CHAPTER -IV

INFLUENCE OF CHEMICAL STRUCTURE OF THE CARBON SURFACE ON THE ADSORPTIVE REMOVAL OF Pb(II) IONS BY ACTIVATED CARBONS

4.1 Introduction

Lead is a heavy metal that finds its way into air, water, food and soil. In air it is derived from lead emissions from automobiles while in water it is released through effluents from lead treatment and recovery plants especially from lead battery manufacturing units. The amount of lead in water exceeds many times the toleration limit. In the human body lead tends to form complexes which interfere with several synthetic and metabolic processes. Consequently, the removal of lead from water using activated carbon has attracted the attention of a large number of investigators.

Netzer and Hughes (1), Corapcioglu and Huang(2) and Shekinah et al (3) studied the adsorptive removal of Pb (II) ions from aqueous solutions by activated carbons at different solution pH values and observed that the adsorption involved hydrolysis, complex ion formation, ion exchange and the precipitation of the metal as Pb(OH)$_2$. Cheng et al (4) and Taylor and Kuennnen (5), while studying the adsorption of Pb (II) ions on activated carbons associated with different carbon - oxygen surface groups, suggested that the adsorption was a function of the amount of the carbon - oxygen surface groups. However, these workers did not dwell upon the nature of the carbon oxygen surface groups which influence the adsorption of lead. Macias - Garcia et al (6) investigated the adsorption of Pb (II) ions on heat treated and sulphurised activated carbons at different pH values and temperatures and observed that the adsorption decreased strongly with decreasing pH and temperature. Park et al (7), while studying the adsorption of several heavy metal ions on an activated carbon and on activated carbon fiber, observed that the activated carbon fiber had higher adsorption capacity and a higher rate of adsorption. The optimum pH for maximum adsorption of Pb (II) ions in the case of activated carbon fiber was about 8 while it was 11 for the activated carbon. Mohamed and Fahmi (8) and Kobya et al (9), however found a pH between 5-6 as the optimum pH for the maximum adsorption of Pb (II) ions.
Malik et al (10) adsorbed Pb (II) ions from aqueous solutions in the presence of Cu (II) ions on activated carbons associated with heteroatom such as oxygen and phosphorus and suggested that the carboxylic groups were responsible for the adsorption of Pb (II) ions. Ferro - Garcia et al (11) studied the adsorptive removal of Pb (II) ions from aqueous solutions using activated carbons prepared from almond shells, olive stones and peach stones. They observed that although the adsorption increased with increase in surface area but the surface covered by Pb (II) ions was only a fraction of the BET surface area indicating that many of the micropores were not accessible to larger hydrated Pb (II) ions.

Goel et al (12) observed that multicomponent metal adsorption by coconut based activated carbon using single, binary and ternary systems composed of Cu(II), Pb(II) and Hg(II) ions followed both the Langmuir and the Freundlich models of adsorption. Bansode et al (13) also found that the removal of metal ions from a ternary system of Cu(II), Pb(II) and Zn(II) ions using a Peacon shell based activated carbon activated with steam and acid were more effective. Mostafa (14) prepared steam activated and zinc chloride activated carbons from rice husk and studied the adsorption of Pb (II) ions before and after modification of their surface. It was observed that the surface chemistry of the carbon surface was important factor in determining the removal capacity of the metal ion.

It appears from the above perusal of literature that although the influence of chemisorbed oxygen on the adsorption of Pb (II) ions has been recognized, the exact nature of the carbon-oxygen surface groups which influence the adsorption of Pb (II) ions has not been identified. The role of electrostatic interactions which arise as a result of the carbon surface charge at different pH values of the solution also needs to be examined. The present work was, therefore, undertaken.

Two samples of granulated activated carbons (GAC-S and GAC-E) obtained from Norit N.V., The Netherlands and a sample ICEG obtained from Industrial carbons Pvt. Ltd., India have been used in these investigations. The activated carbons have been oxidized with nitric acid, ammonium persulphate, hydrogen peroxide in solution phase and with oxygen gas at 350°C to enhance the amount of carbon-oxygen surface functional groups. The oxidized carbons were then degassed at 400°, 650° and 950°C to gradually eliminate varying amounts of these carbon-oxygen surface groups (15-18). The adsorption of Pb (II) ions was determined by contacting a known weight
(0.5g) of each carbon sample, dried in an electric oven at 120°C and cooled in a desiccator, with 50 ml solutions of lead nitrate of different concentrations. The concentration of the solution before and after adsorption was determined using analytical procedures (19). The details of the experimental procedures are given in the experimental part of the thesis (chapter -II).

4.2 Results And Discussion

Adsorption isotherms of Pb (II) ions from aqueous solutions on three samples of activated carbons in the concentration range 50-500 mg/L are presented in Fig 4.1. The adsorption studies have been carried out at a solution pH=5 which was maintained by the addition of small amounts of acid or base. The adsorption isotherms are Type I of the BET classification showing a rapid adsorption at lower concentrations which tends to level off at higher concentrations. All the three carbons adsorb appreciable amounts of Pb (II) ions, the amount adsorbed varying between 3.2 to 7.5%. It is seen that the amount adsorbed increases with increase in surface area but there is no linear relationship between the amount adsorbed and the surface area (cf. Table 4.1). The adsorption data obeys Langmuir isotherm equation. The linear Langmuir plots are shown in Fig 4.2 and the values of \( X_m \), the Langmuir monolayer capacity, as calculated from the linear plots are included in Table 4.1.

Pb (II) ions in aqueous solution exist as hydrated ions. Assuming the hydration number to be between 4 and 7.5, Burges (20) has suggested that the average diameter of a hydrated Pb (II) ion may be taken as 0.802 nm. Thus only pores having diameters larger than this value will be accessible to Pb (II) ions. The surface area of each activated carbon occupied by hydrated Pb (II) ions was calculated using Langmuir monolayer capacities. These values along with the BET surface areas of carbons are also given in Table 4.1. It is interesting to note that only a small fraction amounting to between 8.2-8.3% of the BET surface area is occupied by the Pb (II) ions. This indicates that the BET surface area of microporous activated carbons does not play an important role in the adsorption of Pb (II) ions from aqueous solutions. This receives further support from the amounts adsorbed on the oxidized activated carbons discussed in the next section. The adsorption of Pb (II) ions increases several times on oxidation in some cases even though the BET surface area slightly decreases on oxidation.
Fig 4.1 Adsorption isotherms of Pb(II) ions on as-received activated carbons

- ICEG
- GAC-E
- GAC-S

Amount adsorbed (mg/g)

Concentration (mg/L)
Fig 4.2 Linear Langmuir adsorption isotherms of Pb (II) ions on different as-received activated carbons.

- □ GAC-E
- ○ ICEG
- △ GAC-S

Concentration (mg/L) vs. $C/x$ (g/L) graph.
Table - 4.1

Fraction of BET Surface area occupied by Pb(II) ions

<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>BET(N₂) Surface area (m²/g)</th>
<th>Monolayer capacity (X_m) (from linear Langmuir plots)</th>
<th>Surface area occupied by Pb²⁺ ions (m²/g)</th>
<th>(\frac{S_{Pb^{2+}}}{S_{BET}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICEG</td>
<td>550</td>
<td>37.6</td>
<td>45.3</td>
<td>8.2</td>
</tr>
<tr>
<td>GAC-E</td>
<td>1190</td>
<td>79.4</td>
<td>98.1</td>
<td>8.2</td>
</tr>
<tr>
<td>GAC-S</td>
<td>1256</td>
<td>88.0</td>
<td>104.7</td>
<td>8.3</td>
</tr>
</tbody>
</table>

Chemical structure of an activated carbon surface which is due to the presence of chemisorbed oxygen is another factor which can strongly influence the adsorption of cations by carbons from aqueous solutions (4, 5, 21-24). As these carbons have been prepared using different source raw materials and processing procedures, they are expected to be associated with different amounts of chemisorbed oxygen. This oxygen in carbons is present in the form of carbon–oxygen surface functional groups some of which are acidic in character. Since the pH of the aqueous solution has a great influence on the adsorption of cations and since these acidic groups can ionize in water producing H⁺ ions (23, 25), the presence of acidic surface groups is likely to influence the adsorption of Pb (II) ions from aqueous solutions.

It has been mentioned earlier (chapter-III) that the chemisorbed oxygen on the carbon surface is present in the form of two types of carbon–oxygen surface groups: one of which is acidic in character and is evolved as CO₂ on degassing in the temperature range 400 – 700°C. The other group which is evolved as CO in the temperature range 600-950°C is non-acidic in character (15–18). The acidic groups have been postulated as carboxyls and lactones while the non-acidic groups have been identified as quinones (26–28).

The amounts of these surface groups which are evolved as CO₂ and CO on degassing at temperatures up to 950°C were determined and are recorded in Table - 4.2. It is seen that these carbons are associated with varying amounts of the carbon–oxygen
surface groups. While the activated carbons GAC-S and GAC-E have larger amounts of the surface groups evolved as CO₂, the carbon ICEG has a larger amount of surface groups evolved as CO. As the adsorption of Pb (II) ions is smaller in the case of ICEG carbon it appears that the acidic surface groups evolved as CO₂ may have a larger influence on the adsorption of Pb (II) ions.

Table – 4.2
Gases evolved on degassing different as received activated carbons at 950°C

<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>Oxygen evolved (g/100 g) as</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂</td>
</tr>
<tr>
<td>GAC-E</td>
<td>2.12</td>
</tr>
<tr>
<td>GAC-S</td>
<td>2.21</td>
</tr>
<tr>
<td>ICEG</td>
<td>1.75</td>
</tr>
</tbody>
</table>

In order to examine the influence of these surface groups on the adsorption more clearly, two of the carbon samples namely GAC-E and GAC-S were oxidized with nitric acid, ammonium persulphate and hydrogen peroxide in the solution phase and with oxygen gas at 350°C. These treatments are known to enhance the amount of carbon-oxygen surface groups on the carbon surface. The adsorption isotherms on the oxidized carbon samples are shown in Figs 4.3 and 4.4. The adsorption increases on oxidation in both the carbons. The increase in adsorption, however, depends on the nature of the oxidative treatment. The increase in adsorption is at a maximum in case of the carbon samples oxidized with nitric acid and is minimum in case of the samples oxidized with hydrogen peroxide. Incidentally the oxidation of the carbons with nitric acid enhances the amount of chemisorbed oxygen by considerably larger amounts compared to their oxidations with other oxidizing agents (cf Table 4.3). It is interesting that the increase in adsorption has the same order as the increase in the amount of carbon-oxygen groups evolved as CO₂.
Fig 4.3 Adsorption isotherms of Pb(II) ions on GAC-E carbon after different oxidative treatments

- As received
- Nitric acid oxidised
- Ammonium persulphate oxidised
- Oxygen oxidised
- Hydrogen peroxide oxidised

Amount adsorbed (mg/g)

Concentration (mg/L)
Fig 4.4 Adsorption isotherms of Pb (II) ions on GAC-S carbon after different oxidative treatments

- As received
- Nitric acid oxidised
- Ammonium persulphate oxidised
- Oxygen oxidised
- Hydrogen peroxide oxidised

Concentration (mg/L)
Amount adsorbed (mg/g)
Table 4.3
BET surface areas and gases evolved on degassing different oxidized activated carbons at 950°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET 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><strong>GAC-E</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-received</td>
<td>1190</td>
<td>2.12</td>
<td>1.21</td>
<td>1.20</td>
<td>4.53</td>
</tr>
<tr>
<td>NHO₃-oxidized</td>
<td>1095</td>
<td>12.70</td>
<td>6.40</td>
<td>1.75</td>
<td>20.85</td>
</tr>
<tr>
<td>(NH₄)₂S₂O₈-oxidized</td>
<td>1000</td>
<td>5.52</td>
<td>6.10</td>
<td>1.54</td>
<td>13.16</td>
</tr>
<tr>
<td>O₂-oxidized</td>
<td>1150</td>
<td>3.56</td>
<td>6.15</td>
<td>1.30</td>
<td>11.01</td>
</tr>
<tr>
<td>H₂O₂-oxidized</td>
<td>1120</td>
<td>2.34</td>
<td>7.62</td>
<td>1.20</td>
<td>11.16</td>
</tr>
<tr>
<td><strong>GAC-S</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As-received</td>
<td>1256</td>
<td>2.21</td>
<td>1.72</td>
<td>1.34</td>
<td>5.27</td>
</tr>
<tr>
<td>HNO₃-oxidized</td>
<td>1180</td>
<td>12.42</td>
<td>7.10</td>
<td>1.40</td>
<td>20.92</td>
</tr>
<tr>
<td>(NH₄)₂S₂O₈-oxidized</td>
<td>1190</td>
<td>6.10</td>
<td>6.82</td>
<td>1.30</td>
<td>14.22</td>
</tr>
<tr>
<td>O₂-oxidized</td>
<td>1170</td>
<td>3.81</td>
<td>7.25</td>
<td>1.30</td>
<td>12.36</td>
</tr>
<tr>
<td>H₂O₂-oxidized</td>
<td>1205</td>
<td>2.48</td>
<td>6.95</td>
<td>1.25</td>
<td>10.68</td>
</tr>
</tbody>
</table>

The oxidized activated carbon samples were then degassed at gradually increasing temperatures to eliminate varying amounts of the carbon–oxygen surface groups. The adsorption isotherms on the degassed carbon samples are presented in Fig 4.5 for GAC–E and in Fig 4.6 for GAC–S. It is seen that the adsorption of Pb (II) ions decreases gradually as the temperature of degassing is enhanced. The decrease in adsorption is only slight between 0.03 – 0.35% when the degassing is carried out at
400°C for both GAC-E & GAC-S carbon samples. However, the decrease in adsorption is considerably larger for the 650°C-degassed carbon samples (cf Figs 4.5 and 4.6). The 950°C degassed samples show a still lower adsorption of Pb (II) ions.

The amounts of carbon-oxygen surface groups associated with the different degassed carbon samples are given in Table 4.4. It is evident that the 400°C degassed carbon samples have lost only a small portion (~ 15%) of their acidic surface groups while the 650°C-degassed carbon samples have lost a larger portion of their acidic groups although they still retain a greater portion of the non-acidic surface groups. The 950°C-degassed carbon samples are almost completely free of any acidic or non-acidic surface groups.

It is apparent that the adsorption of Pb (II) ions is determined largely by the presence of carbon-oxygen surface groups and more so by the presence of acidic surface groups which are evolved as CO$_2$. The acidic surface groups on the carbon surface provide sites for the adsorption of Pb (II) ions. The 950°C-degassed carbon samples show smaller adsorption because of the absence of any acidic sites on their surface.

The presence of acidic surface groups and their ionization in water also changes the pH of the carbon suspension. The pH of the as-received activated carbons varied between 9 and 10. However, the pH of these carbons was reduced to between 3 and 4 on oxidation with nitric acid and to 4 and 5 on oxidation with other oxidizing agents. This decrease in pH of the carbon surface due to the presence of acidic surface groups probably results in an increase in the adsorption of Pb (II) ions. In order to verify this point, the adsorption studies were carried out from solutions of different pH values. The pH of the solution was controlled by the addition of nitric acid or sodium hydroxide. The adsorption of Pb (II) ions as a function of solution pH is shown in Fig 4.7. It is seen that the adsorption is small below a pH value of 2 in all the three carbons. However, when the pH was increased a maximum in adsorption is obtained at pH 3-4. At pH values higher than 7, the adsorption studies could not be carried out because of the precipitation of lead hydroxide.

It appears that a change in pH of the solution results in a change in the carbon surface charge, being different at different pH values of the solution (2). A sudden
Fig 4.5 Adsorption isotherms of Pb (II) ions on nitric acid oxidised GAC-E after degassing

- Nitric acid oxidised
- Nitric acid oxidised and degassed at 400°C
- Nitric acid oxidised and degassed at 650°C
- Nitric acid oxidised and degassed at 950°C

Concentration (mg/L)

Amount adsorbed (mg/g)

Concentration (mg/L)
Fig 4.6 Adsorption isotherms of Pb (II) ions on nitric acid oxidised GAC-S after degassing

- •—Nitric acid oxidised
- •—Nitric acid oxidised and degassed at 400°C
- •—Nitric acid oxidised and degassed at 650°C
- x—Nitric acid oxidised and degassed at 950°C

Amount adsorbed (mg/g) vs Concentration (mg/L)
Table - 4.4

Gases evolved on degassing different oxidized and degassed activated carbon samples at 950°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxygen evolved (g/100g) as</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂</td>
<td>CO</td>
</tr>
<tr>
<td><strong>GAC-E</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HNO₃- oxidized</td>
<td>12.70</td>
<td>6.40</td>
</tr>
<tr>
<td>NHO₃ oxidized and</td>
<td>5.52</td>
<td>6.10</td>
</tr>
<tr>
<td>degassed at (°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>10.95</td>
<td>6.12</td>
</tr>
<tr>
<td>650</td>
<td>2.10</td>
<td>5.85</td>
</tr>
<tr>
<td>950</td>
<td>Traces</td>
<td>Traces</td>
</tr>
<tr>
<td><strong>GAC-S</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HNO₃- oxidized</td>
<td>12.42</td>
<td>7.10</td>
</tr>
<tr>
<td>HNO₃ oxidized and</td>
<td>6.10</td>
<td>6.82</td>
</tr>
<tr>
<td>degassed at (°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>10.95</td>
<td>6.95</td>
</tr>
<tr>
<td>650</td>
<td>1.90</td>
<td>6.10</td>
</tr>
<tr>
<td>950</td>
<td>Traces</td>
<td>Traces</td>
</tr>
</tbody>
</table>
Fig. 4.7 Effect of solution pH on the adsorption of Pb (II) ions from aqueous solutions.

ICEG
GAC-S
GAC-E
increase in the adsorption of Pb (II) ions in the pH range 3-4 indicates that the zero point of charge (ZPC) of the carbon surface lies between these values. At pH values lower than ZPC, there is excessive protonation of the carbon surface which gives it a positive charge. This enhances the electrostatic repulsive interactions between the carbon surface and the positively charged Pb (II) cations resulting in a lower adsorption.

As the pH of the solution increases beyond ZPC, the carbon surface attains a negative charge due to the ionization of acidic surface groups. This causes attractive electrostatic interactions between the carbon surface and the lead cations resulting in increased adsorption. At higher pH values the preponderance of OH⁻ ions in the solution generates a competition between the negatively charged carbon surface and the solution OH⁻ ions for the Pb (II) ions resulting in a decrease in the adsorption of Pb (II) ions.

4.3 Mechanism of Adsorption

It appears from the results obtained on the adsorption of Pb (II) ions that the mechanisms involved in the adsorption is similar to the one involved in the adsorption of Hg (II) ions (Chapter III). The ionisation of acidic carbon – oxygen surface groups renders the carbon surface negatively charged. This results in attractive electrostatic interactions between the negatively charged surface sites and the positively charge Pb (II) cations. When the activated carbon surface is given an oxidative treatment, the number and concentration of acidic surface groups and hence those of negatively charged sites increases. This enhances the attractive interactions and results in higher adsorption of Pb (II) cations. On degassing of the oxidized surface, the oxygen groups are eliminated depending upon the temperature of degassing. This results in a decrease of the negatively charged sites which in turn decreases the adsorption of Pb (II) ions. When the acidic oxygen groups are removed almost completely on degassing at 950°C, the carbon surface loses all of its negative sites and attains more or less a positive charge. This enhances the repulsive interactions between the carbon surface and the Pb (II) ions thereby decreasing the adsorption. Whatever adsorption takes place in the case of 950°C – degassed carbon samples may be attributed to take place in pores.
4.4 References


