

ACID AND BIO-ACTIVATION OF CARBON PREPARED FROM CORNCOB FOR ADSORPTION OF Cd(II) FROM AQUEOUS SOLUTION

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ABSTRACT

Chemical and physical activation processes, which are relatively expensive and non-eco-friendly, are conventionally employed for activated carbon preparation. In this study, aqueous cashew bark extract was used to activate carbon prepared from corncob (CBAC). Its ability to adsorb Cd(II) from an aqueous solution was compared with the H₃PO₄ activated variant (CCAC). The pH of optimum adsorption was 4 (80.4% efficiency for CCAC and 75.6% for CBAC). Adsorption with CBAC attained equilibrium in 60 min compared to 90 min required with CCAC. The adsorption data followed the Elovich model. For CCAC the process was feasible at all temperatures. However, for CBAC, the process was spontaneous at temperatures higher than 303 K. The efficiency of CCAC was a little higher than CBAC for all the variables investigated, yet the adsorptive capability of CBAC was comparably favourable. Hence, cashew bark extract can be utilized as a cheaper and less eco-toxic alternative to H₃PO₄ for activating carbon produced from corncob.

Keywords: Bio-Activation, Acid Activation, Cadmium, Cashew Extract, Activated Carbon

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INTRODUCTION

The aquatic habitat happens to be the final, direct or indirect, destination of most the pollutants introduced into the environment. Inorganic pollutants of heavy metals are of major concern because of their high toxicity, non-biodegradability, and bioaccumulation tendency.¹⁻³ Cadmium, which has eight stable isotopes of which ¹¹²Cd and ¹¹⁴Cd are the most common, has no known physiological function within the human body but has a severe risk to human health.^{4,5} Most conventional methods employed in removing Cd from wastewater have some disadvantages. Generally, adsorption using activated carbons (AC) has been proven to be the most effective technique due to its peculiar characteristics.^{6,7} High cost of commercial activated carbon (CAC) for adsorption necessitates the search for the production of activated carbon from low-cost precursors. To this end, activated carbons from the following precursors have been exploited: Xanthoceras sorbifolia Bunge hull⁷, spent brewery barley husk⁸, sugar cane bagasse⁹, etc.

The cell walls of corncobs have been noted to contain cellulose and polysaccharide¹⁰ which can be manipulated to produce activated carbon. It is reported that cashew bark has certain natural organic acids like anacardic acid, palmitic, oleic acid with other alkyl phenolic compounds.¹¹ This study was conducted to compare the potential of cashew bark extract-activated carbon for cadmium removal with that H₃PO₄ activated variant.

EXPERIMENTAL

General Procedure

Corncoobs were obtained from a farm in Ado - Ekiti, Nigeria. They were washed several times with distilled water to get rid of debris from them. The sample was dried and later ground to the desired size. Cashew (*Anacardium occidentale*) bark was obtained from Afe Babalola University farm. The extract was obtained as described in the literature.¹² Carbonization and bio-activation of the corncoobs were carried out as described in literature.^{8, 12} Chemical activation was conducted as described previously.⁸ All experiments were conducted by agitating known amount of activated carbon with 30 mL of 50 mg/L cadmium solution at 298 K. The effects of contact time, pH, and temperature variation were investigated. The mixture was filtered and Cd concentration in the filtrate was determined using AAS.

RESULTS AND DISCUSSION

SEM and Elemental Characterization of Activated Carbons

SEM micrographs (Fig.-1) indicated that CCAC and CBAC had pores of different sizes for Cd (II) adsorption. While inactivated carbon had a blunt and smooth surface, both CCAC and CBAC had relatively rough and porous surfaces. The elemental compositions of the activated carbons, as revealed by EDX analysis are presented in Table-1. It can be observed that the samples were highly carbonaceous.

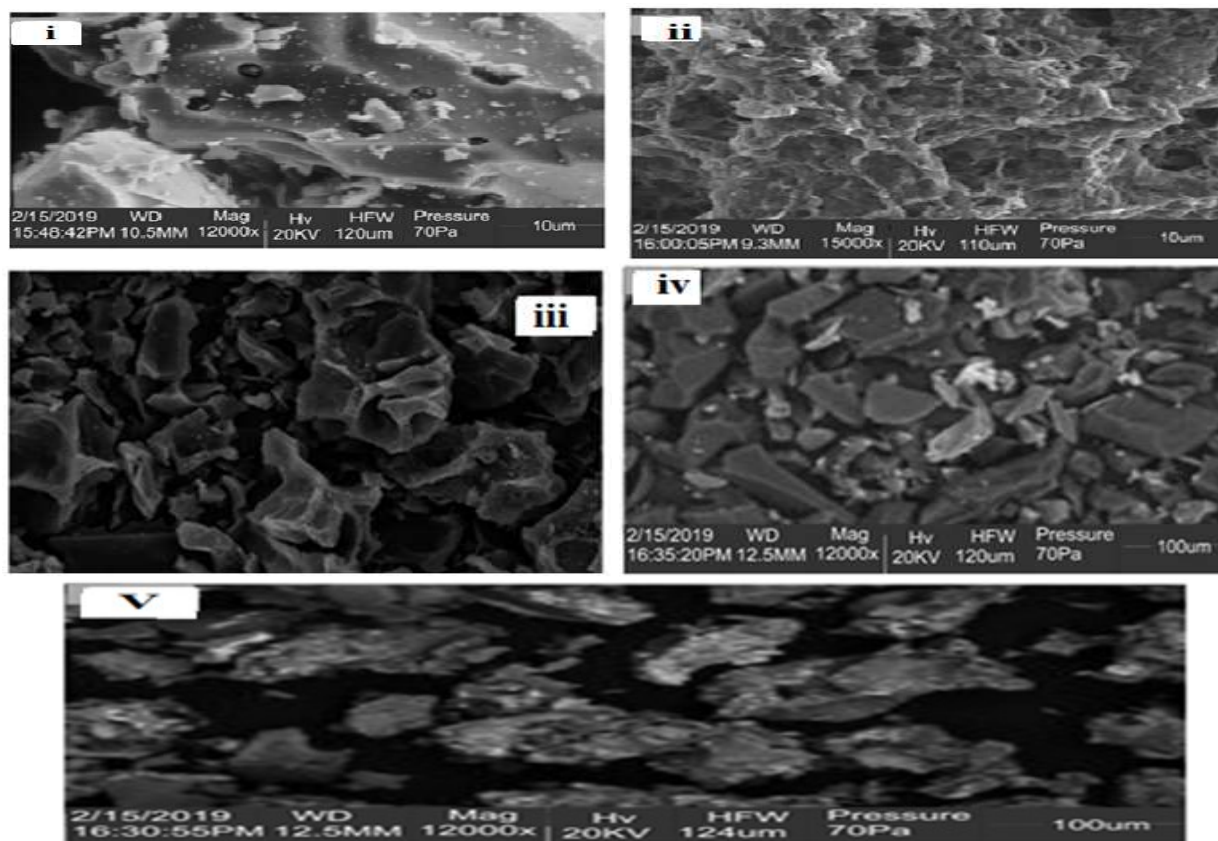


Fig.-1: Scanning Electron Micrographs of (i) Inactivated Carbonized Corncob, (ii) CCAC, (iii) CBAC, (iv) CCAC after Adsorption and (v) CBAC after Adsorption

Effect of pH on the Adsorption of Cadmium

The percentage removal of cadmium increased with an increase in pH until the pH was 4 for both CCAC and CBAC, making the pH of 4 the optimum pH (Fig.-2). Similar reports have been made for Cd adsorption.^{13,14} It can be observed that there was a sharp decline in the removal efficiency of the two activated carbons when the pH was increased from 4 to 5 and thereafter, a change in pH seems to have negligible influence on the removal efficiency. These observations can be explained by the saturation of the surface of the activated carbon with high concentration of H^+ at low pH. This would not only create a repulsion between the $Cd(II)$ and the H^+ ions but also create competitive adsorption for both Cd^{2+} and H^+ ions onto the binding sites of the activated carbons. As the pH increased beyond 3, there was a consequent increase in the concentration of hydroxyl group on the activated carbon which would increase the amount of $Cd(II)$ adsorbed due to electrostatic attraction between the Cd^{2+} and OH^- . The decrease in the percentage adsorption of $Cd(II)$ by both CCAC and CBAC when the solution pH increased above 4 could be attributed to the formation of neutral cadmium (complexes).¹⁵

Influence of Time Variation

The results presented in Fig.-3 shows that the adsorption rate was very rapid at the initial stage for both samples. About 54.4% and 32% of $Cd(II)$ were adsorbed within the first five minutes by CCAC and CBAC

respectively. The second stage involved slow adsorption of Cd(II) from 5 to 60 minutes of adsorption for CBAC while for CCAC, the adsorption rate continued steadily from agitation time of 5 to 90 minutes before proceeding at a constant rate. These observations can be attributed to a large number of available sites for Cd(II) adsorption at the initial stage of the process which later became reduced until the activated carbon samples were completely saturated.

Table-1: Elemental Composition of CCAC and CBAC

Element	Composition (%)			
	CCAC	CCAC after adsorption	CBAC	CBAC after adsorption
O	9.27	10.36	20.36	15.48
C	70	68.20	65.39	60.27
H	16.03	11.07	10.53	8.35
S	4.70	2.97	3.72	4.20
Cd	-	7.40	-	12.50

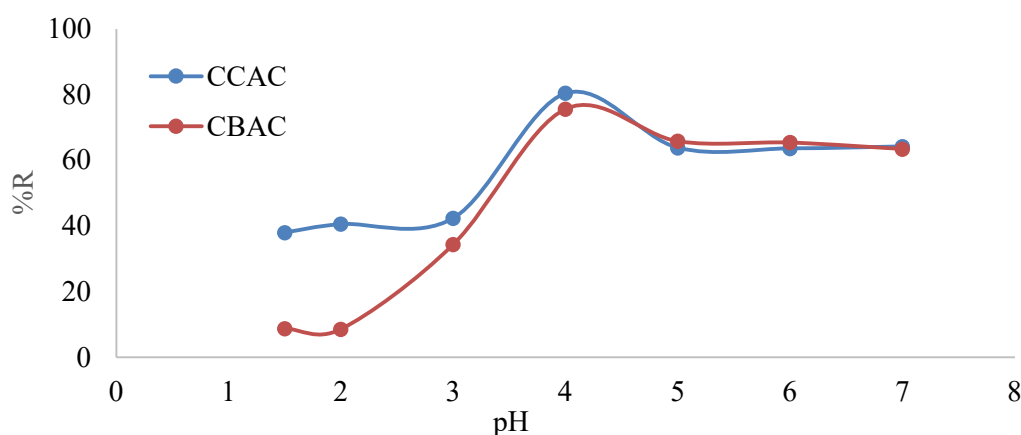


Fig.-2: Influence of pH on the Adsorption of Cadmium Using CCAC And CBAC

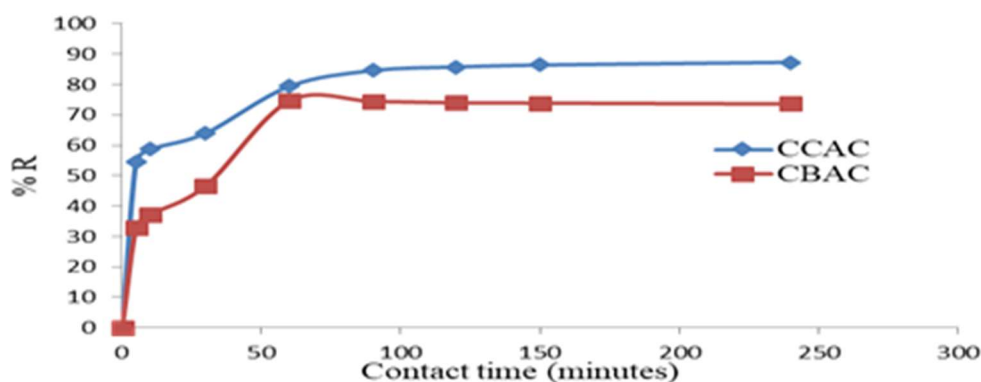


Fig.-3: Influence of Time Variation on Cadmium (II) Adsorption by CCAC And CBAC

Kinetic Parameters

Three kinetic equations (pseudo-first-order, pseudo-second order, and Elovich) were applied in their natural forms as presented in Eqns.-1, 2, and 3 respectively.

$$q_t = q_e \left[1 - \exp(-k_1 t) \right] \quad (1)$$

$$q_t = q_e \left[1 - \frac{1}{1 + q_e k_2 t} \right] \quad (2)$$

$$q = \frac{1}{\beta} \ln(\alpha \cdot \beta \cdot t + 1) \quad (3)$$

Where q_e , q_t , t , k_1 , k_2 , α , and β have their usual meanings with their units indicated in Table-2. Average Regression Error (ARE) was employed to compare the experimental and the predicted data using the solver add-in function, Microsoft Excel, Microsoft Corporation.

$$ARE = \frac{100}{n} \sum_{i=1}^n \left| \frac{q_{ecal} - q_{e \exp}}{q_{e \exp}} \right| \quad (4)$$

Where q_{cal} is the calculated amount of Cd(II) adsorbed onto activated carbon, q_{exp} is the experimental amount of Cd(II) adsorbed and n is the number of data points.

The Elovich model was found to fit the adsorption of Cd(II) by both CCAC and CBAC best (Table-2) judging from the R^2 and ARE values. This simply implies that the chemisorption mechanism with negligible desorption played a prominent role in the adsorption process.¹⁶

Table-2: Information on the Kinetics of Cadmium(II) Adsorption by CCAC and CBAC

Kinetic model	Parameter	CCAC	CBAC
Pseudo-first-order	q_e (mg/g)	13.09	11.04
	k_1 (min)	0.24	0.21
	R^2	0.7508	0.7863
	ARE	12.52	22.16
Pseudo-second-order	q_e (mg/g)	13.09	11.04
	k_2 (g/mg/min)	18.98	15.73
	R^2	0.8626	0.8679
	ARE	20.16	35.40
Elovich	α (mgg ⁻¹ min ⁻¹)	79.68	4.86
	β (gmg ⁻¹)	0.69	0.54
	R^2	0.9707	0.9367
	ARE	3.35	7.94

Adsorption Thermodynamics

The evaluated thermodynamic parameters are presented in Table-3. The table shows that the process was spontaneous for CCAC at all temperatures. However, for CBAC, the process seemed to be spontaneous at temperatures fairly greater than 303 K. The adsorption process by both CCAC and CBAC was endothermic. The positive entropy values for the adsorption of cadmium by both samples indicated that the particles of the metal ions at the activated carbon-liquid interphase were in a high state of disorder.¹⁷

Table-3: Thermodynamics of Cadmium(II) Removal Using CCAC and CBAC

Sample	T (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/K/mol)
CCAC	298	-1.45	8.09	32
	303	-1.61		
	313	-1.93		
	323	-2.25		
CBAC	298	1.52	66.19	217
	303	0.44		
	313	-1.73		
	323	-3.9		

CONCLUSION

This study revealed that the adsorption of cadmium by CCAC and CBAC was pH and contact time-dependent. The pH of 4 was sufficient for optimum performance of both adsorbents. The morphological characterization of the adsorbents showed that both CCAC and CBAC were more porous than the inactivated carbon from corncob. The kinetic modelling of adsorption revealed that chemisorption played a prominent role in the adsorption of Cd(II) by both CCAC and CBAC. The adsorption of cadmium by the activated carbon variants was feasible. The use of CBAC could be more advantageous than CCAC from an environmental point of view, while H_3PO_4 is non-environment friendly, cashew bark extract is environment friendly.

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