



## Phosphoric Acid and Cashew Bark Extract Activated Carbons derived from Coconut (*Cocos nucifera*) Shells for Cr (VI) Adsorption

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### Abstract

THIS study was conducted to activate and characterize carbons prepared from coconut shells for subsequent adsorption of Cr (VI) from synthetic wastewater. The adsorption process was carried out through batch studies. The results showed that the process was pH, contact time and temperature dependent. The optimum pH for Cr (VI) adsorption was 2 for both cashew bark extract activated (CNAC<sub>1</sub>) and H<sub>3</sub>PO<sub>4</sub> activated (CNAC<sub>2</sub>) carbons. Characterization of the activated carbons using Fourier Transform-Infrared Spectroscopy (FTIR) revealed that OH and C=O were some of the prominent functional groups involved in the adsorption of Cr (VI). The EDX analysis results confirmed the adsorption of Cr (VI) on the surfaces of the activated carbons (ACs). Furthermore, SEM characterization showed that the free ACs were coarser and more porous than their Cr (VI) loaded counter-parts while elemental composition of the activated carbons showed that the samples were carbonaceous. The adsorption process was feasible and followed pseudo-first-order kinetic model. Generally, the efficiency of CNAC<sub>2</sub> was higher than that of CNAC<sub>1</sub>. However, cashew bark extract could be used as an activating agent for the preparation of activated carbon from coconut shells for Cr (VI) adsorption because it is cheaper and eco-friendlier than H<sub>3</sub>PO<sub>4</sub>.

Keywords: Cashew bark extract, Activated carbon, Coconut Shells, Chemical Activation, Cr (VI)

### 1. Introduction

Metals are versatile natural endowment located in the earth crust as ores in different deposits across the globe. Man, in his quest for survival and easier life, has explored and exploited these metal ores and consequently converted them into different applications. These applications range from sophisticated mechanical equipment/tools, industrial machine parts, automobile and aircraft parts, clinical tools, agricultural implements, road and house construction equipment, laboratory apparatus/engineering workshop equipment and domestic/kitchen utensils. The most recent applications of metals are in the electronic and telecommunication world. These metals get into the environment during the processes that lead to their extraction from natural ores, deterioration due to

corrosion, wear and tears during use and from industrial wastewater from different metal processing and application technologies. Many metals (particularly heavy metals) are known to be toxic, and some of these toxic metals are indiscriminately introduced into the environment [1].

Chromium compounds, which are constantly released into the environment through effluent from industrial processes such as electroplating, metal finishing, leather tanning, textile industries, wood preservation, chromate preparation paint, ink and aluminium manufacturing industries, are among the toxic inorganic aquatic pollutants [2 – 4]. Chromium is principally encountered in the environment as a trivalent ion, Cr (III) (which occurs naturally and is an essential nutrient) and as hexavalent ion, Cr (VI), [5]. While Cr (III) is less mobile, less toxic, and is mainly found bound to organic matter in soil and aquatic environments, Cr (VI) is classified to be top

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16th hazardous substance which has been reported to cause human health challenges such as cancer, liver damage, pulmonary congestions, skin irritation, DNA damage, asthma, dermatitis and severe diarrhoea [2, 6, 7]. Due to the acute toxicity of Cr (VI), the USEPA has set the maximum contaminant concentration of Cr (VI) in domestic water supplies as 0.05 mg/L while its permissible limit for effluent discharged into inland surface water is set at 0.1 mg/L [6].

Consequently, several methods have been used to remove Cr (VI) from aqueous medium. Some of these methods are: chemical precipitation, membrane filtration, ion exchange, liquid extraction, bioaccumulation, reduction of Cr (VI) to Cr (III), followed by Cr (III) precipitation under the alkaline condition, adsorption, etc. [8, 9]. Adsorption technology is considered to be cheaper, easier to operate, more efficient even at low metal concentration and more eco-friendly than other conventional processes [3]. Meanwhile, the high porosity, relative cheapness, high mechanical strength, large surface area, variable characteristic, surface chemistry and a high degree of surface activity and high affinity of activated carbon for metals have made it a veritable technology for heavy metal removal [8, 10, 11]. Due to high cost associated with adsorption using commercial activated carbon, efforts have been geared towards the search for activated carbon produced from cheap agricultural wastes/ or and by-products. However, most of the studies were based on the use of chemical or physical activation methods. In this study, bio-activation of carbon prepared from coconut shells was carried out using aqueous extract of cashew stem bark.

The term coconut is derived from the 16th-century Portuguese and Spanish word *coco*, meaning 'head' or 'skull' after the three indentations on the coconut shell that resemble facial features [12]. The coconut tree (*Cocos nucifera*) is a member of the palm tree family (*Arecaceae*) and the only known living species of the genus *Cocos* [13]. The term "coconut" (or the archaic "cocoanut" can refer to the whole coconut palm, the seed, or the fruit, which botanically is a drupe, not a nut [14]. A mature coconut is made up of three parts- a fibrous husk, a hard shell and the innermost edible flesh tightly enclosed in the shell [12]. While the flesh forms a regular part of the diets of many people in the tropics and subtropics, the husk is usually locally converted to foot mat, and the hard shell is mostly thrown away [13]. Coconut shells were employed for this study because they are available all year round as agricultural by-products and have advantage properties like high carbon content, low ash content,

high yield, mechanical strength and resistance to attrition [15].

The bark and leaves of cashew (*Anacardium occidentale*) are a rich source of tannins, a group of plant chemicals with documented biological activity [16]. Cashew stem bark and leaves are also known to contain certain natural acids such as anacardic acid, palmitic acid, oleic acid with other alkyl phenolic compounds [17]. The presence of these acids and other natural chemicals could aid cashew bark extract to perform the process of carbon activation which other conventional but less eco-friendly chemicals and acids are used for. Hence, this study was conceived to prepare chemical-activated (using  $H_3PO_4$ ) and bio-activated (using aqueous cashew stem bark extract) carbon from coconut shells and compare their morphological and Cr (VI) adsorptive characteristics.

## 2. Materials and Methods

### *Sample collection and preparation*

Coconuts were purchased from Bisi local market, Ado-Ekiti, Ekiti State, Nigeria and were broken to obtain the shells. The shells were sun-dried and later washed thoroughly with distilled water to remove dust and other impurities. The shells were then oven-dried at 105 °C to a constant weight and were crushed into smaller forms. The cashew (*Anacardium occidentale*) stem bark was obtained from Afe Babalola University Farm, Ado-Ekiti. The cashew stem bark was thoroughly washed with distilled water to remove sand and dust particles. The bark was air-dried for three days, washed again with distilled water, chopped into smaller sizes and was soaked in 500 mL distilled water for 48 hours (with intermittent stirring) to obtain the extract. The extract was later used for carbon activation. All chemicals used for the study were of analytical reagent grade. A stock solution containing 1000 mg/L of Cr (VI) was prepared by weighing 2.83 g of  $K_2Cr_2O_7$  into a 1 L standard flask. This was dissolved and made to mark with distilled water. Standard solutions of different concentrations as might be required were prepared by stepwise dilution from this stock solution.

### *Carbonization and activation*

The carbonization of the coconut shells was carried out as described in literature [10]. The pulverized coconut shells were loaded in crucibles into a furnace and carbonized at 400°C for 45 min. For chemical activation,  $25.0 \pm 0.01$  g of the carbonized sample (425  $\mu$ m mesh size) was weighed

into a beaker containing 500 mL of 0.1 M phosphoric acid ( $\text{H}_3\text{PO}_4$ ). The contents of the beaker were thoroughly mixed and heated at a temperature of 60 °C on a magnetic stirrer with a hot plate until a paste was formed. The paste was transferred to an evaporating dish which was placed in a furnace and heated at 500 °C for 30 min. This was then allowed to cool overnight. It was then neutralized with KOH and washed with distilled water until the pH was constant ( $6.89 \pm 0.2$ ). This was further oven-dried at a temperature of 105 °C to constant weight and was kept in an airtight container. For bio-activation,  $25 \pm 0.01$  g of the carbonized coconut shell was soaked in 100 mL of the *Anacardium occidentale* extract for 24 hours. It was then stirred for 60 mins, filtered using mesh net and washed with distilled water severally. The residue was oven-dried at a temperature 105 °C for 60 min to obtain the *Anacardium occidentale* extract-treated carbonized coconut shell. This was then stored in an airtight container in readiness for Cr (VI) adsorption.

#### Characterization of adsorbents

The adsorbents were characterized using Scanning Electron Microscope (SEM), Energy Dispersion X-ray (EDX) and Fourier Transform-Infrared Spectroscopy (FTIR). FTIR analysis in the solid phase was performed on the samples before and after chromium adsorption using Fourier Transform Infrared Spectrometer (Shimadzu 100 series spectrometer USA). The spectra of the adsorbents were measured within the range of 4000–400  $\text{cm}^{-1}$  wave number. The spectra were plotted using the same scale on the transmittance axis for all the adsorbents. The elemental composition and the morphology of the different activated carbons were determined using SEM-EDX couple (JEOL JSM-7600F).

#### Batch studies

Unless otherwise stated, all experimental runs were carried out in 100 mL conical flasks for 60 minutes at room temperature. Fifty millilitres (50 mL) of 50  $\text{mgL}^{-1}$  Cr (VI) solution prepared from the stock solution of  $\text{K}_2\text{Cr}_2\text{O}_7$  was agitated with 0.1 g activated carbon on a SearchTech Instrument SHZ-82 thermostatic water bath shaker (India) operated at a constant speed. The mixture was filtered using whatman filter paper, and the concentration of residual chromium in the filtrate was determined using Atomic Absorption Spectrometer (Buck Scientific 210 VGP).

Experiments on the effect of pH were conducted by adjusting the pH of different standard solutions of the same concentration from a pH of 2 to 8 using 0.1 M HCl or 0.1 M NaOH. Subsequent experiments were conducted at the optimum pH obtained from the

experiment on pH variation. The effect of contact time was determined by varying the agitation time from 3 to 240 min. Experiments were performed at different temperatures of 298 K, 303 K, 313 K and 323 K to determine the effect of temperature.

The adsorption capacity ( $q_e$ ) in  $\text{mg/g}$  of activated carbon was determined using the following equation:

$$q = \frac{(C_o - C_f)V}{m} \quad (1)$$

Where;  $m$  is the mass of activated carbon used (g),  $V$  is the volume of the solution (L),  $C_f$  is the initial metal concentration ( $\text{mg/L}$ ), and  $C_o$  is the final metal concentration ( $\text{mg/L}$ ) in the filtrate.

The removal efficiency (%R) of each activated carbon was calculated using the following expression:

$$\%R = \frac{(C_o - C_f) \times 100}{C_o} \quad (2)$$

### 3. Results and Discussion

#### Effect of pH

The results of the effect of pH change on the removal of Cr (VI) from aqueous solution using cashew bark extract activated carbon from coconut shell (CNAC<sub>1</sub>) and  $\text{H}_3\text{PO}_4$  activated carbon from coconut shell (CNAC<sub>2</sub>) are presented in Fig. 1. It has been pointed out that pH is an important parameter for adsorption of metal ions from the aqueous solution because it affects the chemistry/speciation of the metal ions and the nature of the functional groups present on the surface of the adsorbent [18]. It can be observed that the percentage removal (%R) of Cr (VI) decreased steadily from 75.18% to 70.89% for CNAC<sub>1</sub> and from 84.6% to 70.32% for CNAC<sub>2</sub> when the pH was increased from 2 to 5. This observation can be explained based on the fact that chromium (VI) exists as oxyanions in solutions [6, 8]. It has been reported that chromium (VI) exhibits different types of pH-dependent equilibrium in aqueous solutions. As the pH changes, the equilibrium also changes. In the pH range of 1.0–6.0, chromium (VI) ions co-exist in different forms, such as  $\text{HCrO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{Cr}_3\text{O}_{10}^{2-}$ ,  $\text{Cr}_4\text{O}_{13}^{2-}$  of which  $\text{HCrO}_4^-$  predominates and as the pH of the solution increases the predominant species becomes  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  [3, 6, 19]. At low pH values, there is a high concentration of  $\text{H}^+$  on the activated carbon surface. This enhances an electrostatic attraction between the negatively

charged chromate ions and the H<sup>+</sup> laden surface of the activated carbon. It can also be observed from Fig.1 that there was a slight steady increase in chromium removal as the pH was increased from 5 to 8. This can be linked to literature reports on the coexistence of trivalent chromium (as Cr<sup>3+</sup>, CrOH<sup>2+</sup>, Cr(OH)<sub>3</sub>, CrOH<sup>2+</sup> or Cr<sub>2</sub>O<sub>3</sub>) and hexavalent chromium at different pH values occasioned by the reduction of Cr (VI) to Cr (III) by superficial carbon groups [8, 20]. It has also been reported that Cr<sub>2</sub>O<sub>3</sub> specie dominates at pH higher than 5 [20, 21]. At high pH, the surface of the activated carbon is concentrated with OH<sup>-</sup> ions, this apparently creates an electrostatic attraction between the surface and the trivalent chromium cations which eventually enhances chromium adsorption between pH 5 and 8. Adsorption efficiency of both CNAC<sub>1</sub> and CNAC<sub>2</sub> followed the same pattern at different pH values with both reaching optimum at pH of 2. However, the adsorption efficiency of CNAC<sub>1</sub> is slightly less than that of CNAC<sub>2</sub> at nearly all pH values. Though the optimum pH for adsorption of a particular metal ion to some extent depends on the adsorbent type, similar optimum pH of 2 has been reported by several other authors for hexavalent chromium adsorption [3, 6, 22, 23, 24]. The pH of 2 was applied for further experiments.

#### Kinetics and effect of contact time

Kinetics is one of the physicochemical parameters to be considered in the evaluation of adsorption as a unit operation, and it is one of the parameters required to determine the efficiency of the operation [20]. It can be observed from Fig. 2 that the percentage adsorption of Cr (VI) increased with increase in contact time. There was a rapid removal of Cr (VI) within the first 5 minutes by both samples and then dropped slightly after 10 minutes. The adsorption then continued almost steadily after 60 minutes of agitation for both CNAC<sub>1</sub> and CNAC<sub>2</sub>. This observations could be explained based on the fact that the number of vacant site available for adsorption at the initial stages is high compared to the number of adsorbate particles. This number of vacant sites decreases as the agitation time increases [25]

The kinetic data for Cr (VI) adsorption were simulated using three kinetic models which are: pseudo-first-order, pseudo-second-order and Elovich models. The pseudo-first-order and pseudo-second-order kinetic models are as presented in Equations 3 and 4 respectively.

$$q_t = q_e \left[ 1 - \text{Exp}(-k_1 t) \right] \quad (3)$$

$$q_t = q_e \left[ 1 - \frac{1}{1 + q_e k_2 t} \right] \quad (4)$$

Where  $q_e$  and  $q_t$  are the amounts of solute adsorbed at equilibrium and time  $t$  (mg/g) respectively;  $k_1$  is the pseudo-first-order rate constant (/min), and  $k_2$  is the pseudo-second-order rate constant (g/mg/min).

The non-linear form of Elovich's equation which has been used to describe kinetics of chemisorption of gases and metal ions onto solid materials [26] is presented in Equation 5:

$$q = \frac{1}{\beta} \ln(\alpha \cdot \beta \cdot t + 1) \quad (5)$$

Where  $\alpha$  and  $\beta$  are constants. The parameter  $\alpha$  represents the rate of chemisorption at zero coverage, the parameter  $\beta$  is related to the extent of surface coverage and to the activation energy for the adsorption.

In most reported adsorption studies, the linearized forms of these naturally non-linear equations are employed, thereby bringing about bias in the evaluated values. Due to the inherent bias resulting from the transformation of non-linear equations to their linear forms which often tends towards a diverse form of parameters estimation errors and fits distortion, several mathematically rigorous error functions have lately been introduced [27]. Hence, the non-linear forms of both pseudo-first-order and pseudo-second-order kinetic models were employed, and both Average Regression Error (ARE) and the Chi square ( $X^2$ ) were used to minimize the error distribution between the experimental kinetic data and those predicted by the kinetic models using the *solver* add-in function, Microsoft Excel, Microsoft Corporation. The Average Regression Error (ARE) function is given by Equation 6, while Chi square ( $X^2$ ) is presented in Equation 7.

$$\text{ARE} = \frac{100}{n} \sum_{i=1}^n \left| \frac{q_{i, \text{cal}} - q_{i, \text{exp}}}{q_{i, \text{exp}}} \right| \quad (6)$$

$$X^2 = \sum_{i=1}^n \frac{(q_{e \text{ cal}} - q_{e \text{ exp}})^2}{q_{e \text{ exp}}} \quad (7)$$

Where  $q_{e \text{ cal}}$  is each value of  $q$  theoretically predicted by the fitted model and  $q_{e \text{ exp}}$  is each value of  $q$  determined experimentally, and  $n$  is the number of experiments performed.

The model with the best fit was chosen based on the values of the correlation coefficient ( $R^2$ ) and the error function. The model that presented the highest  $R^2$  value and lowest error value was adjudged to fit the data best. Hence, the pseudo-first-order model was found to fit the adsorption of chromium (VI) by both CNAC<sub>1</sub> and CNAC<sub>2</sub> best (Table 1). The values of kinetic constants and  $q_e$  values of Cr (VI) sorption onto CNAC<sub>1</sub> and CNAC<sub>2</sub> are given in Table 1.

#### *Effect of temperature and adsorption thermodynamics*

Fig.3 displays the relationship between adsorption capacities and variations in temperature. It can be observed that CNAC<sub>1</sub> showed an increase in metal uptake from 13.59 to 20.59 mg/g with increase in temperature from 298 to 323 K. This can be explained based on the fact that increase in temperature increases the rate of diffusion of the adsorbate molecules across the external boundary layer and within the internal pores of the adsorbent particle, due to decrease in the viscosity of the solution [28]. For an initial metal concentration of 50 mg/L, when the temperature was increased from 298 to 323 K, the uptake (mg/g) of CNAC<sub>2</sub> decreased from 22.03 to 12.59 mg/g.

The determination of thermodynamic parameters-standard entropy change ( $\Delta S^\circ$ ), standard enthalpy change ( $\Delta H^\circ$ ) and standard free energy change ( $\Delta G^\circ$ ) is important to ascertain the spontaneity of the adsorption process. In this study, the thermodynamic parameters were determined using the equilibrium data obtained at different temperatures according to the following equations:

$$\Delta G^\circ = -RT \ln K_e \quad (8)$$

$$K_e = C_{Ae}/C_e \quad (9)$$

Where,  $C_{Ae}$  is the solid phase concentration of the metal at equilibrium (mg/L),  $C_e$  is the equilibrium concentration of the metal in solution phase (mg/L),  $K_e$  is the equilibrium constant,  $T$  is the temperature in Kelvin and  $R$  is the gas constant (kJ/mol/K).

$$\ln K_e = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (10)$$

The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  were respectively obtained from the slope and intercept of the plot of  $\ln K_e$  against  $1/T$ , while values of  $\Delta G^\circ$  at different temperatures were obtained using the equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

The negative free energy values obtained showed that the process was feasible for CNAC<sub>2</sub> at all temperatures considered. However, for CNAC<sub>1</sub>, the adsorption of Cr (VI) was only feasible at temperatures above 298 K. The adsorption of Cr (VI) by CNAC<sub>1</sub> was endothermic while its adsorption by CNAC<sub>2</sub> was found to be exothermic (Table 2). The entropy values for the adsorption of chromium (VI) by both CNAC<sub>1</sub> and CNAC<sub>2</sub> indicated that the particles of the metal ions on the surfaces of the activated carbons were in a high state of disorder.

#### *FTIR, SEM and EDX analysis of adsorbents*

Fig.4 presents the FTIR spectra of the activated carbons before and after chromium (VI) adsorption. For H<sub>3</sub>PO<sub>4</sub> activated carbon (CNAC<sub>2</sub>), the vibrational bands 3550.5, 3500.6, 3421.7, 3312.8 and 3234.9 cm<sup>-1</sup> (Fig. 4a) are due to the hydroxyl group with hydrogen bonding of OH stretching vibration. The bands at 2918.9 and 2103.4 cm<sup>-1</sup> can be attributed to C-H stretching vibration of methylene and carbon-carbon triple bond stretching vibration of terminal alkyne respectively. The bands at 1746.5 and 168.0 cm<sup>-1</sup> can be assigned to C=O of ester while the band at 1073.6 cm<sup>-1</sup> is attributed to C-O stretching of alkyl-substituted ether. After Cr (VI) adsorption, the stretching vibrational bands due to OH group were increased to 3561.0, 3514.4, 3492.2, 3425.5, 3324.2 and 3237.9 cm<sup>-1</sup> respectively (Fig. 4b). Increases in vibrational bands after Cr (VI) adsorption by acid activated carbon (CNAC<sub>2</sub>) were also recorded at 1687.4 cm<sup>-1</sup> attributed to the carbonyl group of conjugated ketone, 1614.7 cm<sup>-1</sup> assigned to C=C stretching vibration of an aromatic ring, 1299.4 cm<sup>-1</sup> assigned to primary or secondary OH in-plane bending vibration and the large increase in band 1129.8 cm<sup>-1</sup> assigned to C-O stretching of alkyl-substituted ether.

For CNAC<sub>1</sub>, in addition to the bands attributed to hydroxyl, C=O of ester and ketones, C=C stretching and other functional groups; a new vibrational band at 2811.7 cm<sup>-1</sup> assigned to C-H

stretching of methoxy (O-CH<sub>3</sub>) was observed (Fig. 4c). After chromium adsorption, the vibrational stretching bands 3572.8, 3527.1, 3487.2, 3435.5, 3331.2 and 3244.0 cm<sup>-1</sup> (Fig. 4c), which can be attributed to hydroxyl group with hydrogen bonding were shifted to 3559.4, 3517.9, 3473.0, 3427.5, 3339.0 and 3226.2 cm<sup>-1</sup> respectively (Fig. 4d). There was an increase in the vibrational band 1759.3 cm<sup>-1</sup> assigned to C=O of ester and a decrease in the band 1699.9 cm<sup>-1</sup> assigned to C=O of conjugated ketone after chromium adsorption.

The scanning electron micrographs of adsorbents are employed to observe clear and direct pictures of surface microstructures of different adsorbents. The scanning electron micrographs of CNAC<sub>1</sub> and CNAC<sub>2</sub> before and after Cr (VI) adsorption are displayed in Fig. 5. The micrographs

of CNAC<sub>1</sub> and CNAC<sub>2</sub> (Fig. 5a and 5c) are observed to be coarser, more homogeneous and porous than their Cr (VI) loaded counter-parts (Fig. 5b and 5d). A reduction in the number of pores in the Cr (VI) loaded activated carbons were observed, and this can be attributed to the adsorption of chromium on the activated carbon surfaces.

EDX analysis was used to estimate the elemental composition of the activated carbon samples under investigation, and the results are presented in Fig. 6. It can be observed that carbon had the highest percentage of all the samples. The presence of chromium after adsorption can also be observed in the samples.

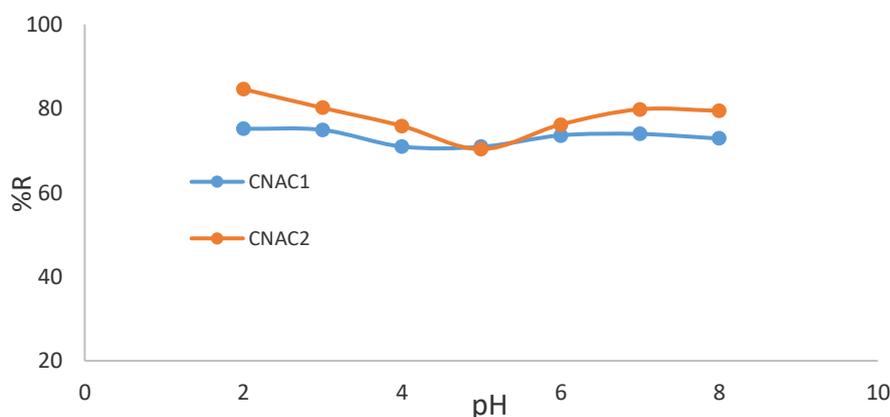


Fig. 1. Effect of pH on the removal of Cr (VI) from aqueous solution using CNAC<sub>1</sub> and CNAC<sub>2</sub>

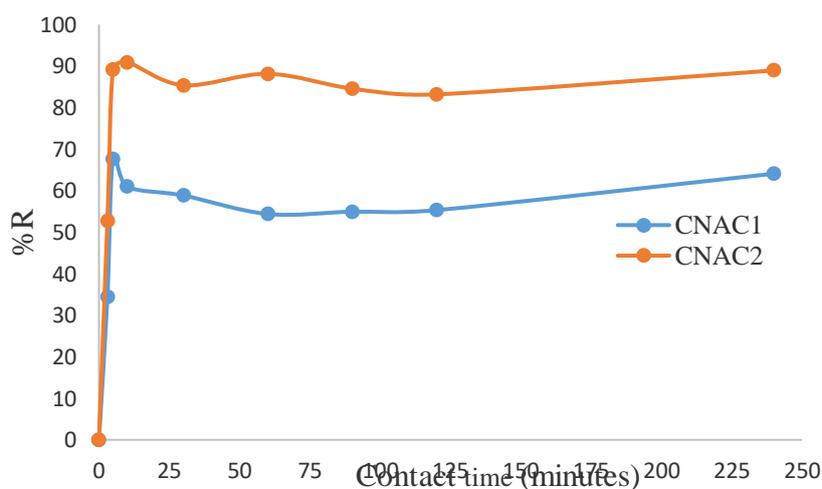
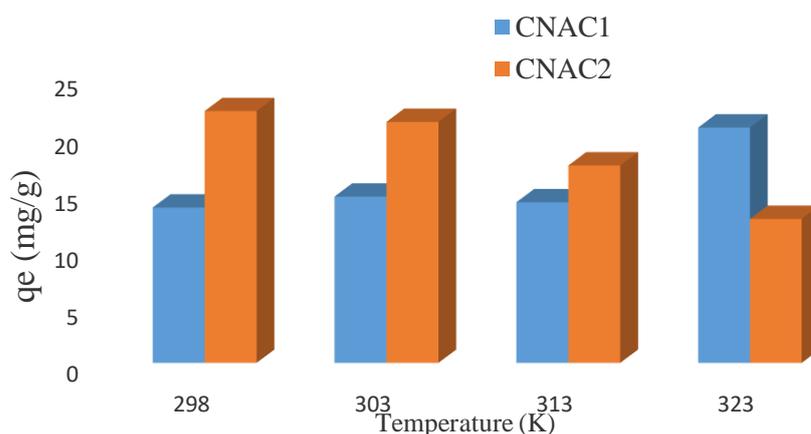


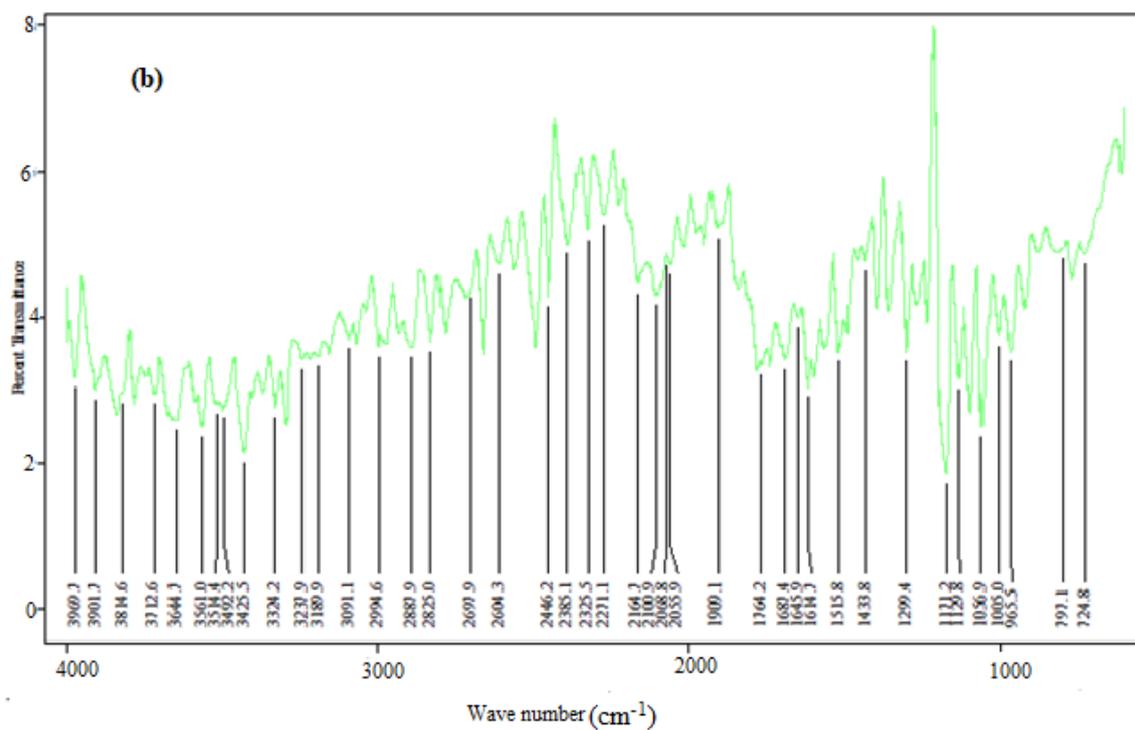
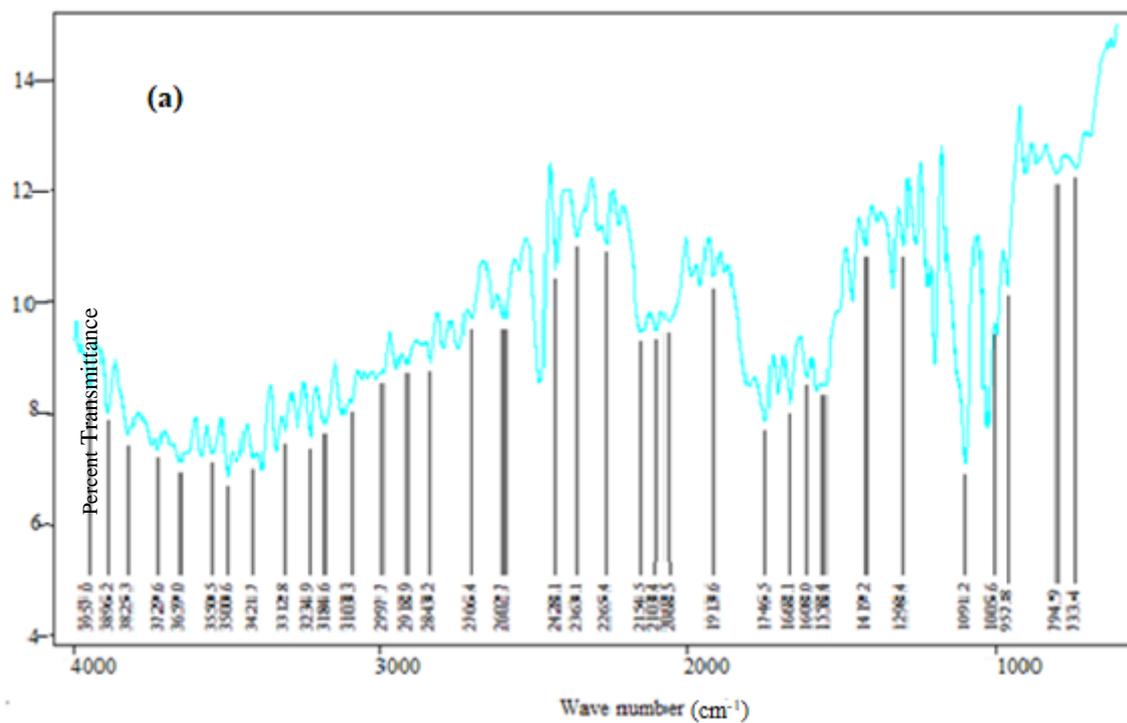
Fig. 2. Effect of contact time on the removal of Cr (VI) from solution using CNAC<sub>1</sub> and CNAC<sub>2</sub>

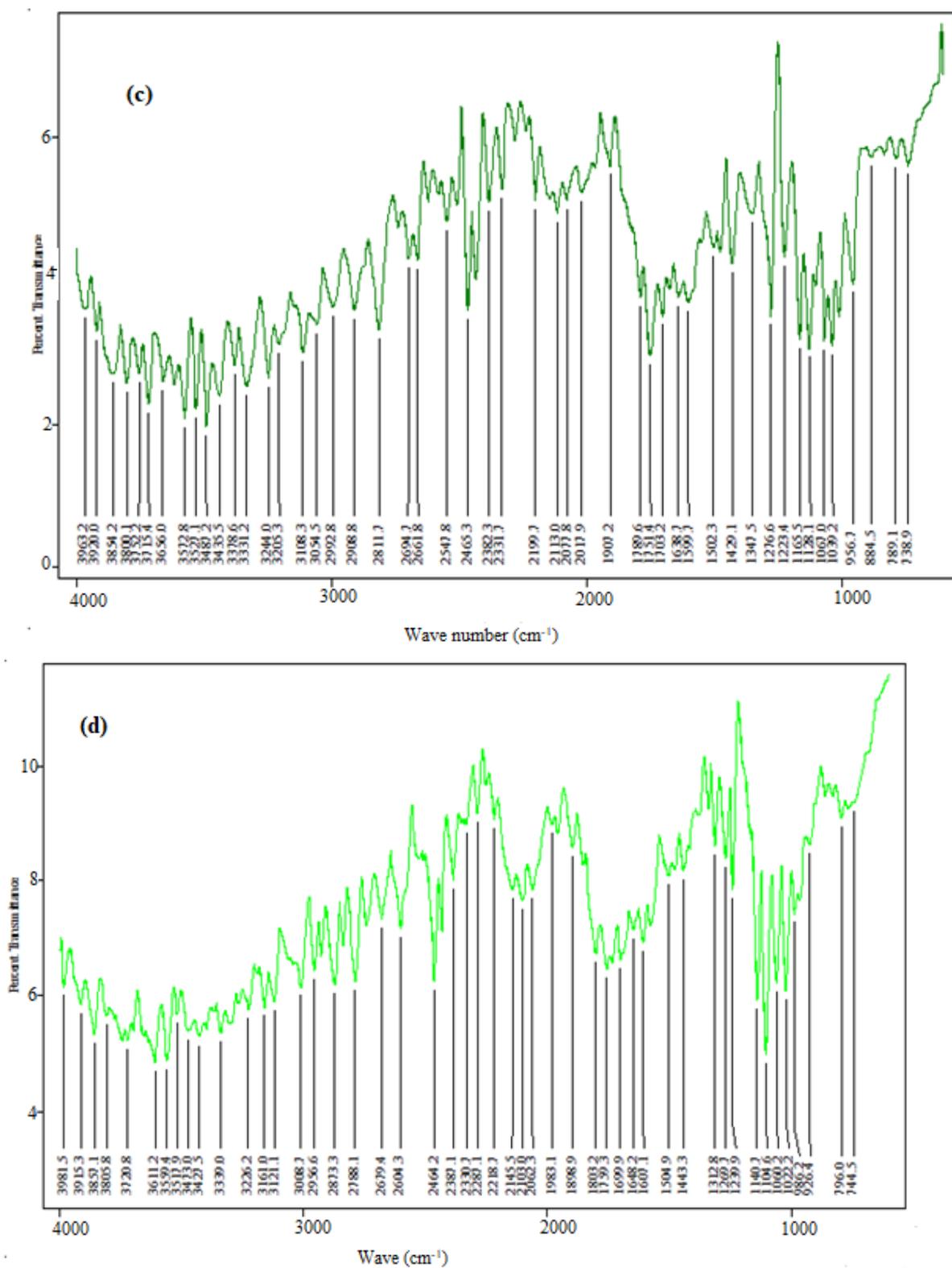
**TABLE 1. Kinetic parameters for the adsorption of Cr (VI) using CNAC<sub>1</sub> and CNAC<sub>2</sub>**

Kinetic model	Parameter	CNAC <sub>1</sub>	CNAC <sub>2</sub>
Pseudo-first-order	q <sub>e</sub> (mgg <sup>-1</sup> )	13.74	21.34
	k <sub>1</sub>	4.45	7.09
	R <sup>2</sup>	0.8804	0.9774
	ARE	12.12	10.38
	χ <sup>2</sup>	3.88	5.26
Pseudo-second-order	q <sub>e</sub> (mgg <sup>-1</sup> )	13.74	21.34
	k <sub>2</sub>	0.11	12.27
	R <sup>2</sup>	0.4669	0.7450
	ARE	12.09	10.36
	χ <sup>2</sup>	3.84	5.23
Elovich	α(x10 <sup>2</sup> )	2.50	2.56
	β	0.70	0.44
	R <sup>2</sup>	0.1667	0.4906
	ARE	13.76	12.04
	χ <sup>2</sup>	5.15	5.25

Fig. 3. Effect of temperature on the adsorption of Cr (VI) using CNAC<sub>1</sub> and CNAC<sub>2</sub>**TABLE 2. Thermodynamic parameters for the adsorption of Cr (VI) CNAC<sub>1</sub> and CNAC<sub>2</sub>**

Sample	T (K)	ΔG <sup>0</sup> (kJ/mol)	ΔH <sup>0</sup> (kJ/mol)	ΔS <sup>0</sup> (kJ/K/mol)
CNAC <sub>1</sub>	298	0.09	38.83	0.13
	303	-0.56		
	313	-1.86		
	323	-3.16		
CNAC <sub>2</sub>	298	-134.49	-74.89	0.20
	303	-135.47		
	313	-137.50		
	323	-139.49		





**Fig.4.** FTIR spectral of: (a) CNAC<sub>2</sub>, (b) Cr (VI) loaded CNAC<sub>2</sub>, (c) CNAC<sub>1</sub> and (d) Cr (VI) loaded CNAC<sub>1</sub>

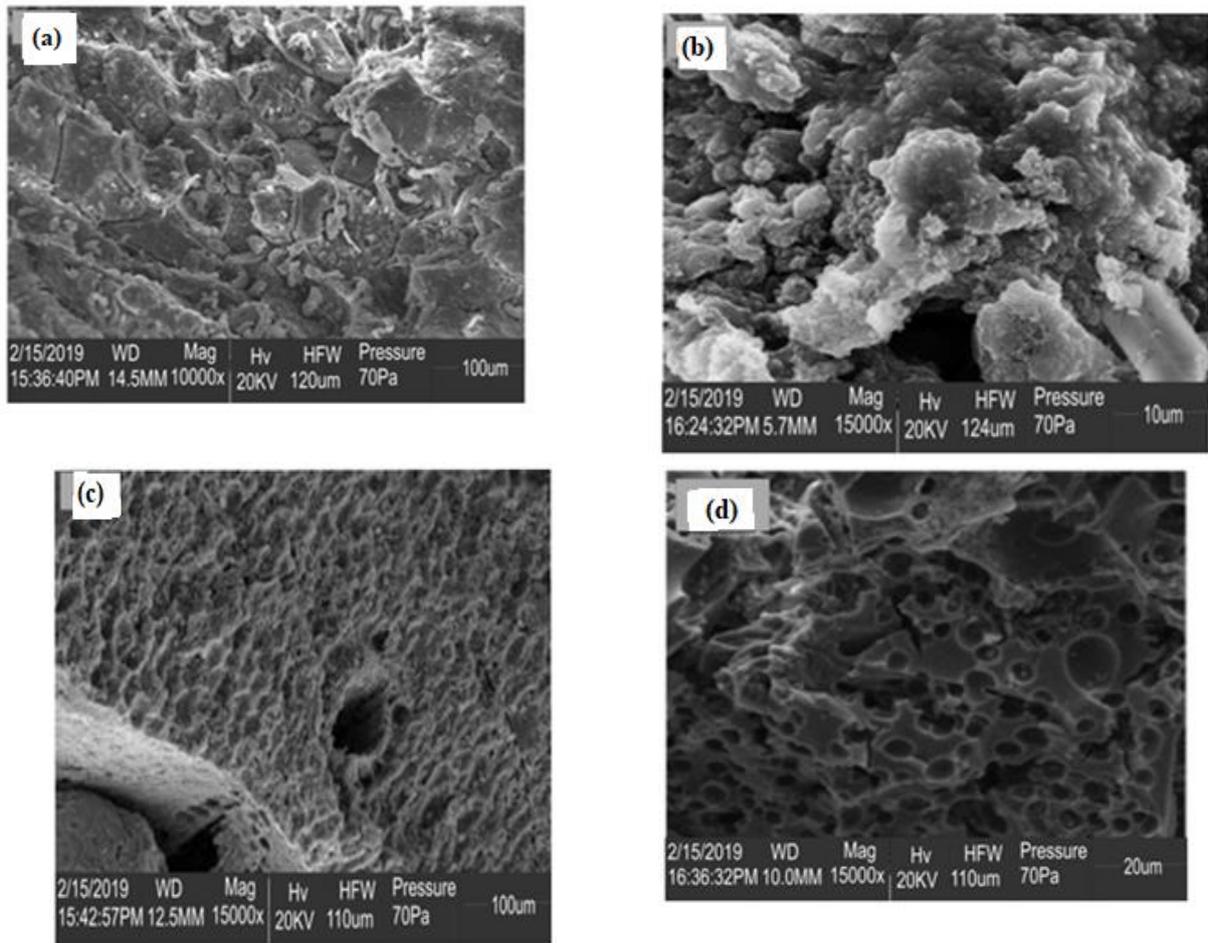
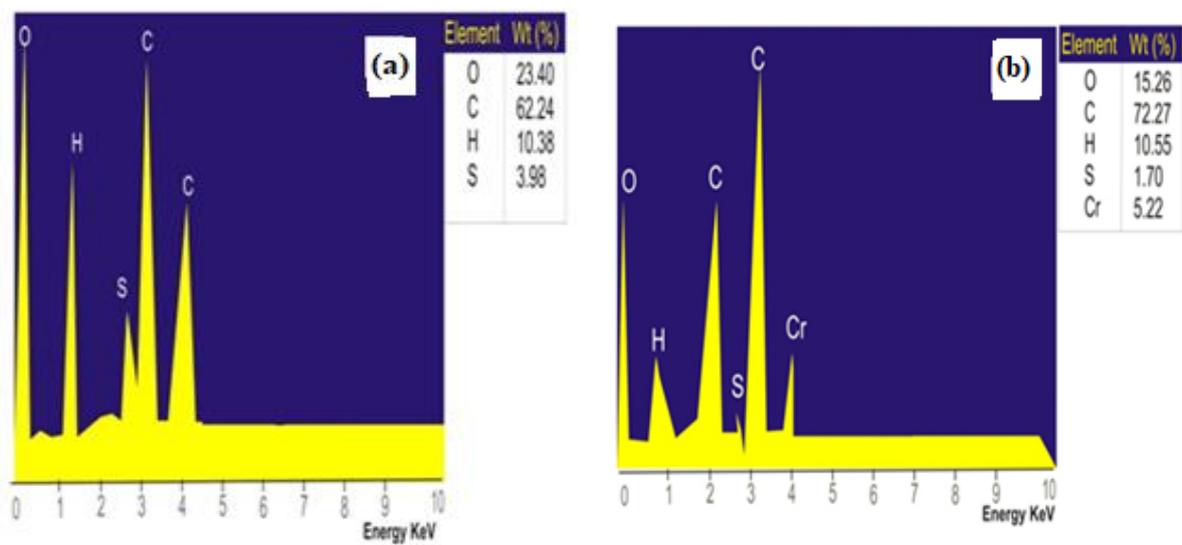


Fig. 5. SEM micrographs of: (a) CNAC<sub>1</sub>, (b) Cr(VI) loaded CNAC<sub>1</sub>, (c) CNAC<sub>2</sub> and (d) Cr(VI) loaded CNAC<sub>2</sub>



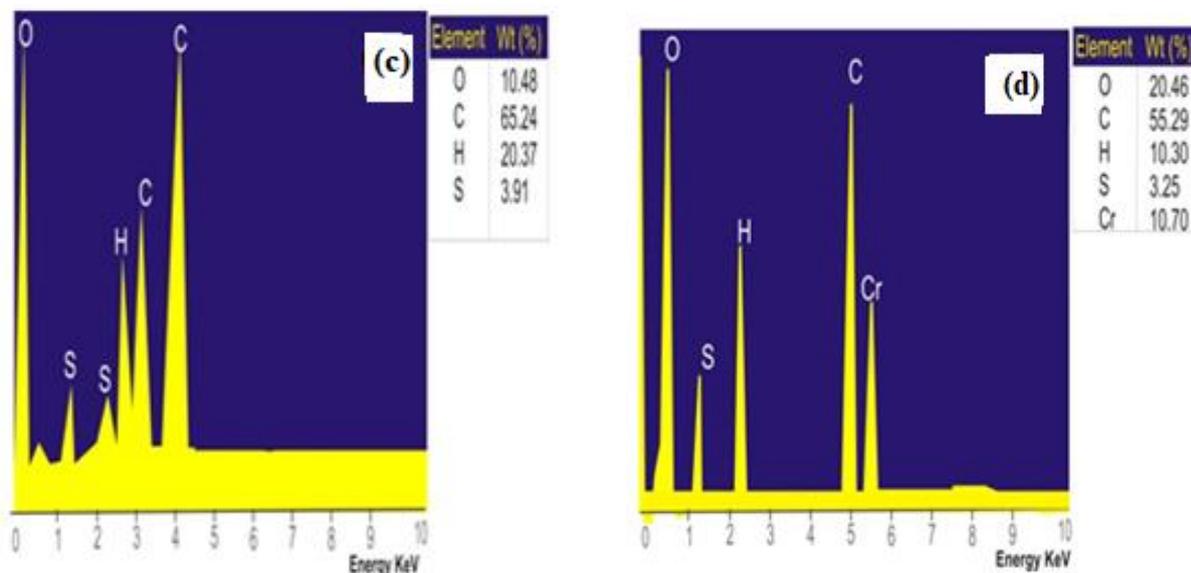


Fig. 6. EDX spectra of: (a) CNAC<sub>1</sub>, (b) Cr (VI) loaded CNAC<sub>1</sub>, (c) CNAC<sub>2</sub> and (d) Cr (VI) loaded CNAC<sub>2</sub>

## Conclusions

This study revealed that Cr (VI) adsorption by cashew bark extract activated carbon (CNAC<sub>1</sub>) and phosphoric acid activated carbon (CNAC<sub>2</sub>) was pH, contact time and temperature-dependent. The pH of maximum adsorption was 2, with percentage removal of 75.18% recorded for CNAC<sub>1</sub> and 84.6% for CNAC<sub>2</sub>. Kinetic studies revealed that the pseudo-first-order model best described the adsorption of Cr (VI) by both CNAC<sub>1</sub> and CNAC<sub>2</sub> and the process was found to be very rapid within the first five minutes of agitation and decreased with approaching equilibrium. Experiments conducted at different temperatures showed that adsorption capacity for CNAC<sub>1</sub> increased with temperature while for CNAC<sub>2</sub>, adsorption capacity decreased with increase in temperature. Thermodynamic parameters revealed that adsorption of Cr (VI) by CNAC<sub>1</sub> was endothermic while for CNAC<sub>2</sub>, it was exothermic. In addition, the process was found to be feasible and spontaneous with CNAC<sub>2</sub> showing higher spontaneity and better adsorption capacity. Meanwhile, the adsorption of Cr (VI) by CNAC<sub>1</sub> was found to be feasible at temperatures greater than 298 K. It can be concluded that CNAC<sub>2</sub> recorded higher adsorption capacity/ percent removal for all parameters studied and more favourable thermodynamic parameters than CNAC<sub>1</sub>. However,

the eco-friendliness and cheapness of aqueous extract of cashew bark could make it serve as an alternative to H<sub>3</sub>PO<sub>4</sub> as an activating agent for carbon preparation from coconut shells for Cr (VI) adsorption.

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