CHAPTER 3

EXPERIMENTAL METHODS AND ANALYSIS

3.1 MATERIALS

Sunflower seed hulls were collected from a dehulling unit at Dindugul, Tamil Nadu, India. Synthetic textile dyes such as C.I. Acid Blue 15 (AB 15), C.I. Acid Red 114 (AR 114) and C.I. Acid Violet 17 (AV 17) were supplied by Sigma-Aldrich Corporation, Bangalore, India and were used as such without further purification. Sulphuric acid used for the activation of sunflower seed hull; Potassium dichromate, Silver nitrate, Ferrous Ammonium Sulphate and Ferroin indicator for Chemical Oxygen Demand (COD) analysis of textile wastewater; Hydrochloric acid and Sodium hydroxide for pH studies; Potassium nitrate used in the determination of zero point charge were of analytical grade and were purchased from Qualigens Fine Chemicals, Mumbai, India.

3.2 PREPARATION OF ACTIVATED CARBONS

The raw material, sunflower seed hulls (SH), was repeatedly washed with distilled water to remove dirt, dust and other impurities. The washed hulls were then sun dried for 48 h and treated with 18 N sulphuric acid at different temperatures. The first sample (SH1) was prepared by immersing sunflower seed hulls in 18 N sulphuric acid, 1:2 (W/V), for 24 h at room temperature. The second sample (SH2) was prepared by immersing sunflower seed hulls in 18 N sulphuric acid, 1:2 (W/V), for 24 h at 80°C in a muffle furnace (Gambaks Instruments, Chennai, India). The third sample
(SH3) was prepared by immersing sunflower seed hulls in 18 N sulphuric acid, 1:2 (W/V), for 24 h at 120°C in a muffle furnace. After treatment, all the samples were cooled to room temperature, washed with distilled water until the pH of the filtrate becomes neutral. The three samples were soaked in 1% sodium bicarbonate solution overnight to remove any residual acid. The resulting activated carbon materials were dried in a hot air oven at 105°C, powdered and sieved through a 0.25 mm sieve. These samples were stored in separate airtight containers, free from moisture until further use.

3.3 CHARACTERISATION OF THE ADSORBENTS

Prior to making all characterization tests, the samples were first oven dried at 110°C for five hours under vacuum. The physico-chemical characteristics of the prepared activated carbons are given in Table 3.1. The surface chemistry of the activated carbons, such as specific surface area, pore volume distribution and pore diameter were determined from N₂ isotherm (Figure 3.1) data collected at 77 K (Autosorb-1-MP, Quantachrome, USA). Surface area of the adsorbents was measured using Brauner Emmer Teller (BET) method in the relative pressure range between 0.05 to 0.999 over twenty adsorption points. Pore volume and pore size distributions (Figure 3.2) were evaluated from the nitrogen adsorption isotherms using the Barrett Joyner Halenda (BJH) method (Brubauer et al 1938; Harkins and Jura 1944; Barrett et al 1951).

As the activation temperature increases, the adsorbed amount raises, which indicates a development of both micro and mesoporosity of the activated carbon. The BET surface areas, pore volume and pore size distribution of adsorbents were obtained from N₂ adsorption isotherm data are presented in Table 3.1. The results illustrate that the BET surface areas of the
SHs increased with increasing activation temperature. Increases in BET surface area were primarily attributable to increase in micropore volume.

Table 3.1 Physico-chemical characteristics of SH1, SH2 and SH3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Adsorbents</th>
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<tbody>
<tr>
<td></td>
<td>SH1</td>
</tr>
<tr>
<td>Surface area, m²/g</td>
<td>110.35</td>
</tr>
<tr>
<td>Pore volume (cm³ g⁻¹) *</td>
<td>0.134</td>
</tr>
<tr>
<td>Micropore volume (cm³ g⁻¹) **</td>
<td>0.086</td>
</tr>
<tr>
<td>Zero point charge (PZC)</td>
<td>4.2</td>
</tr>
<tr>
<td>Yield (%)</td>
<td>82</td>
</tr>
<tr>
<td>pH</td>
<td>6.1</td>
</tr>
<tr>
<td>Moisture content, %</td>
<td>14.2</td>
</tr>
<tr>
<td>Bulk density, g/mL</td>
<td>0.72</td>
</tr>
<tr>
<td>Ash content, %</td>
<td>4.99</td>
</tr>
<tr>
<td>Water soluble matter, %</td>
<td>1.32</td>
</tr>
<tr>
<td>Acid soluble matter, %</td>
<td>9.3</td>
</tr>
<tr>
<td>Decolourising power, mg/g</td>
<td>25.2</td>
</tr>
<tr>
<td>Ion exchange capacity, meq./g</td>
<td>2.3</td>
</tr>
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</table>

Ash analysis, %

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<tr>
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<tbody>
<tr>
<td>SiO₂</td>
<td>16</td>
<td>15.8</td>
<td>15.7</td>
</tr>
<tr>
<td>Na₂O</td>
<td>5.02</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.69</td>
<td>0.689</td>
<td>0.68</td>
</tr>
<tr>
<td>P</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>CaO</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>

* Total pore volume, obtained at p/p₀=0.992
** Micropore volume calculated using BJH method
Figure 3.1  Adsorption isotherms of N\textsubscript{2} at 77K for SH1, SH2 and SH3

Figure 3.2  Pore size distribution of adsorbents
3.3.1 FT-IR spectra of adsorbents

FT-IR analysis permits spectrophotometric observation of the adsorbent surface in the range 400–4000 cm\(^{-1}\), and useful for the identification of the organic functional groups on the surface. An examination of the adsorbent surface provides information regarding the surface functional groups that might have participated in the adsorption reaction. Figures 3.3-3.6 shows FT-IR spectrum of all the three adsorbents used in this study. The FT-IR spectrum of the adsorbents shows a number of absorption peaks, indicating many functional groups present in the adsorbent.

Peak positions were noticed around 3400, 2924, 1713, 1620, 1453, 1215, 1055 and 610 cm\(^{-1}\). The band around 3400 cm\(^{-1}\) is due to O-H and N-H stretching which was reduced considerably in SH3. The pair of peaks observed around 2853 and 2924cm\(^{-1}\) can be assigned to symmetric and asymmetric stretching vibrations of the C-H group, respectively and their bending vibrations appeared around 1450 cm\(^{-1}\). The peaks around 1710 and 1620 cm\(^{-1}\) reflects the carbonyl group stretching and –C=\(\text{C}\)– stretching, respectively. The peak around 1060 cm\(^{-1}\) is due to OCH\(_3\) group which may be attributed to the lignin aromatic groups. Peaks around 609 cm\(^{-1}\) can be assigned to the bending modes of aromatic compounds (Pavia et al 1987). Figure 3.4 shows that SH2 contains high concentrations of surface functional groups when compare with SH1 and SH3. In SH3 most of the functional groups present in the surface get vanished as clearly seen in the figure. The presence of polar functional groups on the surface is likely to give considerable anion exchange capacity to the adsorbents (Tsai et al 2001).
Figure 3.3 FT-IR spectra of SH1
Figure 3.4 FT-IR spectra of SH2
Figure 3.5  FT-IR spectra of SH3
3.3.2 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) has been a primary tool for characterizing the surface morphology and fundamental physical properties of the adsorbent. It is useful for determining the particle shape, porosity an appropriate pore size distribution of the adsorbent. SEM images of SH1, SH2 and SH3 are shown in Figure 3.6. From the figure it is clear that all the adsorbents have considerable number of pores where, there is a good possibility of dyes to be trapped and adsorbed into these pores.

3.3.3 Point of Zero Charge

The point of zero charge of the adsorbents was determined by the solid addition method (Balistrieri and Murray 1981). To a series of 100 mL conical flasks, 45 mL of KNO₃ solution of known strength was transferred. The pHᵢ values of the solution were roughly adjusted from 2 to 12 by adding either 0.1 N HNO₃ or NaOH. The total volume of the solution in each flask was made exactly to 50 mL by adding the KNO₃ solution of the same strength. The pHᵢ solutions were then accurately noted and 0.1 g of the adsorbent was added to each flask, which were securely capped. The suspensions were then manually shaken and allowed to equilibrate for 48 h with intermittent manual shaking. The pH values of the supernatant liquid were noted. The difference in the initial and final pH values (pHᵢ) was plotted against the pHᵢ. The point of intersection of the resulting curve is taken as pHᵥc (Figure 3.7). The values are given in Table 3.1.
Figure 3.6 SEM images of SH1, SH2 and SH3
3.5 ADSORPTION STUDIES

To study the effect of parameters such as adsorbent dosage, pH and initial concentration batch experiments were carried out for the adsorption of anionic dyes onto three activated carbons in a thermostatic orbital shaker (Orbitek, Scigenics Biotech, Chennai, India) at a constant speed of 175 cycles per minute at room temperature. The adsorption isotherm experiment was carried out by agitating 50 mL of dye solutions of various concentrations. After agitation, the dye solution was separated from the adsorbent by centrifugation for 10 minutes. Dye concentrations in the supernatant solutions were measured using a UV-Vis spectrophotometer. The effect of pH on dye removal was studied over a pH range of 2-11. The Initial pH of the dye solution was adjusted by the addition of 0.1 N solution of HCl or NaOH. To find the optimum amount of adsorbent per unit mass of the adsorbate, 50 mL of dye solution was contacted with different amounts of adsorbent till equilibrium was reached. The kinetic experiments were carried out using a
known weight of adsorbent and employing dye in the concentration range of 60-100 mg/L in a 1000 mL beaker using a mechanical stirrer. The samples were withdrawn at predetermined time intervals and centrifuged. The effect of temperature on the adsorption characteristics was studied by determining the thermodynamic parameters at 35, 40 and 45ºC with a fixed dye concentration and dosage. The dye removal percentage and amount adsorbed were calculated using the following relationships

\[
\text{Percentage removal} = \frac{C_o - C_e}{C_o} \times 100
\]  

(3.1)

\[
\text{Amount adsorbed (} q_e \text{)} = \frac{(C_o - C_e)V}{m}
\]  

(3.2)

where \(C_o\) and \(C_e\) are, respectively, the initial and equilibrium concentrations (mg/L) of dye, \(m\) is the mass (g) of the adsorbent and \(V\) is the volume of the dye solution (L). The experimental procedure carried out for the selected dyes is given below individually.

3.6 \hspace{1cm} \textbf{CALCULATION OF COD}

Chemical oxygen demand is a measure of presence of total amount of oxidizable organic and inorganic matter. The value is expressed in terms of parts per million (ppm) of oxygen. The calculation of COD is based on the chemical oxidation of the pollutants present in the textile effluent by \(K_2Cr_2O_7\) in \(H_2SO_4\) in the presence of a catalyst \(Ag_2SO_4\) (Moore et al 1949, Dobbs and Williams 1963).

50 mL of the textile effluent was taken in a 250 mL conical flask. To this 10 mL of 0.1 N \(K_2Cr_2O_7\) in 18 mL \(H_2SO_4\) and 0.1g \(Ag_2SO_4\) were added and the mixture was refluxed for about 3 h. The unreacted dichromate
in the effluent was titrated against standard Ferrous Ammonium Sulphate (FAS) using Ferroin as the indicator. The oxygen equivalent of K$_2$Cr$_2$O$_7$ consumed was taken as the value of COD.

$$\text{(CH}_2\text{O)}_n + \text{Cr}_2\text{O}_7^{2-} + \text{H}^+ \rightarrow \text{Cr}^{3+} + n(\text{CO}_2) + n(\text{H}_2\text{O})$$  \hspace{1cm} (3.3)

COD is determined by using the relation,

$$\text{COD in ppm} = \frac{(A - B) N}{V} \times 8000$$  \hspace{1cm} (3.4)

where

A - Volume of FAS required in the blank titration
B - Volume of FAS required in the titration of the sample
N - Normality of FAS
V - Volume of the sample taken.

### 3.7 CALCULATION OF TDS

The total dissolved solid is the organic and inorganic ions dissolved in the effluent. TDS was calculated using methods given by Howard (1933). To calculate the amount of dissolved solids present in any effluent, 50 mL of water sample was taken and filtered using Whatman filter paper No-44. The filtrate was taken in a dry, previously weighed crucible and evaporated to dryness in a hot air oven at 98° C, followed by one hour drying at 103-105°C. The crucible with residue was cooled in a dessicator and weighed.

\[
\begin{align*}
\text{Weight of empty crucible} & = W_1 \text{ g} \\
\text{Weight of residue + crucible} & = W_2 \text{ g} \\
\text{Weight of residue} & = (W_2 - W_1) \text{ g} \\
\text{Total Dissolved Solids (mg/L)} & = \frac{(W_2 - W_1) \text{ mg}}{V} \times 1000 \\
V & - \text{Volume of the sample in mL.}
\end{align*}
\]