CHAPTER III

ADSORPTION OF COBALT FROM AQUEOUS SOLUTION BY ACTIVATED CARBONS

INTRODUCTION

Cobalt is one of the heavy metals which is present in the effluent of several industries. Consequently its removal from water by adsorption on different adsorbents has been studied by several investigators. Kaya and Akyol [1] studied the adsorption of Co (II), Cu (II) and Cd (II) ions from aqueous solution by activated bentonite as a function of metal ion concentration, temperature, contact time and observed that appreciable amounts of these metal ions could be removed. Shakir et al. [2] examined the removal of Co (II) ions from radioactive process waste water using activated charcoal as the adsorbent and gelatin as a collector. The effect of pH of the solution and that of the charcoal and the amount of collector was also studied. These workers found that removals better than 97% could be achieved under optimum conditions in the pH range 7.5-10.0. The results have been discussed in terms of hydrolysis of the metal ion. In a later publication Shakir et al. [3] used Kaolinite for the removal of Co(II) ions from aqueous solutions in the presence of cationic and anionic surfactants. The removal of Co(II) increased with increase in pH. The presence of strongly ionised cationic or anionic surfactants decreased the removal while the presence of weakly ionised surfactants enhanced the removal of Co (II) ions.

Rivera-Utrilla and Ferro-Garcia [4] investigated the adsorption of Co (II) ions from aqueous solution by activated carbons derived from almond shells. The Co (II) ion
uptake on these activated carbons increased with increasing activation time. Considerable enhancement of Co (II) uptake was found when these carbons were treated with concentrated nitric acid. These workers also studied the influence of pH on the adsorption of Co (II) ions.

It appears that the adsorptive removal of Co (II) ions by activated carbons varying in surface area and carbon-oxygen surface structures has not been studied. The present work was, therefore, undertaken.

Two samples of fibrous activated carbons and two samples of granulated activated carbons have been used in these studies. The carbons were oxidised with nitric acid ammonium persulphate and with gaseous oxygen and then degassed at 400°, 650° and 950°C. The oxidation and degassing procedures have been discussed in detail in the experimental part (Chapter VII) of the thesis.

0.2 g of each carbon sample was placed in contact with 20 mL solution of cobalt acetate of different concentrations and the amount adsorbed was determined spectrophotometrically using standard analytical procedures (Chapter VII).

RESULTS AND DISCUSSION

The adsorption isotherms of Co (II) ions from aqueous solutions of cobalt acetate in the concentration range 20-1000 mg/L on the four samples of activated carbons are presented in Fig. 1. All the four samples adsorb appreciable amounts of Co (II) ions although the amount adsorbed is different in different carbons. In general, the granulated activated carbons GAC-S and GAC-E adsorb larger amount of Co (II) than the fibrous activated carbons ACF-307 and ACF-310. This cannot be attributed to surface area alone because GAC-E has smaller surface area (1113 m²/g) than ACF-310 (1284 m²/g), although it adsorbs larger amounts of Co (II) ions. It appears that besides surface area the
FIG. 1 ADSORPTION ISOTHERMS OF Co(II) IONS ON DIFFERENT ACTIVATED CARBONS.

Amount adsorbed (mg/g)

Concentration (mg/L)

ACF-307
ACF-310
GAC-S
GAC-E
nature of the carbon surface also influences the adsorption of Co (II) ions from aqueous solutions.

The adsorption isotherms are Langmuirian in shape showing a rapid adsorption at low concentrations and ultimately leveling off at higher concentrations. The Langmuir adsorption isotherm can be represented by the equation:

\[ x = \frac{x_m (KC)^n}{(1+KC)^n} \]

where \( x \) is the amount adsorbed at equilibrium concentration \( C \), \( x_m \) is the maximum amount of Co(II) adsorbed, \( K \) is the Langmuir constant and \( n \) is the parameter characterising quasi-Gaussian energetic heterogeneity of the adsorption system. The above equation leads to Freundlich adsorption isotherm at low concentration, when \((KC)^n < 1\),

\[ x = x_m (KC)^n \]

For lower solute concentration both the above isotherms give good agreement with the linear form of the Freundlich equation [5]:

\[ \ln x = \ln K + n \ln C \]

where \( K = x_m K \).

The linear Freundlich adsorption isotherms on log-log scale for the four activated carbons are shown in Fig. 2. The values of Freundlich equation constant \( n \) obtained from linear plots along with the maximum amount adsorbed \( x_m \) are recorded in Table I. It is seen that the value of \( n \) which is a measure of the surface heterogeneity is different for different carbons. In fact, the heterogeneity of the surface increases as the value of \( n \) decreases. This indicates that fibrous activated carbons have slightly more heterogeneous surfaces than the granulated activated carbons. This may be attributed to the fact that the fibrous activated carbons are associated with larger amounts of carbon-oxygen surface structures compared to granulated activated carbons (cf. Table I of Chapter II).
FIG. 2 FREUNDLICH ADSORPTION ISOTHERMS FOR Co(II)IONS ON DIFFERENT ACTIVATED CARBONS.

- ACF-307
- ACF-310
- GAC-S
- GAC-E
Table-I
Parameters of Freundlich adsorption isotherms on four different as-received activated carbons

<table>
<thead>
<tr>
<th>Sample</th>
<th>$x_m$ (mg/g)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAC-S</td>
<td>38.5</td>
<td>0.41</td>
</tr>
<tr>
<td>GAC-E</td>
<td>21.2</td>
<td>0.39</td>
</tr>
<tr>
<td>ACF-307</td>
<td>11.3</td>
<td>0.38</td>
</tr>
<tr>
<td>ACF-310</td>
<td>9.4</td>
<td>0.37</td>
</tr>
</tbody>
</table>
This receives support from the values of $n$ obtained from Freundlich adsorption isotherms for oxidised and degassed carbon samples (Fig. 3-6, Table II and III). It is evident that the value of $n$ decreases on oxidation of the carbons with nitric acid, ammonium persulphate and gaseous oxygen. However, when these oxidised carbons are degassed at gradually increasing temperatures between 400° and 950°C, the $n$ value show a gradual increase. Furthermore, the value of $n$ is minimum in case of the oxidation with nitric acid which incidentally causes a maximum increase in the amount of carbon-oxygen surface structures while the value of $n$ is maximum for the 950°-degassed sample which contains little or no associated oxygen.

In order to examine the influence of associated oxygen on the adsorption of Co(II) ions, the adsorption isotherms were determined on the oxidised carbon samples. These adsorption isotherms are presented in Figs. 7 and 8. The adsorption isotherm on the as-received sample are also reproduced in these figures. It is seen that the adsorption increases considerably on oxidation. The increase in adsorption is maximum in case of the samples oxidised with nitric acid, the increase being between 80-100%. In case of the treatment with oxygen gas the increase in adsorption is minimum. This may be attributed to the fact that nitric acid is a stronger oxidative treatment and results in the formation of larger amount of carbon-oxygen surface chemical groups (cf. Table II of Chapter V). These carbon-oxygen surface structures provide sites for the adsorption of Co (II) ions.

It has been shown in Chapter II of the thesis that the oxidation with nitric acid creates surface structures which are largely acidic in character. The treatment with ammonium persulphate and oxygen gas on the other hand produces both acidic and non-acidic surface groups. The increase in adsorption of Co(II) ions which is much larger in the case of carbon samples oxidised with nitric acid is due to the formation of larger amount of acidic surface groups.
FIG. 3 FREUNDLICH ADSORPTION ISOTHERMS FOR Co(II) IONS ON OXIDISED ACF-307 BEFORE AND AFTER DEGASSING.
FIG. 4 FREUNDLICH ADSORPTION ISOTHERMS FOR Co(II) IONS ON OXIDISED ACF-307 BEFORE AND AFTER DEGASSING.
FIG. 5 FREUNDLICH ADSORPTION ISOTHERMS FOR Co(II) IONS ON OXIDISED GAC-E BEFORE AND AFTER DEGASSING.

- Oxidised with HNO₃
- Degassed at 400°
- Degassed at 650°
- Degassed at 950°

log (amount adsorbed, mg/g)
log (concentration, mg/L)
FIG. 6 FREUNDLICH ADSORPTION ISOTHERMS FOR Co(II) IONS ON OXIDISED GAC-E BEFORE AND AFTER DEGASSING.

- Oxidised with O₂
- Degassed at 400°
- Degassed at 650°
- Degassed at 950°

log (amount adsorbed, mg/g) vs. log (concentration, mg/L)
### Table-II

Parameters of Freundlich adsorption isotherms on oxidised and degassed ACF-307

<table>
<thead>
<tr>
<th>Sample</th>
<th>$x_m$ (mg/g)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidised with HNO$_3$</td>
<td>30.4</td>
<td>0.29</td>
</tr>
<tr>
<td>Oxidised and then degassed at (°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>21.6</td>
<td>0.47</td>
</tr>
<tr>
<td>650</td>
<td>17.4</td>
<td>0.51</td>
</tr>
<tr>
<td>950</td>
<td>7.7</td>
<td>0.63</td>
</tr>
<tr>
<td>Oxidised with O$_2$</td>
<td>13.1</td>
<td>0.35</td>
</tr>
<tr>
<td>Oxidised and then degassed at (°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>10.6</td>
<td>0.42</td>
</tr>
<tr>
<td>650</td>
<td>8.2</td>
<td>0.47</td>
</tr>
<tr>
<td>950</td>
<td>6.1</td>
<td>0.57</td>
</tr>
</tbody>
</table>
### Table-III
Parameters of Freundlich adsorption isotherms on oxidised and degassed GAC-E

<table>
<thead>
<tr>
<th>Sample</th>
<th>( x_m ) (mg/g)</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidised with HNO(_3)</td>
<td>34.9</td>
<td>0.38</td>
</tr>
</tbody>
</table>
| Oxidised and then degassed at (°C)--
  400                                        |                  |         |
| 650                                         | 30.1             | 0.47    |
| 950                                         | 25.1             | 0.51    |
|                                              | 17.5             | 0.63    |
| Oxidised with O\(_2\)                      |                  |         |
| Oxidised and then degassed at (°C)--
  400                                        | 24.5             | 0.39    |
| 650                                         | 19.6             | 0.54    |
| 950                                         | 15.1             | 0.66    |
|                                              | 12.6             | 0.67    |
FIG. 7 ADSORPTION ISOTHERMS OF Co(II) IONS ON ACF-307 BEFORE AND AFTER OXIDATION.

- ACF-307
- Oxidised with HNO₃
- Oxidised with O₂

Amount adsorbed (mg/g) vs. Concentration (mg/L)
FIG. 8 ADSORPTION ISOTHERMS OF Co(II) IONS ON GAC-E BEFORE AND AFTER OXIDATION.
The oxidation of carbons and the formation of acidic groups also causes a change in the pH of the carbon surfaces. The pH of as-received ACF-307 is about 7 while that of GAC-E is about 10. When these carbons are oxidised with nitric acid, the pH is reduced to between 4 and 5. The oxidation with $O_2$ reduces the pH to between 5 and 6. As the adsorption of metal ions is very sensitive to pH of the solution and as it increases with decrease in pH of the solution in this range (cf. Fig. 9), the increase in adsorption of Co(II) ions can be visualised.

This receives support from the adsorption isotherms of Co(II) ions on oxidised carbon samples degassed at 400°C, 650°C and 950°C. This treatment eliminates varying amounts of the two types of surface chemical structures depending upon the temperatures of degassing. The results of these studies are presented in Figs. 10-13. It is interesting to note that the adsorption of Co(II) ions decreases gradually as the chemisorbed oxygen is being eliminated from the carbon surface. As in the case of adsorption of Cr(III) ions (Chapter-II), the decrease in adsorption is very small in case of the 400°C-degassed carbon samples. This can be attributed to the fact that this temperature results in the elimination of only a very small part of the acidic surface oxygen groups (Table II and III of Chapter V). When the carbon samples are degassed at 650°C, a larger part of the acidic surface oxygen groups are eliminated as CO$_2$ resulting in a considerable decrease in the adsorption of Co(II) ions, although this sample still retains a larger proportion of the non-acidic surface groups evolving as CO. In case of the sample degassed at 950°C, the adsorption of Co(II) ions is even smaller. This is due to the fact that this sample is almost completely free of any carbon-oxygen groups. The adsorption of Co(II) ions in the case of 950°C-degassed samples is even smaller than that of the as-received samples because as-received samples do contain small amounts of carbon-oxygen surface groups.
FIG. 9 ADSORPTION OF Co(II) IONS ON GACs AT DIFFERENT pH VALUES.
FIG. 10 ADSORPTION ISOTHERMS OF Co(II) IONS ON OXIDISED ACF-307 BEFORE AND AFTER DEGASSING.
FIG. 11 ADSORPTION ISOTHERMS OF Co(II) IONS ON OXIDISED ACF-307 BEFORE AND AFTER DEGASSING.

Amount adsorbed (mg/g) vs Concentration (mg/L)

- Oxidised with O₂
- Degassed at 400°
- Degassed at 650°
- Degassed at 950°
FIG. 12 ADSORPTION ISOTHERMS OF Co(II) ION ON OXIDISED GAC-E BEFORE AND AFTER DEGASSING.

- Oxidised with HNO₃
- Degassed at 400°
- Degassed at 650°
- Degassed at 950°

Amount adsorbed (mg/g) vs. Concentration (mg/L)
FIG. 13 ADSORPTION ISOTHERMS OF Co(II) IONS ON OXIDISED GAC-E BEFORE AND AFTER DEGASSING.
It appears from the results presented above that the adsorption of Co(II) ions depends upon the amount of acidic surface oxygen groups. The non-acidic surface groups do not influence the adsorption of Co(II) ions. The acidic surface groups which have been postulated as carboxyls or lactones when placed in aqueous solutions ionise to produce H\(^+\) ions which are released into aqueous phase and are exchanged by Co (II) ions on the carbon surface. Consequently the adsorption of Co (II) ions increases as the acidic groups are enhanced on oxidation and decreases on degassing when the acidic surface groups are eliminated as CO\(_2\).
REFERENCES

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2. Shakir, K., Benyamin, K. and Aziz, M.

3. Shakir, K. Flex, H. and Benyamin, K.

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5. Jaroniec, M.
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