Kinetics and isotherm studies on the adsorption of hexavalent chromium onto sulphuric acid activated Mimusops elengi leaves carbon

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Abstract

Hexavalent chromium [(Cr (VI))] ion is toxic and voluntarily adsorbed by some adsorbents; then, its captivating away from wastewater is very important. This study reports on the adsorption of Hexavalent Chromium from aqueous solution using activated carbon prepared from leaves of Mimusops elengi by sulphuric acid activation. Adsorption experiments were approved out in a batch process with various experimental parameters such as effect of contact time; initial chromium ion concentration, carbon dosage and pH on percentage removal have been studied. Kinetics of the system was studied with linearised forms of Lagergren, Ho and Webber Morris models. Equilibrium data were fitted with Langmuir, Freundlich, Temkin and Dubinin-Raduskevich isotherms.

Keywords: Activated carbon, sulphuric acid activation, Isotherms, Kinetics, and Hexavalent Chromium.

1. Introduction

Heavy metals are non biodegradable and be inclined to mount up in living organisms. Then, they are careful to be potentially dangerous and can cause physiological and neurological disorders [1]. Out of the variety of toxic pollutants chromium and its compounds are measured as the most hazardous inorganic water pollutants. Chromium compounds present in the effluents as a result of electroplating, metal finishing, magnetic tapes, wood preservation, leather tanning, pigments, and chemical manufacturing industries [2, 3]. Cr (VI) causes genetic mutations and cancer because of its eminent hyper toxicity [4], mutagenicity [5] and carcinogenicity [6]. Adsorption by activated carbon is one of the effective techniques for Cr (VI) ion removal from wastewater because of the high surface area, highly spongy character, and comparatively low cost of the adsorbent [7]. Activated carbon is particularly recognized for the effectual taking away of organic chemicals, inorganic and heavy metal ion pollutants from wastewater in the laboratory as well as in a variety of industries [8, 9]. In the past years, several investigations have been reported the removal of metal ions using activated carbons urbanized from industrial or farming wastes [10].

Mimusops elengi is a medium-sized evergreen tree found in tropical forests in South Asia, Southeast Asia and northern Australia. Hence activated carbon is prepared from the leaves of Mimusops elengi using sulfuric acid as activating agent and ability of the prepared carbon to remove Cr (VI) ions from aqueous solution from side to side adsorption was investigated.
2. Experimental

2.1 Preparation of activated carbon

Preparation of adsorbent using H$_2$SO$_4$

The dried Memsops elengi leaf powder was carbonized by treating with concentrated sulphuric acid in the weight ratio of 1:1 (w/v). Thus obtained charred masses were heated for 8 hours in a muffle furnace at 400°C to complete carbonization and activation. The resulting carbons were washed with distilled water until a constant pH of the slurry was reached. Then the carbon was dried for four hours at 100°C in a hot air oven. The dried material was ground well to a fine powder and sieved well using the sieves of desired particle size range. The carbon obtained from the Memsops elengi leaf powder was after this chosen as Sulphuric acid Treated Memsops elengi Activated Carbon (STMAC).

2.2 Preparation of stock solution

Cr (VI) ions stock solution (1000 mg/L) was prepared by dissolving 2.835 g K$_2$Cr$_2$O$_7$ (AR grade) in one litre of double distilled water. The experimental solutions were prepared by proper dilution [14–15].

2.3 Adsorption experiments

The effect of adsorption parameters such as initial concentration of Cr (VI), ion adsorbent dose and contact time was studied by batch mode technique because of its cleanness. Fixed dose of the adsorbent was taken in 250 mL iodine flask and 50 mL and fixed concentration of the Chromium solution was poured into the flask. Desired pH of the solution was brought by adding drops of Con HCl or 6 N NaOH. Then the content of the flask was agitated using rotary shaker with 180 rpm for predetermined duration. Then adsorbents were then separated by centrifugation and the concentration of the solution was determined by ‘Diphenylcarbazide’ method. The percentage removal of the Cr (VI) from the solution was calculated by the mass balance association. To study the effect of pH were brought to 2 to 10

2.4 Diphenyl carbazide method

1 mL of the sample solution was pipette out into 25 mL standard flasks. To this 1 mL of 6 N H$_2$SO$_4$ was added followed by 1 mL of diphenylcarbazide (A 0.25% (W/V) solution of diphenylcarbazide was prepared in 50% (V/V) acetone) and the total volume was made up to 25 mL using double distilled water. Concentration of Cr (VI) ion was estimated by measuring concentration of the reddish brown color developed due to complex configuration using Systronics Double Beam UV-Visible Spectrophotometer: 2202 at the wave length of 540 nm [16, 17].

3. Data processing tools

3.1 Determination of percentage of removal and quantity adsorbed

The percentage removal of the Cr(VI) ions from the solution was calculated by the following mass balance relationships.

\[
\% \text{ of Removal} = \frac{(C_i - C_t) \times V}{C_i}
\]

\[
q_e = \frac{(C_i - C_e) \times V}{W}
\]

\[
q_t = \frac{(C_i - C_t) \times V}{W}
\]

Where, $C_i, C_t, and C_e$ are the liquid phase concentrations in mg/L of Cr(VI) ion at initial, at the time ‘t’ and at equilibrium respectively. $V$ is the volume of the adsorbate solution in liter (L) and $W$ is the mass of the adsorbent in gram (g) used.

3.2 Isotherms

3.2.1 Langmuir isotherm

Langmuir equation is written in the following form [18]

\[
Q_e = \frac{Q_0 b C_e}{1 + b C_e}
\]

This equation is often written in linear forms as

\[
\frac{C_e}{Q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}
\]

where $Q_e$ is the amount of solute adsorbed per unit weight of adsorbent (mg/g), $C_e$ the equilibrium concentration of solute in the bulk solution (mg/L), $Q_0$ is adsorption efficiency and also called as the maximum monolayer adsorption capacity or saturation capacity (mg/g) and $b$ is the adsorption energy, ‘b’ is the reciprocal of the concentration at which half saturation of the adsorbent is reached.

The essential characteristics of Langmuir isotherm can be described by a separation factor, $R_L$, which is defined by the following equation.

\[
R_L = \frac{1}{1 + b C_0}
\]

Where, $C_0$ is the initial concentration of the adsorbate solution. The separation factor, $R_L$, indicates the shape of the isotherm and the nature of the adsorption process which is given below,

<table>
<thead>
<tr>
<th>$R_L$ value</th>
<th>Nature of the process</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_L &gt; 1$</td>
<td>Unfavourable</td>
</tr>
<tr>
<td>$R_L = 1$</td>
<td>Linear</td>
</tr>
<tr>
<td>$0 &lt; R_L &lt; 1$</td>
<td>Favourable</td>
</tr>
<tr>
<td>$R_L = 0$</td>
<td>Irreversible</td>
</tr>
</tbody>
</table>
3.2.2 Freundlich isotherm

This equation has the following form [18]

\[ \log Q_e = \log K_f + \frac{1}{n} \log C_e \]

Where \( Q_e \) is the amount of adsorbate adsorbed (mg/g), \( C_e \) is the equilibrium concentration of adsorbate solution (mg/L) and \( K_f \) and \( n \) are the constants incorporating all factors affecting the adsorption capacity and intensity of adsorption respectively.

3.2.3 Temkin Isotherm

The linear form of Temkin equation is [19].

\[ q_e = \frac{RT}{b_T} \ln a_T + \frac{RT}{b_T} \ln C_e \]

Where, \( b_T \) is the Temkin constant related to heat of sorption (J/mg) and \( a_T \) the equilibrium binding constant corresponding to the maximum binding energy (L/g) The Temkin constants \( a_T \) and \( b_T \) are calculated from the slopes and intercepts of \( q_e \) vs \( \ln C_e \).

3.2.6 Dubinin–Raduskevich Isotherm

The Linear form of Dubinin-Radushkevich isotherm, [18].

\[ \ln q_e = \ln q_0 - B \varepsilon^2 \]

Where, \( q_0 \) is the theoretical saturation capacity (mg/g) B is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2/J) and \( \varepsilon \) is Polanyi potential which is related to the equilibrium as follows;

\[ \varepsilon = RT \ln (1+1/C_e) \]

The constants \( q_0 \) and B were calculated from the slope and intercept of straight line obtained from the plot of \( \ln q_e \) vs \( \varepsilon^2 \). The mean free energy of adsorption E calculated from B using the following equation

\[ E = 1/ (2B)^{1/2} \]

3.3 Kinetics studies

3.3.1 Pseudo First order kinetics

Legergren equation is[20].

\[ \log (q_e-q_t) = \log q_e - k_1 / 2.303 \times t \]

Where \( q_e \) and \( q_t \) are the amounts of adsorbate adsorbed (mg/g) at equilibrium and at time \( t \) (min), respectively and \( k_1 \) is the rate constant of adsorption (l/min).

3.3.2 Pseudo Second order kinetics

Ho equation is [21].

\[ t/q_t = 1/k_2 q_e^2 + 1/q_e t \]

The initial adsorption rate, \( h \) (mg/(g min)), as \( t \rightarrow 0 \) can be defined as

\[ h = k_2 q_e^2 \]

The initial adsorption rate (h), the equilibrium adsorption capacity (\( q_e \)), and the second-order constants \( k_2 \) (g/ (mg. min)) can be determined experimentally from the slope and intercept of plot of \( t/q_t \) versus \( t \).

3.3.4 Intra particle diffusion

Weber–Morris equation is[22].

\[ q_t = k_p t^{1/2} + C \]

Where \( k_p \) is the intra-particle diffusion rate constant, a plot of \( q \) versus \( t^{1/2} \) should be a straight line with a slope \( k_p \) which is the rate constant for intra particle diffusion and intercept \( C \) is the thickness of the boundary film.

3.3.5 Test for Kinetics Models

The sum of error squares is given as follows;

\[ SSE(\%) = \sqrt{\sum [(q_e)_{exp} - (q_e)_{cal}]^2 / N} \]

Where \( N \) is the number of data points, \( (q_e)_{exp} \) the experimental \( q_e \), \( (q_e)_{cal} \) is the calculated \( q_e \).

4. Results and Discussion

4.1 Effect of pH

Figure 1 shows the effect of initial pH of the solution on the removal of Cr(VI) ion. The pH of the solution is a significant changeable which controls the adsorption. Therefore, the power of pH on the adsorption of Cr (VI) ions onto activated carbon was examined in the pH range of 2 to 10. The percentage removal of Cr (VI) ions augmented considerably with the decrease of solution pH value and the maximum removal was attained at pH (2.0).This kind of result was reported earlier [23].
4.2 Effect of Contact time and Initial concentration on adsorption

The effect of contact time on the percentage removal was studied by taking 10 mg/L, 20 mg/L, 30 mg/L, 40 mg/L and 50 mg/L solutions as initial concentrations. The adsorption process was characterized by a rapid uptake of the adsorbate at the initial stages. Then the rate of percentage removal was found to decrease slowly as the contact time increases and become constant after attaining equilibrium stage in all the cases.

4.2 Isotherm studies

The equilibrium data obtained from the experiments were processed with different isotherm models such as Langmuir, Freundlich, Temkin and Dubinin-Radushkevich. Inference obtained from each isotherm was discussed in detail one by one [24].

4.2.1 Langmuir Isotherm

The Langmuir isotherm represents the equilibrium distribution of adsorbate molecules flanked by the solid and liquid phases [25]. The squares of correlation coefficient ($R^2$) values ranged from 0.993 to 1.000 for the three studied temperatures viz. 305, 315, 325 and 335 K. These results show the best fitting of the equilibrium data with Langmuir isotherm. The monolayer adsorption capacity $Q_m$ values (mg/g) for adsorption of Cr (VI) ions onto STMAC ranged from 52.356 to 59.172 mg/g. The adsorption capacity increased with the increase of temperature [26]. The limit removal of Cr (VI) ions was 200 mg/g. The values of $R_L$ in all cases lie between 0 and 1, indicating that the adsorption process was favourable.
Table 1: Langmuir isotherm results for the adsorption of Cr (VI) ion onto STMAC

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Q_0 (mg/g)</th>
<th>B (L/mg)</th>
<th>R²</th>
<th>RL</th>
</tr>
</thead>
<tbody>
<tr>
<td>305</td>
<td>52.356</td>
<td>0.088</td>
<td>0.981</td>
<td>0.32</td>
</tr>
<tr>
<td>315</td>
<td>56.497</td>
<td>0.098</td>
<td>0.988</td>
<td>0.28</td>
</tr>
<tr>
<td>325</td>
<td>58.140</td>
<td>0.112</td>
<td>0.991</td>
<td>0.23</td>
</tr>
<tr>
<td>335</td>
<td>59.172</td>
<td>0.132</td>
<td>0.990</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Figure 3: Langmuir Isotherm

4.2.2 Freundlich Isotherm

The Freundlich adsorption capacity constant K_f (mg/g) values ranged from 6.8234 to 14.0929 mg/g. The magnitude of ‘n’ reveals the favorability of the adsorption. The values of 0< 1/n< 1 represent favourable adsorption conditions [27].

Table 2: Freundlich isotherm results for the adsorption of Cr(VI) ion onto STMAC

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>1/n</th>
<th>K_f (mg/g)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>305</td>
<td>1.7547</td>
<td>6.0814</td>
<td>0.958</td>
</tr>
<tr>
<td>315</td>
<td>1.7655</td>
<td>7.0146</td>
<td>0.961</td>
</tr>
<tr>
<td>325</td>
<td>1.8067</td>
<td>7.9799</td>
<td>0.955</td>
</tr>
<tr>
<td>335</td>
<td>1.8577</td>
<td>9.0782</td>
<td>0.947</td>
</tr>
</tbody>
</table>

Figure 4: Freundlich Isotherm
4.2.3 Temkin isotherm

Equilibrium binding constant $a_T$ values (L/g) ranged from 4.74 to 1.89 L/g and the heat of sorption constant $b_T$ values ranged from 205.45 J/mg to 200.80 J/mg for the three studied temperatures viz. 305, 315, 325 and 335 K. The lower values of $a_T$ and $b_T$ with respect to adsorption of Cr (VI) ion adsorption point out physisorption rather than chemisorption.

Table 3 Temkin isotherm results for the adsorption of Cr (VI) ion onto STMAC.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$b_T$ (J/mg)</th>
<th>$a_T$ (L/g)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>305</td>
<td>205.45</td>
<td>4.74</td>
<td>0.978</td>
</tr>
<tr>
<td>315</td>
<td>197.65</td>
<td>2.51</td>
<td>0.985</td>
</tr>
<tr>
<td>325</td>
<td>198.35</td>
<td>1.20</td>
<td>0.987</td>
</tr>
<tr>
<td>335</td>
<td>200.80</td>
<td>1.89</td>
<td>0.983</td>
</tr>
</tbody>
</table>

4.2.4 D-R Isotherm

‘E’ is a parameter used in predicting the type of adsorption. An E value less than 8 kJ/ mol is an indication of physisorption. The mono layer adsorption capacity $q_d$ values (mg/g) are ranged from 81.22 to 87.54 mg/g for all the studied temperatures. Additional it is noticed that adsorption capacity increased with the increase of temperature. The very low value of E infers the physisorption interaction.

Table 4 D-R isotherm results for the adsorption of Cr (VI) ions onto STMAC

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$q_d$ (mg/g)</th>
<th>E (kJ/mol)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>305</td>
<td>81.22</td>
<td>0.31</td>
<td>0.927</td>
</tr>
<tr>
<td>315</td>
<td>83.94</td>
<td>0.40</td>
<td>0.929</td>
</tr>
<tr>
<td>325</td>
<td>85.98</td>
<td>0.40</td>
<td>0.932</td>
</tr>
<tr>
<td>335</td>
<td>87.54</td>
<td>0.50</td>
<td>0.932</td>
</tr>
</tbody>
</table>
4.3 Kinetic study

A number of adsorption kinetic models have been conventional to appreciate the adsorption kinetics and rate-limiting step. These comprise pseudo-first and second-order and Weber Morris sorption kinetic models [28].

The pseudo first order rate constant, \( k_1 \) (min\(^{-1}\)) ranged from 0.0507 to 0.0426 min\(^{-1}\). The pseudo first order theoretical adsorption capacity (\( q_{e,\text{cal}} \)) values, obtained from the intercept of the linear plots, were compared with the experimental adsorption capacity (\( q_{e,\text{exp}} \)) values. The initial sorption rate ‘\( h \)’ increased directly with the increase of initial Cr (VI) ion concentration (1.23–3.24 mg/g.min\(^{-1}\)), as an opposite association exists flanked by the in general sorption rates and initial Cr (VI) ion concentrations.

Results obtained in the two kinetic models are presented in Table 5. Second order kinetic model seems to best illustrate the above adsorption system as it has \( R^2 \) value which was very close to agreement. Furthermore, the difference between calculated adsorption capacity (\( q_{e,\text{cal}} \)) and experimental adsorption capacity (\( q_{e,\text{exp}} \)) values of second order is little when compared to the first order kinetic model. Statistically it is tested with the tool ‘Sum of error squares’ (SSE %) [29]. Low SSE value for pseudo second order kinetic model infers that this model is more appropriate.

Table 5 Kinetics results for the adsorption of Cr (VI) ions onto PTMAC.

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>First Order Kinetics</th>
<th>Second Order Kinetics</th>
<th>Intra Particle Diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( k_1 ) (min(^{-1}))</td>
<td>( q_{e,\text{cal}} ) (mg/g)</td>
<td>( q_{e,\text{exp}} ) (mg/g)</td>
</tr>
<tr>
<td>10</td>
<td>0.0507</td>
<td>12.5026</td>
<td>11.17</td>
</tr>
<tr>
<td>20</td>
<td>0.0316</td>
<td>18.5780</td>
<td>20.33</td>
</tr>
<tr>
<td>30</td>
<td>0.0302</td>
<td>26.0615</td>
<td>28.92</td>
</tr>
<tr>
<td>40</td>
<td>0.0309</td>
<td>31.6228</td>
<td>34.67</td>
</tr>
<tr>
<td>50</td>
<td>0.0426</td>
<td>37.7572</td>
<td>36.00</td>
</tr>
</tbody>
</table>
4.3.1 Intra particle diffusion

The $k_p$ values were initiate to increase with an increase of Cr (VI) ion concentration which reveals that the rate of adsorption governed by the dissemination of Cr (VI) ions within the pores of the adsorbent. [30].

<table>
<thead>
<tr>
<th>Concentration mg/L</th>
<th>$k_p$ (mg/g.min)</th>
<th>$h$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.55</td>
<td>1.23</td>
<td>0.890</td>
</tr>
<tr>
<td>20</td>
<td>0.68</td>
<td>1.42</td>
<td>0.974</td>
</tr>
<tr>
<td>30</td>
<td>1.45</td>
<td>1.98</td>
<td>0.983</td>
</tr>
<tr>
<td>40</td>
<td>1.59</td>
<td>2.44</td>
<td>0.934</td>
</tr>
<tr>
<td>50</td>
<td>1.86</td>
<td>3.24</td>
<td>0.794</td>
</tr>
</tbody>
</table>
5. Conclusion

This learns shows that sulphuric Acid Treated *Mimusops elengi* Activated Carbon (STMAC) was a successful adsorbent for the elimination of Cr (VI) ions from aqueous solution. Adsorption of Cr(VI) ion was extremely pH dependent and the results showed that the most favorable pH for the removal was originate to be 2.0, at which Cr(VI) exists as the most easily absorbable form. Symmetry adsorption was achieved approximately 80 minutes for the dosage of 30 mg/50 mL of solution at room temperature of 305 K for the initial concentration of Chromium (VI) solution ranging from 10 to 50 mg/L. The equilibrium parameter R_L value consequently obtained from Langmuir isotherm revise were in between 0 and 1 showing the favourable adsorption method. The values of ‘n’ the intensity of adsorption, obtained from Freundlich isotherm were found to be greater than one representative a favourable adsorption. Values obtained for other parameters from Freundlich, Temkin and Dubinin-Radushkevich isotherms discovered the possibility of multi-layer, physisorption and heterogeneous aperture distribution. The statistical tool ‘Summation of error square test’ exposed that present adsorbent – adsorbate system followed second order kinetics. The variation of intra particle diffusion constant k_p values with the initial adsorbate concentrations indicates that the intra-particle diffusion limits the rate of the process.

References


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