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Adsorption of hexavalent chromium from aqueous solution by granulated activated carbon from *Canarium schweinfurthii* seed shell

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ABSTRACT

Activated carbons were prepared from agricultural waste Canaruim schweinfurthii seed shell with zinc chloride ($ZnCl_2$) and Phosphoric acid (H_3PO_4) as chemical activation agent. The activated carbons were prepared by carbonization at 500^0C for 15minutes. Batch adsorption trials were used to assess the effectiveness of using activated carbon as a sorbent for the removal of hexavalent chromium from solution. Based on linear regression analysts, the data obtained from the batch studies showed a good compliance with both the Langmuir and the Freundlich equations. The values obtained for the isotherm constants showed that the maximum adsorption capacity, Q_o was 0.757 mg/g with activated carbon prepared with Phosphoric acid.

Key words: Chromium (VI), *Canaruim schweinfurthii*, activated carbon, Adsorption

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INTRODUCTION

Water pollution by chromium is of considerable concern, as this metal has found widespread use in electroplating, leather tanning, metal finishing, nuclear power plant, textile industries, and chromate preparation. Chromium exists in two oxidation states as Cr (III) and Cr (VI). The hexavalent form is 500 times more toxic than the trivalent [1]. Due to its high solubility, Cr (VI) is the most hazardous, since it can accumulate in the food chain and cause several ailments[2,3].

In general, chromium (VI) is removed from waste water by various methods such as chemical precipitation, electrochemical reduction, sulfide precipitation, cementation, ion-exchange, reverse osmosis, electrodialysis, solvent extraction, and evaporation, etc. [4]. These methods are, however, cost intensive and are unaffordable for large scale treatment of wastewater that is rich in chromium (VI). Among all these, adsorption is the most promising technique and a feasible alternative[5]. A variety of materials have been tried as adsorbents for Cr (VI) and a number of studies have been reported using adsorbents like granular activated carbon [2] Soya cake [6], rubber tyres and sawdust [8], activated sludge [9], unmodified natural clay [7]lingocellular substrate[10], fly ash [11], rice husk based activated carbon [12], etc. Adsorption using activated carbon is an effective method for the treatment of industrial effluents contaminated with chromium (VI) and quite popular [13, 14].

Canaruim schweinfurthii seed shell is very cheap and available in the middle belt region of Nigeria; studies on the utilization of *Canaruim schweinfurthii* seed shell as a precursor for manufacturing activated carbons are minimal or none. In addition information concerning the adsorption of chromium onto *Canaruim schweinfurthii* seed shell has not been reported. In view of the health problems caused by Cr (VI), the present study was performed to evaluate activated carbon as adsorbents for the removal of Cr (VI) from polluted water by systematic evaluation of the parameters involved such as Cr concentration. Furthermore, the Freundlich and Langmuir adsorption isotherms were applied to study adsorption and to calculate isotherm parameters.

MATERIALS AND METHODS

2.1 Adsorbent

In the present study, *Canaruim schweinfurthii* Seed Shell was used for the preparation of activated carbon. The seeds were washed and sundried it was crushed using jaw crusher into smaller particle sizes. They were further pulverized into fine granular form. The sample was sieved into a particle size of 850µm-1.18mm. The granular was carbonized at 250^0C for 3 hours in oven. The carbonized sample was allowed to chemical activation, by the addition of 1M $ZnCl_2$ and 1 M H_3PO_4 separately. The sample was activated in the furnace for 15 minutes at 500^0C. The activated carbon produced was washed with distilled water to remove the excess activating agent it was oven dried at 120^0C and stored in sealed air tight polythene bags for further experiment. All the chemicals used were of analytical reagent grade obtained from B.D.H and E.Merck except were stated.

2.2 Adsorbate

Cr (VI) stock solution (5 mg/L) was prepared in 1000 ml distilled water using 141.4 mg dried $K_2Cr_2O_7$. The working solution was obtained by diluting the stock solution in distilled water.

2.3 Batch mode adsorption studies

The working solution of 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 mg/L 0f Cr (VI) was prepared from stock solution. Batch mode adsorption studies were carried out with 60mg of the activated carbons and 20ml of Cr (VI) solution of desired concentration at pH of 4.0 ± 2, agitated at 200rpm in a mechanical shaker at room temperature for 1 hour. The adsorbate solution was separated from the adsorbent by centrifugation at 3000rpm and estimated The concentration of free chromium (VI) ions in the solution was determined spectrophotometrically by developing a purple-violet color with 1,5-diphenyl carbazide in acidic solution as an complexing agent. The absorbance of the purple-violet colored solution is read at 540 nm after 20 min[15].

The amounts of adsorbates adsorbed at time, *qt*and at equilibrium condition, *qe*were calculated using the Equations below

$$q_t = \frac{(C_o - C_t)\,V}{w}$$

$$q_e = \frac{(C_o - C_e)\,V}{w}$$

Where *Co* and *Ce*are initial and equilibrium adsorbate concentrations, mg/L. *Ct* is the adsorbate concentration at time, mg/L. *V* is volume of solution, L and *w* is weight of adsorbent, g.

RESULTS AND DISCUSSION

3.1 Characterization of Canaruim schweinfurthii Seed Shell

Important physical properties of *Canaruim schweinfurthii* seed shell used such as bulk density, moisture content, Ash content, dry matter content and pH were determined using the methods reported by Allen [16]. The resulted is presented on Table 1

3.2 Adsorption of Chromium (VI)

3.2.1Adsorption Isotherms

An adsorption isotherm describes the relationship between the amounts of adsorbate which is adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium[17]. The adsorption isotherm of Chromium (VI) onto the prepared activated carbon was fitted by several well-known isotherms models, namely the Langmuir and Freundlich models, to assess their utility. The Langmuir model is obtained under the ideal consumption of a totally homogeneous adsorption surface, whereas the Freundlich model is suitable for a highly heterogeneous surface. In this work, both models were used to describe the relationship between the amount of Chromium (VI) adsorbed and its equilibrium concentration.

3.2.2 Langmuir Isotherms

The Langmuir adsorption isotherm is often used for adsorption of the solute from a liquid solution. The Langmuir adsorption isotherm is perhaps the best known of all the isotherms describing adsorption, and it is often expressed as:

$$q_e = \frac{Q^0 K_L C_e}{(1 + K_L C_E)}$$

Where:
q_e = Adsorption capacity at equilibrium solute concentration, *Ce*(mg/g)
C_e= Concentration of adsorbate in solution (mg/L)
Q_o= Maximum adsorption capacity corresponding to complete monolayer coverage (Mg/g)
K_L = Langmuir constant related with affinity of the points of union (L/mg)
The above equation can be rearranged to create the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 K_L} + \frac{C_e}{Q^0}$$

The linear form can be used for the linearization of experimental data by plotting C_e / q_e against C_e. Meanwhile, the Langmuir constant Q_o and K can be evaluated from the slope and intercept of linear equation, respectively, as shown in *Fig. 1*. The essential characteristics of the Langmuir equation can be expressed in terms of dimensionless separation factor, R_L, defined as:

$$R_L = \frac{1}{(1 + K_L C_o)}$$

Where C_o is the highest initial solute concentration. The R_L value implies the adsorption to be favourable (R_L>1), linear (R_L=1), favourable (0<R_L<1), or irreversible (R_L=0). The values of R_L were found to be 0.097 for adsorption with Zinc chloride activated carbon and 0.7 with Phosphoric acid activated carbon and this confirmed that the prepared activated carbon are favourable for the adsorption of Chromium (VI) under conditions used in the present study .

3.2.3 Freundlich Isotherms

The Freundlich isotherm is the earliest known relationship describing the adsorption equation which is often expressed as:

$$q_e = K_f C_e^{1/n}$$

Where:
q_e= Adsorption capacity at equilibrium solute concentration, C_e(mg/g)
C_e= Concentration of adsorbate in solution (mg/L)
K_f= Empirical constants depending on several environmental factors
n = Empirical parameter representing the energetic heterogeneity of the adsorption sites

The equation is conveniently used in the linear form by taking the logarithmic of both sides as:

$$\text{Log}q_e = \text{Log}K_f + 1/n \text{ Log}C_e$$

A plot of (log q_e) against (log C_e) yields a straight line which indicates the confirmation of the Freundlich isotherm for adsorption. The constant can be obtained from the slope and the intercept of the linear plot of the experimental data, as shown in *Fig. 2*. The value of *n* indicates favourable adsorption when 1<*n*<10. The *n* values were found to be 1.75 for Zinc chloride activated carbon and 0.837 for Phosphoric acid activated carbon. Therefore, the present adsorption systems appear to be favourable[18]. The Langmuir constants Q_o and K_L and the Freundlich constants K_F and n are given in the Table 2. Both isotherm models were found to fit the adsorption data of the prepared activated carbon with correlation coefficient, R^2 value 0.770 and 0.824, respectively for the Zinc chloride activated carbon with 0.880 and 0.922 for the Phosphoric acid activated carbon respectively. The adsorption capacity of the adsorbent was obtained from the Langmuir model up to 0.12 mg/g for the Zinc chloride activated carbon and 0.792 mg/g for the Phosphoric acid activated carbon. This result shows that the prepared activated carbon in this study has a very high adsorption capacity as compared to the other works listed in Table 3. This is probably due to the different activation methods used, which eventually resulted in different surface characteristics [19].

3.2.4 Comparison of adsorption capacity of Canaruim schweinfurthii with other adsorbents

Direct comparison of *CanariumScweinfurthii* with other adsorbent materials is difficult, owing to the different applied experimental conditions. In the present study, activated carbon from *Canaruim schweinfurthii* has been compared with other adsorbents based on their maximum adsorption capacity for Cr (VI) and shown in Table 3. It can be observed that the activated carbon prepared compares well with the other adsorbents listed in Table 2. Activated rice husk carbon and modified oak sawdust and wheat bran are adsorbents that exhibited higher adsorption capacity. This could be primarily due to the initial carbon content, activation process as well as the pore development due to the basic morphology of the raw material [20]. Hence, *Canaruim schweinfurthii* activated carbon can be considered to be viable adsorbent for the removal of Cr (VI) from aqueous solutions.

Table 1: Physicochemical properties of raw sample of *Canaruim schweinfurthii* and carbonized sample

Parameters	Raw sample
% moisture	5.10
% Dry matter	81.0
% Ash Content	0.5
Bulk density(g/cm^3)	1.33
% yield carbon	18.56
pH measurement	
(i) Raw	4.93
(ii) Carbonized	9.0

Table 2: Langmuir and Freundlich isotherm constants for Chromium (VI) on the prepared activated carbons

	Langmuir isotherm model				Freundlich isotherm model		
Type of adsorbent	Q_o (mg/g)	K_L (1/mg)	R_L	R^2	K_F (mg/g)(L/mg)$^{1/n}$	n	R^2
Activated carbon with H_3PO_4	0.792	0.384	0.700	0.88	0.44	0.837	0.922
Activted carbon with $ZnCl_2$	0.12	9.30	0.097	0.77	0.18	1.750	0.824

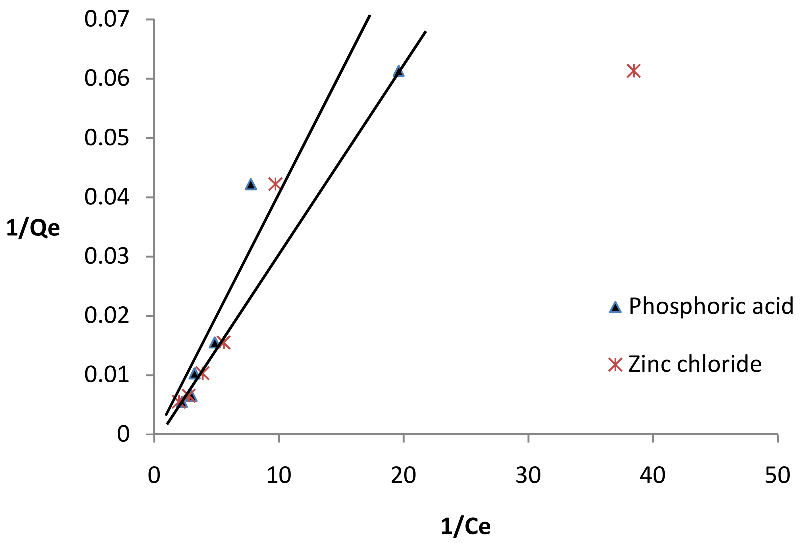

Fig. 1:Langmuir adsorption isotherm of Chromium(VI) onto activated carbon

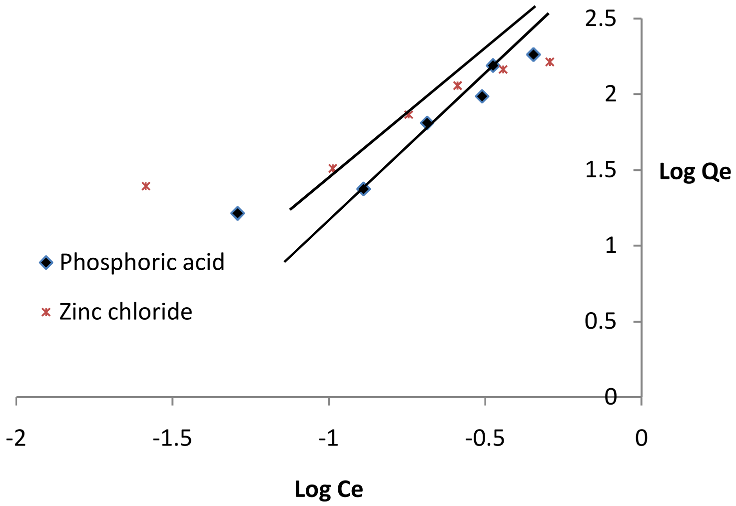

Fig. 2: Freundlich adsorption isotherm of Chromium (VI) onto activated carbon

Table 3: Comparison of adsorption capacities of Cr (VI) with other adsorbents

Adsorbents	Adsorption capacity (mg/g)	pH	Co (mg/L)	Reference
Activated rice husk carbon	0.8	2	10	[21]
Activated alumina	1.6	4	10	[21]
Sawdust	0.229	2	5	[22]
Pine leaves	0.277	2	5	[22]
Raw rice bran	0.07	2	5	[24]
Modified oak sawdust	1.7	3	-	[25]
CETYL-amended zeolite	0.65	-	-	[23]
EHDDMA-amended zeolite	0.42	-	-	[23]
Wheat bran	0.942	3	5	[26]
Canaruim schweinfurthii	0.792	4	5	Present study

CONCLUSION

The experimental data of the adsorption studies on Chromium (VI) using prepared activated carbon from *Canaruim schweinfurthii* was described well by both Langmuir and Freundlich isotherm models. This indicates that the adsorption of Chromium (VI) from aqueous solutions could be either monolayer or multilayer. The adsorption capacity of the adsorbent, obtained from the Langmuir model, was up to 0.792mg/g which is the maximum adsorption capacity of the adsorbent use. The present study concludes that the production of the activated carbon adsorbents, from *Canaruim schweinfurthii*, can provide a two-fold environmental and economic benefit; new low-cost adsorbents are produced for commercial use in wastewater treatment. The preliminary and adsorption studies show that the activated carbon prepared from *Canaruim schweinfurthii* seed shell can be used effectively in the treatment of tannery wastewaters. As the raw material is an agricultural waste, its application in the treatment process is expected to be cheap and commercially viable.

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