Evaluation Of Removal Of Chromium (VI) Using Sulphuric Acid Processed Cyprus Rotundus Carbon

S. Vijayakumar, M. Senthil

Kandaswamy Kandar’s College, Department of Chemistry, P. Velur, Namakkal District 638181.

Abstract

Activated carbon was prepared from Cyprus rotundus roots by pyrolysis, chloride, sulphate, carbonate and acid processes and their Cr(VI) removing capacities were found experimentally. The same experiment was repeated using the commercially available activated carbon. Both the results were compared. The experiments were repeated by altering various parameters like pH, concentration and the carbon dosage. Langmuir and Freundlich adsorption isotherms were plotted and the equilibrium isotherms were determined. The levels of adsorption capacity of the activated carbons which were obtained by plotting Langmuir adsorption isotherms were found to be 83.325 mg/g, 104.175 for Sulphuric acid processed Cyprus rotundus carbon (SCRC) in distilled water and tap water respectively. The same values of adsorption capacity from Langmuir isotherm were 227.275 mg/g and 58.15 mg/g for Commercially activated carbon (CAC) in distilled water and tap water respectively. It was found that the R² values obtained for both the isotherms are in excellent agreement. It can be employed to explain the adsorbing capacity of Sulphuric acid treated Cyprus rotundus carbon and Commercially activated carbon. The Kinetics experiment data follows pseudo first order kinetics. The results reveal that Cr(VI) from tanneries are effectively removed by using Sulphuric acid treated Cyprus rotundus carbon.

Keywords:
Cr (VI) removal, Cyprus rotundus carbon, Sulphuric acid treated Cyprus rotundus carbon (SCRC), Commercially activated carbon (CAC), Langmuir and Freundlich Adsorption isotherms, Kinetics, Chromium effluents from tanneries.

INTRODUCTION:

Cr(VI) as chromate (CrO₄²⁻), dichromate (Cr₂O₇²⁻), and CrO₃ are treated to be the most poisonous forms of chromium because of its greater oxidizing potential, greater dissolution, and movement across the membranes in living systems and in the ecosystem. Cr(III) as oxides, hydroxides, and sulphates is of lesser toxicity since it remains almost insoluble in water, shows lower moving ability. Cr(VI) is a very strong irritant for the epithelial tissues and a human carcinogen. The growth of paddy and its uptake of macro nutrients and micro nutrients gradually decreased with increasing concentrations of chromium in the soil (Perumal Sundaramoorthy et al., 2010). Municipal waste water sludge derived from biochar acts as an excellent sorbent for Cr (VI) ions (Weihua Zhang et al., 2013). Activated carbon developed from P. capicillacea, a red alga removes chromium (Ahmed El Nemr et al., 2015). Adsorbents like peanut shell (Z.A. Al-Othman et al., 2012), corn cob bio mass magnetized
by magnetite nanoparticles (S. Nethaji et al., 2013), Tea waste and date pits (Ahmad B. Albadarin et al., 2013), modified walnut shells (T. Altun and E. Pehlivan, 2012), mesoporous carbon nitride (Huan Chen et al., 2014), Moso and Ma bamboo (Sheng-Fong Lo et al., 2012), Trapa natans husk (Weifeng Liu et al., 2010), activated carbon-based, iron containing adsorbents (Weifeng Liu et al., 2012), sunflower waste (Monika Jain et al., 2010), fungal biomass of Termitomyces clypeatus (Lata Ramrakhiani), pistachio hull powder (Gholamerza Moussavi et al., 2010), neem saw dust (V. Vinodhini et al., 2010), wheat straw (Xue Song Wang et al., 2010), Eichhornia crassipes root biomass (Anil Kumar Giri et al., 2012), algal bloom residue (Hong Zhang et al., 2010), Wheat and Barley straw (Rumi Chand et al., 2009), walnut hull (Xue song wang et al., 2009), pomegranate husk (Ahmed El Nemr), Tamarind wood (J.N. Sahu et al., 2009), saw dust (Suresh Gupta et al., 2009), Bael fruit shell (J. Anandkumar et al., 2009), sugar beet bagasse charcoal and saw dust (T.P. Dhungana et al., 2009), wool from merino sheep (Nilgun Balkaya et al., 2012), Gular fruits (Rifaqat A.K. Rao et al., 2010), coir pith (C. Namasivayam et al., 2007), Green alga ulva lactuca (Amany El-Sikaily), Wheat bran (A. Ozer and D. Ozer, 2010), brown sea weed (Donghee Park et al., 2004), bamboo charcoal (Li Qiao-ling et al., 2008), salvinia cucullata weed (S.S. Baral et al., 2008), bacterial biofilm supported granular carbon (C. Quintelas et al., 2001).

The point of this study is to find out the adsorption capacities of sulphuric acid activated Cyprus rotundus carbon (SCRC) for the removal of Cr (VI) from tanneries and comparing it with the capacity of the Commercially Activated Carbon (CAC). The conditions of the experiments were determined by varying the pH, carbon dosage and concentration. To study the adsorption process, adsorption isotherms were determined and kinetics studies were done.

DESCRIPTION OF THE PROCESS AND PRINCIPLES

Preparation of Cyprus rotundus carbon by pyrolysis followed by activation:

50 g of Cyprus rotundus roots were washed, chopped into tiny pieces and made dry in the sun. The dried sample was heated at a temperature of 450 – 700 °C. Volatile products escape out. The substance chars and produces fumes. It is heated until the fumes stop. Then the substance is thermally activated in an inert atmosphere at 850 – 900 °C for half an hour.

Preparation of Cyprus rotundus carbon by chloride process:

20 g of Cyprus rotundus roots were soaked in 205 solutions of Zinc chloride, Calcium chloride, Manganese chloride and ammonium chloride salts for one day. The filtrate is decanted. The wet residue is spread on plates and dried slowly. The dried residue is heated at 600 – 650 °C. Then the sample is activated thermally at 850 – 900 °C for half an hour without air. The carbonized material is washed with water followed by dilute HCl and then dried.

Preparation of Cyprus rotundus carbon by sulphate process:

20 g of Cyprus rotundus is dipped in a 10 % solution of ammonium sulphate or sodium sulphate for one day. The filtrate is decanted. The wet residue is spread on plates and then dried. The dried residue is heated at 600 – 650 °C. Then the sample is activated thermally at 850 – 900 °C for half an hour without air. Then it is treated with water followed by dilute HCl. It is again treated with water to eliminate any acid residues. Then it is dried.

Preparation of Cyprus rotundus carbon by acid process:

50 g of dried Cyprus rotundus roots is treated with 200 ml of concentrated sulphuric acid. For the same purpose, the sample is treated with sulphuric acid in a container with fast stirring. The sample chars with the release of some gases. When the reaction ceases, the contents are placed in an oven maintained at 150°C for one day. Finally the mixture is treated with water to eliminate the traces of acid from the sample. It is again dried at 110°C.
Preparation of Cyprus rotundus carbon by carbonate process:

Cyprus rotundus roots are washed with water and treated with Manganous chloride for 1 day. Then the sample is dipped in a 10 % solution of sodium carbonate for one day. The sample is isolated by decantation and then heated at 110 °C to make it dry. The sample is treated to pyrolysis at 700 °C and activated at 850 °C for half an hour in the absence of air. The sample is treated with 10 % HCl. The sample is then treated with water and heated at 110 °C to make it free from moisture.

Choice of Cyprus rotundus carbon:

The average chemical composition of Cyprus rotundus carbon is listed in the following table below:

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Constituent</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Moisture content</td>
<td>7.30</td>
</tr>
<tr>
<td>2</td>
<td>Essential oil</td>
<td>78.4</td>
</tr>
<tr>
<td>3</td>
<td>Cypere</td>
<td>9.76</td>
</tr>
<tr>
<td>4</td>
<td>Humulen</td>
<td>7.97</td>
</tr>
<tr>
<td>5</td>
<td>Selinene</td>
<td>7.88</td>
</tr>
<tr>
<td>6</td>
<td>Zierone</td>
<td>4.62</td>
</tr>
<tr>
<td>7</td>
<td>Campholenic aldehyde</td>
<td>3.83</td>
</tr>
<tr>
<td>8</td>
<td>Pinene</td>
<td>3.51</td>
</tr>
<tr>
<td>9</td>
<td>Longeverbenone</td>
<td>2.72</td>
</tr>
<tr>
<td>10</td>
<td>Vatirenene</td>
<td>2.32</td>
</tr>
<tr>
<td>11</td>
<td>Other organic compounds</td>
<td>14.65</td>
</tr>
<tr>
<td>12</td>
<td>Ash ( Dry basis)</td>
<td>4.30</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ash Analysis</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Silica</td>
</tr>
<tr>
<td>2</td>
<td>K₂O</td>
</tr>
<tr>
<td>3</td>
<td>Na₂O</td>
</tr>
<tr>
<td>4</td>
<td>CaO</td>
</tr>
<tr>
<td>5</td>
<td>MgO</td>
</tr>
<tr>
<td>6</td>
<td>P₂O₅</td>
</tr>
</tbody>
</table>

Cyprus rotundus carbon prepared by the sulphuric acid process is best suited for adsorption studies and the characteristics of CAC (Commercially activated carbon) and carbon prepared by different processes are listed in the table below:
### Table 2: Characteristics of CAC (Commercially activated carbon) and carbon prepared by different processes.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Parameters</th>
<th>CAC</th>
<th>Pyrolysis process</th>
<th>Chloride process</th>
<th>Sulphate process</th>
<th>Carbonate process</th>
<th>Acid process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Moisture %</td>
<td>7.20</td>
<td>3.01</td>
<td>8.17</td>
<td>7.10</td>
<td>9.27</td>
<td>11.30</td>
</tr>
<tr>
<td>2</td>
<td>Ash %</td>
<td>3.68</td>
<td>20.28</td>
<td>21.38</td>
<td>27.63</td>
<td>23.48</td>
<td>4.94</td>
</tr>
<tr>
<td>3</td>
<td>Bulk Density</td>
<td>0.61</td>
<td>0.23</td>
<td>0.26</td>
<td>0.25</td>
<td>0.23</td>
<td>0.45</td>
</tr>
<tr>
<td>4</td>
<td>Matter soluble in water %</td>
<td>1.69</td>
<td>5.60</td>
<td>8.32</td>
<td>10.00</td>
<td>7.43</td>
<td>2.50</td>
</tr>
<tr>
<td>5</td>
<td>Matter soluble in Acid%</td>
<td>1.75</td>
<td>9.64</td>
<td>9.45</td>
<td>11.30</td>
<td>8.32</td>
<td>2.12</td>
</tr>
<tr>
<td>6</td>
<td>Free Carbon %</td>
<td>85.68</td>
<td>61.46</td>
<td>52.68</td>
<td>70.97</td>
<td>74.76</td>
<td>80.0</td>
</tr>
<tr>
<td>7</td>
<td>Phenol number</td>
<td>20</td>
<td>68</td>
<td>78</td>
<td>70</td>
<td>74</td>
<td>67</td>
</tr>
<tr>
<td>8</td>
<td>Methylene Blue Value</td>
<td>78</td>
<td>28</td>
<td>50</td>
<td>56</td>
<td>60</td>
<td>42</td>
</tr>
<tr>
<td>9</td>
<td>Ion exchange capacity Meq/g</td>
<td>NIL</td>
<td>NIL</td>
<td>NIL</td>
<td>NIL</td>
<td>NIL</td>
<td>0.56</td>
</tr>
<tr>
<td>10</td>
<td>Surface area Sq.meters/g</td>
<td>563</td>
<td>235</td>
<td>216</td>
<td>200</td>
<td>210</td>
<td>40.32</td>
</tr>
<tr>
<td>11</td>
<td>pH</td>
<td>8.40</td>
<td>9.44</td>
<td>7.82</td>
<td>9.10</td>
<td>8.72</td>
<td>3.35</td>
</tr>
<tr>
<td>12</td>
<td>Iron %</td>
<td>0.005</td>
<td>0.063</td>
<td>0.063</td>
<td>0.07</td>
<td>0.065</td>
<td>0.015</td>
</tr>
</tbody>
</table>

**Preparation of Cr (VI) solution:**
0.1414 g of Potassium dichromate is dissolved in a litre of distilled water to get a stock solution of Cr (VI) containing 50 mg/ml.

**Preparation of S – Diphenylcarbazide reagent:**
0.2 g of S – Diphenyl carbazide is made upto 100 mL using isopropyl alcohol. To this solution 400 mL of 3.6 N sulphuric acid is added with regular stirring. The solution is placed in a refrigerator stable for one month.
Determination of Cr (VI):

To aliquots of 50 mL solution add 2.5 ml Diphenylcarbazide reagent is added and mixed well and made up to the mark. The absorbance is measured against a reagent blank at 540 nm using 1.0 cells. The measurements are completed within 50 minutes. A standard graph in the range 10 – 50 microgram of Cr (VI) is to be prepared.

Adsorption Studies:

In all the experiments, 100 ml of Cr (VI) solution with a needed concentration and altered to the required pH were placed in 300 mL high density polyethylene (HDPE) bottles and an adsorbent of required dose was added to it. The pH of the solution was altered using 0.1 M HNO₃ or KOH. The solutions were constantly shaken for different contact times at 30 °C and carbon particles were centrifuged at 500 rpm and the clear supernatant liquid was tested for Cr (VI) by Atomic Adsorption Spectra. The above liquid was treated with KMnO₄ in an acidic medium of Sulphuric acid. This is done to oxidize all Cr (II) and Cr (III) to Cr (VI) (Gupta et al., 2010). This is done before determining the total amount of Cr (VI) in the medium of adsorption. Solute and blanks free from adsorbents were utilized as control in all the above procedures. The solution is equilibrated for about one day and adsorption isotherms were calculated and reaction kinetics were studied for different concentrations of Cr (VI) and a constant adsorbent dose was maintained. AAS that operates with an air-acetylene flame was used to find out the amount of Cr (VI) that remains unadsorbed in the clear liquid. The apparatus consists of a 15mA operated hollow cathode lamp. It operates at a wavelength of 358 nm. The adsorbents’ removal efficiency (E) of the for Cr (VI) was determined by using the given equation:

\[ E(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad \ldots \quad (1) \]

Where \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations (mg/L) of Cr (VI) solutions, respectively.

RESULTS AND DISCUSSION

Effect of contact time:

So as to find out the equilibration time effect on the removal of Cr (VI), experiments were done using 500 mL of Cr (VI) of concentration 100 mg/L containing 0.34 g carbon at pH 2.5. A set of solutions was equilibrated for varying periods ranging from 1 to 10 hours. After the agitation time, the solutions were centrifuged, analyzed and the percentage of Cr (VI) removed in each case was established. The results are predicted in figure:

It is evident from the graph that 6 hours and 5hours equilibration time were required for the maximum removal of 92.12 % and 90% of Chromium (VI) by commercially activated carbon and Sulphuric acid treated Cyprus rotundus carbon, respectively. Hence Cyprus rotundus carbon treated with sulphuric acid is superior to CAC (commercially activated carbon) to remove Cr (VI) from aqueous solutions.
Effect of pH:

The experiments were carried out in different pH ranging from 1 to 12 so as to determine the desired pH for the highest removal of Cr (VI). After the equilibration time, the solutions were analyzed and the percentage of Cr (VI) elimination was established and the results are depicted in the figure.

It is noted from the figure that highest removal of Cr (VI) occurs at a lower pH and when the pH value is increased, the percentage removal of Cr (VI) decreases. At low range of pH, the surface of the adsorbent carries a large positive charge and is therefore able to attract more Chromium ions that are having a negative charge in the given solution. Chromium (VI) removal of Sulphuric acid treated Cyprus rotundus carbon (SCRC) at pH 2.6, 3.67, 4.5 and 5.4 are 99.10, 77.00, 79.00 and 66.67 respectively. Thus Chromium (VI) removal is maximum at a pH of 2.6. Chromium (VI) removal for Commercially activated carbon (CAC) at 2.1, 4.0 and 6.0 are 97, 90 and 77 respectively. Hence Chromium (VI) removal is maximum at a pH of 2.1. It is clearly evident that Chromium (VI) removal by SCRC is superior to CAC at lower pH levels.
Effect of Carbon dose:

We need to determine the minimum quantity of carbon that is required for the highest removal of Chromium (VI) for sulphuric acid treated Cyprus rotundus carbon (SCRC) and Commercially activated carbon (CAC). We conduct experiments with 500 mL of 20 mg/L of Chromium (VI) solution which contain different amounts of carbon which ranges from 50 mg to 600 mg/100mL at an optimum pH of 2.5 to 3 for Sulphuric acid treated Cyprus rotundus carbon (SCRC) and 2.8 to 3 for Commercially activated carbon (CAC) respectively. Respective equilibration times were maintained for these carbons and the Chromium (VI) removal in each instance was established. The results are presented in figure. A minimum carbon dose of 200 mg/100mL for both Sulphuric acid treated Cyprus rotundus carbon (SCRC) and Commercially activated carbon (CAC) was required for the removal of 99.9 % and 97 % of Chromium (VI) removal respectively. This indicates that Sulphuric acid treated Cyprus rotundus carbon (SCRC) is more efficient in the removal of Cr (VI) in preference
to Commercially activated carbon (CAC). Hence based on the optimization studies it is suggested that Sulphuric acid treated Cyprus rotundus carbon (SCRC) is a better adsorbent than CAC to remove Cr (VI) from aqueous solutions.
FIGURE 3: EFFECT OF CARBON CAC AND CARBON SCRC

Figure 4: EDAX CAC RAW MATERIAL

Figure 5: EDAX CAC Cr (VI) ADSORBED

Figure 6: EDAX SCRC RAW MATERIAL

Figure 7: EDAX SCRC Cr (VI) ADSORBED
FIGURE 8: SEM IMAGES FOR CAC RAW MATERIAL

FIGURE 9: SEM IMAGES FOR CAC Cr (VI) ADSORBED

FIGURE 10: SEM IMAGES FOR SCRC RAW MATERIAL
FIGURE 11: SEM IMAGES FOR SCRC Cr (VI) ADSORBED

FIGURE 12: IR IMAGES FOR CAC RAW MATERIAL

FIGURE 13: IR IMAGES FOR CAC Cr (VI) ADSORBED
Adsorption Isotherm:

Adsorption isotherms help us understand the interaction between the solute and the adsorbents. They are useful and essential in optimizing the usage of adsorbents. Langmuir, Freundlich and Tempkin isotherms are very useful in the study of adsorbents. Langmuir (1918) equation is as below:

\[
\frac{1}{q_e} = \frac{1}{b} + \frac{1}{a b C_e} \quad \text{........ (2)}
\]

Where \( C_e \) is the concentration at equilibrium (mg/L), \( q_e \) is the equilibrium adsorbed amount of Cr (VI) (mg/g), Langmuir constants which correspond to adsorption energy in (L/mg) capacity of adsorption in (mg/g) are ‘a’ and ‘b’ respectively. When we plot \( 1/q_e \) vs \( 1/C_e \), we get a linear graph. Figure depicts the Langmuir adsorption isotherm of Cr (VI) adsorption on adsorbents for an equilibration time for one day. From the slopes and intercepts obtained from the graph, constants, ‘a’ and ‘b’ were found and listed in the tabular column.

The highest capacity of adsorption for adsorbents were found using the Langmuir isotherm. The capacity of adsorption levels for activated carbons which were obtained by plotting Langmuir adsorption isotherms are determined to be 83.325 mg/g, 104.175 for Sulphuric acid processed Cyprus rotundus carbon (SCRC) in distilled water and tap water respectively. \( R_L \) is a constant without dimension. It is a separation factor that is utilized to predict the favourability of a sorption system in
the adsorption process. The value of $R_L$ from 0 and 1 favours adsorption. The values of $R_L$ can be determined by the equation based on the Langmuir isotherm $R_L = (1/1+aC_0)\ldots\ldots\ldots(3)$

Where, $C_0$ is the concentration of Cr (VI) at the initial stage and ‘a’ is a constant that indicates adsorption energy.

The value of $R_L$ helps us to determine adsorption process nature. The $R_L$ values of for the favourability of the process, irreversible nature, linearity and unfavourability of the process are $0 < R_L < 1$, $R_L = 0$, $R_L = 1$ and $R_L > 1$, respectively. The $R_L$ values for Sulphuric acid treated Cyprus rotundus carbon (SCRC) and Commercially Activated Carbon (CAC) were found to be between 0 and 1 at all concentrations investigated, this clearly tells us that the sorption of Cr (VI) is favourable using the above SCRC and CAC as adsorbents. The Freundlich isotherm is determined by the equation given below (Freundlich and Helle, 1939):

$$\log x/m = \log K_f + 1/n (\log C_e) \quad \ldots\ldots \ldots (4)$$

where $C_e$ is concentration at equilibrium (mg/L) and x/m is the amount adsorbed per unit weight of adsorbent (mg/g). The plot of $\log(x/m)$ vs $\log C_e$ gives a linear graph indicating the favourability of adsorption. The Figure depicts, Freundlich adsorption isotherms for adsorption of Cr (VI) on SCRC and CAC. Using the intercepts and slopes from the graph, the values of $K_f$ and $n$ were calculated. The capacity of adsorption ($K_f$), intensity of adsorption ($n$) and coefficient of correlation($R^2$) are presented in table. Plot of $\log x/m$ vs $\log C_e$ is a linear graph with $1/n$ as the slope and the intercept of $\log x/m$ is $\log K_f$ at $\log C_e = 0 (C_e = 1)$. The linearity of the graphs show that the process follows Freundlich adsorption type. The values of $K_f$ for Freundlich adsorption equation were obtained for Sulphuric acid treated Cyprus rotundus carbon (SCRC) and Commercially Activated Carbon (CAC) from the intercept of $\log x/m$ axis. From the slopes of the linear curves, the sorption intensities ‘1/n’ were obtained for both SCRC and CAC.

The adsorption is favourable for intensity of adsorption values between 1 and 10 ($1 < n < 10$). The values of ‘n’ range from 1 to 10, indicating the favourability of these adsorbents on Cr (VI) adsorption. The values of Correlation coefficient of correlation ($R^2$) are obtained from the linear graphs for both the isotherm models and are tabulated in the table. The values of $R^2$ obtained tell us that Langmuir and Freundlich adsorption isotherms operate at the same time on the layer of carbon adsorbents for the complete elimination of Cr (VI) from aqueous solutions.

**Adsorption Kinetics:**

To explain the kinetics of adsorption for Cr (VI) for these adsorbents, 2 kinetic models were used. Lagergren’s pseudo-first order and pseudo-second order models were used for this purpose. The rate equation for the pseudo-first order Lagergren is given as (Lagergren 1998).

$$\ln (q_t (exp) - q_t (theo)) = \ln q_e (theo) - k_1 t \quad \ldots\ldots \ldots (5)$$

where, $q_t (exp)$ and $q_t (theo)$ are the adsorbed metal ions concentration (mg/g) at equilibrium and at time $t$ (min), respectively and pseudo-first order equilibrium rate constant is $k_1 (min^{-1})$. When we plot $ln (q_t (exp) - q_t (theo))$ vs $t$, we get a linear graph whose slope is $k_1$ and $q_e (theo)$ as the intercept. The linearity of the graph shows that pseudo-first order rate equation is applicable. Graphs depict pseudo first order kinetics for the adsorption of Cr (VI) onto Sulphuric acid treated Cyprus rotundus carbon (SCRC) and Commercially Activated Carbon (CAC) respectively. The rate equation for pseudo-second order model is given below (Ho and Mckay, 1999):

$$t / q_t (theo) = 1/k_2 q_e^2 (theo) + 1 / q_e (theo) \quad \ldots\ldots \ldots (6)$$
where, \( k_2 \) is adsorption rate constant for pseudo-second order (g/mg, min). When \((t/q_e^{(exp)}) vs 't'\) is plotted, we get a straight line whose slopes are \(1/q_e^{(theo)}\) and \(1/k_2 q_e^{2 (theo)}\). This validates the application of the pseudo-second order model. Graphs represent the application of pseudo second order kinetics for the adsorption of Cr (VI) for Sulphuric acid treated Cyprus rotundus carbon (SCRC) and Commercially Activated Carbon (CAC) respectively.

To quantitatively compare the feasibility of kinetic models in fitting to data, the percent of relative deviation \((P)\), is calculated as per the equation:

\[
P = \frac{100}{N} \left\{ \sum q_e^{(exp)} q_e^{(theo)} / q_e^{(exp)} \right\}
\]  

(7)

For any value of \( C_c \), \( q_e^{(exp)} \) is the experimentally determined value of \( q_e \), the theoretical value that corresponds \( q_e \) is \( q_e^{(theo)} \) and number of observations is \( N \). For lesser values of percentage deviation, the fit is found to be good. If the value of \( P<5 \), the fit is found to be excellent (Ayranci and Duman, 2005). Equations were used to verify the results. The experimental data found very well fitted to both the equations. The theoretical values of \( q_e^{(theo)} \) values that were calculated from the models are compared with experimentally determined values and tabulated. It was evident that the \( q_e \) values \((q_e^{(theo)})\) obtained by pseudo-first order kinetic model very well contrasted to the experimental \( q_e \) values \((q_e^{(exp)})\). The percent of relative deviation \((P)\) was found to be maximum. When pseudo-second order kinetics equation was used, the \( q_e^{(theo)} \) values and \( q_e^{(exp)} \) were in good agreement. The values of percent relative deviation \((P)\) were in good agreement and the values of correlation coefficients \((R^2)\) nearly approaches unity when pseudo-second order kinetics was applied. This evidently depicts that the adsorption of Cr (VI) on SCRC and CAC follows by pseudo-second order kinetics.

**FIGURE 16**: Kinetic fit curve for SCRC

![Kinetic fit curve for SCRC](image-url)
Application to wastewater

Waste water was collected from tanneries and experiments were done to find out the efficiency of these adsorbents in the removal of chromium. The chemical composition of chrome-plating industry wastewater is tabulated and listed in the table. As the waste water contains high concentration of Chromium to an extent of 320 mg/L, 6 times the amount of distilled water was used before adsorption studies were carried out with Sulphuric acid treated Cyprus rotundus carbon (SCRC) and Commercially Activated Carbon (CAC). The diluted waste water was adjusted to a pH of 2 for Sulphuric acid treated Cyprus rotundus carbon (SCRC) and a pH of 3 for Commercially Activated Carbon (CAC) respectively. Maintaining an optimum pH and time, the effect of dose of adsorbents on the removal of chromium was carried out. It is found that at carbon doses 300 mg/100mL, 400 mg/100mL and 500 mg/100mL at a pH of 2.6, the removal of chromium was found to be 99.1% for Sulphuric acid treated Cyprus rotundus carbon (SCRC). It is 90% for Commercially activated carbon (CAC). It is therefore found that the chromium (VI) removing capacity of Sulphuric acid treated Cyprus rotundus carbon (SCRC) is superior to that of Commercially activated carbon (CAC).

Conclusion:

1. Studies show that 99.1%, 77%, 79% and 66.67% of Chromium (VI) removal were removed at pH 2.6, 3.67, 4.5 and 5.4, at a carbon dose of 500mg/mL, 600mg/mL, 600 mg/mL and 600 mg/mL respectively at a Chromium (VI) concentration of 20 mg/L for Sulphuric acid treated Cyprus rotundus carbon (SCRC). Chromium (VI) removal for Commercially activated carbon (CAC) were found to be 10%, 20%, 84% and 96% at pH 5.4, 4, 3 and 2.6 at a carbon dose of 700mg/mL, 400 mg/mL, 700 mg/mL and 400 mg/mL. Hence it is found that the Sulphuric acid treated Cyprus rotundus carbon (SCRC) removes Chromium (VI) from aqueous solutions at lower pH and lower carbon dose than that of Commercially activated carbon (CAC).
2. Freundlich adsorption capacity for Sulphuric acid treated Cyprus rotundus carbon (SCRC) is found to be more higher than Commercially activated carbon (CAC).

3. It is found that Chromium (VI) adsorption on Sulphuric acid treated Cyprus rotundus carbon (SCRC) and Commercially activated carbon (CAC) follows pseudo-first order kinetics.

4. It is found that Sulphuric acid treated Cyprus rotundus carbon (SCRC) is superior to commercially activated carbon for the removal of Chromium (VI) obtained from waste water obtained from chrome plating.

5. Hence it is concluded that Sulphuric acid treated Cyprus rotundus carbon (SCRC) can be used as an adsorbent alternatively for the elimination of Chromium (VI) from aqueous solutions and chrome plating waste waters.

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