Kinetics, equilibrium and thermodynamics investigation on the adsorption of Cr (VI) ions from wastewater using activated *Kigelia africana* rind nano carbon

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**ABSTRACT**

The goal of this research is to investigate the feasibility of using activated *Kigelia africana* rind nano carbon (KANC) to adsorb Cr (VI) ions from aqueous solutions through batch experiments. Effect of contact time, initial Cr(VI) ion concentration, activated KANC dose, initial solution pH, other ions and temperature on the Cr (VI) ions adsorption were examined. The sorption process was examined by applying Elovich, pseudo-second order and intraparticle diffusion rate. The best pH for Cr (VI) ions removal is in the range of 2.0-7.0 with more than 80-85% of Cr (VI) ions removed. The equilibrium time was found to be 45min and the adsorption data followed the pseudo-second-order kinetics. Isotherm data followed Langmuir isotherm model. The adsorption was endothermic and spontaneous in nature.

Keywords: Adsorption, *Kigelia africana* nano carbon, Cr (VI), Isotherm, Kinetics, Thermodynamics, Equilibrium models.
1. Introduction

Chromium has been considered as one of the top 16th toxic pollutants and because of its carcinogenic and teratogenic characteristics on the public, it has become a serious health concern [1-3]. Chromium is a redox active element, with oxidation states from +2 to +6, but only the +3 and +6 states are prevalent in the aquatic environment. The two environmentally stable oxidation states, Cr(III) and Cr(VI), exhibit very different toxicities and mobilities [4]. Cr(III) is relatively insoluble in aqueous systems, and exhibits little or no toxicity [5]. In contrast, Cr(VI) usually occurs as the highly soluble and toxic chromate anion, and is a suspected carcinogen and mutagen [6]. Chromium is used in a variety of applications including tanning processes, electroplating, steel production, anodizing of aluminium, wood preservation, pigmentation, catalyst, and as corrosion inhibitors [7-11]. The maximum levels permitted in wastewater are 5mg/l for trivalent and 0.05 mg/l for hexavalent chromium [12]. Therefore removal of Cr (VI) ions from wastewater is very important for public health. The various methods adopted for the removal of Cr (VI) ions are chemical precipitation [13], ion exchange [14], solvent extraction [15] and adsorption [16]. Among these methods, adsorption has been proved to be an efficient and economical technique [17].

In the present investigation the adsorption of chromium (VI) ions onto activated carbon prepared from rinds of Kigelia africana nano carbon by carbonization with sulphuric acid has been achieved. The kinetic and equilibrium adsorption data obtained were utilized to characterize the sample prepared [7]. The amounts and rates of adsorption of Cr (VI) ion using activated KANC from wastewater were then measured. Three simplified kinetic models including pseudo-second-order and Elovich equations intraparticle diffusion model were used to describe the adsorption process.

2. Materials and methods

All the reagents used for the current investigation were of GR grade. Stock solution (1000 mg/L) of Cr(VI) was prepared by dissolving 5.6578g of K₂Cr₂O₇ in double distilled water. The solution was further diluted to the required concentrations before use. Before mixing the activated
KANC, the pH of each Cr (VI) solution was adjusted to the required value by 0.1 M NaOH or 0.1 M HCl solution.

2.1 Preparation of activated KANC

*Kigelia africana* rinds were collected from local area of Pudukkottai district, Tamilnadu, India (Fig.1). It was dried, charred with excess quantity of concentrated sulphuric acid keeping at 120°C for 10 h. Then the resultant carbon was washed with excess quantity of distilled water and dried at 110°C for 1 h and the material obtained was soaked in 5% sodium bicarbonate solution and allowed to stand overnight to remove any residual acid. The material was thoroughly washed with hot distilled water until washings were nearly of neutral effect. To eliminate surface groups by thermal activation, the carbonized material was treated at 1100 ºC for 6 h in a furnace [18]. The resulting carbons were ground in a mill, washed with pure water and finally dried at 120 ºC. The dried powders were sieved by a mesh.

![Fig.1 Kigelia africana plant](image)

2.2 Adsorbent characterization

The characterization of activated KANC was performed by means of spectroscopic and quantitative analysis. The surface area of the activated KANC was determined by Quanta chrome surface area analyzer. The pH of aqueous slurry was determined by soaking 1g of biomass in 50 mL distilled water, stirred for 24 h and filtered and the final pH was measured [19]. The physicochemical characteristics of the activated KANC were determined using standard procedures and are list in Table 1 [20]. The concentrations of sodium and potassium were determined by Flame Photometer (Model
No. Systronics126). The equilibrium Cr(VI) concentration was determined by using 1,5-diphenylcarbazide as the complexing agent and a UV-VIS Spectrophotometer (Systronics, Vis double beam Spectro 1203) at a $\lambda_{\text{max}}$ of 540 nm. For stirring purpose magnetic stirrer was used. The pH of zero-point charge or $\text{pH}_{\text{ZPC}}$ was determined based on the previous method [20].

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{pH}_{\text{slurry}}$</td>
<td>5.5</td>
</tr>
<tr>
<td>$\text{pH}_{\text{zpc}}$</td>
<td>6.00</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>0.195</td>
</tr>
<tr>
<td>Moisture content, %</td>
<td>0.105</td>
</tr>
<tr>
<td>Bulk density, g cm$^{-3}$</td>
<td>0.117</td>
</tr>
<tr>
<td>Particle density, g cm$^{-3}$</td>
<td>0.285</td>
</tr>
<tr>
<td>Conductivity, $\mu$S/cm</td>
<td>41.63</td>
</tr>
<tr>
<td>Surface area, m$^2$/g</td>
<td>25.25</td>
</tr>
<tr>
<td>Na$^+$, mg L$^{-1}$</td>
<td>98</td>
</tr>
<tr>
<td>K$^+$, mg L$^{-1}$</td>
<td>440</td>
</tr>
</tbody>
</table>

### 2.3 Batch Adsorption experiments

The Batch adsorption experiments were conducted in 250 mL Erlenmeyer flask with 50mL of standard Cr(VI) ion solution and were agitated in a thermo state-controlled shaker at 120 rpm. All experiments were conducted at 30-60 °C.

The effect of initial pH on the adsorption of the Cr(VI) ion onto the activated KANC was studied across a pH range of 2.0-9.0 with a fixed activated KANC concentration (25 mg/50ml of 20mgL$^{-1}$ of Cr(VI) ion solution). The pit value of the initial metal solution (50mgL$^{-1}$) was adjusted using a 0.1M HCl or NaOH solution. Activated KANC (0.0250g) was then added to the solution and agitated for enough time to achieve equilibrium. The effect of the agitation period was also studied at a constant concentration of 20 mg L$^{-1}$ Cr(VI) ion solution and a fixed activated KANC concentration of 25mg/50mL at the optimum pH. After agitation the sample solution was withdrawn at different
time intervals (15-60min) and centrifuged at 1000 rpm for 10 min. Subsequently an aliquot of the supernatant was used for determination of the remaining Cr(VI) ion concentration, and the remainder was poured back into the original solution.

The determination of the effect of the initial concentration of the uptake of the Cr(VI) ion was conducted by varying the Cr(VI) ion concentration from 10 to 50 mg L\(^{-1}\) at a constant activated KANC dosage of 25 mg at optimum pH and agitation period.

The effect of temperature on the adsorption characteristics was studied by determining the adsorption isotherms from 303 - 333K at a Cr(VI) ion concentration of 10-50mg/L.

The percentage removal of the Cr(VI) ions and the amount of Cr(VI) ions taken up by the activated KANC was calculated by applying following equations.

\[
\% \text{ Removal} = \frac{C_i - C_t}{C_i} \times 100 \quad \text{...................................(1)}
\]

\[
Q = \frac{(C_i - C_t)}{m} V \quad \text{.......................... (2)}
\]

Where \(C_i\) and \(C_t\) are the initial and liquid phase concentrations of Cr(VI) at time ‘t’ (mg L\(^{-1}\)) \(Q\) is the amount of Cr(VI) ion adsorbed on the activated KANC of at any time (mg g\(^{-1}\)), \(m\) (g) the mass of the activated KANC used and \(V\) the volume of the Cr(VI) ion solution (L).

3. Results and Discussion

3.1 Effect of contact time

The effect of contact time on the adsorption of Cr (VI) ions using activated KANC was studied and the results are shown in figure 1. From the results, it was observed that the adsorption of Cr(VI) ions from an aqueous solution reached equilibrium within 45 min. The adsorption of Cr(VI) ions by activated KANC sharply increased in the first 45 min. The rapid adsorption at the initial stage was probably due to the great concentration gradient between the Cr(VI) ions in solution and the Cr(VI) ions in the activated KANC because there must be a number of vacant sites available in the beginning [21]. The progressive increase in adsorption and, consequently, the attainment of equilibrium adsorption is initially due to the limited mass transfer of the Cr(VI) ions from the bulk solution to the
external surface of the activated KANC, and is subsequently due to the slower internal mass transfer within the adsorbent particles [22].

![Graph showing effect of contact time on Cr(VI) ion removal]

**Fig: 2- Effect of contact time on the removal of Cr(VI) ion**

[Cr(VI)]=20 mg/L; dose=0.025g/50ml; Temp.=30°C; pH=6.7

### 3.2 Effect of initial Cr(VI) ion concentration

The experimental results of adsorption of Cr(VI) ions on the activated KANC at various initial concentration (10, 20, 30, 40 and 50 mg/L) for Cr (VI) ions in terms of equilibrium data are given in Table 2.

**Table: 2. Equilibrium parameters for the adsorption of Cr (VI) ion onto activated KANC**

<table>
<thead>
<tr>
<th>Cr (VI) ion concentration (mg/L)</th>
<th>C_e (mg / L)</th>
<th>Q_e (mg / g)</th>
<th>Cr (VI) ion Removed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>10</td>
<td>1.9082</td>
<td>1.4082</td>
<td>1.1588</td>
</tr>
<tr>
<td>20</td>
<td>3.4082</td>
<td>3.1594</td>
<td>2.9187</td>
</tr>
<tr>
<td>30</td>
<td>6.6788</td>
<td>6.1093</td>
<td>5.4083</td>
</tr>
<tr>
<td>40</td>
<td>9.4292</td>
<td>8.6794</td>
<td>8.2668</td>
</tr>
<tr>
<td>50</td>
<td>13.658</td>
<td>13.207</td>
<td>12.930</td>
</tr>
</tbody>
</table>
The initial concentration provides an important driving force to overcome the mass transfer resistance of all of the molecules between the aqueous and solid phase, the Fig.2 plots the percentage of Cr(VI) ion removal versus the initial Cr(VI) ion concentration of the KANC. While increasing the initial Cr(VI) ion concentration from 10 to 50 mgL⁻¹, the percentage of Cr(VI) ion removal by the KANC decreased from 86-75% respectively, the percentage removal of the Cr(VI) ion decreased slowly in the concentration range of 10-50 mgL⁻¹, but reduced rapidly from 10 to 30 mgL⁻¹ Cr(VI) ion removal is highly concentration dependent at higher concentrations. This can be explained by the fact that the activated KANC has a limited number of active sites that become saturated above a certain concentration [23]. At low Cr(VI) ion concentrations, the ratio of surface active sites to the total Cr(VI) ion in the solution is high and hence all Cr(VI) ion may interact with the active functional groups on the surface of the activated KANC and be removed from the solution. However, with increased Cr(VI) ion concentrations, the number of active adsorption sites is not enough to accommodate the Cr(VI) ion. Therefore, the initial Cr(VI) ion concentration was fixed at 20 mg L⁻¹ in the following experiments.

3.3 Effect of activated KANC dose

In this study, five different activated KANC dosages were selected ranging from 0.025 to 0.125 g while the Cr(VI) concentration was fixed at 20 mg/L. The results are presented in Fig. 3. From the results, it was observed that percentage of Cr(VI) ion removal increased with increase in activated KANC dose. Such a trend is mostly attributed to an increase in the sorptive surface area and the availability of more active binding sites on the surface of the activated KANC. This may be due to the decrease in total adsorption surface area available to Cr(VI) ion resulting from overlapping or aggregation of adsorption sites. Thus with increasing activated KANC mass, the amount of Cr(VI) ion adsorbed onto unit mass of adsorbent gets reduced, thus causing a decrease in qₑ value with increasing adsorbent mass concentration. Furthermore maximum Cr(VI) ions removal (85.86%) was recorded by 0.025 g activated KANC and further increase in activated KANC dose did not significantly change the
adsorption yield. This is due to the non-availability of active sites on the activated KANC and establishment of equilibrium between the Cr(VI) ion on the adsorbent and in the solution.

![Graph showing the effect of adsorbent dose on the removal of Cr(VI) ion](image)

**Fig 3:** Effect of adsorbent dose on the removal of Cr(VI) ion

- $[\text{Cr(VI)}]=20\text{mg/L}; \text{contact time }45\text{ min}; \text{pH}=6.7; \text{Temp. }30^\circ\text{C}$

### 3.4 Effect of initial solution pH

Adsorption of Cr (VI) ion onto activated KANC was carried out to examine the effect of pH (in a range of 2-9) on the removal of aged disperse Cr(VI) ion from aqueous solution and the results are represented in the Figure 4. From the results, it was observed percent Cr(VI) ions removal increased rapidly with the increase in pH of the solution initially, and the optimal pH as observed at 6.7. Further increase in pH, causes a drastic decrease in the adsorption percentage and the maximum percentage removal of Cr (VI) ions is 87.7%. This might be due to the weakening of electrostatic force of attraction between the oppositely charged Cr (VI) ions and activated KANC which ultimately leads to the reduction in sorption capacity [24]. The pH of an initial Cr(VI) ion solution exerts profound influence on the adsorptive uptake of adsorbate molecules, presumably due to its influence on the surface properties of the adsorbent and ionization/ dissociation of the adsorbate molecule [25, 26].
Therefore investigation of the effect of pH on the adsorption process is helpful to determine the optimized operational parameters for application and to reveal the adsorption mechanism [27].

![Graph showing the effect of initial pH on the removal of Cr(VI) ion](image)

**Fig.4- Effect of initial pH on the removal of Cr(VI) ion**

[C(VI)] = 20 mg/L; contact time = 45 min; dose = 0.025 g/50 ml; Temp. 30°C

### 3.5 Effect of other ions

The effect of other ions like Cl⁻ on the adsorption process studied at different concentrations. The ions added to 20 mg/L of Cr(VI) ion solutions and the contents were agitated for 60 min at 30 °C. The results had reveals that low concentration of Cl⁻ does not affect the percentage of adsorption of Cr(VI) ion on activated KANC, because the interaction of Cl⁻ at available sites of adsorbent through competitive adsorption is not so effective. This is so because ions with smaller hydrated radii decrease the swelling pressure within the sorbent and increase the affinity of the sorbent for such ions [28, 29].

### 3.6 Effect of Temperature

It is well known that temperature plays an important role in the adsorption process. The Cr(VI) ions removal increase rapidly from 303K to 333K, this result suggests that the experimental
temperature had a greater effect on the adsorption process implying that the surface coverage increased at higher temperatures. This may be attributed to the increased penetration of Cr(VI) ion inside micro pores or the creation of new active sites at higher temperatures. This indicates the endothermic nature of the controlled adsorption process.

3.7 Adsorption isotherm models

Adsorption isotherms [30-34] describes the relation between the amount or concentration of adsorbate that accumulates on the adsorbent and the equilibrium concentration of the dissolved adsorbate. Equilibrium studies were carried out by agitating a series of beakers containing 100 mL of Cr(VI) solutions of initial concentration 20 mg/L with 0.025 g of activated KANC at 30°C with a constant agitation. Agitation was provided for 1.0 h, which is more than sufficient time to reach equilibrium.

Formula used for calculation of $q_e$ is as follows:

$$q_e = \frac{C_0 - C_e}{m} X V$$

.................(3)

3.7.1 Freundlich adsorption isotherm

The Freundlich adsorption isotherm is based on the equilibrium sorption on heterogeneous surfaces. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to heat of adsorption. The Freundlich adsorption isotherm [35] is expressed by the following equation:

$$q_e = K_F C_e^{1/n_F}$$

................. (4)

Which, can be linearized as,

$$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e$$

.................(5)

Where, $q_e$ is the amount of Cr(VI) adsorbed at equilibrium (mg/g) and $C_e$ is the concentration of Cr(VI) in the aqueous phase at equilibrium (ppm). $K_F$ (L/g) and $1/n_F$ are the Freundlich constants related to adsorption capacity and sorption intensity, respectively.
The Freundlich constants $K_F$ and $1/n_F$ were calculated from the slope and intercept of the $\ln q_e$ Vs $\ln C_e$ plot, as shown in Fig. 5, and the model parameters are shown in Table 3. The magnitude of $K_F$ showed that the activated KANC had a high capacity for Cr(VI) ions adsorption from the aqueous solutions studied. The Freundlich exponent, $n_F$, should have values in the range of 1 and 10 (i.e., $1/n_F < 1$) to be considered as favourable adsorption [36]. A $1/n_F$ value of less than 1 indicated that Cr(VI) is favorably adsorbed by the activated KANC. The Freundlich isotherm did not show a good fit to the experimental data as indicated by SSE and Chi-square statistics.

![Fig. 5 Freundlich adsorption isotherm for the removal of Cr(VI) ion](image)

**3.7.2 Langmuir adsorption isotherm**

The Langmuir adsorption isotherm is based on the assumption that all sorption sites possess equal affinity to the adsorbate. The Langmuir isotherm in a linear form [37] can be represented as:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad \text{.................(6)}$$
Where, $q_e$ is the amount of Cr(VI) adsorbed at equilibrium (mg/g), $C_e$ is the concentration of Cr(VI) in the aqueous phase at equilibrium (ppm), $q_m$ is the maximum Cr(VI) uptake (mg/g), and $K_L$ is the Langmuir constant related to adsorption capacity and the energy of adsorption (g/mg).

A linear plot of $C_e/q_e$ Vs $C_e$ was employed to determine the value of $q_m$ and $K_L$, as shown in Fig. 6, and the data so obtained were also presented in Table 3.

**Table 3. Langmuir and Freundlich isotherm parameters for the adsorption of Cr (VI) ions onto activated KANC**

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Constant</th>
<th>Temp., °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td><strong>Freundlich</strong></td>
<td>$K_f$ (mg/g) (L/mg)$^1/n$</td>
<td>11.3793</td>
</tr>
<tr>
<td></td>
<td>$N$</td>
<td>1.35494</td>
</tr>
<tr>
<td><strong>Langmuir</strong></td>
<td>$Q_m$ (mg/g)</td>
<td>148.888</td>
</tr>
<tr>
<td></td>
<td>$b$ (L/mg)</td>
<td>0.07140</td>
</tr>
</tbody>
</table>

The model predicted a maximum value that could not be reached in the experiments. The value of $K_L$ decreased with an increase in the temperature. A high $K_L$ value indicates a high adsorption affinity. The Langmuir isotherm in term of dimensionless constant separation factor or equilibrium parameter ($R_L$) defined in the following equation:

$$R_L = \frac{1}{1+K_L C_0} \quad \text{(7)}$$

Where, $C_0$ is the initial Cr(VI) concentration (ppm). Four scenarios can be distinguished:

The sorption isotherm is unfavorable when $R_L > 1$, the isotherm is linear when $R_L = 1$, The isotherm is favorable when $0 < R_L < 1$ and the isotherm is irreversible when $R_L = 0$. The values of dimensionless separation factor ($R_L$) for Cr(VI) removal were calculated at different concentrations and temperatures. As shown in Table 4, at all concentrations and temperatures tested the values of $R_L$ for Cr(VI) adsorptions on the activated KANC were less than 1 and greater than zero, indicating favorable adsorption.
Table: 4. Dimensionless separation factor ($R_L$) for the adsorption of Cr(VI) ion onto activated KANC

<table>
<thead>
<tr>
<th>Cr (VI) ion concentration (mg/L)</th>
<th>Temp., °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>0.3591</td>
</tr>
<tr>
<td>20</td>
<td>0.2188</td>
</tr>
<tr>
<td>30</td>
<td>0.1573</td>
</tr>
<tr>
<td>40</td>
<td>0.1228</td>
</tr>
<tr>
<td>50</td>
<td>0.1008</td>
</tr>
</tbody>
</table>

The Langmuir isotherm showed a better fit to the adsorption data than the Freundlich isotherm as shown in Fig. 5 and Fig. 6. The fact that the Langmuir isotherm fits the experimental data well may be due to homogeneous distribution of active sites on the activated KANC surface, since the Langmuir equation assumes that the activated KANC surface is energetically homogeneous.
3.5 Kinetic parameters

The rate and mechanism of the adsorption process can be elucidated based on kinetic studies. Cr(VI) adsorption on solid surface may be explained by two distinct mechanisms: (1) An initial rapid binding of Cr(VI) molecules on the adsorbent surface; (2) relatively slow intra-particle diffusion. To analyze the adsorption kinetics of the Cr(VI), the pseudo-second-order and intra-particle diffusion models were applied. The model and its linear mode equation [38] is presented below:

<table>
<thead>
<tr>
<th>Model</th>
<th>Nonlinear Form</th>
<th>Linear Form</th>
<th>Number of Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pseudo-second-order</strong></td>
<td>dq/dt = k₂(qₑ-qₜ)²</td>
<td>t/qₑ = 1/k₂qₑ² + (1/qₑ)t</td>
<td>(8)</td>
</tr>
</tbody>
</table>

Where, qₑ and qₜ refer to the amount of Cr(VI) adsorbed (mg/g) at equilibrium and at any time, t (min), respectively and k₂ (g/mg.min) is the equilibrium rate constant of pseudo-second order model.

In the pseudo-second order model, the slope and intercept of the t/qₑ Vs t plot were used to calculate the second-order rate constant, k₂. The values of equilibrium rate constant (k₂) are presented in Table 7. According to Table 5, the value of R² (0.999) related to the pseudo-second order model revealed that Cr(VI) adsorption followed this model.

3.5.1 Simple Elovich Model

The simple Elovich model [39] is expressed in the form,

\[ q_t = q_l + \beta \ln t \]  \( \quad \text{(9)} \)

Where, qₜ is the amount adsorbed at time t, α and β are the constants obtained from the experiment. A plot of qₜ against ln t should give a linear relationship for the applicability of the simple Elovich kinetic. The Elovich kinetics of Cr(VI) on to activated KANC for various initial concentrations (10, 20, 30, 40 and 50 mg/L) of volume 50 mL (each), adsorbent dose 0.025g, temperature 28 °C and pH 6.0.

The Elovich model equation is generally expressed as

\[ \frac{dq_t}{dt} = \alpha \exp (-\beta q_t) \]  \( \quad \text{(10)} \)
Where; \( \alpha \) is the initial adsorption rate (mg g\(^{-1}\) min\(^{-1}\)) and \( \beta \) is the desorption constant (g/mg) during any one experiment. To simplify the Elovich equation, it is assumed that \( \alpha \beta t \gg t \) and by applying boundary conditions \( q_t = 0 \) at \( t = 0 \) and \( q_t = q_e \) at \( t = t \) Eq.(10) becomes:

\[
q_t = \frac{1}{\beta} \ln (\alpha \beta) + \frac{1}{\beta} \ln t 
\]

Since, Cr (VI) ions adsorption fits with the Elovich model, a plot of \( q_t \) vs. \( \ln(t) \) should yield a linear relationship with a slope of \( (1/\beta) \) and an intercept of \( (1/\beta) \ln (\alpha \beta) \). The Elovich model parameters \( \alpha, \beta, \) and correlation coefficient (\( \gamma \)) are summarized in Table 5. The experimental data such as the initial adsorption rate (\( \alpha \)) adsorption constant (\( \beta \)) and the correlation coefficient (\( \gamma \)) calculated from this model indicates that the initial adsorption (\( \alpha \)) increases with temperature similar to that of initial adsorption rate (\( h \)) in pseudo-second–order kinetics models. This may be due to increase the pore or active site on the activated KANC.

### 3.9.2 The Intraparticle diffusion model

The kinetic results were analyzed by the Intraparticle diffusion model to elucidate the diffusion mechanism [40, 41]. The model is expressed as [42]:

\[
q_t = K_{id} t^{1/2} + I
\]

Where \( I \) is the intercept and \( K_{id} \) is the intra-particle diffusion rate constant. The intercept of the plot reflects the boundary layer effect. Larger the intercept, greater is the contribution of the surface sorption in the rate controlling step. The calculated diffusion coefficient \( K_{id} \) values are listed in table 5. The \( K_{id} \) value was higher at the higher concentrations. Intraparticle diffusion is the sole rate-limiting step if the regression of \( q_t \) versus \( t^{1/2} \) is linear and passes through the origin. In fact, the linear plots at each concentration did not pass through the origin. This deviation from the origin is due to the difference in the rate of mass transfer in the initial and final stages of the sorption. This indicated the existence of some boundary layer effect and further showed that Intraparticle diffusion was not the only rate-limiting step.

### Table 5. The Kinetic parameters for the adsorption of Cr (VI) ion onto activated KANC
Cr (VI) ion concentration (mg/L) | Temp., °C | Pseudo-second-order | Elovich model | Intraparticle diffusion |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
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<td>k&lt;sub&gt;2&lt;/sub&gt;</td>
<td>γ</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td>19.702</td>
<td>0.0035</td>
<td>0.9834</td>
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<td></td>
<td>40</td>
<td>18.476</td>
<td>0.0098</td>
<td>0.9835</td>
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<td></td>
<td>50</td>
<td>18.459</td>
<td>0.0166</td>
<td>0.9891</td>
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<tr>
<td></td>
<td>60</td>
<td>18.463</td>
<td>0.0177</td>
<td>0.9861</td>
</tr>
<tr>
<td>20</td>
<td>30</td>
<td>36.533</td>
<td>0.0035</td>
<td>0.9895</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>36.784</td>
<td>0.0039</td>
<td>0.9842</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>37.142</td>
<td>0.0044</td>
<td>0.9875</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>37.642</td>
<td>0.0049</td>
<td>0.9837</td>
</tr>
<tr>
<td>30</td>
<td>30</td>
<td>49.657</td>
<td>0.0037</td>
<td>0.9845</td>
</tr>
<tr>
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<td>40</td>
<td>51.383</td>
<td>0.0041</td>
<td>0.9902</td>
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<tr>
<td></td>
<td>50</td>
<td>53.405</td>
<td>0.0034</td>
<td>0.9887</td>
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<td></td>
<td>60</td>
<td>53.018</td>
<td>0.0050</td>
<td>0.9903</td>
</tr>
<tr>
<td>40</td>
<td>30</td>
<td>65.591</td>
<td>0.0037</td>
<td>0.9878</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>65.985</td>
<td>0.0035</td>
<td>0.9836</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>67.732</td>
<td>0.0037</td>
<td>0.9867</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>68.692</td>
<td>0.0037</td>
<td>0.9898</td>
</tr>
<tr>
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<td>30</td>
<td>77.610</td>
<td>0.0022</td>
<td>0.9845</td>
</tr>
<tr>
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<td>40</td>
<td>78.658</td>
<td>0.0021</td>
<td>0.9904</td>
</tr>
<tr>
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<td>78.830</td>
<td>0.0023</td>
<td>0.9839</td>
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<td>60</td>
<td>80.576</td>
<td>0.0021</td>
<td>0.9862</td>
</tr>
</tbody>
</table>

It is clear from the Table 5, that the pseudo-second-order kinetic model showed excellent linearity with high correlation coefficient (R<sup>2</sup>&gt;0.99) at all the studied concentrations in comparison to the other kinetic models. In addition, the calculated q<sub>e</sub> values also agree with the experimental data in the case of pseudo-second-order kinetic model. It is also evident from table 5 that the values of the rate
constant $k_2$ decrease with increasing initial Cr (VI) concentrations. This is due to the lower competition for the surface active sites at lower concentration but at higher concentration the competition for the surface active sites will be high and consequently lower sorption rates are obtained.

### 3.8 Adsorption Thermodynamics

Thermodynamic parameters were evaluated to confirm the adsorption nature and the inherent energetic changes involves during sorption [43]. The thermodynamic constants, free energy change, enthalpy change and entropy change were calculated to evaluate the thermodynamic feasibility and the spontaneous nature of the process [44]. Enthalpy change ($\Delta H$), and entropy change ($\Delta S$) may be determined from Van’t Hoff equation:

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \text{ .................................. (13)}$$

By plotting ln K as ordinate and 1/T as abscissa, we will get $\Delta S$, $\Delta H$ and by using the following equation. We can get the value of have $\Delta S$, $\Delta H$ and by this equation, get the value of $\Delta G$.

$$\Delta G = \Delta H - T\Delta S \text{ ......................... (14)}$$

Where, $\Delta G$ is the free energy change (kJ mol$^{-1}$), $R$ is the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $K$ the thermodynamic equilibrium constant and $T$ is the absolute temperature (K).

$$\Delta G = \Delta H - T\Delta S = -RT \ln K_e \text{ ................. (15)}$$

$$\ln K_e = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \text{ ................. (16)}$$

$$2.30 \log \frac{q_e}{C_e} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \text{ ................. (17)}$$

$$\log \frac{q_e}{C_e} = \frac{\Delta S}{R \times 2.303} - \frac{\Delta H}{RT \times 2.303} \text{ ................. (18)}$$

The values of $\Delta S$, $\Delta H$, $\Delta G$ was obtained from a plot of log ($q_e/C_e$) vs. 1/T.

Heat of reaction (-$\Delta H$) for physical adsorption is reported to be -3 to 63 kJ/mol in literature. The value of $-\Delta H$ range from -3 to -22 kJ/mol from Table 6 which indicate that the nature of adsorption of Cr(VI) onto activated KANC is physical adsorption. The negative value of $\Delta H$ and $\Delta G$ indicates exothermic and spontaneous process of adsorption of Cr(VI) onto activated KANC.
respectively [45]. The positive value of $\Delta S$ reflects the affinity of the activated KANC for the Cr (VI) ions and suggests some structural changes in adsorbate and adsorbent [46].

In order to support that physical adsorption is the predominant mechanism, the values of activation energy ($E_a$) and sticking probability ($S^*$) were calculated from the experimental data [47]. They were calculated using modified Arrhenius type equation related to surface coverage ($\theta$) as follows [48]:

$$\theta = \left(1 - \frac{C_s}{C_i}\right) \quad \ldots \ldots (19)$$

$$S^* = (1 - \theta) e^{-\frac{E_a}{RT}} \quad \ldots \ldots (20)$$

The sticking probability, $S^*$, is a function of the adsorbate/adsorbent system under consideration but must satisfy the condition $0 < S^* < 1$ and is dependent on the temperature of the system [49]. The values of $E_a$ and $S^*$ can be calculated from slope and intercept of the plot of $\ln(1-\theta)$ versus $1/T$ respectively and are listed in Table 6.

Table: 6. Thermodynamic parameters for the adsorption of Cr (VI) ion onto activated KANC

<table>
<thead>
<tr>
<th>Cr (VI) ion concentration (mg/L)</th>
<th>$\Delta G^o$ (KJ/mol)</th>
<th>$\Delta H^o$ (KJ/mol)</th>
<th>$\Delta S^o$ (KJ/mol)</th>
<th>$E_a$</th>
<th>$S^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30 40 50 60</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>-3639.3 -4706.2 -5456.8 -5695.5</td>
<td>-17.458</td>
<td>70.229</td>
<td>14887.8</td>
<td>0.0005</td>
</tr>
<tr>
<td>20</td>
<td>-3987.1 -4354.7 -4744.7 -5504.6</td>
<td>-10.915</td>
<td>48.938</td>
<td>9332.26</td>
<td>0.0043</td>
</tr>
<tr>
<td>30</td>
<td>-3150.0 -3548.7 -4067.0 -4416.6</td>
<td>-9.9544</td>
<td>43.239</td>
<td>8018.14</td>
<td>0.0092</td>
</tr>
<tr>
<td>40</td>
<td>-2963.1 -3339.6 -3612.2 -3927.5</td>
<td>-6.6325</td>
<td>31.739</td>
<td>5207.95</td>
<td>0.0296</td>
</tr>
<tr>
<td>50</td>
<td>-2465.3 -2666.1 -2828.3 -3130.4</td>
<td>-4.0491</td>
<td>21.452</td>
<td>3001.47</td>
<td>0.0834</td>
</tr>
</tbody>
</table>

From Table 6, it is illustrated that the reaction is spontaneous in nature and also confirms that the sorption is exothermic in nature. The positive value of $\Delta S^o$ reflects the affinities of the activated KANC for the Cr(VI) ions. From Table 6, It was observed that the probability of the Cr(VI) to stick on surface of biomass is very high as $S^*<< 1$, these values confirm that, the sorption process is physisorption [50, 51].
3.10 Desorption studies

In order to assess the reusability of chromium-loaded activated KANC desorption experiments were carried out [52, 53]. The effect of strength of desorbing solution (NaOH) on the recovery of Cr (VI) ion. When the strength of the desorbing solution increased from 0.5 to 2.0 M, Cr (VI) desorption percentage increased from 28.5% to 79%. Thus a significant amount of Cr (VI) ion is being desorbed, which shows that the activated KANC biomass can be effectively reused after desorption.

4. Conclusion

This study highlights the potential of using activated KANC as an efficient adsorbent for Cr (VI) ion in wastewater to remove. The adsorption of Cr (VI) ions onto activated KANC was affected by pH, adsorbent dosage, and temperature. The Cr (VI) ion uptake percentage by activated KANC was found to be 85% when 0.025 g of activated KANC was agitated with 50mL of Cr(VI) solution of 20 mg/L for 45 min at pH 6.7. The adsorption data was fitted well by pseudo-second order kinetic indicating that chemical reaction is involved in the adsorption process. The temperature equilibrium data fitted well with Langmuir isotherm. An increase of $Q_m$ value with the increase of temperature implied that chemisorption occurs in the process. Thermodynamic constants were also evaluated using equilibrium constants from Langmuir isotherm. The negative values of $\Delta G^0$ and $\Delta H^0$ indicated the spontaneity of Cr(VI) adsorption process and the positive value of $\Delta S^0$ showed the endothermic nature. In conclusion, high adsorption capacity and rapid adsorption suggested activated KANC may be a promising adsorbent for removing Cr (VI) ions from wastewater.

References


