Adsorption of hexavalent chromium from aqueous solution by *Leucaena leucocephala* seed pod activated carbon: equilibrium, kinetic and thermodynamic studies

Adeyinka S. Yusuff

Department of Chemical and Petroleum Engineering College of Engineering, Afe Babalola University, Ado-Ekiti, Nigeria

**ABSTRACT**

This study is initiated to launch an activated carbon derived from *Leucaena leucocephala* seed pod as an adsorbent for the removal of hexavalent chromium from aqueous solution. The prepared activated carbon was characterized by proximate analysis, Brunauer-Emmett-Teller (BET) surface area measurement, scanning electron microscopic-energy dispersive X-ray (SEM-EDX) spectroscopy and Fourier transform infrared (FTIR) spectroscopy. The effects of various variables, initial Cr(VI) concentration, contact time, adsorbent dosage, temperature and pH, which influence the adsorption process, were investigated. Equilibrium adsorption isotherms, kinetic and thermodynamic behaviour of the process were studied. The pH at point of zero charge (pHpzc) of 5.20 suggested that surface of the activated carbon was positively charged for pH below the pHpzc, attracting anions. The obtained results showed that 100 min contact time, 1.0 g adsorbent dose, 45 °C temperature and solution pH of 6.0 resulted in maximum Cr(VI) uptake. The experimental data better fitted to the Langmuir isotherm with monolayer adsorption capacity of 26.94 mg/g. The kinetic analysis revealed that pseudo-second-order model fitted well to the acquired experimental data. The thermodynamic behaviour of Cr(VI) adsorption onto activated carbon was found to be spontaneous and endothermic in nature.

**1. Introduction**

The presence of toxic heavy metals in a water environment has been attributed to human and industrial activities, which has raised considerable public concern regarding the negative consequences on plants, animals (aquatic and terrestrial) and human lives (Lim & Lee, 2015). Intimate contact with toxic heavy metals such as copper, lead, nickel, cadmium and also chromium can lead to detrimental effects on flora and fauna (Singh, Gautam, Mishra, & Gupta, 2011). The chromium ion exists in two different oxidation states: trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)]. According to Gorzin and Abadi (2017), the second form is far more toxic than the other because of its high solubility in water. Therefore, it is necessary to treat industrial wastewater or effluent in order to reduce the concentration of Cr(VI) below the permissible level before discharging it into water bodies (Gorzin & Abadi, 2017).

Numerous treatment techniques have been employed to separate hexavalent chromium from wastewater. Coagulation, membrane separation, reverse osmosis, ion exchange, electro-Fenton process, co-precipitation, nanofiltration and adsorption are among these techniques. Due to high efficiency, low cost, eco-friendliness and simple operating conditions, adsorption is applied as a general purification process in many industries (Lim & Lee, 2015). The adsorption process is a unit operation involving separation of contaminants from liquid or gaseous mixture by using an appropriate porous solid material called adsorbent.

Recently, rapid removal of Cr(VI) from water/wastewater has been proven to be possible by use of activated carbon based adsorbents. Today research is therefore being focused on preparation of adsorbents from carbon based materials such as coconut tree sawdust (Selvi, Pattabhi, & Kadirvelu, 2001), walnut shell (Derdour, Bouchelta, Naser-Eddine, Medjram, & Magri, 2018), hazelnut shell (Koby, 2017), peanut shell (Al-Othman, Ali, & Naushad, 2012), paper mill sludge (Gorzin & Abadi, 2017), apricot stone (Abbas & Trari, 2015), corn cob (Murugesan, Vidhyadevi, Kirupha, Ravikumar, & Sivanesan, 2013), *Delonix regia* pods (Renuga, Manjusha, & Latitha, 2010), bamboo waste (Dula, Siraj, & Kitt, 2014), and palm seed-based biochar.
2. Materials and methods

2.1. Materials

The *Leucaena leucocephala* seed pods were picked up under the tree situated behind Owolabi Hall, Afe Babalola University, Ado-Ekiti, Nigeria. All the chemical compounds used in this study, including potassium hexa­toxochromate ($K_2Cr_2O_7$), sodium hydroxide (NaOH) and sulphuric acid (H$_2$SO$_4$), were of analytical grade purchased from Sigma-Aldrich and used as received. The commercial adsorbent used for comparison purposes was Burgoyne activated charcoal powder (Burbidges and Co. Mumbai, India) with 300 mesh particle size; 2.83 g of $K_2Cr_2O_7$ was dissolved in 1000 mL of distilled water in order to prepare 1000 mg/L of Cr(vi) stock solution. Various solutions of the necessary initial Cr(vi) concentrations were obtained by diluting the stock solution with the required amount of distilled water.

2.2. Preparation of activated carbon

The collected pods were opened to remove the seeds and thoroughly washed with distilled water to remove dust and other impurities. It was thereafter heated at 105°C for 24 h in an oven. The dried pods were crushed into smaller pieces by mortar and pestle and ground into powder with a mechanical grinder. The obtained powder was sieved to a particle size of 150 µm. In order to activate the powder, an aliquot of 30 g of the powder was soaked in 50 mL of 0.5, 1.0, 1.5, 2.0 and 2.5 M NaOH solutions and left overnight for full impregnation. The impregnate was heated overnight in an oven. The five samples were then carbonized at 550°C for two hours in a muffle furnace. The obtained *L. leucocephala* seed pods activated carbon samples which were treated using 0.5, 1.0, 1.5, 2.0 and 2.5 M NaOH solutions, and were denoted as LLAC-1, LLAC-2, LLAC-3, LLAC-4 and LLAC-5, respectively.

2.3. Characterization of activated carbon

The proximate properties such as yield recovery, bulk density and ash content were determined by applying standard procedures. The textural characteristics of the prepared activated carbon (LLAC) and CAC, including specific surface area, pore volume and pore diameter were determined by the Brunauer, Emmett, and Teller (BET) method using a Quantachrome instrument (Nova station A, version 11.03, USA) based on the principle of adsorption/desorption of nitrogen at 77 K and 60/60 s (ads/des) equilibrium time. The surface morphology and elemental composition of the LLAC samples were simultaneously examined using a scanning electron microscopic-energy dispersive X-ray (SEM-EDX, JEOL-JSM 7600F) spectroscope, while the surface functional groups present on the LLAC samples before and after adsorption of Cr(vi) as well as that of the CAC sample were determined by a Fourier transform infrared (FTIR) spectrophotometer (IR Affinity 1S, Shimadzu, Japan).
2.4. Determination of pH at point of zero charge (pH_{pzc}) of LLAC

Point of zero charge (pzc) of an adsorbent is a parameter that determines the net surface charge of the ion in solution. The pH at pzc (pH_{pzc}) is the value of pH at which the total external and internal surface of the ion is fixed at zero (Arlette, Jorge, & Ruben, 2012; Eletta, Ajayi, Ogunleye, & Akpan, 2016). The pH_{pzc} of LLAC was determined by the salt addition method (Nodoushan, Parvizi, Nodoushan, & Ghaneian, 2017). 0.5 g of LLAC sample and 50 mL of 0.010 M NaCl solution were mixed in six conical flasks. The solution pH was adjusted to the required initial pH (pHi) value of 2, 4, 6, 8, 10 and 12 by adding several drops of HCl (0.1 M) or NaOH (0.1 M) solution. The content in each flask was then agitated in an isothermal water bath shaker at 150 rpm for 36 h and the final pH (pHf) of each solution was carefully measured. The difference between the initial and final pH (pHf – pHi) of each solution was thereafter determined. The plot of (pHf – pHi) versus pHi was constructed and the pH_{pzc} was obtained as the intercept on an x-axis.

2.5. Batch adsorption studies

The influences of initial adsorbate concentration (50–250 mg/L), contact time (20–100 min), pH (2–10), adsorbent dosage (0.2–1.0 g) and temperature (25–45 °C) on the adsorption process were investigated. The batch mode adsorption experiments were conducted by bringing into contact the 50 mL of different Cr(VI) solutions with a specified quantity of as-synthesized LLAC in a set of each 250 mL conical flasks. The solution pH was adjusted to the required value and the content of each flask was agitated in a water bath shaker (SearchTech Instrument) operating at related temperature and a constant stirring rate of 150 rpm. After the equilibrium was attained, each sample was centrifuged at 350 rpm for 10 min and decanted. The concentration of un-adsorbed Cr(VI) was then determined by an Atomic Absorption Spectrophotometer (AAS, Buck Scientific 210VGP, USA). The Cr(VI) removal efficiency, R (%), and equilibrium amount of Cr(VI) adsorbed, q_{e}, mg/g, were calculated by Equations (1) and (2) below:

\[
R, \% = \left( \frac{C_o - C_e}{C_o} \right) \times 100\% \tag{1}
\]

\[
q_e = \frac{(C_o - C_e)V}{M} \tag{2}
\]

where \(C_o\) and \(C_e\) (mg/L) are the initial and equilibrium concentration of the Cr(VI) in aqueous phase. \(V\) (L) is the volume of the Cr(VI) solution, and \(M\) (g) is the mass of the activated carbon.

2.6. Equilibrium adsorption isotherm

The correlation between the amount of Cr(VI) adsorbed onto LLCA and the equilibrium concentration of Cr(VI) in the aqueous phase was evaluated using two-parameter isotherm models. The experimental data acquired was analysed by Langmuir and Freundlich models.

The Langmuir isotherm model is employed based on monolayer adsorption of adsorbate on homogeneous active sites and thus saturation is attained, beyond which no further attachment of adsorbate on adsorbent takes place. It also operates with the assumption that there is no interaction between the adsorbed molecules on adjacent sites (Oyedoh & Ekwonu, 2016). The non-linear model which was proposed by Langmuir (1918) is presented in Equation (3).

\[
q_e = \frac{q_{max}bC_e}{(1 + bC_e)} \tag{3}
\]

where \(q_{e}\) (mg/g) is the amount of Cr(VI) adsorbed at equilibrium, \(C_e\) (mg/L) is the equilibrium concentration of Cr(VI) in aqueous solution, \(q_{max}\) (mg/g) is the maximum adsorption capacity, and \(b\) is the Langmuir constant.

The separation factor (\(R_L\)) whose value determines the nature of the isotherm shape is an important feature of the Langmuir isotherm. It represents favourable (0 < \(R_L\) < 1), unfavourable (\(R_L\) > 1), linear (\(R_L\) = 1) or irreversible adsorption (\(R_L\) = 0). The dimensionless parameter is given by Equation (4).

\[
R_L = \frac{1}{1 + bC_o} \tag{4}
\]

where \(C_o\) (mg/L) is the maximum initial Cr(VI) concentration and \(b\) (L/mg) is the Langmuir equilibrium constant.

The Freundlich isotherm is the oldest known two-parameter adsorption model, which is applied for multilayer, heterogeneous adsorption sites and is expressed as follows (Freundlich, 1906).

\[
q_e = k_F C_e^{1/n} \tag{5}
\]

where, \(C_e\) (mg/L) is the equilibrium concentration of Cr(VI) in solution, \(k_F\) (mg/g(L/mg)^{1/n}) indicates the adsorption capacity of the adsorbent and \(n\) represents adsorption intensity.

2.7. Adsorption kinetics

Pseudo-first-order, pseudo-second-order and intraparticle diffusion models were applied to evaluate the experimental data in order to gain insight into the controlling mechanism of the adsorption of Cr(VI) onto LLAC. The linear forms of the pseudo-first-order (Langergren, 1898), pseudo-second-order (Ho &
Mckay, 1998) and intraparticle diffusion models are given in Equations (6–8), respectively.

\[
\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{6}
\]

\[
t = \frac{1}{k_2 q_e} + \frac{t}{q_e} \tag{7}
\]

\[
q_t = k_D t^{1/2} + C \tag{8}
\]

where \(q_e\) (mg/g) is the amount of Cr(VI) adsorbed at equilibrium, \(q_t\) is the amount of Cr(VI) adsorbed at time \(t\) (mg/g), \(k_1\) is the pseudo-first-order rate constant \((\text{min}^{-1})\), \(k_2\) is the pseudo-second-order constant \((\text{g mg}^{-1} \text{min}^{-1})\), \(k_D\) is the intraparticle diffusion rate constant \((\text{mg g}^{-1} \text{min}^{-0.5})\), and \(C\) is the intercept.

### 2.8. Adsorption thermodynamic study

The thermodynamic behaviour of Cr(VI) adsorption onto LLCA was evaluated based on the thermodynamic parameters including standard Gibbs free energy change, \(\Delta G^o\) (kJ/mol), enthalpy change, \(\Delta H^o\) (kJ/mol), and entropy change, \(\Delta S^o\) \((\text{J} \text{ mol}^{-1} \text{K}^{-1})\) which were determined using the following equations.

\[
\Delta G^o = -RT \ln K_c \tag{9}
\]

\[
\Delta G^o = \Delta H^o - T \Delta S^o \tag{10}
\]

\[
K_c = \frac{C_{\text{ad}}}{C_e} \tag{11}
\]

where \(C_{\text{ad}}\) is the adsorbed Cr(VI) concentration on the surface of the LLCA adsorbent, \(K_c\) is equilibrium constant, \(T\) (K) is the temperature and \(R\) \((8.314 \text{ J mol}^{-1} \text{K}^{-1})\) is the gas constant.

### 2.9. Adsorbent reusability study

The reusability of the adsorbent was tested to check its stability after reuse. The procedures reported by Gazi et al. (2018) were adopted in the present study.

0.75 g of Cr(VI) ions loaded-LLAC-3 was charged into a conical flask containing 20 mL of 0.5 M NaOH (desorption agent) and vigorously agitated for 100 min at 90°C. Consecutive desorption-adsorption experiments were thereafter conducted and the desorption efficiency was determined by dividing the mass of Cr(VI) ion regenerated by the mass of the metal ions adsorbed (Oladipo & Gazi, 2015). Regeneration characteristics of spent LLAC-3 adsorbent were further studied by considering the kinetic mechanism of Cr(VI) desorption. However, detailed studies on desorption kinetics for activated carbon have not been reported. In this work, the desorption kinetic has been considered using the pseudo-first-order and pseudo-second-order kinetic models (Equations (6) and (7)).

### 3. Results and discussions

#### 3.1. Characterization of activated carbon

The preliminary experiment revealed that LLAC-3 possessed active molecular adsorption sites and was able to adsorb a larger amount of Cr(VI) ions from aqueous solution compared with other prepared LLAC samples (Figure 1). Therefore, the LLAC-3 adsorbent was studied in more detail under different batch mode adsorption conditions to determine the optimum performance.

The results of elemental composition and ultimate analyses conducted on the LLAC are presented in Table 1. The prepared activated carbon contained 60.0% of carbon, which is the dominant element in the sample. The yield recovery of the LLAC was found to be 48.7%, which can be compared to the value of 49% for a Scirpus acutus stem activated carbon (Jambulingam, Karthikeyan, Sivakumar, Kiruthika, & Maiyalagan, 2007) and 36.25% for activated carbon prepared from orange peel (Sahu, 2015). However, the low yield of LLAC could be due to the method of preparation applied. The bulk density of the prepared activated carbon (0.523 g/cm³) was greater than that reported for Conocarpus pruning waste activated carbon (0.49 g/cm³) (El-Naggar, Alzhrani, Ahmad, Usman, & Alwabel, 2016), Ceiba pentandra shell activated carbon (0.48 g/cm³) (Jambulingam et al., 2007) and Pongamia pinnata shell activated carbon (0.33 g/cm³) (Jambulingam et al., 2007). The prepared activated carbon has low incombustible mineral matter content as indicated by the value of ash content (3.41%).

The textural properties of LLAC-3 and CAC including BET surface area, total pore volume and average pore radius are presented in Table 2. The BET surface area of LLAC-3 was found to be larger than that of CAC and the value of 88.05 m²/g reported for activated carbon prepared from apricot stone (Abbas et al., 2016).
The adsorption of Cr(VI) and identify and compare the particles was observed. Blocked and agglomeration of the occupied adsorbent pores on the surface of fresh LLAC-3 are observed (Figure 2(b)). In addition, the textural properties obtained suggest that the external surface of the LLAC-3 sample is occupied by active adsorption centres which facilitate rapid adsorption of Cr(VI) (Gorzin & Abadi, 2017). This is corroborated by the preliminary result presented in Figure 1. A similar observation was reported for removal of Cr(vi) from aqueous solution by using walnut shell based activated carbon (Ghasemi, Ghoreyshi, & Younesi, 2015). However, the pore radii obtained for both prepared and CAC indicated that they are mesoporous materials because their pore diameters fall between 2 and 50 Å. The pore radii obtained for both prepared and CAC indicated that they are mesoporous materials because their pore diameters fall between 2 and 50 Å. The findings of the present study agree reasonably well with the results reported by Tan, Abdullah, Lim, and Yeo (2017).

The SEM images of LLAC-3 before and after adsorption of Cr(vi) are depicted in Figure 2(a) and (b), respectively. As seen in Figure 2(a), the prepared activated carbon possesses an undefined structure with pores of different size on its rough surface which favours the adsorption of Cr(vi). However, there were changes in adsorbent structure due to Cr(vi) adsorption (Figure 2(b)). In addition, the observed pores on the surface of fresh LLAC-3 are blocked and agglomeration of the occupied adsorbent particles was observed.

In order to evaluate the mechanism of the adsorption of Cr(vi) and identify and compare the functional groups present on the surfaces of both the newly prepared activated carbon (LLAC-3) and CAC, the FTIR were recorded. Figure 3 depicts the FTIR spectra of the LLAC-3 sample before and after adsorption of Cr(vi) and CAC. The broad bands centred at 3431 to 3460 cm⁻¹ for the three samples correspond to the O–H groups which indicate physisorbed moisture on the adsorbent surface (Olutoye & Hameed, 2013). The band 1632 cm⁻¹, which was shifted to 1634 cm⁻¹ in used LLAC-3 sample can be attributed to the binding between Cr(vi) ions with C–O group (Gorzin & Abadi, 2017). The absorption band around 1462 cm⁻¹ is assigned to CH₃ antisymmetric deformation (Tan et al., 2017), while the band at 1427 cm⁻¹ is due to the C–O stretching of dimers or in-plane OH bending (Hameed, Krishni, & Sata, 2009). The presence of peak 1383 cm⁻¹ comes from the CH₂ symmetric deformation. The feature emerging at 941 cm⁻¹ confirms the formation of Cr=O chromate anion bonds which indicates adsorption of Cr(vi) onto LLAC-3 surface (Oyedoh & Ekwonu, 2016). The bands between 890 cm⁻¹ and 805 cm⁻¹ can be assigned to CH out-of-plane deformation. The peaks between 680 cm⁻¹ and 580 cm⁻¹ can be attributed to C≡C–H. The high efficiency of the prepared activated carbon in the removal of Cr(vi) ions from aqueous solution may be ascribed to the presence of the surface functional groups, among which carboxylic (C–O and C=O) and hydroxyl (OH) groups play the main role.

The value of pHₚᵢₐₚ on the surface of prepared activated carbon was determined to be 5.20 as can be seen in Figure 4. The result indicates that Cr(vi) adsorption is favourable at pH value higher than pHₚᵢₐₚ, while anion (HCrO₄⁻) adsorption is favoured at pH values lower than pHₚᵢₐₚ (Nomanbhay & Palanisamy, 2005). This suggests that adsorption of Cr(vi) is highly favourable at the value of pH less than 5.20 and this might be attributed to strong electrostatic attraction between anion (HCrO₄⁻) and protonated oxygen-containing functional groups (C–O and C=O) present on the surface of LLAC-3. The result obtained here is in agreement with the findings of many researchers who reported higher adsorption of Cr(vi) at pH values 3–6 (Doke & Khan, 2015). In addition, the total pore volume and average pore radius of the LLAC-3 sample were found to be higher than those of CAC. This implied that the modification of raw LLAC with 1.5 M aqueous NaOH solution which was coupled with carbonization at 550 °C for two hours successfully improved the surface properties of the prepared activated carbon. Thus, the textural properties obtained suggest that the external surface of the LLAC-3 sample is occupied by active adsorption centres which facilitate rapid adsorption of Cr(vi) (Gorzin & Abadi, 2017).

### Table 1. Elemental composition and proximate analyses of LLAC-3.

| Parameter | C | H | S | O | Yield recovery (%) | Bulk density (g/cm³) | Ash content (%) |
|-----------|---|---|---|---|-------------------|---------------------|------------------|
| Value     | 60 | 12 | 10 | 18 | 48.7              | 0.523               | 3.41             |

### Table 2. Textural properties of prepared and commercial activated carbons.

| Sample | BET surface area (m²/g) | Total pore volume (cm³/g) | Average pore diameter (Å) |
|--------|-------------------------|---------------------------|---------------------------|
| LLAC   | 89.74                   | 0.0232                    | 3.59                      |
| CAC    | 67.87                   | 0.0108                    | 2.88                      |

### Table 3. Two-parameter isotherm constants and correlation coefficients for adsorption of Cr(vi) onto LLAC-3.

| Isotherm | Value |
|----------|-------|
| Langmuir |       |
| qₘₐₓ (mg/g) | 26.94 |
| b (L/mg)   | 0.044 |
| R²         | 0.9873|
| Rₜ         | 0.083 |
| Freundlich |       |
| kᵢ (mg/gL/mg)¹/𝑛 | 2.64 |
| N          | 1.99  |
| R²         | 0.9634|
3.2. Effects of various variables on Cr(VI) adsorption

3.2.1. Effect of initial Cr(VI) concentration

The influence of the initial concentration (50–250 mg/L) on the removal of Cr(VI) from aqueous solution using 0.5 g adsorbent dose at 40 °C and pH of 6.0 was investigated. As shown in Figure 5, the equilibrium amount of Cr(vi) adsorbed increased from 4.53 to 19.36 mg/g and the removal efficiency decreased from 90.61 to 77.42% when initial adsorbate concentration was increased from 50 to 250 mg/L. These observations were due to the presence of the same active centres on the LLAC-3 surface despite the increase in the initial adsorbate concentration which leads to the saturation of the active centres on the adsorbent. A similar result was reported by studies on Cr(VI) removal from aqueous solution by paper mill sludge-based...
activated carbon (Gorzin & Abadi, 2017) and walnut shell-based activated carbon (Ghasemi et al., 2015). The decrease in the removal efficiency also reflects that the protons in the acidic medium could easily expand the pore diameter and thus reduce the surface area of the adsorbent (Caglar, Afsin, Koksal, Tabak, & Eren, 2013).

### 3.2.2. Effect of contact time

The effect of contact time (20–100 min) on the Cr(VI) removal efficiency and the amount of adsorption at equilibrium of Cr(VI) was investigated. When the contact time increased from 20 to 100 min, the removal efficiency of Cr(VI) from aqueous solution increased from 76.47 to 85.6% and the loading capacity of LLAC-3 increased from 3.82 to 4.28 mg/g as seen in Figure 6. It is obvious that rapid removal of Cr(VI) occurs during the first 20 min of the interaction. However, both output variables slow down slightly towards the equilibrium position. This observation may be attributed to the presence of more than enough surface adsorption sites on the surface that facilitates rapid attachment of Cr(VI) on LLAC-3 surface and penetration into the adsorbent pores in a short period of time (Kumar, Bishnoi, & Bishnoi, 2008; Seyf-Laye et al., 2018).

### 3.2.3. Effect of adsorbent dosage

Adsorbent dosage is another important factor affecting the adsorption process through determining the amount of adsorbate removed (Gorzin & Abadi, 2017). In the present study, the effect of adsorbent on removal of Cr(VI) from aqueous solution was determined by changing the doses of LLAC-3 from 0.2 to 1.0 g at 40 °C, for a contact time of 100 min and at a fixed initial Cr(VI) concentration of 50 mg/L. As shown in Figure 7, the removal efficiency of Cr(VI) increased from 78.55 to 89.47%, while adsorption capacity of LLAC-3 decreased from 9.82 to 2.23 mg/g when the adsorbent dosage was increased from 0.2 to 1.0 g. The discrepancy between the binding sites and holding capacity of the adsorbent makes it less efficient towards removal of Cr(VI) ions at low adsorbent dosage. However, when the adsorbent dosage is increased, more chromium ions are retained by excess surface centres which have not yet been saturated (Ridha, Ahmed, & Raoof, 2017). Therefore, adsorbent dosage of 1.0 g was chosen for the subsequent studies.

### 3.2.4. Effect of temperature

The influence of temperature on the adsorption process was studied in the temperature range of 25–45 °C. The removal efficiency of Cr(VI) from aqueous solution increased from 67.52% at 25 °C to 81.22% at 45 °C and loading capacity of LLAC-3 also increased from 1.74 to 2.03 mg/g as shown in Figure 8. Cr(VI) uptake increases with temperature and the positive effect of temperature on removal of Cr(VI) from aqueous solution is an indication that active sites present on the surface increase and thus improves adsorption performance (Yusuff, Olateju, & Ekanem, 2017). A similar observation was reported for heavy metal adsorption on NALCO plant sand (Mohapatra, Khatum, & Anand, 2009).

### 3.2.5. Effect of pH

The effect of pH on the adsorption of Cr(VI) from aqueous solution was investigated over a pH range of 2–10 while keeping other variables constant as follows: initial Cr(VI) concentration of 50 mg/L, 1.0 g adsorbent dosage, temperature of 45 °C and contact time of 100 min. The removal efficiency of Cr(VI) by 76.64% at pH 2 increased to 81.32% at pH 6.0, while the loading capacity of LLAC-3 showed a similar trend (Figure 9). The results obtained implied that the maximum Cr(VI) uptake by the LLAC-3 sample could be achieved in an acidic medium whereas the basic condition would not be in favour of efficient removal of Cr(VI) and loading capacity of the adsorbent. The hexavalent chromium exists in different
forms, such as HCrO$_4^-$, H$_2$CrO$_4$, Cr$_2$O$_2^{7-}$, and CrO$_2^{4-}$ in the aqueous phase as a function of pH, and among these chromium species HCrO$_4^-$ is more dominant in an acidic medium (Doke & Khan, 2017).

The pH dependency on adsorption of Cr(vi) can further be explained by chromium species speciation and the adsorbent surface at zero point charge (pH$_{pzc}$). At pH below pH$_{pzc}$, the LLAC-3 surface becomes positively charged, which facilitates a strong interaction between the anion (HCrO$_4^-$) and the adsorbent surface oxygen-containing functional groups (C=O, C=O and O-H) as shown in Equation (12). However, at pH above pH$_{pzc}$, the LLAC-3 becomes dominated by the hydroxyl group (OH$^-$), which inhibits attraction between the anions and the LLAC-3 surface, lowering the adsorbate uptake (Mohapatra et al., 2009; Gupta, Rastogi, & Naya, 2010). Therefore, at pH below pH$_{pzc}$, the interactions prevailing between the adsorbent centres and Cr(vi) ions could be described as of an electrostatic nature (Gupta et al., 2010).

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**Figure 6.** Effect of contact time on Cr(vi) adsorption at initial Cr(vi) concentration = 50 mg/L, adsorbent dosage = 0.5 g, temperature = 40 °C, and pH = 6.0.

**Figure 7.** Effect of adsorbent dosage on Cr(vi) adsorption at initial Cr(vi) concentration = 50 mg/L, contact time = 100 min, temperature = 40 °C, and pH = 6.0.

**Figure 8.** Effect of temperature on Cr(vi) adsorption at initial Cr(vi) concentration = 50 mg/L, contact time = 100 min, adsorbent dosage = 1.0 g, and pH = 6.0.


\[ \text{LLAC-OH}_2^+ + \text{HCrO}_4^- \rightarrow \text{LLACHCrO}_4^+ + \text{H}_2\text{O}, \quad \text{pH} < \text{pH}_{\text{pzc}} (5.20) \]  

(12)

where [LLAC–OH\(_2\)]\(^+\) represents one of the protonated functional groups on the surface of the adsorbent.

### 3.3. Adsorption isotherms

The data obtained from the batch adsorption experiments were analysed by non-linear forms of Langmuir and Freundlich isotherms. The validity of the models was compared, referring to the value of the linear correlation coefficient (\(R^2\)). The adsorption parameters of the two models (Equations (3) and (5)) determined from Figure 10 are listed in Table 3. The plot obtained from the experimental data is compared with those obtained from the Langmuir and Freundlich isotherm models in Figure 10, and this model fits better the acquired experimental results. The values of \(R^2\) suggest that the Langmuir isotherm provides the best conformity with experimental data. Thus, it indicates that LLAC-3 contains uniform adsorption sites and thus enables the anion species to form a monolayer. A similar result was reported for Cr(\(vi\)) removal from aqueous solution by peanut shell (Al-Othman et al., 2012), walnut shell (Ghasemi et al., 2015), bamboo waste (Dula et al., 2014) and paper mill sludge (Gorzin & Abadi, 2017).

The value of separation factor (\(R_L\)), which was obtained as 0.083 at optimum conditions, indicated that the adsorption of Cr(\(vi\)) onto LLAC-3 is a favourable process. This is corroborated by the value of the Freundlich exponent (\(n = 1.99\)) which is higher than 1.0 (Table 3).

### 3.4. Adsorption kinetics

Adsorption kinetic parameters were determined following the pseudo-first-order, pseudo-second-order and intraparticle diffusion models and are listed in
Figure 11. (a) Pseudo-first-order, (b) pseudo-second-order and (c) intraparticle diffusion models for adsorption of Cr(Ⅵ) by prepared activated carbon at different initial concentrations. Plot of InKc against 1/T (K⁻¹) for the adsorption of Cr(Ⅵ) onto LLAC-3 between 298–318 K.

Figure 12. Plot of lnKc against 1/T (K⁻¹) for the adsorption of Cr(Ⅵ) onto LLAC-3 between 298–318 K.
In the present study, kinetic analysis was carried out at three initial Cr(VI) concentrations: 50, 150 and 250 mg/L. The linear plots of the three models for Cr(VI) adsorption onto LLAC-3 are depicted in Figure 11. The best fitting model was chosen based on the linear correlation coefficient ($R^2$). The values of $R^2$ for all initial concentrations of Cr(VI), which are generally lower than 0.970 (Table 4), indicate that the pseudo-first-order model does not fit the adsorption experiment data well. However, the $R^2$ values (0.988–0.9983) coming from the pseudo-second-order model suggest a better fit of the model with the experimental data. Therefore, it may be concluded that the adsorption process of Cr(VI) by LLAC-3 is of the type chemisorption controlled.

As seen in Figure 11(c), the plot of $q_t$ against $t^{1/2}$ is not linear, indicating that the adsorption process of Cr(VI) onto LLAC-3 involves more than one step. In the first step, the mass transfer of the adsorbate to the external surface of the adsorbent takes place. The intraparticle transport of adsorbate in the adsorbent pores occurs in the second step. The values of $R^2$ for the three initial concentrations found when the intraparticle diffusion model is applied are lower than those for the pseudo-second-order model (Table 4), which is further evidence supporting a better correlation between pseudo-second-order model and the experimental data.

### 3.5. Thermodynamics of adsorption

The values of thermodynamic parameters for adsorption of Cr(VI) by LLAC-3 were determined from Figure 12 and are listed in Table 5. The negative $\Delta G^o$ values determined at all temperatures indicate that the adsorption process is spontaneous in nature. The positive value of $\Delta S^o$ highlights the affinity of the prepared activated carbon towards Cr(VI) ions and also an increased degree of disorder at the adsorbent/adsorbate interface (Ridha et al., 2017), and occurrence of some structural changes during the adsorption process (Yusuff, Gbadamosi, Lala, & Ngochindo, 2018). The positive value of $\Delta H^o$ suggests an endothermic nature of the adsorption of Cr(VI) by the adsorbent over the temperature range of 298–318 K. The value of $\Delta H^o$, which is below the value corresponding to physical adsorption (Abbas & Trari, 2015) indicates that Cr(VI) ions are physisorbed to the LLAC-3 surface. A similar observation was reported for Cr(VI) adsorption onto walnut shell (Ghasemi et al., 2015), activated carbon resorcinol formaldehyde xerogels (Oyedoh & Ekwonu, 2016) and paper mill sludge (Gorzin & Abadi, 2017).

### 3.6. Adsorbent reusability study

The adsorption-desorption efficiencies of the LLAC-3 after three cycles are presented in Table 6. Desorption efficiencies for the three cycles conducted were 63.42%, 58.22% and 47.56%,
respectively. The reason for the reduction in regeneration efficiency is probably due to the repeated desorption process on the LLAC-3 adsorbent, which decreased its adsorption capacity (Fatma, Hariani, Riyanti, & Sepriani, 2018). In addition, several metal ions cannot be separated from the adsorbent due to the saturation of the active centres of the adsorbent by Cr(VI) ions.

Also, the application of NaOH as a desorption agent increases the pH of the solution and enhances the negativity of the LLAC-3 surface. Therefore, electrostatic force between negatively charged adsorbent and positively charged Cr(VI) ions reduces the desorption process (Gazi et al., 2018). Finally, it is important to note that further improvement or optimization may be considered by varying pH, temperature, and contact time. Application of several desorption agents as well as their effects on desorption efficiency is necessary due to the prevailing world environmental needs.

### 3.7. Desorption kinetics

Desorption kinetic data obtained were analysed using pseudo-first-order and pseudo-second-order models. The values of parameters contained in the two models were determined from the combined plots of log(\(q_e - q_t\)) against t and \(t/q_t\) against t (Figure 13) and are presented in Table 7. The correlation coefficient \(R^2\) value of the pseudo-second-order kinetic model was found to be 0.999, which is greater than the \(R^2\) value obtained for the pseudo-first-order kinetic model. Thus, the desorption of Cr(vi) from spent LLAC-3 could be better described by the pseudo-second-order kinetic model.

### 3.8. Comparison of prepared activated carbon with CAC and other adsorbents

The performances of the Leucaena leucocephala seed pod based activated carbon and commercial activated carbon (CAC) were compared by using each adsorbent separately for the removal of Cr(vi) from aqueous solution under optimum conditions: 50 mg/L initial Cr(VI) concentration, 100 min contact time, 1.0 g adsorbent dosage, 45°C temperature and solution pH of 6.0. The Cr(vi) removal efficiencies by the prepared activated carbon and CAC were determined as 90.68% and 77.92%, respectively. The performance of the newly prepared activated carbon is seen well above the adsorption efficiency of CAC, which may be ascribed to its large BET surface area and the presence of the active functional groups at the surface, which enhances the adsorption process.

A comparison of the maximum monolayer adsorption capacity of Cr(VI) on Leucaena leucocephala seed pod based activated carbon with some other adsorbents used previously for Cr(VI) removal (Table 8) showed that the prepared activated carbon possessed larger adsorption capacity (26.94 mg/g), implying that LLAC could be considered as an efficient adsorbent for the removal of heavy metals from aqueous medium.

### 4. Conclusion

In this work, the ability of activated carbon derived from Leucaena leucocephala seed pod to remove Cr(vi) from aqueous solution was investigated. It was found that the prepared activated carbon acted as an effective adsorbent for the removal of Cr(vi) from
aqueous solution. Since the *Leucaena leucocephala* tree is abundantly and locally available, it may be regarded as an economically viable raw material for removing toxic heavy metals from aqueous medium. Equilibrium data were well described by the Langmuir model with the monolayer adsorption capacity of 26.94 mg/g at optimum conditions. The pseudo-second-order kinetic model was best fitted with the experimental data, indicating chemisorption of Cr(VI) by the newly prepared activated carbon. Studies on thermodynamic behaviour of Cr(VI) adsorption showed that the process was spontaneous and endothermic in nature. Higher performance of *Leucaena leucocephala* seed pod based activated carbon for the removal of Cr(VI) than commercial activated carbon imply that the LLAC adsorbent can be regarded as an efficient material and viable adsorbent for the removal of heavy metals from an aqueous environment.

**Disclosure statement**

No potential conflict of interest was reported by the author.

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