Chapter III
CHAPTER-III

REMOVAL OF SOME PHENOLS BY ACTIVATED CARBON
DEVELOPED FROM USED TEA LEAVES

Key Words
Activated Carbon Developed from Used Tea Leaves
Phenols
Adsorption /Desorption
Adsorption Isotherms
Phenol Removal Unit

An important group of anionic organic pollutants in natural waters are phenols\(^1\). Many industries are characteristic sources of phenolic pollutants, including oil refineries, chemical plant, explosive manufacture, resin manufacture and coke ovens\(^2\). Phenols as a class of organics are similar in structure to more common herbicides and insecticides resistant to biodegradation, besides the effect of their presence in water supplies, noticed as bad tastes and odour\(^3\). Very small concentration of phenols cause disagreeable odour, particularly when waters containing phenols are chlorinated. Moreover, they are harmful to mankind and other organisms causing pain, renal irritation, severe shock and possibly death at higher concentrations\(^4\). Consequently, phenolics were considered to constitute the 11th of 126 chemicals which have been designated as priority pollutants by the US Environmental Protection Agency\(^5\).

Various processes are available for reducing the concentration
of phenols in aqueous solutions. Adsorption is one of the more useful techniques. Activated carbons have been suggested as adsorbent and are being employed for the removal of phenols\textsuperscript{6-10}. Chlorophenols, o-, m- and p-cresols, p-nitrophenol, 2,4-dinitrophenol, 2,4-dichlorophenol, dihydroxy and trihydroxy benzenes have also been reported recently in relation to studies on the adsorption capacities of activated carbons\textsuperscript{3,5,11-16}.

Commercially available activated carbons are expensive. Therefore, there is a need to produce low-cost activated carbons that can be applied to pollution control. A search for cheap and readily available starting material has identified used tea leaves, to prepare potential and commercially viable activated carbon for water treatment.

The present chapter deals with the adsorption of phenols from aqueous solutions by chemically (H\textsubscript{3}PO\textsubscript{4}) activated carbon obtained from used tea leaves (UTL). The raw material is an easily available kitchen waste. The adsorption capacities of these carbons towards several phenolics are studied and the effects of pH, adsorbate concentration and contact time have been investigated. Adsorption isotherms, cyclic capacity and regeneration methods have been studied.

**MATERIALS AND METHODS**

**Reagents**

The phenols selected for investigation are: phenol(P), o-cresol (o-Cr), m-cresol(m-Cr), 4-nitrophenol(4-NP), 4-chlorophenol
(4-CP), 2,4-dinitrophenol (2,4-DNP), 2,4-dichlorophenol (2,4-DCP). All chemicals used were of analytical grade.

**Instrumentation**

Automatic surface area analyser Coulter SA 3100, shaking machine IEC - 56, Chemito UV-Vis spectrophotometer UV-2500 and systronic digital pH meter were used for surface area determination, shaking, spectrophotometric, and pH measurements, respectively.

**Preparation of Activated Carbons**

Used tea leaves procured locally were treated with hot distilled water to remove sugar and milk contents and dried in sun. Activated carbons were prepared from $\text{H}_3\text{PO}_4$ impregnated powdered UTL and carbonised at 300-500°C as outlined in Table 3.1. For impregnation, a ratio of acid volume : weight of UTL powder of 2:1 was employed. Before utilisation the carbons were washed with distilled water and dried in a hot air oven at 100 ± 5°C. These carbons were ground and sieved to 170-240 mesh.

**Characterization of Activated Carbon**

Moisture content, bulk density, solubility and pH of activated carbons (UTLC) were determined adopting the standard procedures$^{17-19}$ as mentioned below:

**Moisture and Ash content**

The moisture content of the activated carbon was determined
by heating a known weight of sample in hot air oven maintained at 105 ± 5°C for 4 h. Heating, cooling and weighing were repeated at 30 min interval until the constant weight was obtained. The difference in weights gave the amount of moisture content. After the determination of moisture content the same sample was ignited in muffle furnace at 1000°C for about 3h. The process of heating and cooling was repeated until constant weight was obtained. Ash content was calculated by difference between initial and final weights.

**Bulk density**

A 50 ml graduated cylinder was weighted accurately and filled to 50 ml mark with carbon and weighed again accurately. The density was calculated by dividing the weight of carbon by 50.

**Solubility**

Accurately weighed carbon sample (5g) was transferred into 500 ml pyrex glass beaker. About 100 ml 4 mol dm$^{-3}$ HCl was added and heated to boiling with continuous stirring. The material was then allowed to settle and the supernatant liquid was filtered through a gooch crucible fitted with an asbestos mat. The procedure was repeated thrice with the residue remaining in the beaker using 100 ml 4 mol dm$^{-3}$ HCl each time. The combined filtrate was concentrated on a water bath upto about 50 ml volume, transferred to china dish, evaporated to dryness on a water bath and finally dried in hot air oven at 105 ± 5°C.
This was cooled and weighed. The weight of residue represented the matter soluble in 4 mol dm$^{-3}$ HCl. The matter soluble in 2 mol dm$^{-3}$ NaOH was determined with the same procedure.

**pH Measurement**

Dried carbon (5g) was added to 100 ml of freshly boiled and cooled water (pH 7) and heated to boiling. After digestion for 10 min the solution was filtered while hot and cooled to room temperature. pH was determined using pH meter.

**Infrared Spectrum**

Infrared analysis of active carbon UTLC-5 was performed using KBr technique.

**Adsorption Experiments**

50 ml aliquots of stock solutions of each phenol were mixed with 20 mg of the active carbon (UTLC-5) in glass stoppered conical flasks. These flasks were then shaken for 6 h to achieve an equilibrium. Each mixture was filtered and the filtrate was analysed for phenol spectrophotometrically using the UV absorbance maxima.

**Adsorption Isotherms**

Various concentrations ranging from 20-500 mg/l of stock solutions were added to 20 mg of active carbon, UTLC-5 and shaken to achieve equilibration. Each mixture was filtered and analysed spectrophotometrically.
Breakthrough Test

Seven cycles of down flow breakthrough test using 10 g (25 ml) of UTLC-5 in 20 mm ID glass column and flow rate 2 ml/min (empty-bed contact time 12 min), were conducted with 4-CP bearing distilled water (100 mg/l). The column was run until phenol was detected in the effluent. The UTLC-5 column was then regenerated in situ by backwashing with 100 ml of 1N NaOH solution. This was followed by backwashing with distilled water until the influent and effluent pH were comparable. This constitutes one cycle of breakthrough test. The spent regenerant and backwash water were analysed spectrophotometrically for the recovered phenol.

Small Phenol Removal Unit

A small phenol removal unit (Fig.3.8) was fabricated and its performance in removing phenol from municipal wastewater of Kanpur City (pH 7.5-8.4, BOD 200-280 mg/l, COD 500-650 mg/l, suspended solids 200-412 mg/l, total Kjeldahl nitrogen 40-100 mg/l, NH$_3$-N 20-80 mg/l, hardness 410-650 mg CaCO$_3$/l) was evaluated. The wastewater was filtered and spicked with 4-CP (100 mg/l). The unit comprised of pyrex column (18 cm i.d. x 44 cm height) containing 1 kg (2.4 l) of UTLC-5 medium upto a height of 9.4 cm. An average flow rate was 6 l/h (empty bed contact time 24 min).
RESULTS

The conditions of preparation of active carbons from H₃PO₄-impregnated powdered tea leaves and their properties: surface area, solubility, pH, moisture content and bulk density are given in Table 3.1.

The results of adsorbability of five activated carbons to adsorb phenol, o-cresol, m-cresol, 4-nitrophenol, 4-chlorophenol, 2,4-dinitrophenol and 2,4-dichlorophenol from aqueous solutions are summerized in Table 3.2. On the basis of highest adsorbablity, UTLC-5 was choosen for exhaustive studies. For comparison activated charcoal was also studied under similar experimental conditions (Table 3.2).

Infrared spectrum of UTLC-5 is given in Fig.3.1. Kinetic plots of adsorption of 4-NP and 4-CP on activated carbon, UTLC-5 to determine the minimum contact time to attain equilibrium are shown in Fig.3.2.

In order to find out effect of pH and concentration the experiments were performed for the adsorbability of 4-NP and 4-CP on activated carbon UTLC-5 at different pH (2-10) and concentrations (20-100 mg/l). The adsorbability data are summerized in Table 3.3.

In batch reactor with rapid stirring there is also a possibility that the transport of adsorbate ions from solution into the pores of the adsorbent is the rate controlling step²¹,²². This possibility
was tested and graphical relationship between the amount adsorbed and the square root of time is plotted in Fig. 3.3.

Effect of carbon dose on per cent phenol removal at optimum pH 6 has been studied. The results of % removal and carbon added for 4-NP and 4-CP are plotted in Fig. 3.4.

The application of Langmuir isotherm model \((1/q_e \text{ Vs } 1/C_e)\) for 4-NP and 4-CP is shown in Fig. 3.5. The application of Freundlich isotherm model \((\log q_e \text{ Vs } \log C_e)\) for 4-NP and 4-CP is shown in Fig. 3.6.

Langmuir and Freundlich parameters for adsorption of 4-NP and 4-CP are given in Table. 3.4.

Removal and regeneration of column is an important process in wastewater treatment. To achieve this and in order to assess the practical utility of the adsorbent, studies were undertaken on column operation. The results of seven cycles of breakthrough test of 4-CP removal are plotted in Fig. 3.7.
TABLE 3.1
Preparation and Properties of Activated Carbons

<table>
<thead>
<tr>
<th>% H$_3$PO$_4$ (w/v)</th>
<th>Carbonization temperature (°C)</th>
<th>Notation</th>
<th>Surface area (m$^2$/g)</th>
<th>Solubility in 1M HCl (mg/50ml)</th>
<th>Solubility in 1M NaOH (%)</th>
<th>pH</th>
<th>Moisture content (%)</th>
<th>Bulk density (g/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>300</td>
<td>UTLC-1</td>
<td>90.8</td>
<td>--</td>
<td>--</td>
<td></td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>30</td>
<td>300</td>
<td>UTLC-2</td>
<td>295.0</td>
<td>Nil</td>
<td>Nil</td>
<td></td>
<td>--</td>
<td>0.50</td>
</tr>
<tr>
<td>40</td>
<td>300</td>
<td>UTLC-3</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td></td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>50</td>
<td>300</td>
<td>UTLC-4</td>
<td>300.4</td>
<td>--</td>
<td>--</td>
<td></td>
<td>6.0</td>
<td>--</td>
</tr>
<tr>
<td>50</td>
<td>500</td>
<td>UTLC-5</td>
<td>344.2</td>
<td>Nil</td>
<td>Nil</td>
<td>6.3</td>
<td>5.8</td>
<td>0.51</td>
</tr>
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</table>
TABLE 3.2

Adsorption Capacity of Phenols (mg/g) to Activated Carbons

Initial Concentration of Phenols = 500 mg/l
Concentration of Adsorbent = 400 mg/l

<table>
<thead>
<tr>
<th>Notation</th>
<th>P</th>
<th>O-Cr</th>
<th>m-Cr</th>
<th>4-CP</th>
<th>4-NP</th>
<th>2,4-DCP</th>
<th>2,4-DNP</th>
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</thead>
<tbody>
<tr>
<td>UTL-C-1</td>
<td>80.2</td>
<td>87.4</td>
<td>83.2</td>
<td>134.4</td>
<td>110.5</td>
<td>200.8</td>
<td>198.6</td>
</tr>
<tr>
<td>UTL-C-2</td>
<td>120.0</td>
<td>152.9</td>
<td>152.0</td>
<td>218.9</td>
<td>180.2</td>
<td>326.5</td>
<td>297.6</td>
</tr>
<tr>
<td>UTL-C-3</td>
<td>125.0</td>
<td>156.9</td>
<td>159.4</td>
<td>230.0</td>
<td>187.6</td>
<td>335.8</td>
<td>308.5</td>
</tr>
<tr>
<td>UTL-C-4</td>
<td>128.0</td>
<td>160.7</td>
<td>168.9</td>
<td>244.6</td>
<td>198.9</td>
<td>362.0</td>
<td>327.4</td>
</tr>
<tr>
<td>UTL-C-5</td>
<td>145.8</td>
<td>178.6</td>
<td>185.8</td>
<td>266.1</td>
<td>240.2</td>
<td>430.2</td>
<td>386.9</td>
</tr>
<tr>
<td>Activated*</td>
<td>149.3</td>
<td>235.2</td>
<td>240.4</td>
<td>298.9</td>
<td>274.1</td>
<td>438.4</td>
<td>397.9</td>
</tr>
<tr>
<td>Charcoal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* A. R. grade, Ranbaxy, India.
### TABLE 3.3

**Adsorbability of 4-NP and 4-CP to Activated Carbon UTLC-5 at Different pH and Concentration**

<table>
<thead>
<tr>
<th>Phenol (mg/l)</th>
<th>Conc.</th>
<th>Adsorbability (mg/g) at pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>20</td>
<td>19.97</td>
<td>25.31</td>
</tr>
<tr>
<td>4-NP 50</td>
<td>31.62</td>
<td>46.21</td>
</tr>
<tr>
<td>100</td>
<td>39.00</td>
<td>52.67</td>
</tr>
<tr>
<td>20</td>
<td>20.14</td>
<td>29.75</td>
</tr>
<tr>
<td>4-CP 50</td>
<td>38.47</td>
<td>57.76</td>
</tr>
<tr>
<td>100</td>
<td>65.36</td>
<td>93.86</td>
</tr>
</tbody>
</table>
TABLE 3.4

Langmuir and Freundlich Adsorption Parameters of UTLC-5

<table>
<thead>
<tr>
<th>Phenol</th>
<th>$b \times 10^8$ (mg/l)</th>
<th>$\theta^e$ (mg/g)</th>
<th>$1/n$</th>
<th>$k$ (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-NP</td>
<td>0.82</td>
<td>285.7</td>
<td>0.4405</td>
<td>18.91</td>
</tr>
<tr>
<td>4-CP</td>
<td>1.20</td>
<td>333.3</td>
<td>0.3922</td>
<td>33.11</td>
</tr>
</tbody>
</table>
Fig. 3.1. IR Spectrum of ULTC-5 Using KBr Disc Method
Fig. 3.2 Kinetic Plots of Adsorption of 4-NP and 4-CP on Activated Carbon UTLC-5
Fig. 3.3 Intraparticle Diffusion Plots for the Adsorption of 4-NP and 4-CP on Carbon UTLC-5
Fig. 3. % Phenol Removal Vs Carbon (UTLC-5) Added at pH 6 and Contact Time 6h
Fig. 3.5 Langmuir Adsorption Model of 4-CP and 4-NP on Activated Carbon UTLC-5
Fig. 3.6 Freundlich Adsorption Models of 4-CP and 4-NP on Activated Carbon UTLC-5
Fig. 3.7. Performance of UTLC-5 in 4-CP Removal in Column Test.
Fig. 3.8 Small Phenol Removal Unit

1. Influent
2. Perforated splash plate
3. UTLC-5 medium
4. Glass wool
5. Glass beads
6. Effluent
DISCUSSION

Activated Carbon

The conditions for the preparation of active carbon samples and their properties summarized Table 3.1 reveal that the increased \( \text{H}_3\text{PO}_4 \) concentration and carbonization temperature resulted in an increase in surface area. Some activation is due to dehydrating power of phosphoric acid. During heating carbon is eroded by being partly oxidised by the phosphoric acid. The adsorption capacity of UTLC-5 lies between 77.2 to 97.7% for different phenols in question as compared to activated charcoal A.R. grade (Table 3.2). UTLC-5 shows promising capacity particularly for chloro and nitrophenols.

Infrared Spectrum

The IR spectrum of UTLC-5 (Fig.3.1) shows characteristic peak of hydrogen bonded \(-\text{OH} \) group (3600-3400 cm\(^{-1}\)). The sharp peaks at 3000 and 2980 cm\(^{-1}\) represent C—H stretching vibration (aliphatic). The bands attributed to acidic \( \text{HPO}_4^{2-} \) are found at 2320, 1120, 1105, 1055 and 990 cm\(^{-1}\). The peak at 690 cm\(^{-1}\) corresponds to P—O stretching and the peak at 1405 cm\(^{-1}\) may be assigned to the deformation vibration of P—OH.

Contact Time

The kinetic plots of adsorption (\( q_e \) Vs Time) of 4-NP and 4-CP on activated carbon UTLC-5 (Fig.3.2) show that initial uptake of adsorbate up to 60 min is quite fast (~83%). The contact time required to reach equilibrium is 180 min.
Effect of pH

The removal/adsorption of phenols from aqueous solutions using UTLC-5 has been found to be highly dependent on pH (Table 3.3), which affects surface charge of the adsorbent, degree of ionization and speciation of phenols. Adsorption gradually increases up to pH 6. The lower pH results in the protonation of phenol molecules as well as active carbon surface which leads to the extensive repulsion of protonated phenols. With the increase of pH from 2 to 6, the molecular form of phenol persists in the medium and surface protonation will be minimum, resulting in increased adsorption. Reduction at pH above 6 seems due to increasing ionization of phenols.

Intraparticle Diffusion

In the intraparticle diffusion plots for the adsorption of 4-NP and 4-CP (Fig. 3.3), the double nature of the plots may be explained as: The initial curved portions are attributed to boundary layer diffusion effects\(^\text{24}\) while the final linear portions are due to intraparticle diffusion effects\(^\text{25}\).

Effect of Adsorbent Dose

The variation of phenol removal against adsorbent dose for 4-CP and 4-NP removal (Fig. 3.4) shows that per cent removal
of phenol increases with the increase in adsorbent dose. It is apparent that the equilibrium concentration decreases with increasing adsorbent dose for an initial solute concentration of 100 mg/l. Such a situation is expected because, for a fixed initial solute concentration and volume, increasing adsorbent dose provides a greater surface area (net adsorption sites).

**Adsorption Isotherms**

Adsorption equilibrium data which express the relationship between mass of adsorbate adsorbed per unit weight of adsorbent and liquid phase equilibrium concentration of adsorbate are represented by adsorption isotherms and provide important design data for adsorption system. The equilibrium data for removal of 4-NP and 4-CP in the present investigations have been analysed using Freundlich and Langmuir isotherms.

The linear plots of $1/q_e$ Vs $1/C_e$ for 4-NP and 4-CP (Fig.3.5) suggest the applicability of the Langmuir model.

$$\frac{1}{q_e} = \frac{1}{\theta^o b} \cdot \frac{1}{C_e} \theta^o$$

.............(3.1)

Where, $q_e$ = amount of dye adsorbed per unit weight of adsorbent (mg/g), $C_e$ is the equilibrium concentration of dye in aqueous solution (mg/l), $\theta^o$ and $b$ are Langmuir constants related to the capacity and energy of adsorption, (mg/g) and (l/mg) respectively.
The adsorption data (Fig. 3.6) were also fitted to the linear form of Freundlich equation

\[ \log q_e = \log k_f + \frac{1}{n} \log C_e \]  

Where, \( k_f \) and \( 1/n \) are Freundlich constants related to the adsorption capacity and adsorption intensity, respectively.

The isotherm parameters of 4-CP and 4-NP on UTLC-5 (Table 3.4) suggest that the adsorption capacity of 4-CP is higher than that of 4-NP while the intensity of adsorption of 4-CP is lower than that of the 4-NP. The values of \( 1/n \) observed between 0.1 and 0.5, show the best adsorption character\(^{28} \theta^\circ \) value of 4-CP in greater than 4-NP (Table 3.4) indicating that adsorbability of 4-CP is comparatively greater. It is further evidenced by the adsorption capacity data given in Table 3.2.

**Breakthrough Test**

The results of seven cycles of breakthrough tests plotted in Fig. 3.7 show that 320-240 bed volumes of 4-CP per cycle (corresponding to 800-600 mg 4-CP) could be passed through the column without any trace being detected in the effluent.

**Small Phenol Removal Unit**

The unit demonstrated (Fig. 3.8) for 4-CP removal from municipal wastewater produced 745 l (298 bed volumes) water
in the first cycle. During regeneration, 95.3% of the removed 4-CP was recovered. In the second cycle the unit produced 712 l (285 bed volumes) water. No phenol was detected in the effluent. The small unit appeared promising for phenol removal from wastewaters.
REFERENCES


