Application of Quaternized Activated Carbon Derived from Macadamia Nutshells for the Removal of Hexavalent Chromium from Aqueous Solutions

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ABSTRACT

In this paper, the feasibility of quaternized activated carbon derived from Macadamia nutshells was explored in the removal of hexavalent chromium (Cr(VI)) from aqueous solutions. The amino-modified activated carbon was achieved by cross-linking native Macadamia activated carbon (MAC) with epichlorohydrin and grafting diethylenetriamine and triethylamine (EDT) on the surface and the product was labelled as MAC-EDT. The adsorbent was characterized by Fourier transform infrared spectroscopy (FTIR), Brunauer-Emmett-Teller (BET), scanning electron microscope (SEM) and the CHNS analyzer. The optimum parameters for Cr(VI) removal found were pH (5), contact time (120 min) and sorbent mass (0.10 g) where removal efficiencies were >90% in all cases. Langmuir model fitted the data best and the adsorption capacity was 145.5 mg g⁻¹ after surface modification with EDT. The Cr(VI) ion was found to be adsorbed more as compared to other anions, and the sorption order was: SO₄²⁻ < PO₄³⁻ < NO₃⁻ < Cr₂O₇²⁻. The removal mechanism involved adsorption of Cr(VI) and/or subsequent reduction of Cr(VI) to Cr(III).

KEYWORDS

Activated carbon, amination, Macadamia, chromium(VI), adsorption, reduction.

1. Introduction

Petroleum refining, electroplating, chrome mining, leather tanning, paint and pigments manufacturing industrial activities may generate chromium waste. In addition to these, natural causes like volcanic eruptions also may lead to seepage of chromium compounds into the environment. Like other metal pollutants, chromium is non-biodegradable and toxic. In the environment, chromium may exhibit different oxidation states ranging from +2 to +6, but the trivalent (Cr(III)) and hexavalent (Cr(VI)) oxidation states are the most prevalent. These forms of chromium have different mobilities and levels of toxicity in aqueous environment. In fact Cr(III) is 500 times less toxic than Cr(VI). On the contrary, while the United States Environmental Protection Agency has classified Cr(VI) as a group A carcinogen because of its chronic effects, Cr(III) is a micronutrient needed for biological processes. However, both forms are toxic at high concentrations. Cancer of the digestive tract and lungs are some common effects of chromium exposure. 

The World Health Organization (WHO) has set guidelines (WHO) has set rules which have set maximum tolerable concentration limits of 0.05 mg L⁻¹ of Cr(VI) in drinking water and 0.1 mg L⁻¹ in inland surface water. A variety of methods including chemical precipitation, ion exchange, reverse osmosis, adsorption, reduction and electrochemical precipitation, have been investigated for Cr(VI) removal from various sample matrices. The adsorption method, particularly utilizing waste agricultural materials as precursors for activated carbons (ACs), has gained more popularity because of its abundance, low cost and effectiveness in removing pollutants from aqueous solutions.

ACs derived from various agricultural waste and biomass including Moringa oleifera seed powder, peanut shell, oil palm endocarp, bamboo bark and logan seed, have been examined for Cr(VI) adsorption. Well-developed internal pore structure, high surface area and tunable surface chemistry are some of the properties making ACs excellent adsorbents. ACs can be produced by either chemical or physical activation, and it is common that oxidizing conditions are employed in order to impart the surface oxygen groups to the carbon making the surface of the carbon acidic. However, acidic groups, particularly carboxylic groups, tend to attract water molecules through H-bonding forming water clusters thereby reducing adsorption efficiency of ACs.

Therefore, in this study, the AC was modified by amination to –NH which at low pH might lead to protonation and subsequent electrostatic attraction of anionic Cr(VI) as well as adding the quaternary functionality, –N+(CH₂CH₃)₃Cl⁻, on the surface. No study has been reported on the use of amino-functionalized AC produced from Macadamia nutshells for the removal of Cr(VI) from aqueous solutions, as far as we know. The removal mechanism of Cr(VI) by activated carbon is complex and may include adsorption of Cr(VI) onto carbon surface followed by subsequent reduction of Cr(VI) to Cr(III), and release back into the solution of reduced Cr(III) or adsorption of Cr(III) onto the carbon surface. Therefore, variable parameters such as effect of pH, concentration and contact time were studied to explore Cr(VI) interaction with MAC-EDT.

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2. Materials and Methods

2.1. Chemicals and Instrumentation

Potassium dichromate ($K_2Cr_2O_7$), sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Merck Chemical Co (Johannesburg, South Africa). Epichlorohydrin, diethylenetriamine, triethylamine, N,N-dimethylformamide and 1,5-diphenylcarbazide were purchased from Sigma-Aldrich (Johannesburg, South Africa). Commercial Macadamia activated carbon (MAC) was supplied by Innovation Carbon FILTATECH (Johannesburg, South Africa).

Ultrapure water from LaboStar equipment by Siemens (Warrendale, Pennsylvania, USA) was used to make all solutions. The pH of solutions was monitored by the ADWA AD111 OPR pH meter from Adwa Instruments (Szeged, Hungary). A Multichannel stirrer MS-53M model Jeio Tech (Seoul, Korea) was used for stirring solutions in batch adsorptions. Atomic absorption spectrophotometer AA7000 from Shimadzu (Kyoto, Japan) was used for measuring total chromium concentration in solutions whilst Cr(VI) was determined by UV-VIS (T80+) supplied by PG Instruments. CL10 ThermoScientific centrifuge supplied by Labotec (Johannesburg, South Africa) was utilized for centrifugation. KhyPlot 2.0 software (Quasi-Newton algorithm) was used to plot the data for isotherm and kinetic models.

Elemental analysis of activated carbon was determined on a Thermo Flash 2000 series CHNS/O Organic Elemental Analyser. The surface area was measured on a Micromeritics Flow Prep Thermo Flash 2000 series CHNS/O Organic Elemental Analyser. Proximate and component analysis was done following a method reported by Li et al. from Tristar instrument. Element analysis of activated carbon was determined on a Thermo Flash 2000 series CHNS/O Organic Elemental Analyser. The surface area was measured on a Micromeritics Flow Prep Thermo Flash 2000 series CHNS/O Organic Elemental Analyser. Proximate and component analysis was done following a method reported by Li et al. The evaluation of morphology and surface texture was conducted on an FEI Quanta 200 SEM (FEI, Hillsboro, OR, USA). A PerkinElmer Spectrum 400 FT-IR/FT-NIR spectrometer (Waltham, MA, USA) was used for recording FTIR spectra. An STA 600 Simultaneous Thermal Analyzer from PerkinElmer (Waltham, USA) was used for the thermogravimetric analysis.

2.2. Preparation of Amino-modified Activated Carbon

A method described by Xu et al. was used. Briefly, about 2 g of powdered AC was weighed and transferred into a 50 mL round-bottom flask, 5 mL of epichlorohydrin and 5 mL of N,N-dimethylformamide were added to contact with 2 g of MAC and the contents were refluxed at 80 °C for 1 h. Then, 3 mL of diethylenetriamine was added and agitated for 1 h. Finally, 5 mL of triethylamine was introduced for grafting. After mixing for 1 h, the product (labelled as MAC-EDT) was cooled down and washed with distilled water to remove the residual chemicals, subsequently dried at 70 °C and used in the adsorption studies. Fig. 1 shows the general scheme for the synthesis of MAC-EDT.

2.3. Preparation of Stock and Standard Solutions

Chromium(VI) stock solution of 1000 mg L$^{-1}$ was prepared by dissolving pre-dried $K_2Cr_2O_7$ in ultrapure water. Working and standard solutions were prepared from serial dilutions of the stock solution. All chemical reagents used were of high-purity analytical grade.

2.4. Determination of pH of Point of Zero Charge

The point of zero charge ($pH_{pzc}$) of MAC-EDT was determined by a method from literature. Briefly, a solution of $KNO_3$ (0.02 M; 45 mL) was transferred into each of six different 100 mL glass beakers. Dilute solutions of HCl (0.1 M) or NaOH (0.1 M) were used to adjust the pH such that each beaker had a different pH from pH 2 to 12. Following pH adjustments, $KNO_3$ solution was used to make up the final volume in each beaker to 50 mL. The initial (pH) in each beaker was recorded. In each beaker, 0.1 g MAC-EDT powder was then added and the solutions were stirred for 24 h at ambient temperature. The final pH (pHf) of the stirred solution was recorded. The $pH_{pzc}$ was obtained by plotting the change in pH ($ΔpH$) versus the initial pH.

2.5. Adsorption Studies

The effects of adsorption-controlling parameters such as the solution pH, contact time, metal ion initial concentration and adsorbent dosage play a critical role in pollutant sequestration by ACs. Hence, the influence of these parameters on the removal of Cr(VI) by MAC-EDT was investigated in the present study. All adsorption experiments were carried out at room temperature while stirring the solution at 300 rpm. Solutions of HCl and NaOH were used to adjust the initial pH of solution (pH 2–11). The initial concentration of Cr(VI) was varied from 10–180 mg L$^{-1}$ while the adsorbent mass was varied from 0.02–0.12 g and stirring time range studied was from 10–240 min. Binary solutions of Cr(VI) and competing anions were prepared to evaluate the effect of co-existing anions on the removal of Cr(VI) by MAC-EDT. All experiments were conducted in duplicate and the reported results are averages. Following completion of adsorption reactions, the mixtures were centrifuged and Cr(VI) concentration of one part of the supernatant was determined by UV-Vis spectrophotometer ($λ_{max}$ 540 nm). The chromogenic agent used to develop colour was the 1,5-diphenylcarbazide (DPC) reagent (0.2 mL of 10 % $H_2SO_4$ solution and 2 mL DPC) as per the previously reported method. Flame atomic absorption spectroscopy (FAAS) was used to analyze the other fraction of the supernatant solution for total chromium and Cr(III) was obtained from the difference between Cr(VI) concentration and total chromium analysis. Equations (1) and (2) were used to calculate the amount of Cr(VI) adsorbed on the AC surface.

![Figure 1](image-url)
where, $q_e$ is the adsorbed Cr(VI) (mg g–1 adsorbent) on the surface, $b$ is the Langmuir isotherm constant (L mg–1), $q_m$ represents maximum Cr(VI) uptake (mg g–1), $q_o$ is the calculated Cr(VI) uptake (mg g–1) and $C_e$ is the equilibrium Cr(VI) concentration (mg L–1). The Freundlich model relates to a multilayer uptake of adsorption while if the $R_L$ is greater than 1, then an unfavourable adsorption is predicted.36,37

$$q_e = \frac{q_m b C_e}{(1 + b C_e)}$$

(3)

where, $b$ is the Langmuir isotherm constant (L mg–1), $q_m$ represents maximum Cr(VI) uptake (mg g–1), $q_o$ is the calculated Cr(VI) uptake (mg g–1) and $C_e$ is the equilibrium Cr(VI) concentration (mg L–1). The Freundlich model relates to a multilayer uptake of an adsorbate on a heterogeneous surface.38 The equation is supplied below.

$$R_L = \frac{1}{1 + b C_e}$$

(4)

where, $b$ is the Langmuir isotherm constant (L mg–1) and 1/n is the Freundlich exponent. The Freundlich constant $K_F$ is related to adsorption capacity and the exponent 1/n is a measure of the sorption intensity or surface heterogeneity.39

2.7. Kinetic Modelling

Pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic equations were used to evaluate the processes controlling adsorption of Cr(VI) by MAC-EDT and the rate of mass transfer. The PFO and PSO equations for the models are given in their linearized forms in Equations (6) and (7), respectively.40

$$\log(q_t - q_e) = \log q_o - \frac{k_1 t}{2.303}$$

(6)

$$\frac{t}{q_t} = \frac{1}{k_2 q_o^2} + \frac{1}{q_o} t$$

(7)

where, $q_o$ (mg g–1) is the metal ion sorption capacity at time $t$, $k_1$ (min–1) is the PFO rate constant and $k_2$ (g mg–1 min–1) is the PSO rate constant.

3. Results and Discussion

3.1. Characterization of Macadamia Activated Carbon

Proximate and ultimate analysis results of MAC-EDT and other ACs found in literature are displayed in Table 1. The higher %C in MAC-EDT shows that Macadamia nutshellshells are very carbonaceous. The higher %N confirms that nitrogen groups from ethylenediamine and triethylamine were grafted on the surface of MAC-EDT. Accordingly, the %O content of MAC-EDT decreased due to loss of H2O as moisture during the grafting of epichlorohydrin on the surface of MAC. Therefore, this implied MAC-EDT had a low ratio of acidic functional groups on its surface. Proximate analysis showed that ash, volatile and fixed carbon contents of MAC were comparable with other ACs in literature. The fixed carbon content (26.99 %) was slightly higher compared to most ACs and this was related to the higher %C value obtained by the CHNS analyzer. The high percentage of fixed carbon was due to lignin content observed in plant materials, while the cellulose and hemicellulose make up for the volatile matter.41 Therefore, it was concluded that the MAC had physico-chemical properties that are characteristic of ACs derived from plant materials.39 The ash content was very low (0.22 %) as compared to other biomass activated carbons. Low values are always favourable since their presence inhibits surface area development.20 However, upon functionalization of MAC with EDT, the physico-chemical properties changed as evidenced by the elemental analysis results and proximate analysis results (Table 1). For example, there was evident increase in the %N (8.47 %) due to presence of diethylenetriamine and triethylamine on the surface of MAC. The ash content increased after functionalization while the volatile content decreased. Also, the BET surface area decreased from 689 to 0.518 m2 g–1 signifying the closure of pores by the cross-linking reagent. The decrease of BET after functionalization has also been observed in literature.42

Figure 2 shows the FTIR spectra of MAC-EDT before and after adsorption of Cr(VI). Distinct differences between the spectra, particularly in the region of 1600–1000 cm–1 were observed. These differences signified that the AC surface was modified or changed after being in contact with Cr(VI) due to oxidation of

Table 1 Physico-chemical properties of different ACs.

<table>
<thead>
<tr>
<th>Activated carbon source</th>
<th>Ultimate analysis</th>
<th>Proximate analysis/%</th>
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<tr>
<td></td>
<td>%C</td>
<td>%H</td>
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<tr>
<td>MAC</td>
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<td>MAC-EDT</td>
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<tr>
<td>Jatropha wood</td>
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<td>6.3</td>
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<tr>
<td>Coconut shells</td>
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<td>6.1</td>
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<td>ZnCl2 activated groundnut shell</td>
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<tr>
<td>Raw palm kernel shell</td>
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<tr>
<td>Quaternized palm kernel shell</td>
<td>45.08</td>
<td>5.41</td>
</tr>
</tbody>
</table>

*Computed by difference. %0.12 % sulphur detection was considered in the calculation.
certain functional groups. The characteristic broad peak at 3343 cm$^{-1}$ is normally associated with the –OH group of biomaterials and sometimes it overlaps with the –NH group (Fig. 2a). Upon contact with Cr(VI), the intensity of the band decreased which signified its involvement in chromium removal (Fig. 2b). The grafting of amino groups on the surface of activated carbon can be confirmed by the presence of various peaks between 1687 and 1150 cm$^{-1}$. The vibrational peaks at 1687, 1582 and 1453 cm$^{-1}$ were attributed to C=O of activated carbon structure, NR$_3^+$ asymmetric bending and the C-N stretching of CH$_2$-N$^+$R$_3$ group, respectively. The difference in the peaks at 1323 and 1150 cm$^{-1}$ between the Cr(VI)-loaded and unloaded MAC-EDT spectra could be attributed to the symmetric deformation of C-H bands of CH$_3$ group and the symmetric C-O-(H) stretching vibrations, respectively. However, upon contact with Cr(VI) the C-O-H group was oxidized leading to the formation of new peaks at 1547 and 1323 cm$^{-1}$. The peak at 1547 cm$^{-1}$ could be due to the formation of the carboxylate ion due to oxidation of alcohol structure by Cr(VI). Also, elsewhere, it was stated that the disappearance of vibrational bands at 1000–1450 cm$^{-1}$ which were characteristic of C-N stretching vibration region, signified their involvement in metal uptake. Therefore, the observed changes in the spectra of MAC-EDT after contact with Cr(VI) showed that the removal mechanism was not simply adsorption but it also involved transformation of some functional groups because of the oxidative nature of Cr(VI), which was later reduced to Cr(III).

Figure 3 depicts the TGA thermograms of the native (MAC) and the modified activated carbon (MAC-EDT). It was observed that both materials had a moisture content of approximately 10%. The thermal stability of the raw MAC was evident as it was not degradable even at high temperatures (>100 °C). However, for the MAC-EDT, there was drastic weight loss at around 325 °C which was as a result of the degradation. After 600 °C, there remained 46% which was the native MAC content. This, after removing the water content, translated to a loading capacity of 440 mg g$^{-1}$ for the coating organic moiety (EDT).

The morphological properties and texture of MAC-EDT were evaluated using SEM and the micrographs are shown in Fig. 4a. The porosity of the material is evident with interconnected networks. A closer look at the surface shows that pores are actually elongated which confirmed that MAC-EDT retained the structure of lignocellulose-based plant materials proving that the activation process removed more of the non-carbon materials. The fuzziness MAC-EDT micrographs showed better porosity structures, the BET surface area was low (0.518 m$^2$ g$^{-1}$) due to the coating of MAC by EDT. The uncoated MAC material (Fig. 4b) shows well-defined crystal clusters with some visible pores but no interconnected pores as observed in MAC-EDT which were attributed to the EDT coating.

### 3.2. Effect of pH on Adsorption of Chromium(VI)

The influence of solution pH on adsorption of Cr(VI) was investigated by varying the pH from 2 to 11 while other parameters were kept constant. Fig 5a shows the percentage removal of Cr(VI) by MAC-EDT and MAC. Removal of Cr(VI) by MAC-EDT did not show a strong pH dependence. Only about 10% decrease in removal efficiency was observed as the pH was increased from pH 2 to 11. This was attributed to the EDT modification that introduced a permanent positive charge on the MAC-EDT resulting in electrostatic attraction and/or ion exchange mechanism. Similar trends were observed elsewhere. The optimal removal of chromium(VI) occurred at pH 2, but pH 5 was used for subsequent experiments as optimum pH due to observed high reduction of Cr(VI) to Cr(III) occurring at pH 2 (Fig. 5b). In relation to Cr(VI) removal by MAC-EDT, there was not much difference at pH 2 and pH 5 but the amount of Cr(III) left in solution as a result of reduction informed the decision to use pH 5 as the optimum. On the other
hand, the removal of Cr(VI) by MAC showed a strong dependence on pH as the percentage removal decreased with increase in pH. The lower removal efficiency from pH 5 to 11 by MAC compared to MAC-EDT was attributed to competition of binding sites by Cr$_2$O$_4^{2–}$ and OH$^–$ species (from NaOH used for pH adjustment). The different trends in Cr(VI) removal by MAC and MAC-EDT implied that the surface modification of MAC by EDT influenced the removal mechanism of Cr(VI) by the carbons.

Cr(VI) is an oxyanionic species, hence the observed high percentage removal at low pH was due to surface attraction of negatively charged Cr(VI) anion to positively charged MAC-EDT surface which was positive at pH < pH$_{pzc}$ (MAC-EDT was 6.83, Fig. 5a insert) and subsequent reduction of Cr(VI) to Cr(III). On the other hand, presence of hydroxyl ion at basic pH is known to interfere with the removal of Cr(VI) species, hence the decreased removal efficiency at higher pH. Furthermore, the surface of the material tends to be largely negative at pH > pH$_{pzc}$ resulting in repulsion of negatively charged chromium(VI) species.

Total chromium concentration was measured before and after adsorption of Cr(VI) by MAC-EDT to elucidate any reduction potential of Cr(VI) to Cr(III). Fig. 5b displays the results of equilibrium chromium concentration after adsorption from a 100 mg L$^{-1}$ initial Cr(VI) solution. Cr(VI) undergoes reduction to Cr(III) at very acidic conditions$^{47,48}$ and this was observed in Fig. 4b at pH 2. The amount of total chromium in solution after adsorption was high, implying that the formed Cr(III) was repelled into solution.

The basicity character of ACs which is responsible for the reduction of Cr(VI) to Cr(III), is attributable to the presence of heteroatoms such as sulfur and nitrogen on the surface of ACs.$^{49}$ The higher values of equilibrium total chromium concentration suggested that MAC-EDT contained functional groups like heteroatoms or carbon-carbon double bonds capable of reducing Cr(VI) to Cr(III). Further precipitation of Cr(III) to Cr(OH)$_3$ following its reduction from Cr(VI) at neutral to basic conditions could explain the higher recoveries of Cr(III) at basic conditions.$^{49}$ At high concentrations and low pH conditions, HCrO$_4^–$ transforms to its dimerized form Cr$_2$O$_7^{2–}$.50

3.3. Effect of Adsorbent Dosage on Adsorption of Chromium(VI) Ion

Figure 6 displays the percentage removal of chromium(VI) as a function of adsorbent mass (0.02 to 0.14 g). It can be observed that the percentage removal increased from 92 % to 100 % when the sorbent dosage was increased from 0.02 to 0.10 g. This is because the number of the adsorption sites increased as the mass of the MAC-EDT was increased.$^{51}$ From 0.10 g to 0.12 g the percentage removal remained unchanged at 100 %, as it is known that up to a certain weight, the sorbent will reach equilibrium where no appreciable removal extraction will be registered.$^{51}$ An optimal mass of 0.10 g was used in subsequent experiments. Higher removal efficiency by MAC-EDT even at low dosages suggested that the grafted functional groups were well spread in the material as they were responsible for the removal of Cr(VI). On the other hand, the adsorption capacity (mg g$^{-1}$) generally decreases with increase in adsorbent mass and this can be explained by the inverse proportionality relationship between $q_e$ and $m$ in Equation (2).

![Figure 4](image1.png)

**Figure 4** SEM micrographs of MAC-EDT (a) and MAC (b).

![Figure 5](image2.png)

**Figure 5** Effect of solution initial pH and point of zero charge (inset) (a) and total Cr versus Cr(VI) concentration after adsorption with MAC-EDT (b) (Conditions: 100 mg L$^{-1}$ initial Cr(VI) solution; amount of adsorbent 0.1 g; solution volume 25 mL; contact time 2 h) ($n = 2$, error bars showing standard deviation).
3.4. Effect of Initial Concentration and Adsorption Modelling

The effect of initial solution concentration on the removal of Cr(VI) by MAC-EDT was evaluated by changing the concentration, while maintaining other parameters uniform. Almost 100% removal efficiency was achieved up to 100 mg L⁻¹ and then a decrease to 87% at 200 mg L⁻¹ was observed (Fig. 7a). The removal efficiency at higher concentrations decreased due to higher ratio of Cr(VI) ions present in solution as opposed to the number of available adsorption sites on the MAC-EDT. The adsorption capacity of MAC-EDT increased as Cr(VI) initial concentration was increased. Greater chances of Cr(VI) ions colliding with MAC-EDT surface at higher initial concentration of Cr(VI) were pronounced. The result of these interactions was the driving force overcoming all mass transfer resistances between the aqueous and solid phases leading to the sorption of Cr(VI) on MAC-EDT.

Figure 7b shows the trends obtained by fitting the adsorption experimental data to Freundlich and Langmuir isotherms. Langmuir isotherm fitted the MAC-EDT data best. Grafting of amino functionality onto MAC resulted in monolayer adsorption mechanism for Cr(VI).

The Langmuir constant b (described in Equation 3) is related to the free energy change of sorption, \( \Delta G \) (kJ/mol) according to the following formula:

\[
\Delta G = RT \ln b
\]

where R is the universal gas constant (8.314 J mol⁻¹ K⁻¹) and T is the temperature in Kelvin. Since the \( \Delta G \) value was in the range of -80 and -400 kJ mol⁻¹, the sorption was concluded to be chemisorption. A value between -20 and 0 kJ mol⁻¹ would have meant a physisorption adsorption mechanism. This conclusion was similar to that reported by Karmacharya et al. who used activated carbon derived from waste tyre rubber for the removal of arsenic from aqueous solution.

Table 2 summarizes the Langmuir and Freundlich constants. Although the coefficient of determination for the Freundlich model (\( R^2 = 0.825 \)) was higher than that of the Langmuir model (\( R^2 = 0.758 \)), the \( k_f \) value (64.34) which is an indication of the adsorption capacity, was very low as compared to the experimental (\( q_m \)). In contrast, the Langmuir adsorption capacity calculated value (\( q_m = 147.57 \) mg g⁻¹) was close to the experimental value (\( q_m = 145.49 \) mg g⁻¹). Therefore, it was deduced that MAC-EDT data was better described by the Langmuir model. Also, the Langmuir separation constant (\( R_L \)) values lied between 0.01 and 0.05, signifying favourable adsorption of Cr(VI) by MAC-EDT.

3.5. Effect of Contact Time and Kinetic Modelling

The effect of contact time (10–240 min) was investigated while keeping other parameters such as initial concentration (100 mg L⁻¹), pH (5) and sorbent dosage (4 g L⁻¹) at constant. For the first 30 min, the percentage removal of Cr(VI) by MAC-EDT was observed to increase steadily then reached equilibrium at about 60 min. However, 120 min was used as optimum to allow the reactions to reach completion.

Table 3 shows the results obtained by fitting time dependency data into PFO and PSO kinetic models. The PSO kinetic model fitted the MAC-EDT data better due to the observed higher \( R^2 \) value (0.919) and lesser MSq error (11.22). These results revealed that the chemisorption process was more favoured. It has also been reported elsewhere that the sorption of Cr(VI) by ACs followed the PSO kinetic rate model.
The influence of competing anions, phosphate, sulphate and nitrate, was investigated in a batch mode by using binary solutions with Cr(VI). In all solutions, the initial anion concentration was 100 mg L\(^{-1}\), solution pH 5, contact time was 2 h, adsorbent mass used was 0.1 g and volume of solution used was 25 mL. Following completion of reaction time, Cr(VI) remaining in solution was measured by the UV-Vis method. The removal efficiency of Cr(VI) in the presence of competing ions decreased compared to the control (Fig. 8). The interaction between the Cr(VI) species and the adsorbent is through ionic bonding due to the opposite charges on the adsorbent and adsorbate. Therefore, it is not surprising that the removal efficiency of Cr(VI) decreased a bit in the presence of other competing anions due to the fact that these competing ions also carry a negative charge while the adsorbent is positively charged. The order of removal of the anions was SO\(_4^{2-}\) < PO\(_4^{3-}\) = NO\(_3^-\) < CrO\(_4^{2-}\). It was generally found that the size of the anion played a key role in the suppression of the adsorption of the target Cr(VI). The biggest competitor, the sulphate ion, was seen to be preferentially adsorbed as compared to the phosphate and nitrate ions owing to the similarity of shapes and size between Cr(VI) species (CrO\(_4^{2-}\)) and SO\(_4^{2-}\). This sorption order was almost similar to what was observed by other researchers\(^{32}\). Fig. 8 also illustrates that high recoveries of Cr(VI) were obtained, implying that the grafting of amine groups improved the selective removal of Cr(VI). All the values for the percentage removals were >97 %, further signifying MAC-EDT was effective in adsorbing Cr(VI) in the presence of competing ions in binary solutions.

### 3.7. Comparison of MAC-EDT Adsorption Capacity with Other ACs

Table 4 shows the comparison of adsorption capacity, optimum pH and initial concentrations of different AC adsorbents. As can be seen in Table 4, the adsorption capacity of MAC-EDT was amongst the highest when compared to other ACs produced from agricultural waste materials. The effect of grafting EDT on the MAC which resulted in quaternization improved MAC-EDT adsorption capacity due to stronger electrostatic interaction taking place between the positively charged MAC-EDT surface and the negatively charged Cr(VI) ions.

### 4. Conclusions

Functionalized AC derived from *Macadamia* nutshell (MAC-EDT) was investigated for the adsorption of chromium(VI) from aqueous solutions. It was demonstrated in this study that MAC-EDT could be used as an effective adsorbent for Cr(VI) and optimum conditions found were pH 5, sorbent mass (0.1 g), initial concentration (100 mg L\(^{-1}\)), and contact time (2 h). It was further revealed that during Cr(VI) adsorption by MAC-EDT, fraction of the Cr(VI) was reduced to Cr(III) in almost the entire pH range evaluated. The implications were that MAC-EDT possessed functional groups (electron donors) that were capable of reducing Cr(VI) to Cr(III). While the amount of Cr(VI) left at pH 2 was lesser, the total Cr left at pH 2 was higher in relation to other pH’s indicating that adsorption and reduction took place. However, the amount of Cr(VI) at pH 2 and pH 5 was similar but the amount of total chromium left at pH 5 was lesser than pH 2. Therefore, pH 5 was chosen as optimum pH since it showed less reduction and similar adsorption of Cr(VI) as was observed at pH 2. Characterization of the MAC-EDT with FTIR before and after Cr(VI) adsorption revealed changes of material surface functional groups due to their involvement in chromium removal. The removal efficiency of Cr(VI) in the presence of competing anions was >98 % for all anions studied, PO\(_4^{3-}\), NO\(_3^-\) and SO\(_4^{2-}\) but Cr(VI) sequestration was affected most in the presence of sulphate ions. When compared to other plant based activated carbons in recent literature, MAC-EDT displayed a higher Langmuir adsorption capacity of 145.5 mg g\(^{-1}\) which puts MAC-EDT as an alternative adsorbent for the sequestration of Cr(VI) from aqueous solutions. Overall, MAC-EDT is an alternative adsorbent for the removal of Cr(VI) ions from aqueous solutions.

### Acknowledgements

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**Table 3** Kinetic modelling data for MAC-EDT

<table>
<thead>
<tr>
<th>Kinetic Models</th>
<th>Parameters</th>
<th>MAC-EDT</th>
</tr>
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<tbody>
<tr>
<td>Pseudo-first order</td>
<td>( k_1/\text{min}^{-1})</td>
<td>0.082</td>
</tr>
<tr>
<td></td>
<td>( q_{\text{cal}}/\text{mg g}^{-1})</td>
<td>66.82</td>
</tr>
<tr>
<td></td>
<td>( R^2)</td>
<td>0.886</td>
</tr>
<tr>
<td></td>
<td>MSq error</td>
<td>15.84</td>
</tr>
<tr>
<td>Pseudo-second order</td>
<td>( k_2/\text{g mg}^{-1} \text{min}^{-1})</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>( q_{\text{cal}}/\text{mg g}^{-1})</td>
<td>70.92</td>
</tr>
<tr>
<td></td>
<td>( R^2)</td>
<td>0.919</td>
</tr>
<tr>
<td></td>
<td>MSq error</td>
<td>11.22</td>
</tr>
</tbody>
</table>

Note, MSq = sum of squares divided by degrees of freedom.

**Table 4** Comparison of adsorption capacities from different plant derived activated carbon sorbents for Cr(VI) removal

<table>
<thead>
<tr>
<th>Activated carbon source</th>
<th>pH</th>
<th>Adsorption capacity/mg g(^{-1})</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jatropha</td>
<td>2</td>
<td>140.84</td>
<td>Gueye et al.(^{34})</td>
</tr>
<tr>
<td>Peanut shell</td>
<td>2</td>
<td>106.38</td>
<td>Gueye et al.(^{34})</td>
</tr>
<tr>
<td>Longan seed</td>
<td>3</td>
<td>35.02</td>
<td>Yang et al.(^{35})</td>
</tr>
<tr>
<td>Prawn shell</td>
<td>–</td>
<td>100</td>
<td>Arulkumar et al.(^{35})</td>
</tr>
<tr>
<td>Commercial AC</td>
<td>4</td>
<td>55.6</td>
<td>Jung et al.(^{35})</td>
</tr>
<tr>
<td>Tendu leaf refuse</td>
<td>2</td>
<td>92.5</td>
<td>Mane et al.(^{35})</td>
</tr>
<tr>
<td>Olive stones</td>
<td>1.5</td>
<td>71</td>
<td>Attia et al.(^{28})</td>
</tr>
<tr>
<td>Bael fruit shell</td>
<td>2</td>
<td>17.27</td>
<td>Anandkumar and Mandal(^{32})</td>
</tr>
<tr>
<td>Tamarind wood</td>
<td>5</td>
<td>28.02</td>
<td>Acharya et al.(^{38})</td>
</tr>
<tr>
<td>Waste of Bamboo</td>
<td>2</td>
<td>59.2</td>
<td>Dula et al.(^{34})</td>
</tr>
<tr>
<td>Arundo donax Linn</td>
<td>5</td>
<td>102.88</td>
<td>Sun et al.(^{34})</td>
</tr>
<tr>
<td>Macadamia nutshell (MAC-EDT)</td>
<td>5</td>
<td>145.5</td>
<td>This study</td>
</tr>
</tbody>
</table>

*Figure 8* Removal of Cr(VI) in the presence of competing ions in binary solutions (\( n = 2\), error bars showing standard deviation).
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References


