Influence of Surface area, Surface Chemical Structure and Solution pH on the Adsorption of Pb(II) Ions on Activated Carbons

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Abstract

The influence of carbon surface area, carbon-oxygen groups associated with the carbon surface and the solution pH on the adsorption of Pb(II) ions from aqueous solutions has been studied using three activated carbons. The adsorption isotherms are Type I of BET classification and the data obeys Langmuir adsorption equation. The BET surface area has little effect on the adsorption while it is strongly influenced by the presence of acidic carbon oxygen surface groups. The amount of these surface groups was enhanced by oxidation of the carbons with different oxidizing agents and reduced by eliminating these groups on degassing at different temperatures. The adsorption of Pb(II) ions increases on each oxidation and decreases on degassing the oxidized carbons. The increase in adsorption on oxidation has been attributed to the formation of acidic carbon-oxygen surface groups and the decrease to the elimination of these acidic surface groups on degassing. The adsorption is also influenced by the pH of the aqueous solution. The adsorption is only small at pH values lower than 3 but is considerably larger at higher pH values. Suitable mechanisms consistent with the adsorption data have been suggested.

Keywords: Adsorption, surface groups, carbon surface charge, activated carbon, carbon surface oxidation

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], Coralcioglu and Huang [2] and Shekimah 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 Kuennen [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.

Malik et al. [8] adsorbed Pb(II) ions from aqueous solutions in the presence of Cu (II) ions on activated carbons associated with heteroatoms such as oxygen and phosphorus and suggested that the carboxylic groups were responsible for the adsorption of Pb(II) ions. Ferro-Garcia et al. [9] 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. [10] 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. [11] also found that the removal of metal ions from a ternary system of Cu(II), Pb(II) and Zn(II) ions using a Pecor shell based activated carbon activated with steam and acid were more effective. Mostafa [12] 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 an 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.

2. Experimental

2.1. Materials

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 Private Limited, 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°C, 650°C and 950°C to gradually eliminate varying amounts of these carbon-oxygen surface groups [13, 14].

2.2. Oxidation of activated carbons

2.2.1. Oxidation with Nitric Acid

The activated carbon sample (5 g) was heated with 150 ml of pure nitric acid in a borosil beaker of 250 ml capacity in a water bath maintained at about 80°C. When all but about 10 ml of the acid had evaporated, the contents were cooled, diluted with water and transferred over a filter paper. The carbon sample was washed exhaustively with hot distilled water until the filtrate was free of nitrate ions. The washed carbon sample was dried first in air and then in an electric oven at 120°C, and then stored in a stoppered glass bottle. The suspension was continuously shaken in a mechanical shaker for 48 hr. The carbon was filtered, washed and dried in an oven and stored in a stoppered glass bottle flushed with nitrogen.

2.2.2. Oxidation with Hydrogen Peroxide

5 g of the activated carbon sample was added to 500 ml of 3 N hydrogen peroxide solution in a well stoppered glass bottle. The suspension was continuously shaken in a mechanical shaker for 48 hr. The carbon was filtered, washed and dried in an oven and stored in a stoppered glass bottle flushed with nitrogen.

2.2.3. Oxidation with ammonium persulphate

5 g of the activated carbon sample was mixed with 250 ml of saturated solution of ammonium persulphate in sulphuric acid and the suspension shaken for 48 hr. The carbon was filtered, washed with hot water till free of sulphate ions and dried in an electric oven. The sample was then stored in glass bottle flushed with nitrogen.

2.3. Degassing of the Carbons

About 5 g of each of the activated carbon sample was spread in a thin layer about 5" long in a tube furnace. It was kept in position by means of porous copper gauge plugs. The tube furnace was connected to a Hyvac Cenco Vacuum pump capable of giving vacuum to the order of $3 \times 10^{-3}$ mm of Hg. The temperature of the furnace was raised to the required level slowly. The gases began to be evolved soon after. The temperature was allowed to rise gradually and before it was raised by another 50°C complete elimination of the gases, at the preceding temperature was ensured. After degassing at the required temperature, the sample was allowed to cool in vacuum to room temperature to avoid reformation of the carbon-oxygen surface groups and was then transferred to stoppered bottles flushed with nitrogen. These samples are referred to as "degassed samples" in the text. The details of the procedure are published elsewhere [13, 14].

2.4. Determination of carbon oxygen surface groups

The carbon-oxygen groups present on the as received, oxidized and degassed carbon samples were determined by evacuating one gram portion of each sample at gradually increasing temperatures up to 950°C. The carbon sample dried at 120°C and contained in a platinum boat is placed in a resistance tube furnace. The temperature of the furnace was allowed to rise gradually in steps of 50°C to ensure complete elimination of the gas at the previous temperature. The carbon-oxygen surface groups decompose into CO$_2$, CO and water vapour which were measured using usual analytical procedures. The details of the procedures are already published [15, 16].

2.5. Determination and control of pH of the solution

The pH of the stock solution of lead nitrate was controlled by the addition of small amounts of dilute solution of sodium hydroxide or nitric acid. The pH of the solution was measured using a glass- calomel electrode pH meter.
2.6. Determination of pH of carbon surface

0.5 g of the activated carbon was determined by contacting with 50 ml of CO$_2$-free distilled water. The suspension was shaken in a mechanical shaker for 2 hrs and the pH determined using a glass-calomel electrode pH meter (15).

2.7. Adsorption of Lead

The adsorption of Pb(II) ions was determined by contacting a known weight (0.2 g) 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 suspensions were shaken in a mechanical shaker for 24 hr and then placed in a thermostat and allowed to stand overnight. After 24 hr an aliquot portion of the solution was pipetted out and the concentration determined titrimetrically with 0.005 M solution of EDTA using standard analytical procedures [17].

3. Results and Discussion

3.1. Adsorption Isotherms

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. 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 1). The adsorption data obeys Langmuir isotherm equation. The linear langmuir plots are shown in Fig. 2 and the values of $X_m$, the Langmuir monolayer capacity, as calculated from the linear plots are included in Table 1.

Pb(II) ions in aqueous solution exist as hydrated ions. Assuming the hydration number to be between 4 and 7.5 Burges [18] 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 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.

Table 1. Fraction of BET Surface area occupied by Pb(II) ions

<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>BET (N$_2$) Surface area (m$^2$/g)</th>
<th>Monolayer capacity $X_m$ (from linear Langmuir plots)</th>
<th>$S_{Pb}^{2+}$ (m$^2$/g)</th>
<th>BET area covered (%)</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>

Fig. 1. Adsorption isotherms of Pb(II) ions on as-received activated carbons.
3.2. Influence of Chemical Structure of the Carbon Surface on Adsorption

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, 19-22]. 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 [1-4, 19-22] has a great influence on the adsorption of cations and since these acidic groups can ionize in water producing $\text{H}^+$ ions [21-23], the presence of acidic surface groups is likely to influence the adsorption of Pb(II) ions from aqueous solutions.

It may be worthwhile to mention here 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 $\text{CO}_2$ 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 [13-16]. The acidic groups have been postulated as carboxyls and lactones while the non-acidic groups have been identified as quinones [24-26].

The amounts of these surface groups which are evolved as $\text{CO}_2$ and CO on degassing at temperatures up to 950°C were determined and are recorded in Table 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 $\text{CO}_2$, 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 $\text{CO}_2$ may have a larger influence on the adsorption of Pb(II) ions.

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. 3 and 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.

**Table 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 $\text{CO}_2$</th>
<th>CO</th>
<th>H$_2$O</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAC-E</td>
<td>2.12</td>
<td>1.21</td>
<td>1.20</td>
<td>4.53</td>
</tr>
<tr>
<td>GAC-S</td>
<td>2.21</td>
<td>1.72</td>
<td>1.34</td>
<td>5.27</td>
</tr>
<tr>
<td>ICEG</td>
<td>1.75</td>
<td>4.25</td>
<td>1.58</td>
<td>7.58</td>
</tr>
</tbody>
</table>

![Fig. 2. Linear Langmuir isotherms of Pb(II) ions on various as-received activated carbons.](image)

![Fig. 3. Adsorption isotherms of Pb(II) ions on GAC-E after different oxidative treatments.](image)
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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 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 \( \text{CO}_2 \).

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. 5 for GAC-E and in Fig. 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 (400°-degassed) for both GAC-E & GAC-S carbon samples. However, the decrease in adsorption is considerably larger when the carbon samples are degassed at 650°C (650°-degassed) (cf Figs. 5 and 6). The carbon samples degassed at 950°C (950°-degassed) 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. It is evident that the 400°-degassed carbon samples have lost only a small portion (~15%) of their acidic surface groups while the 650°-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°-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°-degassed carbon samples show smaller adsorption because of the absence of any acidic sites on their surface.

3.3. Influence of solution pH on adsorption

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. 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 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 negatively charged Pb(II) cations resulting in an 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.

3.4. Mechanism of Adsorption

When an activated carbon associated with carbon-oxygen
surface groups is placed in an aqueous solution, the acidic carbon-oxygen surface groups undergo ionization producing H+ ions, the degree of ionization depending on the pH of the solution. The H+ ions are directed towards the solution phase leaving the carbon surface with negatively charged sites. This results in attractive electrostatic interactions between the negatively charged surface sites and the positively charged 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. Conclusions

Adsorption of Pb(II) ions on activated carbons from aqueous solutions obeys Langmuir isotherm equation. The adsorption does not depend on the surface area of the carbon and only a fraction of BET surface is covered by Pb(II) ions. The adsorption increases on oxidation of the carbon surface in proportion to the formation of acidic carbon-oxygen surface group and decreases gradually on degassing at increasing temperatures as these acidic surface groups are gradually eliminated. The adsorption is also influenced by the pH of the aqueous solution, being only small at pH values lower than 3 but attaining a maximum value at pH between 3 and 5. The acidic surface groups on ionization in aqueous solution render the carbon surface negatively charged and enhance the attractive electrostatic interactions between the carbon surface and the positively charged Pb(II) ions. Thus the adsorption of Pb(II) ions takes place on specific sites provided by acidic surface groups present on the carbon surface.

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