Adsorption of nitrobenzene on activated carbon from dilute aqueous solutions

P Aggarwal¹, J C Kapoor¹, S K Kapoor¹, A K Bhalla²* & R C Bansal³
¹Centre for Environment and Explosive Safety, Metcalfe House, Delhi 110 054, India
²Department of Chemical Engineering, Punjab University, Chandigarh 160 014, India

Received 22 August 1995; accepted 5 April 1996

The adsorption isotherms of nitrobenzene from aqueous solutions in the concentration range 20-200 mg/L have been studied on five different commercially available activated carbons with surface areas varying between 650-1300 m²/g. The adsorption depends upon surface area but is not linearly related to it. The adsorption isotherms on oxidised and degassed samples of activated carbons indicate that the adsorption increases on degassing but decreases on oxidation.

Toxic and hazardous nitro compounds are often present in process wastewater from explosive manufacturing plants. These compounds are required to be removed before discharging the wastewater into water streams. Several techniques have been used for the removal of these organics but treatment with activated carbon is one of the promising methods for removing nitro compounds to near ppm level.

The main objective of the present study is to determine adsorption capacity of commercially available coconut based activated carbons to remove nitrobenzene, a major contaminant in wastewater from explosive manufacturing plants. The effect of surface area, carbon-oxygen surface structures (functional groups) created by different oxidation and degassing treatments and the nature of these surface groups on the adsorption behaviour of nitrobenzene in aqueous solution has also been studied.

Experimental Procedure

Five grades of commercially available coconut based activated carbons supplied by M/s Active Carbon, Hyderabad have been used. All chemicals used, were of AR quality and only double distilled water was used for preparing solutions and for washings. The activated carbons were used before and after degassing at 400, 600 and 1000°C⁸⁻¹⁰ and after oxidation with nitric acid¹¹, hydrogen peroxide¹²,¹³ and ammonium persulphate¹³. For degassing and oxidation, standard procedures have been used¹⁴.

Adsorption of nitrobenzene — 0.05 g of the carbon sample dried at 120°C for 3 h was placed in contact with 50 mL solution of different concentrations varying between 20-200 ppm in a 100 mL stoppered conical flask. The contents were shaken for 24 h in a thermostated shaker maintained at 30 ± 1°C. The contents were allowed to settle and filtered using Whatman filter paper No. 42. The concentration of the solution, before and after adsorption, was determined using GBC 916 UV/VIS spectrophotometer at λmax 269 nm. All studies were made at pH 7.

Estimation of surface oxygen complexes — The amount of oxygen associated with each carbon before and after the treatment and its desorption as CO₂ and CO was determined by degassing one gram of each carbon at 1000°C in a silica tube furnace using a standard procedure¹⁰,¹⁴. The amounts of CO₂, CO and H₂O vapour evolved were determined and expressed as g/100g (Table 1).

Results and Discussion

Adsorption isotherms of nitrobenzene from its aqueous solutions on five different grades of active carbons are presented in Fig. 1. It is seen that all the carbons adsorb appreciable amounts of nitrobenzene. The isotherms are of Type I of the BET classification showing a rapid adsorption at lower concentrations tending to be asymptotic at higher concentrations. The amount adsorbed increases with increase in surface area, being maximum in the case of AC-70, which has the largest surface area and minimum in the case of AC-30 carbon sample which has the smallest surface area. However, no direct relationship could be obtained between the maximum amount adsorbed...
Table 1 — Oxygen evolved on outgassing various ACs at 1000°C

<table>
<thead>
<tr>
<th>Carbon sample</th>
<th>BET surface area, m²/g</th>
<th>CO₂, g/100g</th>
<th>CO, g/100g</th>
<th>H₂O, g/100g</th>
<th>Total, g/100g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original AC-30</td>
<td>650</td>
<td>1.033</td>
<td>1.402</td>
<td>1.061</td>
<td>3.496</td>
</tr>
<tr>
<td>HNO₃-treated</td>
<td></td>
<td>11.201</td>
<td>7.086</td>
<td>1.815</td>
<td>20.102</td>
</tr>
<tr>
<td>H₂O₂-treated</td>
<td></td>
<td>1.018</td>
<td>1.829</td>
<td>1.211</td>
<td>4.058</td>
</tr>
<tr>
<td>(NH₄)₂S₂O₇-treated</td>
<td></td>
<td>4.727</td>
<td>2.067</td>
<td>1.824</td>
<td>8.618</td>
</tr>
<tr>
<td>400°C degassed</td>
<td></td>
<td>0.788</td>
<td>1.068</td>
<td>0.552</td>
<td>2.408</td>
</tr>
<tr>
<td>600°C degassed</td>
<td></td>
<td>0.041</td>
<td>0.926</td>
<td>0.576</td>
<td>1.543</td>
</tr>
<tr>
<td>1000°C degassed</td>
<td></td>
<td>traces</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Original AC-50</td>
<td>1000</td>
<td>1.155</td>
<td>1.495</td>
<td>1.323</td>
<td>3.973</td>
</tr>
<tr>
<td>HNO₃-treated</td>
<td></td>
<td>8.713</td>
<td>6.841</td>
<td>2.092</td>
<td>17.646</td>
</tr>
<tr>
<td>H₂O₂-treated</td>
<td></td>
<td>1.415</td>
<td>2.042</td>
<td>1.471</td>
<td>4.928</td>
</tr>
<tr>
<td>(NH₄)₂S₂O₇-treated</td>
<td></td>
<td>2.356</td>
<td>2.921</td>
<td>5.411</td>
<td>10.688</td>
</tr>
<tr>
<td>400°C degassed</td>
<td></td>
<td>0.567</td>
<td>1.132</td>
<td>1.554</td>
<td>3.253</td>
</tr>
<tr>
<td>600°C degassed</td>
<td></td>
<td>0.631</td>
<td>1.097</td>
<td>1.134</td>
<td>2.862</td>
</tr>
<tr>
<td>1000°C degassed</td>
<td></td>
<td>traces</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Original AC-70</td>
<td>1300</td>
<td>1.439</td>
<td>1.161</td>
<td>1.361</td>
<td>3.961</td>
</tr>
<tr>
<td>HNO₃-treated</td>
<td></td>
<td>12.414</td>
<td>7.601</td>
<td>2.741</td>
<td>22.756</td>
</tr>
<tr>
<td>H₂O₂-treated</td>
<td></td>
<td>1.658</td>
<td>2.731</td>
<td>1.752</td>
<td>6.141</td>
</tr>
<tr>
<td>(NH₄)₂S₂O₇-treated</td>
<td></td>
<td>2.175</td>
<td>2.471</td>
<td>3.012</td>
<td>7.658</td>
</tr>
<tr>
<td>400°C degassed</td>
<td></td>
<td>1.123</td>
<td>1.167</td>
<td>1.268</td>
<td>3.558</td>
</tr>
<tr>
<td>600°C degassed</td>
<td></td>
<td>0.489</td>
<td>0.761</td>
<td>0.446</td>
<td>1.716</td>
</tr>
<tr>
<td>1000°C degassed</td>
<td></td>
<td>traces</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1 Adsorption isotherms of nitrobenzene on activated carbon.

*---* AC-30 (650 m²/g), × --- × AC-40 (900 m²/g), ▲ --- ▲ AC-50 (1000 m²/g), ○ --- ○ AC-60 (1150 m²/g), □ --- □ AC-70 (1300 m²/g)

Temp. 30 ± 1°C, pH 7.0, initial concentrations 20-200 mg/L, carbon dose 1.0 g/L.

and the surface area. It appears that surface area is not the only factor which determines the adsorption of nitrobenzene.

Activated carbon surface is known to have two different types of carbon-oxygen surface structures. The surface structures which are evolved...
as CO₂ between 350-700°C are chemically less stable. These surface structures are acidic and polar in character and are postulated as carboxylic or lactonic groups. The second type of surface oxygen structures which are evolved as CO in the temperature range 550-950°C are postulated as quinonic groups. These are neutral and nonpolar in character. The amount of these two types of surface structures on different carbon samples have been studied by degassing at gradually in-
creasing temperatures up to 1000°C and the results are presented in Table 1. It is seen that oxidation enhances the amount of these surface structures while degassing eliminates these structures. Thus, different carbon samples with varying amounts of these two types of surface structures are obtained. In order to examine the influence of associated oxygen on the adsorption of nitrobenzene, the adsorption isotherms were determined on the oxidised and degassed samples.

The adsorption isotherms of nitrobenzene on AC-50 before and after outgassing at different temperatures are shown in Fig. 2. A similar behaviour has been observed with other carbons. It is seen that the adsorption of nitrobenzene increases on degassing and the isotherms moving bodily upward. The adsorption increases with increase in the temperature of degassing up to 600°C and shows a slight decrease in case of 1000°C degassed sample. The maximum adsorption in case of 600°C degassed sample and a consequent decrease at higher degassing temperature can be explained on the basis of the existence of two different types of carbon-oxygen surface structures16,20.

The 600°C degassed carbon sample is devoid of a larger portion of its CO₂-complex but still retains a large proportion of its CO-complex while 1000°C degassed sample is almost free of any of these surface complexes [Table 1]. It thus appears that the presence of acidic CO₂-complexes tends to suppress the adsorption21, while emergence of CO-complex as the dominating oxygen complex enhances its adsorption capacity for nitrobenzene. The 600°C degassed carbon which has lost a large portion of its CO₂-complex (50-70%) and still retains a better part of its CO-complex (60-70%) shows maximum amount of adsorption. The decrease in adsorption in the case of 1000°C degassed sample is due to the elimination of most of its oxygen complexes.

The above postulation receives further support from the adsorption isotherms on the oxidised carbon samples. It is interesting to note (Fig. 3) that the adsorption capacity of carbons for nitrobenzene decreases on oxidation. However, the decrease is only slight in case of the oxidation with hydrogen peroxide or ammonium persulphate. The decrease is maximum in case of the samples oxidised with nitric acid, which incidentally results in a maximum increase in the amount of CO₂-complexes.

It is evident from the results presented above that the adsorption of nitrobenzene is influenced primarily by surface area, although the type of oxygen complexes present on the carbon surface also plays a significant role. While the presence of carboxylic surface groups reduces the adsorption, the presence of quinonic group enhances it. This may be attributed to the probability of interaction of π electron clouds of the benzene ring in nitrobenzene with the partial positive charge on the carbonyl carbon atom22.

Acknowledgement
The authors are thankful to Dr A K Datta, Director, Centre for Environment & Explosive Safety, Delhi, for taking keen interest and for granting permission to publish this work. We also record an appreciation for Dr Kishira Mishra for useful discussions and suggestions during the course of this work.

References