Arsenic removal using chemically modified Kigelia Africana as a low-cost bio-adsorbent: Equilibrium, Kinetics and Thermodynamics studies

Virender Yadav1*, D.P. Tiwari1,2, Mamta Bhagat1

1Department of Chemical Engineering, Deenbandhu Chottu Ram University of Science and Technology, Murthal, (Sonipat) Haryana
2Rajiv Gandhi Government Engineering College, Nagrota Bagwan Taluka (Kangra) Himachal Pradesh

Received: 10 May Revised: 18 May Accepted: 26 May

Abstract

Removal of As (III) from aqueous solution using Kigelia Africana carbons produced by chemically modified is executed in this paper. The Kigelia Africana carbons surface characteristics were studied by FTIR, SEM, and XRD. The influence of different operating parameters such as initial concentration, contact time, amount of adsorbent, temperature, and pH was investigated, and isotherm models and adsorption kinetics on Kigelia Africana carbons are also examined. Under the following conditions, the amount of adsorbent 50 mg, pH of solution 7 with 180 min, the maximum percentage removal was found to be 95.8 %. The equilibrium data were followed by the Langmuir adsorption isotherm model. The maximum adsorption capacity can be calculated 84.21 mg/g by using the Langmuir adsorption isotherm model. The results show that the pseudo-second-order model best depicts adsorption kinetic data. The thermodynamic parameters, such as a change in enthalpy (ΔH°), change in Gibb's free energy (ΔG°), and entropy change (ΔS°), were investigated. The negative estimations of ΔG° at different temperatures affirmed that spontaneity of process at all given temperatures. The positive values of ΔH° confirmed that the adsorption process was endothermic nature.

Keywords: As (III), Adsorption, Activated carbon, Isotherm, Kinetics.

1. Introduction

Water contamination is the ebb and flow issue running all through the world. The arrival of harmful substances in water as a loss by mechanical areas unbalancing the normal earth procedures. Arsenic is an exceedingly dangerous substance for every single living creature [1]. World Health Organization demonstrated this component as a human cancer-causing substance [2]. Arsenic is found in two structures As(III) and As(V)) on the earth and all its structure is effectively solvent in water even dangerous too. As poisonous quality relies upon substance development, so inorganic arsenic mixes, most are the most harmful structures. Numerous examinations have been accounted for its expanded dangers of related ailments with the utilization of mineral water in groupings of less than 50 µg/L [3–6]. Numerous business arsenic expulsion advances incorporate adsorption,
precipitation, and layer forms [7–9] among them; sorption is found so straightforward, effective and minimal effort arsenic evacuation system, particularly advantageous for use in rustic zones. A broad scope of adsorbent materials for watery arsenic evacuation is accessible these days: organic compounds [10], mineral oxides, various soils, initiated carbonaceous materials [11] and polymer gums [12,13]. By and by, achieved modest and active arsenic adsorbents are still profoundly attractive. As detailed in the ongoing article, certain agrarian and also common side-effects, for example, rice husks, squander parasitic tea biomass, fly slag, and red mud was observed to be tremendous and economical arsenic adsorbents [14]. What's more, the use of modern squanders in water treatment pursues the reuse-reuse idea. Adsorbents ought to resemble what is locally accessible, cheap, and with high expulsion effectiveness. Moreover, the warm treatment of the adsorbent additionally improves the physical characteristics of a compound which support the adsorption procedure, (for example, specific surface territory and porosity) [15]. The present analysis addresses the application of chemically modified Kigelia Africana carbons as adsorbents for the elimination of As (III) from aqueous solution. The SEM, BET, XRD, and FTIR methods were utilized to characterize the Kigelia Africana carbons. The various operating parameter, such as contact time, initial concentration, the dosage of adsorbent, temperature, and pH, were investigated. The experimental data have been studied for various adsorption isotherm models. The kinetics data have also been analyzed for adsorption kinetics models. Thermodynamics parameters were studied using change in enthalpy $\Delta H^\circ$, change in Gibb’s free energy $\Delta G^\circ$, and change in entropy $\Delta S^\circ$.

2. **Material and methods**

2.1 **Materials**

A stock arrangement of As (III) was readied (1000 mg/L) by dissolving fitting measure of arsenic trichloride (AR grade) in twofold refined water. All diluted solution prepared in double distilled water to obtain the desired concentration.

2.2 **Preparation of activated carbon from Kigelia Africana**

The Kigelia Africana fruits were collected and kept for solar dry. After drying, fruits were crushed in small piece followed washing with double distilled water and dried in an air oven at 105 °C for 24 hours. The carbonization of crushed materials was done sulfuric acid and further kept in a muffle furnace at 600 °C for 2 hours. The excess sulfuric acid was removed with double distilled water till seven pH was attained. The washed adsorbent was then dried in an oven at 105 °C for 6 for further uses.

3. **Experimental section:**

3.1 **Batch Setup**

The batch method was selected for further experiments. Influence of initial concentration, contact time, pH, adsorbent dose, and temperature were examined at different conditions which affect the removal efficiency. The % removal efficiency was calculated by the equation:
3.2. Equilibrium study

To justify the adsorption phenomenon and also to look out for adsorption parameters that verify the adsorption system during the operation, the number of isotherm models engaged in terms of adsorption equilibrium study like Freundlich, Langmuir, Dubinin – Radushkevich (D-R) and Temkin isotherm models.

\[ \frac{C_e}{q_e} = \left( \frac{1}{K_L q_m} + \frac{C_e}{q_m} \right) \]  

\[ R_L = \frac{1}{(1+K_L C_o)} \]  

Freundlich isotherm \[ \log q_e = \log K_f + \frac{1}{n} \log C_e \]  

Temkin isotherm \[ q_e = B \ln A_T + B \ln C_e \]  

Dubinin – Radushkevich \[ \ln q_e = \ln q_m - (\beta e^2 2) \]  
\[ \varepsilon = RT \ln[1 + \frac{1}{C_e}] \]  
\[ E = \frac{1}{\sqrt[n]{\varepsilon}} \]  

3.3. Kinetic study:

The energy that gives the effectiveness of adsorbent regarding time variety, and furthermore chooses the request of the response. Pseudo-1st-order, Pseudo-2nd-order, and Intra-Particle diffusion models were employed to evaluate various parametric constant in respect of efficiency of the adsorbent.

Pseudo – 1st – order: \[ \ln(q_e - qt) = \ln q_e - \frac{K_1}{2.303} t \]  

Pseudo – 2nd – order: \[ \frac{1}{q_t} = \left( \frac{1}{K_2 q_e^2} \right) = \frac{1}{t} \frac{1}{q_e} \]  

Intra-particle diffusion: \[ qt = K_{id} t^{0.5} + C \]  

3.4. Thermodynamic study:

The thermodynamic properties such as \( \Delta G^o \), \( \Delta H^o \), and \( \Delta S^o \) were examined using the following Equation:
3.5. Characterization of the adsorbent:

The adsorbent was characterized with the help of techniques such as FTIR, SEM, and XRD to ensure that the surface characterization, binding functional group, and crystallinity information.

4. Results and discussion

4.1. Materials characterization

Figure 1(a) shows the SEM pictures of Kigelia Africana, which concludes that few pits have been included during carbonization because of the dissipation of unstable natural mixture. In Figure 1 (b), the XRD spectrum illustrates that amorphous kind of adsorbent surface. The functional group is developed after carbonization of adsorbent is shown in Figure 1 (c). The various peak arises on the adsorbent surface were around at 3709 cm\(^{-1}\), 2945 cm\(^{-1}\) and 1514 cm\(^{-1}\), confirms that sharp hydroxyl groups, a methyl group, and aromatic functional group respectively.

\[ K_c = \frac{C_e}{C_0 - C_e} \]  
\[ \Delta G^o = -RT \ln K_c \]  
\[ \ln K_c = \left( \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \right) \]

Fig.1 (a) SEM image of Kigelia Africana carbon (b) XRD image of Kigelia Africana carbon (c) FTIR spectrum of Kigelia Africana carbon
4.2. Influence of parameters through the batch setup

Effect of initial concentration was analyzed through varying initial concentration of heavy metal ion from 50 to 100 mg/L with fixation of adsorbent dose and pH value. From the figure 2 (a) it was concluded that with an arsenic concentration of 50mg/L, % removal increased up to 95%, whereas adsorption capacity increased 78.3 mg/g upon increasing concentration to 100mg/L. Due to that, the existing site of adsorbent not fully used at maximum adsorbent dosage corresponding to minimum adsorbent dosage. Hence, the adsorption capacity depends upon the adsorbent dosage [16].

Effect of residence time graph confirms that upon varying residence time for adsorbate-adsorbent interaction from 30-210 min, % removal, as well as adsorption capacity, increased 46.1 mg/g at 210 min. More will be an interaction between adsorbate and adsorbent more will be adsorption [17].

Effect of the adsorbent dose was chosen for varying limits 5-50 mg while other factors were fixed. It was observed by the figure 2 (c) that initially % removal was less because of less number of active sites availability but later on getting large active sites % removal was also increased up to 95.8% [17].

Effect of pH was done for acidic or basic nature of adsorbate ion with limit from 1-12. For low pH % removal was less as well as adsorption due to acidic nature but at neutral pH % removal was high 47.9% and then again for high pH value % removal was decreased because of high basic nature. It was due to the reason that zero net positive charge effect [18,19].

Effect of temperature was checked for 20°, 30°, 40°, 50° and 60° C with fixation of other factors. From the graph n, it was clear that % removal increased on varying temperature because at high-temperature molecule becomes active, pores expanded and ready to provide high surface area so that adsorbate molecule can get readily adsorbed on to the surface of the adsorbent and result in high adsorption.
Fig. 2 (a) Effect of the initial concentration of As (III) on Kigelia Africana carbons (b) Effect of contact time and (c) Effect of Kigelia Africana carbons dosage on adsorption of As (III) (d) effect of pH (e) Effect of temperature

4.3. Adsorption isotherms:

To understand the mechanism of the adsorption, various isotherms utilized such as Freundlich, Langmuir, Dubinin–Radushkevich, and Temkin Isotherm concerning different parameters [20]. From
figure 3 observation and calculated parameters, it was concluded that Langmuir isotherm was the best fitted and estimated the highest value of 84.21 mg/g for the adsorption capacity and confirms the monolayer adsorption phenomena. The value of n>1 affirms that the Kigelia Africana carbons are suitable adsorbent for removal of As (III) [21]. Other isotherms were also quite fitted concerning the regression coefficient $R^2 > 0.90$. All the calculated parameters for each isotherm reported in Table 1.

![Figure 3](image-url)

**Fig. 3** (a) Langmuir isotherm (b) Freundlich isotherm (c) Temkin isotherm and (d) D-R adsorption isotherm models

<table>
<thead>
<tr>
<th>Models</th>
<th>Metals ion</th>
<th>As III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$q_m$ (mg/g)</td>
<td>84.21</td>
</tr>
<tr>
<td></td>
<td>$K_L$ (L/mg)</td>
<td>0.6418</td>
</tr>
<tr>
<td></td>
<td>$R_L$</td>
<td>0.0302</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.9998</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$1/n$</td>
<td>0.2085</td>
</tr>
</tbody>
</table>
### 4.4. Kinetics

Kinetic models can determine the efficiency of the adsorbent. For this purpose, Pseudo-1st-order plot, Pseudo-2nd-order plot, intraparticle diffusion plot models were chosen to find out the order of reaction, the rate constant, and whether diffusion occurs inside the pores and outside the pores.

Upon analysis, it was confirmed that adsorption phenomena follows pseudo-2nd-order behavior and comes under chemisorptions. This model was found the best fitted for arsenic removal with adsorption capacity 55.32 mg/g over pseudo-1st-order kinetics. On the other hand, the intra-particle diffusion plot indicates that point on to graph don’t cross the origin, which means that diffusion depends on the boundary layer effect, and it occurs only on the outside of pores. However, the diffusion coefficient value is $2.232 \times 10^{-9} (g \text{ mg}^{-1} \text{ min}^{-0.5})$, which is very nominal for a diffusion process to occur. All the parameters presented in Table 2 below.

Thermodynamic properties were found by variations of temperature and equilibrium constant. Endothermic nature of the adsorption process is confirmed by an increase in the equilibrium constant on increasing temperature. A plot between $\ln K_c$ vs. $1/T$ present Van’t Hoff plot that gives the linearity over variations of temperature. A negative value of $\Delta G^\circ$ indicates the spontaneous process, and the positive value of $\Delta H^\circ$ and $\Delta S^\circ$ confirms the endothermic nature of the process.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of data points ($n$)</td>
<td>4.7964</td>
</tr>
<tr>
<td>Temkin ($K_T$ (mg/g))</td>
<td>4.4584</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
</tr>
<tr>
<td>Temkin ($A_T$ (L/mg))</td>
<td>108.26</td>
</tr>
<tr>
<td></td>
<td>$b_T$</td>
</tr>
<tr>
<td></td>
<td>$B$</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
</tr>
<tr>
<td>Dubinin-Radushkevich ($q_s$ (mg/g))</td>
<td>11.73</td>
</tr>
<tr>
<td></td>
<td>$K_{ad}$ (mol KJ$^{-1}$)</td>
</tr>
<tr>
<td></td>
<td>$E$ (KJ/mol)</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
</tr>
</tbody>
</table>
**Fig. 4** (a) Pseudo-1st-order plot (b) Pseudo-2nd-order plot (c) Intraparticle diffusion plot (d) Von’ Hoff plot

**Table 2** Summary of parameters for various kinetic models for As III on Kigelia Africana carbons

<table>
<thead>
<tr>
<th>Kinetic Model</th>
<th>Parameter</th>
<th>As III</th>
<th>Thermodynamic Parameters</th>
<th>As III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-1st-order</td>
<td>( q_e ) (mg/g)</td>
<td>9.194</td>
<td>( \Delta H^\circ ) (KJ/mol)</td>
<td>23.930</td>
</tr>
<tr>
<td></td>
<td>( k_1 ) (1/min)</td>
<td>0.013</td>
<td>( \Delta S^\circ ) (KJ/mol K)</td>
<td>0.1033</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.9944</td>
<td>( R^2 )</td>
<td>0.9359</td>
</tr>
<tr>
<td>Pseudo-2nd-order</td>
<td>( q_e ) (mg/g)</td>
<td>55.32</td>
<td>( -\Delta G^\circ \times 10^5 ) (kJ/mol)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( K_s ) (g/mg min)</td>
<td>0.0005</td>
<td>293 (K)</td>
<td>6.050</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.9945</td>
<td>303 (K)</td>
<td>7.877</td>
</tr>
</tbody>
</table>
From the comparison study, it was found that in the past years, arsenic was removed by different adsorbents such as activated carbon prepared from different raw materials, clay ash reported various adsorption capacities. But this study reported the highest value for adsorption capacity of 84.21 mg/g, as presented in Table 3 below.

**Table 3 Comparison between adsorption capacities of different activated carbons for As III from aqueous solutions**

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>As III (mg/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron ore sludge</td>
<td>1.113</td>
<td>[22]</td>
</tr>
<tr>
<td>Solvent extracted olive pulp carbons</td>
<td>1.393</td>
<td>[23]</td>
</tr>
<tr>
<td>GAC treated with FeCl₂</td>
<td>2.0</td>
<td>[24]</td>
</tr>
<tr>
<td>Char prepared from oak wood</td>
<td>5.85</td>
<td>[25]</td>
</tr>
<tr>
<td>Char prepared from oak bark</td>
<td>7.40</td>
<td>[25]</td>
</tr>
<tr>
<td>Pine bark char</td>
<td>12.15</td>
<td>[25]</td>
</tr>
<tr>
<td>AC impregnated iron oxide</td>
<td>32.86</td>
<td>[26]</td>
</tr>
<tr>
<td>Iron modified activating carbon</td>
<td>39.2</td>
<td>[27]</td>
</tr>
<tr>
<td>ZrPACM-43 hybrid material</td>
<td>41.49</td>
<td>[28]</td>
</tr>
<tr>
<td>Kigelia Africana carbon</td>
<td>84.21</td>
<td>This Study</td>
</tr>
</tbody>
</table>

5. **Conclusion:**

In this study, we have confirmed the ability of Kigelia Africana carbon to eliminate As (III) in aqueous solution. The Kigelia Africana carbon was characterized using various techniques such as SEM, XRD, and FTIR. The surface area, average pore size, and total pore volume were found to be 79.67 m²/g, 7.15 nm, and 0.22 cc/g, respectively. The percentage of removal and adsorption capacity are much dependent on the initial adsorption concentration of arsenic (III), contact time, adsorbent dosage, pH, and temperature. Under the best condition using 50 mg of Kigelia Africana carbon at 30 °C, with 180 min, percentage removal of Arsenic (III) was 95.8 % observed. The adsorption equilibrium data can follow to be a Langmuir isotherm model with the highest correlation coefficient ($R^2 = 0.9998$). The
maximum adsorption capacity was obtained 84.21 mg/g using Langmuir isotherm. Experimental kinetic data can be best fitted to Pseudo-2nd-order model. In thermodynamics, the adsorption process requires a low amount of energy and ΔG° values for different temperature indicate that the process is spontaneous at all temperatures.

Conflicts of Interest
There are no conflicts to declare.

Acknowledgments
The authors wish to thanks University grant commission for financial support Rajiv Gandhi National Fellowships for Disabilities Students [F/2014-15/RGNF-2014-15D-OBC-HAR-59079].

References


