Isotherm Studies of Adsorption of Cr (Vi) Ions onto Coconut Husk

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Abstract: In this study, the application of ground coconut husk GCH for removal of Cr (VI) from its aqueous solution was investigated. Several batch experiments were carried out with different values of test conditions including sorbent concentration, contact time, temperature and pH. The results obtained showed that adsorption of Cr (VI) followed Freundlich isotherm model. Dubinin-Radushkevich isotherm revealed that adsorption of the three metal ions principally followed chemical adsorption process. Adsorption kinetics was best described by pseudo-second order. Thermodynamic studies revealed that adsorption of Cr (VI) were endothermic process since ΔH was positive. Adsorption of Cr (VI) was spontaneous as evident from the negative value ΔG. Uptake of metal ion from their aqueous solution increases with increase in pH but decreases slightly at pH of 8.

Keywords: Chromium (VI), Adsorption, Coconut Husk

1. Introduction

The last century witnessed accelerated and intensified industrialization and urbanization activities that led to degradation and contamination of our aquatic environment with different serious pollutants [1]. Thus, waste water contaminated with heavy metals has become a global problem which required ongoing evaluation and revision of water resource policy regularly.

Increase in industrial activities has caused many water bodies to receive loads of heavy metals that exceed the maximum permissible limit for waste water discharge designated to protect the environment, humans and animals [2]. Heavy metals have the tendency of accumulating inside the human body when they are incorporated through the food chain [3]. It has been identified that these metals are release into the environment by both natural and anthropogenic means such as mining, smelting, metal plating, explosive manufacture, industrial activities and among many others.

The effect of heavy metals in water and waste water range from beneficial through troublesome to dangerously toxic (even at low concentration). Therefore, it's elimination from waste water is important to protect public health and wild life [4].

Several technologies for heavy metal removal have been proposed [5]. These comprise precipitation [6], reverse osmosis [7], solvent extraction [8], flocculation [9], sorption [10], and activated carbon adsorption and membrane separation process [11]. Nevertheless, these aforementioned techniques are all generally expensive and might possibly generate by-products dangerous to human health [1]. Since the cost of these processes are rather expensive, the use of agricultural residues or industrial by-products having biological activities have been received with considerable attention [12]. Biosorption is put forward as an effective and relatively simple method of waste treatment through riding them of various chemical compounds. The low price of the Biosorbent is an additional assets, this renders the whole method cheap and allows for combining with other sequestering processes [13]. Recent studies have shown that several Biosorbents like cow hooves [14], egg shell [15], Msasa Tree (*brachystegia spiciformis*) Leaf Powder [1],

chick and Duck Feather [16], *pseudomonas aeruginosa DSGPM4 species* [17], *treculia africana* [18], roasted date pits [19], shrimp peel [20], were used for remediation of heavy metals from wastewater.

Coconut husk is a hard protecting cover of coconut. It is made up of exocarp and mesocarp composed of fibre called coir which has many traditional and commercial uses. According to the statistics compiled by Malaysian Ministry of Agriculture, there are more than 408,000t of coconut husk, rice husk and corn cobs produced in Malaysia annually [21]. The use of coconut shell as a Biosorbent material presents strong potential due to its high content of lignin of about 36-45% and cellulose of about 23-43% [22]. Coconut husk is generally considered as a waste. It's abundance in Nigeria cannot be over-emphasized. Thus, regulating these agricultural wastes by converting them into effective adsorbent have become imperative to removing these toxic heavy metals. This work evaluates the use of GCH for the adsorption of Cr (VI) ions with the variation of some experimental factors namely: concentration, contact time, pH and temperature The effects of these parameters and adsorption isotherms were investigated.

2. Materials and Methods

2.1. Sorbent Preparation

Coconut husk were collected from Ihulu, Aguluzigbo in Anaocha Local Government area, Anambra State, Nigeria. It was washed thoroughly with distilled water to remove dirt, sun dried for about a week and then ground to fine powder. The ground adsorbent was sieved and a particle size of 400μm was used in the whole experiment.

2.2. Preparations of Standard Solutions of Cr (VI)

Standard solution containing 1000mg/l Cr (VI) was prepared by dissolving 2.90g of $K_2Cr_2O_7$ in 100ml of deionized water in a volumetric flask and making up to 1000ml. Adsorption experiments involving temperature, concentration and contact time variations were carried out after serial dilution of standard solution.

2.3. Sorption Studies

2.3.1. Adsorption Equilibrium Experiment

3g of powdered coconut husk was weighed into five different beakers each containing 100ml of varying concentration of $K_2Cr_2O_7$ ranging from 10mg/L to 50mg/L. The mixtures were thoroughly stirred and allowed to stand for one hour, after which, 10ml of the mixture was drawn out and filtered. The filtrate was analyzed with AAS for metal ion concentration. Results obtained were treated and analyzed using thirteen different isotherm models shown in table 1 below.

Table 1. Mathematical representation of isotherm models.

S/N	ISOTHERM MODEL	EQUATION	PLOT	REFERENCE
1	HENRY	$q_e = K C_e$	q_e Vs C_e	[23]
2	LANGMUIR I	$\dfrac{C_e}{q_e} = \dfrac{1}{q_m L} + \dfrac{C_e}{q_m}$	$\dfrac{C_e}{q_e}$ Vs C_e	[24]
3	LANGMUIR II	$\dfrac{1}{q_e} = \dfrac{1}{q_m K C_e} + \dfrac{1}{q_m}$	$\dfrac{1}{q_e}$ Vs $\dfrac{1}{C_e}$	[24]
4	LANGMUIR III	$q_e = q_m + \dfrac{q_e}{K C_e}$	q_e Vs $+\dfrac{1}{C_e}$	[24]
5	LANGMUIR IV	$\dfrac{q_e}{C_e} = q_m K + q_e K$	$\dfrac{q_e}{C_e}$ Vs q_e	[24]
6	FREUNDLICH	$\ln q_e = \ln K_F + \dfrac{1}{n} \ln C_e$	$\ln q_e$ Vs $\ln C_e$	[24]
7	TEMKIN	$q_e = B \ln K + B \ln C_e$	q_e Vs $\ln C_e$	[25]
8	DUBININ-RADUSHKEVICH	$\ln q_e = \ln q_D - \gamma \varepsilon^2$	$\ln q_e$ Vs ε^2	[24]
9	HARKINS-JURA	$\dfrac{1}{q_e{}^2} = \dfrac{B_{HJ}}{A_{HJ}} - \dfrac{1}{A} \log C_e$	$\dfrac{1}{q_e{}^2}$ Vs $\log C_e$	[25]
10	FRUMKIN	$\ln\left[\dfrac{\theta}{(1-\theta)C_e}\right] = \ln K - 2a\theta$	$\ln\left[\dfrac{\theta}{(1-\theta)C_e}\right]$ Vs θ	[26]
11	JOVANOVIC	$\ln q_e = \ln q_m - K_J C_e$	$\ln q_e$ Vs C_e	[25]
12	EL-AWARDY	$\log \dfrac{\theta}{(1-\theta)} = \log K' - y \log C_e$	$\log \dfrac{\theta}{(1-\theta)}$ Vs $\log C_e$	[27]
13	SMITH	$q_e = W_b - W \ln(1 - C_e)$	q_e Vs $\ln(1 - C_e)$	[26]

2.3.2. Kinetic Experiment

40ml of $K_2Cr_2O_7$ was drawn from the stock solution. This was made up to 1000ml to produce 40mg/l of Cr (VI) ion. 100ml was then withdrawn using a measuring cylinder and poured into a beaker. 3g of the adsorbed was added to the beaker. The mixture was thoroughly stirred and allowed to stand. At time intervals of 5, 10, 30, 60, 90 and 120 minutes, 15ml of the mixture was drawn out and filtered. The filtrate obtained was then analyzed for metal ion concentration. Results obtained were analyzed using Pseudo first and second order kinetic models.

2.3.3. Thermodynamic Experiment

Adsorption of Cr (VI) ion from their aqueous solution were investigated over the temperature range of 50°C, 70°C and 90°C. 40ml of $K_2Cr_2O_7$ was drawn from the stock solution. This was made up to 1000ml to produce 40mg/l of Cr (VI). 100ml of the prepared solution was put into a beaker. 3g of the adsorbent was added to the beaker and the mixture was stirred for even distribution. The beaker was placed in a thermostat water bath set at temperature of 50°C and allowed to stand in the bath for an hour and after which, sample was drawn from it and filtered for analysis. This was repeated at temperatures of 70°C and 90°C.

2.3.4. pH Experiment

The uptake of Cr (VI) ions as a function of H^+ ion concentration was determined in the pH range of 2-8. The

adjustment of the pH solutions was carried out by adding required amount of conc. H_2SO_4 and NaOH solutions.

Amount of adsorption Qe was calculated using the equation;

$$Q_e = \frac{V(C_o - C_e)}{w} \qquad (1)$$

Where
C_o = concentration of ion at initial time in mg/l
C_e = concentration of ion at equilibrium time in mg/l
V = volume used in litres
W = mass of the adsorbent used in grams

3. Results and Discussion

3.1. Adsorption Isotherm

***Table 2.** Isotherm parameters for adsorption of Cr (VI).*

S/N	Isotherm	Parameters	
1	Henry	K	0.645
		0	0.098
2	Langmuir I	q_m (mg/g)	11.36364
		K_L (l/mg)	0.070513
3	Langmuir II	q_m (mg/g)	-8.92857
		K_L (l/mg)	-10.5042
4	Langmuir III	q_m (mg/g)	0.006
		K_L (l/mg)	1.420455
5	Langmuir IV	q_m (mg/g)	0.037376
		K_L (l/mg)	1.311
6	Freundlich	N	1.132503
		K_F	0.755028
7	Temkin	A	0.436049
		B	1.003
		A	2.129171
8	Dubinin-Radushkevich	γ	$-3.00*10^{-07}$
		q_D or q_m (mg/g)	1.944491
9	Harkins-Jura	A	-0.56593
		B	-1.05942
10	Frumkin	A	2.393
		K	0.075547
		ΔG (J/mol)	6399.568
11	Jovanovic	K_J	0.55
		q_m (mg/g)	0.436049
12	El-Awardy	Y	3.255
		B	0.768742
13	Smith	W	-0.645
		w_b	0.743

Table 2 shows the isotherm parameters of sorption of Cr (VI) ion. The applicability of each isotherm model to data

obtained was evaluated by the correlation coefficient R^2 value. Correlation coefficient R^2 determines the fitness of

models for experimental data. Considering the R^2 values for the various models, Freundlich isotherm best described the adsorption of Cr (VI) which indicates a heterogeneous and multilayer adsorption.

Adsorption intensity n was greater than 1. Hence, heterogeneous distribution on the sorbent surface was favoured.

Dubnin-Raduskevich model was employed to determine the mean adsorption energy, E_m. E_m indicates whether adsorption occurs via physiosorption or chemisorption. The adsorption behaviour might be predicted physiosorption in the range of 1-8 KJ/mol of the mean adsorption energy and chemisorption in more than 8 KJ/mol [8]. The values of mean adsorption energy for Cr (VI) was 13.36 KJ/mol. Thus, it predominantly followed chemisorption process.

3.2. Adsorption Kinetic Studies

3.2.1. Pseudo First Order Kinetics

The pseudo first order kinetic model has been widely used to predict the metal adsorption kinetics. It is derived thus:

$$\frac{dq}{dt} = k_1 (q_e - q) \qquad (2)$$

Where q_t is the amount of metal adsorbed at any time

(mg/g), q_e, amount of metal adsorbed at equilibrium time (mg/g), and k_1 pseudo first order rate constant (min^{-1}).

Integrating equation 2 with respect to boundary conditions q_0 at t_0 and q_q at t_t yields equation 3

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (3)$$

A plot of $\ln(q_e - q_t)$ against t gives a negative slope -k with intercept $\ln q_e$.

3.2.2. Pseudo Second Order Kinetics

The adsorption kinetic data can be further analyzed using pseudo second order kinetics.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \cdots \qquad (4)$$

Where,
t = time in minutes
k_2 = second order rate constant
q_t = amount adsorbed at a given time
A plot of $\frac{t}{q_t}$ versus time t enables the calculation of q_e from the slope and the rate constant k_2 is then evaluated from the intercept.

Table 3. *Kinetic parameters for adsorption of Cr (VI).*

Metals	Model	Slope	Intercept	R^2	Q_e	K_{ad}
Cr	Pseudo- first order	-0.0311	-2.946	0.888	0.052549484	0.0311
	Pseudo- second order	1.2171	0.7374	1	0.821625174	2.0089

Figures 1 and 2 show the kinetic model plots of adsorption. Table 3 shows the kinetic parameters of adsorption of Cr (VI) ion obtained using pseudo first order and pseudo second order models. It can be seen that sorption of the three metal ion fitted better into the pseudo-second order model than pseudo-first order model. This is as a result of the fact that the former has R^2 value close to unity than the latter. Also, greater adsorption rate constant of pseudo-second order model shows that adsorbates are adsorbed faster by the adsorbent.
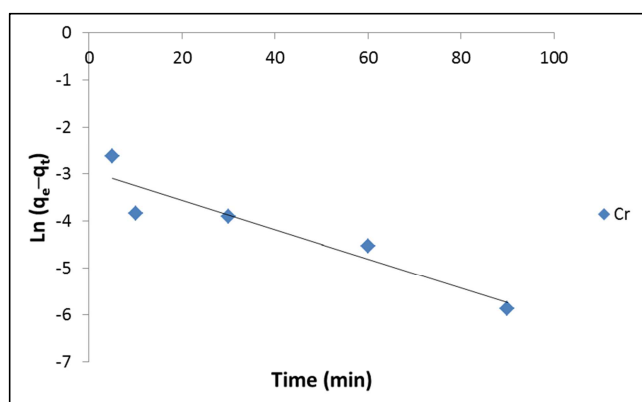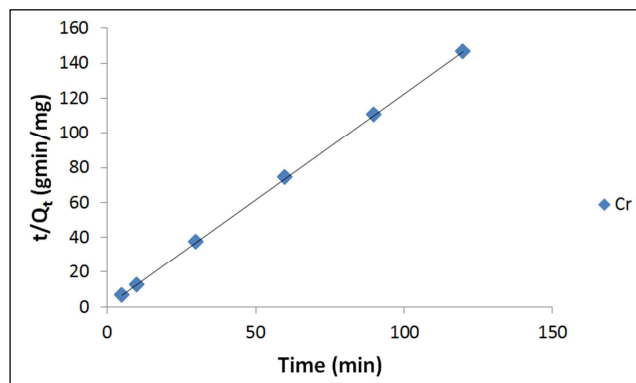

Figure 1. *Pseudo-first order plot for adsorption of Cr (VI).*

Figure 2. *Pseudo-second order plot for adsorption of Cr (VI).*

3.3. Effect of Contact Time

Fig 3 shows the effect of contact time on the removal of heavy metal at time ranging from 5-120 minutes. It was seen from the plot that, increase in contact time facilitates the percentage removal of the named ions from their aqueous solution. However, as time increases, the rate at which biosorption takes place on the sorbent surface diminishes, indicating that the process tends to approach equilibrium state between 80-90 minutes. Therefore, an equilibrium time of 90 minutes was used for further experiments. The initial high biosorption rate may be linked to the abundance of free binding sites on the biosorbent which become saturated resulting in decreased biosorption rate [14].
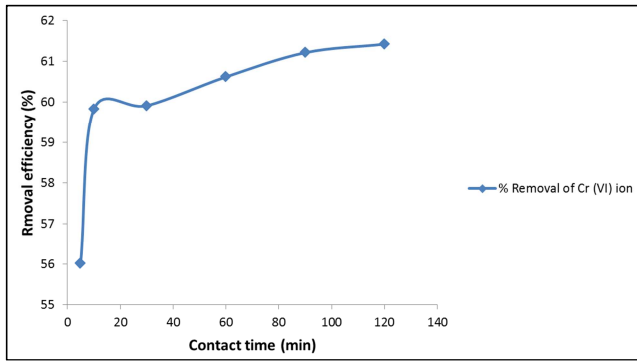
Figure 3. *Effect of time on the Percentage removal of Cr(VI).*

3.4. Thermodynamic Studies

The thermodynamic parameters that must be considered to determine the process include enthalpy of adsorption ΔH, entropy change ΔS and free energy change ΔG. Positive value of ΔH signifies endothermic reaction while negative value indicates exothermicity. Positive or negative value of ΔS relates to the increase or decrease in disorderliness of the adsorption process. ΔG is used to identify the spontaneity and feasibility of the adsorption process. Its value can be determined using the equation below

$$\Delta G = \Delta H - T \Delta S \qquad (5)$$

Gibbs free energy ΔG is also given as

$$\Delta G = -RT \ln K \qquad (6)$$

Where,
K= the equilibrium constant
R = Universal gas constant
Substituting equation 5 into equation 6 and making ln K the subject of the formulae yields:

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (7)$$

A plot of ln K against $\frac{1}{T}$ gives a straight line graph with slope $-\frac{\Delta H}{R}$ and intercept $\frac{\Delta S}{R}$, from which ΔH and ΔS were deduced.

Table 4. *Thermodynamic parameters for the adsorption of Cr (VI).*

ΔH (J/mol)	ΔS (J/K/mol)	ΔG (J/mol)		
		323K	343K	363K
9829.64	36.4336	-1938.4	-2667.1	-3395.8

Thermodynamic parameters deduced from figure 4 are shown in table 4 above. It follows that adsorption of Cr (VI) was endothermic process since ΔH was positive. Thus, there was an interaction between the adsorbate and adsorbent. Positive value of entropy for adsorption of Cr (VI) shows an increase in disorderliness of the system. It can also be seen from the table that the values of ΔG were negative, signifying spontaneity of the adsorption process.
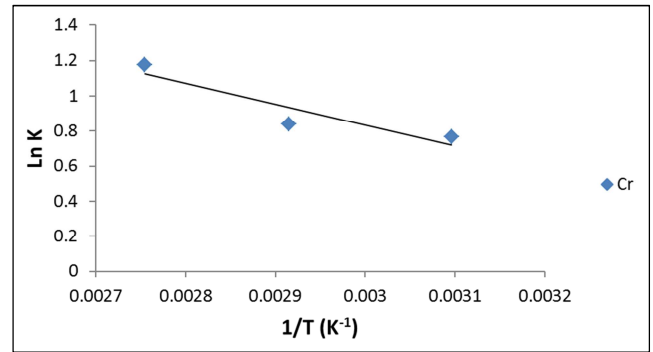

Figure 4. *Thermodynamic plot for the adsorption of Cr (VI).*

3.5. Effect of pH Study

Figure 5 shows the effect of pH on adsorption of Cr (VI) ion from their aqueous solution. From the plot, adsorption increased with increase in pH from 2 to 6. However, the uptake of metal ions decreased slightly from pH of 6 to 8.

Minimum adsorption of metal ion observed at low pH was due to higher concentration and higher mobility of H^+ ion present which favoured the adsorption of hydrogen ion compared to Cr (VI) ion. It suggests that at lower pH value, the surface of the adsorbent is surrounded by hydronium ion thereby preventing the metal ion form approaching the bonding site of the sorbent [11].

In contrast, at higher pH, more negatively charged surface becomes available thus facilitating greater metal ion removal. However, at pH of 8, there is a decrease in the adsorption capacity due to precipitation of metal ion and dual competition of both metal anions and OH to be adsorbed on the surface of the adsorbent on which OH predominates [11].
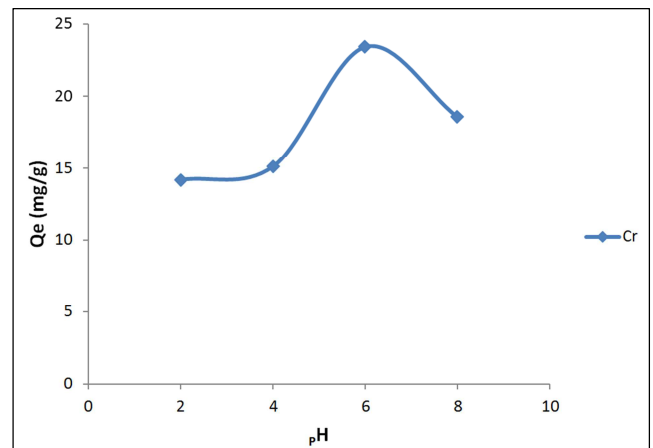

Figure 5. *Effect of pH on Cr (VI), ion removal.*

4. Conclusion

In this study, coconut husk as an underlying medium was investigated for its effectiveness in removing Cr (VI) ion from aqueous solution at different initial metal ion concentration, contact time, temperature and pH. The results obtained showed that adsorption of Cr (VI) followed Freundlich isotherm model DR isotherm revealed that

adsorption followed chemical adsorption process. Adsorption kinetics was better described by pseudo-second order model compared to Lagergren kinetics as evident from correlation regression values (R^2). Uptake of metal ion from their aqueous solution was affected by change in pH. Hence coconut husk can be effectively applied in the treatment of heavy metal-contaminated effluents before they can be discharged into the environment,

Table 5. *Definition of parameters.*

q_e	Amount absorbed at equilibrium (mg/g)
C_e	Equilibrium concentration (mg/l).
q_m	Monolayer adsorption capacity (mg/g).
K	Equilibrium constant in (l/mg),
n	Freundlich exponent
K_F	Freundlich constant in (l/g)
B	B=1/2a = RT/b where a represents the Temkin surface energy
R	Universal gas constant, 8.314J/mol/K
T	Absolute temperature in Kelvin
θ	Fractional surface coverage
b	Rate of change of the standard Gibbs energy of adsorption with θ
γ	DR constant in mol^2/kJ^2 related to the adsorption energy $E = (-2\gamma)^{-0.5}$
q_D	theoretical monolayer saturation capacity in (mg/g)
ε	Polanyi potential, equal to RT ln (1 + 1/Ce).
A_{HJ}	Harkins-Jura parameter which accounts for multilayer adsorption
B_{HJ}	Harkins-Jura constant
a	Frumkin interaction parameter
ΔG	Gibb's free energy (kJ/mol) =-RTlnK
K_J	Jovanovic constant
y	Number of adsorbing molecules
K'	El-Awardy binding constant, $K = K'^{1/y}$
W	Amount in multilayered fraction
w_b	Amount in first adsorbed fraction

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