption Studies of Heavy Metals by Low-Cost Adsorbents

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**ABSTRACT:** In this study, removal of toxic metals Cr(VI) from artificially contaminated water has been investigated with the aim of detoxifying industrial effluents before their safe disposal onto land or into the river. Two low-cost natural adsorbents, Palm Kernel fiber and Coconut husks, were used to remove Cr(VI) ion from synthesized waste water. The effects of, initial concentration, contact time, on adsorption efficiency were investigated. Adsorption isotherm and kinetics were also studied. Generally, the result showed an increase in removal efficiency with increase in contact time and decrease of initial concentration. Kinetic study revealed that pseudo-second order model is suitable to explain all our experimental data. The adsorption equilibrium data correlate well with Freundlich model, with regression coefficient,  $R^2$ . The results showed that efficiencies of ACNH and APKF for Cr(vi) ion removal were 91.14%, and 84.89% respectively. High adsorption capacity of the tested adsorbents makes it preferable and very cheap and environmental-friendly alternative adsorption material.

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**KEY WORDS:** Adsorption, isotherm, kinetics, heavy metals.

Man's activities through industrialization, urbanization, technological development and agriculture, discharge heavy metals into the environment; this has become a matter of global concern over the past few decades because the presence of heavy metal ions in high concentration in the environment is detrimental to life (Benhima and others, 2008).

With increased environmental awareness and activism of the 1970s, Davydova (2005) observed that most countries of the world started adopting tougher legislation to regulate waste water discharged into the environment. This has led to efforts constantly made to develop new idea or modify existing technology on the removal of heavy metals from effluents before they are discharged into the receiving water bodies.

Several methods are currently employed in heavy metal removal from industrial wastewater, but Okoye and others, (2001) summarized their drawbacks as either technical inefficiency or cost ineffectiveness. Badmus and others, in 2007 reported the emergence of new approaches based on the use of natural inexpensive adsorbents for treatment of industrial waste water. In general, an adsorbent can be termed

as a low cost adsorbent if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry (Nasim and others, 2004).

In Nigeria, huge amounts of Palm kernel fibre and coconut husk waste are generated daily, which create environmental and disposal problems. Therefore, application of these wastes as adsorbent offers highly effective technological means in dealing with pollution of heavy metals and solving their disposal problems, with minimum investment required (Adeogun and others 2012). Therefore there is an urgent need that all possible sources of agro-based inexpensive adsorbents, in Nigeria, should be explored and their feasibility for the removal of heavy metals should be studied in detail.

The objective of this study is to therefore contribute in the search for less expensive adsorbents and their utilization possibilities for various agricultural waste by-products which are in many cases also pollution sources.

### MATERIALS AND METHODS

The preparation of chemicals and materials involved are discussed in this chapter. Adsorption experiments

were carried out at the Chemistry Laboratory of the Post Graduate School of University of Port Harcourt.

*sample collection and preparation:* The coconut fruit (see fig. 3.1) was purchased from a local market and palm fruit husk were collected from small scale palm oil processing unit in Rumusi community of Rivers State, Nigeria. Machete was used to cut-off the outermost cover of the coconut before the husk was collected and dried in an oven (see fig. 3.4) at a temperature of 80°C for 24 hours.

The palm fruit fibre (see fig 3.2) was washed with plenty of warm water to remove the oil content and dried in the oven at 80°C for 24 hours. After drying the samples are ground with a hand held grinder (see fig. 3.3), sieved with a sieve size of 500 µm.

*Preparation of Stock Solution: Preparation of Chromium Solution:* 1000mg/l of Chromic Nitrate (Cr (NO<sub>3</sub>)<sub>2</sub>. 9H<sub>2</sub>O) (Source: Hopkins & Williams. with Mw.= 400.15g. Grade: GPR) was prepared for use throughout the experimental work by dissolving 7.6952g of Chromic Nitrate powder in 1000 ml of distilled water.

Fig 3.9 Orbital shaker (SSL1; Stuart®)  
*Estimation of Metal Uptake:* The metal uptake, q<sub>e</sub>, was determined by the following Adeogun and others (2010):

$$q_e = \frac{V(C_1 - C_e)}{m} \quad (3.1)$$

Where q<sub>e</sub> = metal ions per dry adsorbent (mg/g), V = volume of solution (L) C<sub>1</sub> = initial concentration of metal in solution (mg/L) C<sub>e</sub> = final concentration of metal in solution (mg/L) m= the mass of adsorbent (g) The efficiency of heavy metal removal was calculated from the amount of metal ions adsorbed on the adsorbent and the amount of metal ions available in the synthetic solution, as shown in the equation by Adeogun and others (2010).

$$\text{Percentage removal} = \frac{\text{Heavy metal ion removed}}{\text{Heavy metal ion remaining}} * 100\% \quad (3.2)$$

*Adsorption Experiment: 3.4.1 Effect Of Contact Time On Removal Efficiency;* The metal solutions were adjusted to pH6 with NaOH and HCL; pH was measured using Digital pH meter (Labtech pH510). 2g of the coconut or palm kernel Husk were weighed into sample bottles labeled with different contact time (20mins, 40mins, 60mins, 80mins, 100mins, 120mins and 140mins). 50ml of metal solution of initial concentrations (20mg/l, 60mg/l and 100mg/l) which have already been adjusted to pH6 was measured and added. The sample was agitated at each contact time

with orbital shaker (see fig 3.9). At the end of each contact time the sample was filtered and the filtrate used for metal ion concentration determination using Atomic Absorption Spectrophotometer (Optima 7000DV, Perkin Elmer) (see fig. 3.10).

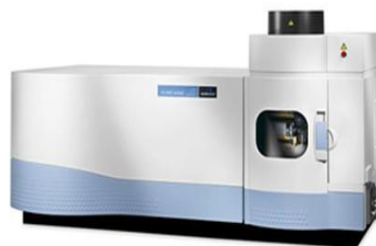


Fig 3 AAS Equipment (Optima 7000DV; Perkin Elmer.)

*Kinetic Models:* Kinetics of adsorption is an important characteristic in defining the efficiency of adsorption. It is of great significance to evaluate the performance of a given adsorbent and gain insight into the underlying mechanisms (Hui Qiu and others 2008).

The pseudo second order equation based on equilibrium adsorption (Malik, 2004) is expressed as:

$$t/q_t = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_t}\right)t \quad (3.4)$$

Where: k<sub>2</sub> (g/mg s) is the rates constant of second-order adsorption. If second-order kinetics is applicable, the plot of t/q<sub>t</sub> versus t should show a linear relationship (Adeogun and others 2012). Values of K<sub>2</sub> and q<sub>e</sub> are determined respectively from Table 3.1.

Table 3.: Kinetic models and their linearized expressions (Abechi E.S, and others 2011)

Models	Plot	Parameters
Pseudo second order	t/q <sub>t</sub> vs. t	K <sub>2</sub> =Slope/intercept q <sub>e</sub> =1/Slope

*Estimation Of Adsorption Isotherm Parameter* The most common representation of the adsorbate concentration and quantity of material adsorbed is the adsorption isotherm; adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity or homogeneity of adsorbents, the type of coverage, and possibility of interaction between the adsorbate species. They are represented by graphs of the amount adsorbed against the equilibrium concentration, at a specific temperature (Yeoh Hong Huei 2012). The nature of the interaction between the adsorbate and adsorbent, i.e. favorable or unfavorable, can be determined from the isotherm shape (Khraisheh and others, 2004).

The Langmuir and Freundlich models are the most widely used models in the case of adsorption of metal ions by adsorbents.

*Langmuir Isotherm:* The model is applicable in the cases where only one molecular layer of adsorbate is formed at the adsorbent surface which remains constant even at higher adsorbate concentrations. The Langmuir model can be presented by the equation (Li and others, 2005):

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{1}{q_{\max}} C_e \quad (3.5)$$

Where :  $q_{\max}$  is the monolayer adsorption capacity of the adsorbent (mg/g), it is the maximum amount adsorbed,  $K_L$  is the Langmuir adsorption constant (L/mg),  $C_e$  is the equilibrium metal ion concentration in the solution (mg/L) and  $q_e$  is the equilibrium metal ion concentration on the adsorbent (mg/g). Values of  $q_{\max}$  and  $K_L$  are calculated respectively from the slope and the intercept of plot of  $C_e/q_e$  vs.  $C_e$ , as shown in Table 3.2.

*Freundlich Model* On the other hand, the Freundlich model is perhaps the most popular adsorption model for a single solute system of monolayer adsorption (Freundlich, 1928).

The equations of the Freundlich adsorption models are expressed as below (Li and others, 2005):

$$\text{Log } q_e = \text{log } K_f + \frac{1}{n} \text{log } C_e. \quad \text{Where} \quad (3.6)$$

$K_F$  is a constant related to the adsorption capacity (Freundlich constant)  $1/n$  is an empirical parameter related to the adsorption intensity (which varies with the heterogeneity of the material).

Values of  $1/n$  and  $K_F$  are calculated respectively from the slope and the intercept of plot of  $\text{log } q_e$  vs.  $\text{log } C_e$ , as shown in Table 3.2.

*Applicability Of Models:* The applicability of each model is determined by comparing the correlation coefficients,  $R^2$ .

The higher the value of correlation coefficients  $R^2$  the better will be the goodness of fit (Adeogun, A. and others 2012).

**Table 3.:** Isotherms and their linearized expressions (Mohammad Salarirad, 2011)

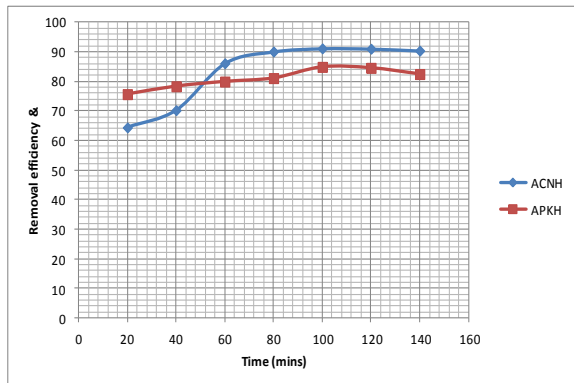
Isotherms	Plot	Parameters
Freundlich	$\text{log } q_e$ vs. $\text{log } C_e$	$K_f = \text{exp}(\text{intercept})$ $n = (\text{slope})^{-1}$
Langmuir	$(C_e/q_e)$ vs. $C_e$	$q_{\max} = (\text{slope})^{-1}$ $K_L = \text{slope}/\text{intercept}$

*Data Analysis:* All charts and calculations were done using Microsoft Excel spreadsheet.

## RESULTS AND DISCUSSION

The results of the experiments at different contact times and concentrations of metal ions are presented in this chapter. Complete results for the adsorption experiment are found in appendix A. The adsorption isotherm, and kinetic parameters of the process are evaluated and the effects of metal ion concentration, and contact time on the adsorption efficiency discussed.

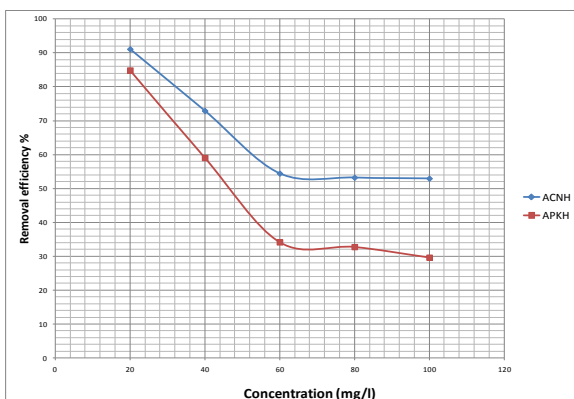
*Effect of Contact Time on Removal Efficiency:* Fig. 4.1 shows the effect of contact time on Cr ions uptake by the selected adsorbents. This was achieved by varying the contact time from 20 to 140 min. in separate experimental runs. As expected, the amount of ion adsorbed into a biomass increases with time, and at some point, reaches a constant value beyond which no more is removed from solution. At this point, the amount of the ion desorbing from the adsorbent is in a state of dynamic equilibrium with the amount being absorbed by the adsorbent. The time required to attain this state of equilibrium is termed the equilibrium time, and the amount of ion adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions. Equilibrium was reached at 100 mins in all cases. This can be explained by the fact that initially, the rate of ion uptake was higher because all sites on the adsorbent were vacant and ion concentration was high, but decrease of adsorption sites reduced the uptake rate. Similar results were found in the study of Mousavi and others (2010).



**Fig 4.1:** The effect of contact time on adsorption efficiency of ACNH and APKF unto Cr ion at 25°C at conc. of 20mg/l

*Effect of Initial Concentration on Removal efficiency:*

The effect of initial ion concentrations on the adsorption efficiency of the studied agricultural wastes is shown in Fig. 4.5 and. Adsorption experiments were carried out at different initial ion concentrations ranging from 20 to 100 mg/L. It was observed as a general trend that there is a decrease of the removal percentage with increase in initial concentration. These results may be explained on the basis that the increase in the number of ions competing for the available binding sites and also because of the lack of active sites on the adsorbent at higher concentrations. Therefore, more metal ions were left un-adsorbed in solution at higher concentration levels (Krishnan & Anirudhan, 2003).



**Fig 4.:** Removal efficiency of Cr by ACNH and APKF with concentration 25°C

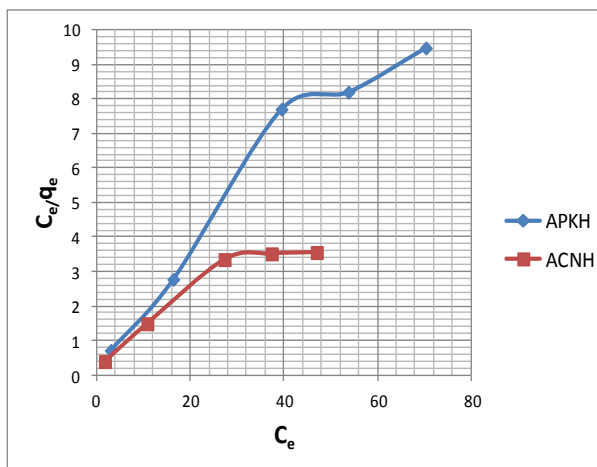
*Adsorption Isotherms; Langmuir isotherm:* Value of Langmuir parameters and correlation coefficients  $R^2$  are summarized in Table 4. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter ( $R_L$ ) (Weber and Chakkravorti, 1974), which is defined by:  $R_L = 1 / (1 + K_L C_0)$  (4.1) Where;

$K_L$  is the Langmuir constant,  $C_0$  is the highest metal concentration ( $mg.L^{-1}$ ). The value of  $R_L$  indicates the type of the isotherm to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ) (Fytianos and others, 2003). Values of  $R_L$  are summarized as follows:

**Table 4.:** Values of  $R_L$  for removal of ion from ACNH and APKF at 25°C

Metal Ions	ACNH	APKF
Cr	0.08	0.57

It will be noted that the value of  $R_L$  was between 0 and 1 indicating the adsorbents prepared are favorable for adsorption of the metal ions under conditions used in this study.



**Fig 4.:** Langmuir isotherm for the adsorption of Cr ion by ACNH and APKF at 25°C

*Freundlich model:* The Freundlich parameters together with correlation coefficients  $R^2$  were summarized in Table 4.3. The slope  $1/n$  ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero (Haghsresht and Lu, 1998). A value for  $1/n$  below one indicates a normal Langmuir isotherm while  $1/n$  above one is indicative of cooperative adsorption (Fytianos and others, 2003). Values of  $1/n$  are summarized as follows:

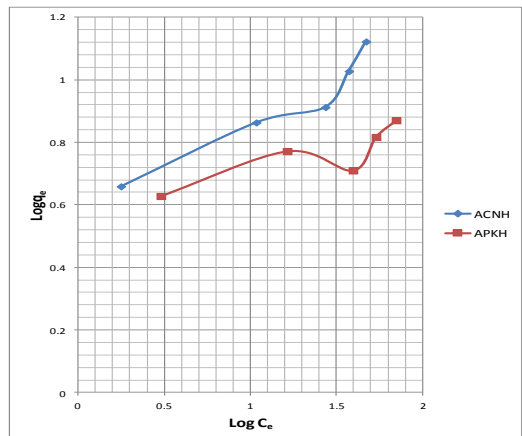
**Table 4.:** Values of  $1/n$  for removal of ion by ACNH and APKF at 25°C

Metal Ions	ACNH	APKF
Cr	0.29	0.14

It will be noted that the value of  $1/n$  was between 0 and 1 indicating the adsorbents prepared are

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favorable for adsorption of the metal ions under conditions used in this study.



**Fig 4** Freundlich isotherm graph for the adsorption of Cr ion by ACNH and APKF at 25°C

**Table 4.:** Isotherms parameters for Cr removal by ACNH and APKF at 25°C

Isotherm model	Parameters	ACNH	APKF
Langmuir	Adsorption constant $K_L$	0.11	0.16
	Adsorption capacity $Q_{max}$	13.69	7.38
	Correlation coefficient $R^2$	0.94	0.97
	Regression equation	$Y=0.07X + 0.64$	$Y=0.13X + 0.82$
Freundlich	Adsorption intensity $i/n$	0.28	0.14
	Adsorption capacity $K_F$	1.77	1.75
	Correlation coefficient $R^2$	0.96	0.85
	Regression equation	$Y=0.28X + 0.57$	$Y=0.14X + 0.56$

**Best-fit Isotherm models:** As seen from Table 4.3, for the adsorption of Cr ions onto ACNH, the Freundlich model presents greater  $R^2$  value (0.957236) than the Langmuir model (0.941493) at 25°C. In this case, Freundlich model fitted better to the adsorption data and thus it is more suitable used to describe the relationship between the amounts of Cr (IV) adsorbed by ACNH and its equilibrium concentration in the solution at 25°C (Adamson, 2001). On the other hand, adsorption of Cr ions onto APKF, fitted better to the Langmuir model under the same conditions. Best fit models are summarized below:

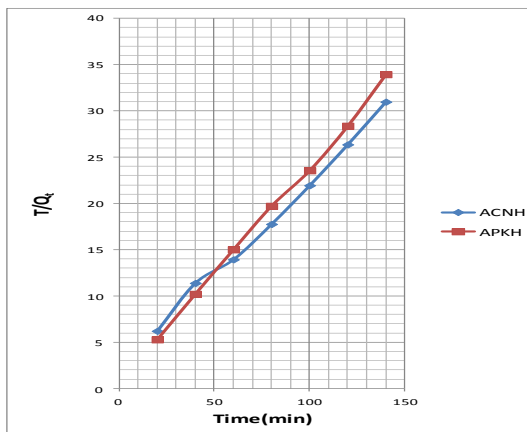
**Table 4.:** Best-fit isotherm model for ion removal by ACNH and APKF at 25°C

	ACNH	APKF
Cr	Freundlich	Langmuir

**Kinetic Models:** The kinetic studies of adsorption of Cr(VI) ions onto coconut husk and palm kernel husk was carried out using the second order models on

experimental data and the values obtained are as seen in Table 4.10.

Values of correlation co-efficient are shown in Tables 4.10.



**Fig 4.** Second order kinetic graph for the adsorption of Cr ion by ACNH and APKF at 25°C

**Table 4.:** Kinetic models for the adsorption of 20mg/l of Cr ion by ACNH and APKF at 25°C

Kinetic model	Parameters	ACNH	APKF
Second order	Rate constant $K_2$	0.08	0.14
	Correlation coefficient $R^2$	0.99	0.99
	Regression equation	$Y=0.20X + 2.32$	$Y=0.23X + 0.75$

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