CHAPTER II

ADSORPTION OF CHROMIUM BY ACTIVATED CARBONS FROM AQUEOUS SOLUTION

INTRODUCTION

Chromium is present in effluent waters of several different industries. It is hazardous because it affects human physiology, accumulates in the food chain and causes several ailments. The stricter environmental regulations related to the discharge of heavy metals makes it necessary to develop processes for their removal from waste water. Activated carbons because of their high surface area, microporous character and the chemical nature of their surface have been considered potential adsorbents for the removal of heavy metals from industrial waste water.

Narayana and Krishnaiah [1,2] and Kannan and Vanangamudi [3] used activated carbon, lignite coal and bituminous coal for the adsorptive removal of chromium from aqueous solutions at different pH values and observed that both adsorption and reduction of Cr(VI) occurred. The adsorption of Cr(VI) was maximum at pH = 3 while the reduction was maximum at pH = 1.

Ouki and Newfeld [4] used column adsorption technique for removal of Cr(VI) from water in the concentration range 250-300 mg/L and found that the removal of Cr(VI) increased significantly at acidic pH values. These workers also observed that at acidic pH values, a redox reaction occurred on the carbon surface when Cr(VI) was reduced to Cr(III). The activated carbon sites, in turn, were oxidised resulting in an increased adsorption capacity.
Cici and Kales [5] studied the adsorption of Cr(VI) on rice husk charcoal activated with ZnCl₂ at two different temperatures and observed that 30-99% Cr(VI) could be removed from solutions containing between 20-200 mg/L of Cr(VI). Andreeva et al. [6] used several different fibrous activated carbons for the adsorption of several heavy metals under static conditions at different pH values and suggested that fibrous activated carbons were very effective for the removal of heavy metals from waste water. The adsorption of chromium followed Freundlich isotherm below 20°C and Langmuir isotherm above 20°C. Dikshit et al. [7] used bituminous coal for the removal of low concentration of Cr(VI) from highly acidic waste water by batch technique. The rate of adsorption followed first order kinetics and the adsorption was suggested to be a diffusion process involving micropores.

Jayson et al. [8] studied the adsorption of chromium ions from aqueous solutions on a sample of activated carbon cloth using radioactive tracer techniques. The results showed that the adsorption of chromium ions from aqueous chromate solutions was always greater by a factor of 10 than that from chromic solutions because chromic ions are too large to enter parts of the microporous system. As the amount of Cr(III) adsorbed exceeded the external surface, it has been postulated that the chromium ions on adsorption dehydrate, become smaller and migrate further into the micropores. Abe [9], Tagashira et al. [10], and Huang and Wu [11] observed that 90-99% chromium present in waste water could be removed using activated carbon.

Yoshida et al. [12] examined the adsorption of Cr(III) and Cr(VI) from aqueous solutions using activated carbon as a function of pH of the solution. Cr(VI) was adsorbed as anionic species and the rate of its adsorption was faster than that of Cr(III). Huang and Wu [13] while studying the adsorption of Cr(VI) and Cr(III) on a filtrasorb carbon also observed that Cr(VI) was adsorbed more readily than Cr(III). The optimum pH for
the removal was between 5.5 and 6.0 for Cr(VI) and 5.0 for Cr(III). These investigators found that Cr(VI) was readily reduced to Cr(III) under acidic conditions in the presence of activated carbon. Huang and Bowers [14], however, found that the removal of chromium ions by activated carbons involved reduction and adsorption consecutively.

Grover and Narayana Swamy [15] and Viraraghavan [16] used fly ash as an adsorbent for the removal of chromium from industrial waste water. While the former observed it to be a case of adsorption into the pores, the latter suggested the adsorption to be a case of chemisorption of Cr(VI).

Bautista-Toledo et al. [17] studied the influence of oxygen surface complexes on the adsorption of chromium ions from aqueous solutions on a commercial activated carbon. The adsorption of both Cr(VI) and Cr(III) was enhanced by the presence of surface oxygen complexes of acid type. The adsorption was also enhanced by addition of NaCl into the solution.

It appears from the above perusal of the literature that the use of activated carbons for the removal of chromium from industrial waste water has a great potential. However, a systematic approach to the mechanism involved has not been made. In the present work the adsorption of Cr(VI) and Cr(III) has been studied using commercially available granulated and fibrous activated carbons associated with varying amounts of different types of carbon-oxygen surface chemical structures.

Two samples of granulated activated carbons and two samples of fibrous activated carbon have been used in these investigations. The activated carbons were oxidised with nitric acid [18-20], ammonium persulphate [21,22] and hydrogen peroxide [23,24] in the solution phase and with gaseous oxygen [25,26] at 350°C to enhance the amount of carbon-oxygen surface chemical structures. The activated carbons were also degassed at different temperatures between 400°C and 950°C [22,27-29] to gradually eliminate...
these surface chemical structures. The details of the oxidation and degassing treatments are described in Chapter VII in the thesis.

0.2 g of each of the activated carbon sample was placed in contact with 20 mL solutions of different concentrations of potassium dichromate for the adsorption of Cr(VI) ions and of chromium chloride for the adsorption of Cr(III) ions. The change in concentration due to adsorption was determined spectrophotometrically using standard procedures as given in Chapter VII.

RESULTS AND DISCUSSION

ADSORPTION OF Cr(III)

Adsorption isotherms of Cr(III) ions from aqueous solutions of chromium chloride in the concentration range 20 to 1000 mg/L on two samples of granulated activated carbons GAC-E and GAC-S and two samples of activated carbon fibers ACF-307 and ACF-310 are shown in Fig. 1. All the isotherms have been determined without addition of any buffer solution to avoid the addition of any external electrolyte which may influence the adsorption process. It is seen that all the activated carbons, granular as well as fibrous, adsorb appreciable amounts of Cr(III) ions and that the amount adsorbed at each concentration is different for different carbons. In general, the granulated activated carbons adsorb larger amounts of Cr(III) ions compared to fibrous activated carbons. The adsorption is maximum in the case of carbon GAC-S and minimum in the case of carbon ACF-307. The adsorption of GAC-S is almost three times the adsorption of ACF-307. This may be attributed to the highly microporous nature of the activated carbon fibers. Activated carbon fibers are known to contain a larger proportion of very small microcapillary pores which may be inaccessible to highly hydrated Cr(III) ions.
FIG. 1 ADSORPTION ISOTHERMS OF Cr(III) ON DIFFERENT AS-RECEIVED ACTIVATED CARBONS.
Cr(III) ion in aqueous solution exists as [Cr(H₂O)₆]³⁺ which has a molecular diameter of 0.922 nm [30] and consequently is accessible only to pores larger than 1 nm. Furthermore, it is seen that the adsorption of Cr(III) on ACF-310 is less than the adsorption on GAC-S, although the surface area of ACF-310 (1284 m²/g) is larger than the surface area of GAC-S (1156 m²/g) (cf. Table I). This once again indicates that ACF-310 has a larger proportion of the micropores inaccessible to hydrated Cr(III) ions.

It is well known that all activated carbons are associated with varying amounts of chemisorbed oxygen, the amount depending upon the source raw material and the history of their preparations. This oxygen in carbons is present in the form of surface oxygen groups, some of which are acidic in character. Since the pH of the solution has a great influence on the adsorption of Cr(III) ions from aqueous solutions and since these acidic surface groups ionise in water producing H⁺ ions, the presence of acidic surface groups are expected to influence the adsorption of Cr(III) ions.

The amounts of these surface groups which are evolved as CO₂ and CO on degassing were determined and are given in Table I. It is seen that different carbons have different amounts of the carbon-oxygen surface groups. While the granulated activated carbons GAC-E and GAC-S have larger amounts of the surface groups evolved as CO₂, the fibrous activated carbons ACF-307 and ACF-310 have larger amounts of the carbon-oxygen surface groups evolved as CO. As the amount of adsorption of Cr(III) is larger in the case of granulated activated carbons, it appears that the surface groups evolved as CO₂ have a larger influence on the adsorption of Cr(III) ions.

In order to examine the influence of these two surface groups more clearly, the activated carbons were oxidised with nitric acid, ammonium persulphate and hydrogen peroxide in the solution phase and with oxygen gas at 350°C. These treatments are known [31] to enhance the amount of chemisorbed oxygen on the carbon surface. The
Table I
Surface areas and amounts of oxygen evolved on degassing different as-received activated carbons at 950°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
<th>Oxygen evolved (g/100g) as CO₂</th>
<th>CO</th>
<th>H₂O</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACF-307</td>
<td>910</td>
<td>1.00</td>
<td>5.30</td>
<td>2.30</td>
<td>8.60</td>
</tr>
<tr>
<td>ACF-310</td>
<td>1284</td>
<td>1.90</td>
<td>4.20</td>
<td>2.40</td>
<td>8.50</td>
</tr>
<tr>
<td>GAC-S</td>
<td>1156</td>
<td>2.10</td>
<td>1.05</td>
<td>1.24</td>
<td>4.39</td>
</tr>
<tr>
<td>GAC-E</td>
<td>1113</td>
<td>2.13</td>
<td>1.66</td>
<td>1.73</td>
<td>5.52</td>
</tr>
</tbody>
</table>
amount of these two types of oxygen groups after oxidation with these different oxidising
agents are recorded in Table II. It is seen that the oxidation with nitric acid enhances the
amount of chemisorbed oxygen by several orders of magnitude while the enhancement is
much less in the case of oxidation with ammonium persulphate, hydrogen peroxide and
gaseous oxygen. The adsorption isotherms of Cr(III) ions on the oxidised samples are
presented in Figs. 2-5. The adsorption increases on oxidation in all the cases although
the increase in adsorption depends upon the nature of the oxidative treatment. The
increase in adsorption is maximum in case of the sample oxidised with nitric acid and
minimum in case of the oxidation with hydrogen peroxide. This may be attributed to the
fact that the oxidation with nitric acid enhances the amount of chemisorbed oxygen by
considerably large amounts compared to other oxidative treatments.

The adsorption isotherms of Cr(III) ions on activated carbon samples degassed at
gradually increasing temperature upto 950°C are presented in Figs. 6-9. It is interesting to
note that the adsorption of Cr(III) ions decreases gradually as the temperature of
degassing is increased. The degassing of the carbon at 400°C decreases the adsorption
of Cr(III) but only slightly. However, when the temperature of degassing is enhanced to
650°C, the adsorption in the case of GAC-S decreases from 1.24% in the case of the as-
received samples to less than 0.65% in the case of the sample degassed at 650°C. (cf. Fig.
6). In the case of other samples also the decrease in adsorption is quite considerable.
When the carbon samples are degassed at 950°C, there is little or no adsorption of
Cr(III). This gradual decrease in the adsorption of Cr(III) with gradual increase in
temperature of degassing is quite interesting.

In order to confirm these observations further, oxidised activated carbon samples
were degassed at 400°, 650° and 950°C and the adsorption isotherms were redetermined.
The results are presented in Figs. 10-13. It is seen that, as before, the adsorption decreases
Table II

Amount of oxygen evolved on degassing different oxidised samples at 950°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxygen evolved (g/100g) as</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂</td>
</tr>
<tr>
<td>ACF-307, Oxidised with—</td>
<td></td>
</tr>
<tr>
<td>HNO₃</td>
<td>12.90</td>
</tr>
<tr>
<td>(NH₄)₂S₂O₈</td>
<td>5.40</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>2.55</td>
</tr>
<tr>
<td>O₂</td>
<td>3.11</td>
</tr>
<tr>
<td>ACF-310, Oxidised with—</td>
<td></td>
</tr>
<tr>
<td>HNO₃</td>
<td>11.96</td>
</tr>
<tr>
<td>(NH₄)₂S₂O₈</td>
<td>4.70</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>1.70</td>
</tr>
<tr>
<td>GAC-S, Oxidised with—</td>
<td></td>
</tr>
<tr>
<td>HNO₃</td>
<td>12.20</td>
</tr>
<tr>
<td>(NH₄)₂S₂O₈</td>
<td>6.34</td>
</tr>
<tr>
<td>GAC-E, Oxidised with—</td>
<td></td>
</tr>
<tr>
<td>HNO₃</td>
<td>12.40</td>
</tr>
<tr>
<td>(NH₄)₂S₂O₈</td>
<td>4.63</td>
</tr>
<tr>
<td>O₂</td>
<td>2.17</td>
</tr>
</tbody>
</table>
FIG. 2 ADSORPTION ISOTHERMS OF Cr(III) ON ACF-307 BEFORE AND AFTER OXIDATION

- As-received
- Oxidised with HNO₃
- Oxidised with O₂
- Oxidised with H₂O₂
- Oxidised with (NH₄)₂S₂O₈

Concentration (mg/L)

Amount Adsorbed (mg/g)

Concentration (mg/L) →
FIG. 3 ADSORPTION ISOTHERMS OF Cr(III) ON GAC-E BEFORE AND AFTER OXIDATION

- As-received
- Oxidised with HNO₃
- Oxidised with O₂
- Oxidised with (NH₄)₂S₂O₈

Amount Adsorbed (mg/g) vs Concentration (mg/L)
FIG. 4 ADSORPTION ISOTHERMS OF Cr (III) ON ACF-310 BEFORE AND AFTER OXIDATION.

- O—O As-received
- ●—● Oxidised with HNO₃
- △—△ Oxidised with (NH₄)₂S₂O₈
- □—□ Oxidised with H₂O₂
FIG. 5 ADSORPTION ISOTHERMS OF Cr(III) ON GAC-S BEFORE AND AFTER OXIDATION

- As-received
- Oxidised with HNO₃
- Oxidised with (NH₄)₂S₂O₈
- Oxidised with H₂O₂
FIG. 6 ADSORPTION ISOTHERMS OF Cr(III) ON GAC-S BEFORE AND AFTER DEGASSING.
FIG. 7 ADSORPTION ISOTHERMS OF Cr (III) ON GAC-E BEFORE AND AFTER DEGASSING

- ○ As-received
- ● 400°-degassed
- ▽ 650°-degassed
- ▼ 950°-degassed
FIG. 8 ADSORPTION ISOTHERMS OF Cr(III) ON ACF-310 BEFORE AND AFTER DEGASSING

- As-received
- 400°-degassed
- 650°-degassed
- 950°-degassed

Amount Adsorbed (mg/g) vs. Concentration (mg/L)
FIG. 9 ADSORPTION ISOTHERMS OF Cr (III) ON ACF-307 BEFORE AND AFTER DEGASSING

- As-received
- 400°-degassed
- 650°-degassed
- 950°-degassed

Amount Adsorbed (mg/g)

Concentration (mg/L)
FIG. 10 ADSORPTION ISOTHERMS OF Cr (III) ON GAC-E BEFORE AND AFTER OXIDATION AND DEGASSING

- As received
- Oxidised with HNO₃
- Oxidised and then degassed at 400°
- Oxidised and then degassed at 650°
- Oxidised and then degassed at 950°

![Graph showing adsorption isotherms of Cr (III) on GAC-E before and after oxidation and degassing.](image-url)
FIG. 11 ADSORPTION ISOTHERMS OF Cr(III) ON GAC-E BEFORE AND AFTER OXIDATION AND DEGASSING

- As-received
- Oxidised with O$_2$
- Oxidised and then degassed at 400$^\circ$C
- Oxidised and then degassed at 650$^\circ$C
- Oxidised and then degassed at 950$^\circ$C
FIG 12 ADSORPTION ISOTHERMS OF Cr(III) ON ACF-307 BEFORE AND AFTER OXIDATION AND DEGASSING

- ○ As received
- ● Oxidised with HNO₃
- ▲ Oxidised and then degassed at 400°
- ▼ Oxidised and then degassed at 650°
- □ Oxidised and then degassed at 950°
FIG. 13 ADSORPTION ISOTHERMS OF Cr(III) ON ACF-307 BEFORE AND AFTER OXIDATION AND DEGASSING

- As-received
- Oxidised with O₂
- Oxidised and then degassed at 400°
- Oxidised and then degassed at 650°
- Oxidised and then degassed at 950°
gradually with gradual increase in the temperature of degassing. It may be worthwhile to mention here that the oxygen on the surface of carbon is present in the form of two types of carbon-oxygen surface complexes, one of which is acidic in character and is evolved as \( \text{CO}_2 \) on evacuation in the temperature range 400°-650°C. The other group which is evolved as \( \text{CO} \) in the temperature range 600°-950°C is non-acidic in character [22,28,32,33]. The former are postulated as carboxylic or lactonic groups while the latter are postulated as quinonic groups. When the carbon is degassed at 400°C only a small part of the acidic surface groups (cf. Table III) is evolved. However, when the carbons are degassed at 650°C, almost all the acidic surface groups are eliminated, while the carbons retain a larger proportion of their non-acidic surface groups. The 950°-degassed carbon samples are almost completely free of any associated oxygen (both acidic and non-acidic) (cf. Table III). It appears that the adsorption of \( \text{Cr(III)} \) is determined largely by the presence of oxygen surface groups and more so by the presence of those oxygen groups which are acidic in character and are evolved as \( \text{CO}_2 \) on degassing.

The surface area occupied by \( \text{Cr(III)} \) ions has been calculated from the Langmuir linear plots and using 0.922 nm [20] as the molecular diameter of \( \text{Cr(III)} \) ion. These values are included in Table IV-VI. It is interesting to note that only a small fraction of the BET surface area in all the carbons is occupied by \( \text{Cr(III)} \) ions. Furthermore, the area covered increases on oxidation and decreases on degassing of the carbons. This indicates that the adsorption of \( \text{Cr(III)} \) ions takes place on certain specific sites. These sites appear to be oxygen groups, more so the acidic oxygen groups, present on the carbon surface. It appears that the \( \text{Cr(III)} \) ions are bonded to the acidic surface sites by forces which may involve hydrogen bonding [34]. The acidic surface groups which have been postulated to be carboxylic [35-38] and lactonic [26,32,35] groups ionise in aqueous solution producing \( \text{H}^+ \) ions. As a result of this ionisation, the activated carbon surface in
Table III

Amount of oxygen evolved on evacuating different degassed samples at 950°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxygen evolved (g/100g) as</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂</td>
<td>CO</td>
<td>H₂O</td>
<td>Total</td>
</tr>
<tr>
<td>ACF-307, degassed at (°C)---</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>0.72</td>
<td>5.24</td>
<td>2.11</td>
<td>8.07</td>
</tr>
<tr>
<td>650</td>
<td>0.21</td>
<td>3.23</td>
<td>Tr</td>
<td>3.44</td>
</tr>
<tr>
<td>950</td>
<td>--</td>
<td>0.07</td>
<td>Tr</td>
<td>0.07</td>
</tr>
<tr>
<td>ACF-310, degassed at (°C)---</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>1.47</td>
<td>4.03</td>
<td>1.92</td>
<td>7.42</td>
</tr>
<tr>
<td>650</td>
<td>0.32</td>
<td>2.17</td>
<td>Tr</td>
<td>2.49</td>
</tr>
<tr>
<td>950</td>
<td>--</td>
<td>0.23</td>
<td>Tr</td>
<td>0.23</td>
</tr>
<tr>
<td>GAC-S, degassed at (°C)---</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>1.67</td>
<td>0.97</td>
<td>1.12</td>
<td>3.76</td>
</tr>
<tr>
<td>650</td>
<td>0.27</td>
<td>0.57</td>
<td>Tr</td>
<td>0.84</td>
</tr>
<tr>
<td>950</td>
<td>--</td>
<td>0.04</td>
<td>Tr</td>
<td>0.04</td>
</tr>
<tr>
<td>GAC-E, degassed at (°C)---</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>1.72</td>
<td>1.52</td>
<td>1.24</td>
<td>4.48</td>
</tr>
<tr>
<td>650</td>
<td>0.40</td>
<td>0.84</td>
<td>Tr</td>
<td>1.24</td>
</tr>
<tr>
<td>950</td>
<td>--</td>
<td>0.09</td>
<td>Tr</td>
<td>0.09</td>
</tr>
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</table>

Tr - Traces

561
Table IV
Data obtained from Langmuir adsorption isotherms of Cr(III) ions on different as-received activated carbons

<table>
<thead>
<tr>
<th>Sample</th>
<th>$x_m$ (mg/g)</th>
<th>$K$ (L/g)</th>
<th>$S_{Cr^{3+}}$ (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAC-S</td>
<td>13.31</td>
<td>0.07</td>
<td>103.1</td>
</tr>
<tr>
<td>GAC-E</td>
<td>10.52</td>
<td>0.08</td>
<td>80.5</td>
</tr>
<tr>
<td>ACF-307</td>
<td>7.08</td>
<td>0.10</td>
<td>58.8</td>
</tr>
<tr>
<td>ACF-310</td>
<td>3.52</td>
<td>0.07</td>
<td>27.3</td>
</tr>
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</table>

$x_m$ is the maximum amount of Cr(III) ions adsorbed by activated carbon, $K$ is Langmuir's constant and $S_{Cr^{3+}}$ is surface area of activated carbon occupied by Cr(III) ions.
Table V

Data obtained from Langmuir adsorption isotherms of Cr(III) ions on oxidised GAC-E and ACF-307

<table>
<thead>
<tr>
<th>Sample</th>
<th>$x_m$(mg/g)</th>
<th>K (L/g)</th>
<th>$S_{Cr^{3+}}$(m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACF-307, Oxidised with</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>20.24</td>
<td>0.33</td>
<td>156.9</td>
</tr>
<tr>
<td>(NH$_4$)$_2$S$_2$O$_8$</td>
<td>15.62</td>
<td>0.25</td>
<td>121.0</td>
</tr>
<tr>
<td>O$_2$</td>
<td>13.66</td>
<td>0.20</td>
<td>105.4</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>6.40</td>
<td>0.06</td>
<td>49.6</td>
</tr>
<tr>
<td>GAC-E, Oxidised with</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>35.16</td>
<td>0.12</td>
<td>272.5</td>
</tr>
<tr>
<td>(NH$_4$)$_2$S$_2$O$_8$</td>
<td>21.93</td>
<td>0.10</td>
<td>169.9</td>
</tr>
<tr>
<td>O$_2$</td>
<td>18.93</td>
<td>0.06</td>
<td>146.7</td>
</tr>
</tbody>
</table>

$x_m$ is the maximum amount of Cr(III) ions adsorbed by activated carbon, K is Langmuir's constant and $S_{Cr^{3+}}$ is surface area of activated carbon occupied by Cr(III) ions.
Table VI

Data obtained from Langmuir adsorption isotherms of Cr(III) ions on degassed GAC-E and ACF-307

<table>
<thead>
<tr>
<th>Sample</th>
<th>$x_m$ (mg/g)</th>
<th>$K$ (L/g)</th>
<th>$S_{Cr}^{3+}$ ($m^2/g$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACF-307, degassed at (°C)---</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>3.20</td>
<td>0.02</td>
<td>24.8</td>
</tr>
<tr>
<td>650</td>
<td>2.06</td>
<td>0.01</td>
<td>16.0</td>
</tr>
<tr>
<td>950</td>
<td>0.66</td>
<td>0.00</td>
<td>5.1</td>
</tr>
<tr>
<td>GAC-E, degassed at (°C)---</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>10.30</td>
<td>0.05</td>
<td>79.8</td>
</tr>
<tr>
<td>650</td>
<td>8.62</td>
<td>0.02</td>
<td>66.8</td>
</tr>
<tr>
<td>950</td>
<td>1.92</td>
<td>0.01</td>
<td>14.9</td>
</tr>
</tbody>
</table>

$x_m$ is the maximum amount of Cr(III) ions adsorbed by activated carbon, $K$ is Langmuir’s constant and $S_{Cr}^{3+}$ is surface area of activated carbon occupied by Cr(III) ions.
aqueous solutions acquires a negative charge depending upon the amount of acidic surface oxygen groups. The surface of carbon oxidised with nitric acid, consequently has a larger negative charge than the surface of the carbon oxidised with hydrogen peroxide, ammonium persulphate and oxygen gas. When the oxygen surface groups which impart negative character to the carbon surface are removed on degassing, the carbon surface becomes lesser and lesser negatively charged. Furthermore, the presence of acidic surface groups on the carbon surface changes the pH of the carbon suspension in aqueous solutions.

The chromic ions in aqueous solutions exist as \([\text{Cr(O}_2\text{H})_6]\)^3+. The associated water molecules around the chromic ions are exchanged with the hydroxyl ions, the number depending upon the pH of the solution [39].

\[
\begin{align*}
[\text{Cr(O}_2\text{H})_6]\]^{3+} & \leftrightarrow [\text{Cr(O}_2\text{H})_2\text{OH}]^{2+} \leftrightarrow [\text{Cr(O}_2\text{H})_4\text{OH}]^{1+} \\
pH=3-4 & \leftrightarrow pH=6-7 & \leftrightarrow pH=8
\end{align*}
\]

Thus a change in pH of the solution, as a result of the change in pH of the carbon surface will change the extent of the positive charge on the chromic ion.

These changes in the charge on the carbon surface as a result of oxidation and the changes in the charge on the Cr(III) ions in solution favour the adsorption of Cr(III) ions because the electrostatic attractive interactions between the carbon surface and the chromium ions present in the solution are enhanced. On degassing, these electrostatic attractive interactions between the carbon surface and the Cr(III) ions in the solution
gradually decreases and result in a decrease in the adsorption of Cr(III) ions. When all the surface oxygen complexes are removed almost completely on degassing at 950°C, the carbon surface lose its capacity to adsorb Cr(III) ions almost completely as the carbon surface tends to acquire a positive charge.

**ADSORPTION OF Cr(VI)**

Adsorption isotherms of Cr(VI) from aqueous solutions of potassium dichromate in the concentration range 20-1000 mg/L on the four samples of activated carbons without adding any buffering reagent are shown in Fig. 14. Each carbon adsorbs appreciable amounts of Cr(VI) ions. However, the amount of Cr(VI) adsorbed is comparatively much larger than the amount of Cr(III) ions adsorbed under similar conditions. This larger adsorption in the case of Cr(VI) may be attributed partly to the smaller size of the Cr(VI) ion in water so that it can enter a larger proportion of the microcapillary pores and partly to the fact that Cr(VI) ion is adsorbed as an anion. As the pH of the carbon suspension of as-received activated carbons is in the range of 7.2-10.0, there is a preponderance of positively charged sites where negatively charged Cr(VI) ions can be adsorbed.

The effect of pH of the solution on the adsorption of Cr(VI) was also examined using buffering reagents to control the pH of the solution. It has been found that the adsorption of Cr(VI) ions is maximum at pH between 5 and 6. However, this increase in adsorption could be attributed to the influence of the buffering electrolytes on the adsorption of Cr(VI) ions. It has been shown that the addition of electrolyte into the solution considerably affects the adsorption of Cr(VI) [17].

In order to examine the effect of the nature of the carbon surface on the adsorption of Cr(VI) ions, the adsorption isotherms of Cr(VI) ions on the oxidised carbons were
FIG. 14 ADSORPTION ISOTHERMS OF Cr (VI) ON FOUR DIFFERENT AS-RECEIVED ACTIVATED CARBONS
determined and are presented in Figs. 15-18. The adsorption isotherms of the as-received activated carbons are also included in these figures for comparison. It is interesting to note that in all the carbons the adsorption of Cr(VI) ions decrease on oxidation. The decrease in adsorption, however, is larger in the case of oxidation with nitric acid and smaller for oxidation with ammonium persulphate or gaseous oxygen.

This decrease in the adsorption of Cr(VI) can be attributed to the formation of carbon-oxygen surface groups which impart negative character to the carbon surface. As the oxidation with nitric acid is a stronger oxidative treatment, it results in the formation of larger amounts of acidic surface oxygen groups compared to other oxidative treatments and hence causes a larger decrease in the adsorption of Cr(VI) ions. It may, however, be mentioned that the oxidation of carbons also enhance the amount of non-acidic carbon oxygen surface groups which have been postulated as quinones [40-42]. These quinonic groups can cause reduction of Cr(VI) into Cr(III) ions. Thus in the case of oxidised carbons two processes are occurring simultaneously: the increase in the removal of Cr(VI) due to its reduction to Cr(III) by the non-acidic quinonic groups and the decrease in adsorption of Cr(VI) ions due to the formation of acidic surface groups. In actual practice, however, the adsorption of Cr(VI) ions is found to decrease in all oxidised carbons. It appears that the increase in the removal of Cr(VI) ions from the solution by reduction of Cr(III) is small. This can be attributed to the fact that the optimum pH for the reduction of Cr(VI) to Cr(III) ions is around 5. As the oxidised carbons generally have pH value of less than 5, there is little or no reduction of Cr(VI) into Cr(III) ions in these cases.

In order to examine this aspect more clearly, adsorption isotherms of Cr(VI) were determined on carbon samples degassed at gradually increasing temperatures. These adsorption isotherms are presented in Figs. 19-20. It is seen that the adsorption of
FIG 15 ADSORPTION ISOTHERMS OF Cr (VI) ON ACF-307 BEFORE AND AFTER OXIDATION

- As-received
- Oxidised with $\text{HNO}_3$
- Oxidised with $(\text{NH}_4)_2 \text{S}_2\text{O}_8$
FIG. 16 ADSORPTION ISOOTHERMS OF Cr(VI) ON ACF-310 BEFORE AND AFTER DEGASSING

- As-received
- Oxidised with HNO$_3$
- Oxidised with (NH$_4$)$_2$S$_2$O$_8$
FIG. 17 ADSORPTION ISOTHERMS OF Cr(VI) ON GAC-S BEFORE AND AFTER OXIDATION

- `O` - As-received
- `●` - Oxidised with HNO₃
- `△` - Oxidised with (NH₄)₂S₂O₈

Amount Adsorbed (mg/g) vs Concentration (mg/L)
FIG. 18 ADSORPTION ISOTHERMS OF Cr (VI) ON GAC-E BEFORE AND AFTER OXIDATION

- ○ As-received
- ● Oxidised with HNO₃
- × Oxidised with O₂
- △ Oxidised with (NH₄)₂ S₂O₈

Amount Adsorbed (mg/g) vs. Concentration (mg/L)
FIG. 19 ADSORPTION ISOTHERMS OF Cr (VI) ON ACF-307 BEFORE AND AFTER DEGASSING

- As received
- 400°-degassed
- 650°-degassed
- 950°-degassed

Amount Adsorbed (mg/g) vs. Concentration (mg/L)
FIG. 20 ADSORPTION ISOTHERMS OF Cr (VI) ON GAC-E BEFORE AND AFTER DEGASSING

- As-received
- 400°C-degassed
- 650°C-degassed
- 950°C-degassed

Amount Adsorbed (mg/g) vs. Concentration (mg/L)
Cr(VI) increases on degassing, being maximum in the case of 650°C-degassed carbon samples. This can be explained in terms of the amount and the type of the surface oxygen groups which are being eliminated at different degassing temperatures.

The evacuation data presented in Table III show that the 400°C-degassed carbon samples have lost only a part (around 20%) of the acidic surface groups (CO₂-evolving groups) while they retain most of their non-acidic surface groups (CO-evolving groups). 650°C-degassed carbons, on the other hand, have lost most of their acidic surface groups (around 80%) and only a small part of the non-acidic surface groups. The 950°C-degassed sample is almost completely free of any surface oxygen groups. As the removal of acidic surface groups tends to decrease the negative character of the carbon surface, the repulsive interactions between the carbon surface and the negatively charged Cr(VI) ions decrease. Thus there is an increase in the adsorption of Cr(VI) ions. As 400°C-degassed carbon samples lose only a small part of the acidic groups, there is a small increase in the adsorption of Cr(VI) ions.

In the case of 650°C-degassed sample, almost all the acidic groups have been eliminated and the dominating groups on the carbon surface are quinonic groups. The pH of the carbon suspensions in these cases is around 5.5. This pH is very favourable for the reduction of Cr(VI) into Cr(III), since the standard reduction potential of the system Cr(VI) - Cr(III) in acid medium is +1.195 V against a quinhydrone electrode potential of +0.699 V [18]. This reduction process of Cr(VI) into Cr(III) at this pH has been supported by FTIR studies carried out by Bautista - Toledo et al. [17]. Thus 650°C-degassed carbon samples show a maximum removal of Cr(VI) ions. In the case of 950°C-degassed carbon samples the adsorption decreases considerably because there are no interactive groups present on the carbon surface. Whatever adsorption takes place may be attributed to the porosity of the carbons.
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