Chapter - IV

Experimental Techniques
CHAPTER – IV

EXPERIMENTAL TECHNIQUES

4.0. Experimental Techniques

4.1. Carbonization Procedure

The plant materials of *Cynodon dactylon* and barks of *Samanea saman* were presented in and around Mannargudi, (Thiruvarur District) and Pattukkottai (Thanjavur District). The materials were dried in absence of sunlight and carbonized with concentrated sulphuric acid in the ratio of 1:1 (w/v). The activated materials were carbonized by heating in a muffle furnace at 500°C for twelve hrs. The activated carbons were washed with double distilled water until a constant pH of the slurry was reached. Then the carbons were dried for four hrs at 100°C in a hot air oven and it was ground well to get a fine powder and sieved. The acid activated carbons obtained from *Cynodon dactylon* and *Samanea saman* would be denoted, hereafter, as CDC and SSC respectively.

4.2. Characterization of activated carbons

Activated carbons are widely used adsorbent due to its high adsorption capacity, high surface area and micro porous structure, high chemical and mechanical stability. The chemical nature and pore structure usually determines the sorption activity. The activated carbons employed in the present study are characterized as follows.
4.2.1. Particle size determination

The Carl Zeiss Light microscope (Axiostar Plus) attached with the ocular micrometer with a dimension of 10x was used to measure the particle size of the adsorbents. The length and breadth of each particle was measured using the ocular micrometer scale. Each division in the scale of the ocular micrometer was 0.01 mm. By application of multiplication factors, the size of the particles was calculated (Muthulakshmi Andal, 2003).

4.2.2. Density

Density was defined as an object mass per unit volume. Mass was a property. The density can be expressed as

\[ \rho = \frac{m}{V} = \frac{1}{v_g} \quad \ldots (4.1) \]

Where,
\begin{align*}
\rho &= \text{density (kg/m}^3), \\
m &= \text{mass (kg)} \\
V &= \text{volume (m}^3) \\
v_g &= \text{specific volume (m}^3/\text{kg})
\end{align*}

Density of the adsorbents was found by mass/volume of the adsorbents. The sieved adsorbents was closely packed in a dry graduated glass tube and weighed. The mean value was obtained by repeating the procedure for ten times. The difference in mass with the initial mass of the graduated tube before close packing was noted, the mean mass/volume determined gave the density of the adsorbent.
4.2.3. Moisture content

Water content or moisture content was the quantity of water contained in a material, such as soil (called soil moisture), rock, ceramics, fruit, or wood. Water content was used in a wide range of scientific and technical areas, and was expressed as a ratio, which can range from zero (completely dry) to the value of the materials porosity at saturation. It can be given on a volumetric or mass (gravimetric) basis.

4.2.4. Loss on ignition

Each adsorbent was taken by one g and it was placed in pre weighed silica crucible and it was ignited at 1000°C for 4 hrs. Then, it was cooled in desiccator for 1hr and then, the final weight was measured. The weight loss was calculated as, loss on ignition.

4.2.5. Acid insoluble matter

Each adsorbent was taken by 500 g and it was placed in an evaporating dish, mixed with distilled water to thin slurry, 10 ml of concentrated hydrochloric acid was added and digested by warming until sample was nearly dry. The digestion was repeated three times with 5 ml of the acid. Then, it was diluted with 100 ml water filtered using a previously weighed sintered crucible and the weight of the insoluble matter was calculated after drying for a constant weight at 100°C.
4.2.6. Water soluble matter

Each adsorbent was taken by one g and added to 100 ml of distilled water and was shaken thoroughly for about 30 min and filtered. The residue i.e. adsorbent was dried, cooled and weighed.

4.2.7. pH of aqueous solution

The adsorbent (100 mg each) was mixed with 50 ml of distilled water and equilibrated for 1 hr by agitating in a thermostated shaker at 120 rpm. The pH of the supernatant was measured using pH meter was calibrated with 4.0 and 9.2 buffers.

4.2.8. Zero point charge ($\text{pH}_{\text{zpc}}$)

The pH at the potential of zero charge ($\text{pH}_{\text{zpc}}$) of the carbons was measured using the pH drift method (Jia et al., 2002). The pH of a solution of 0.01 M NaCl was adjusted between 2 and 12 by adding either hydrochloric acid or sodium hydroxide. Nitrogen was bubbled through the solution at 25°C to remove dissolved carbon dioxide until the initial pH stabilized. Active carbon 50 mg of the activated carbon was added to 50 ml of the solution. After the pH had stabilized (typically after 24 hrs), the final pH was recorded. The graphs of initial pH versus final pH were used to determine the points at which initial and final pH values were equal. This was taken as the $\text{pH}_{\text{zpc}}$ of the carbon.

4.2.9. Titration studies

The strongly acidic carboxylic acid groups are neutralized by NaHCO$_3$, whereas those neutralized by Na$_2$CO$_3$ are thought to be lactones, lactol and
carboxyl group was examined (Jia et al., 2002). The weakly acidic phenolic
groups only react with strong alkali, sodium hydroxide. Therefore, by selective
neutralized using bases of different strength, the surface acidic functional
grouping carbon can be characterized both quantitatively and qualitatively.
Neutralization with hydrochloric acid characterizes the amount of surface basic
groups that are, for example, pyrones and chromenes. The basic properties
have described to surface basic groups and the $\pi$ electron system of carbon
basal planes. The results of the selective neutralization studies are given in
(Table 4.1), the results indicated that the activated carbons used may possess
acidic oxygen functional groups on their surface and this was supported well by
their respective $pH_{zpc}$ values (Syed et al., 2006). The results obtained from the
above characterization studies are given in (Table 4.1)

**Table - 4.1**

<table>
<thead>
<tr>
<th>Characteristics of the adsorbents</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Properties</strong></td>
</tr>
<tr>
<td>Particle size (mm)</td>
</tr>
<tr>
<td>Density (g/cc)</td>
</tr>
<tr>
<td>Moisture content (%)</td>
</tr>
<tr>
<td>Loss on ignition (%)</td>
</tr>
<tr>
<td>Acid insoluble matter (%)</td>
</tr>
<tr>
<td>Water soluble matter (%)</td>
</tr>
<tr>
<td>$pH$ of aqueous solution</td>
</tr>
<tr>
<td>$pH_{zpc}$</td>
</tr>
<tr>
<td>Surface groups (m equiv/g)</td>
</tr>
<tr>
<td>Carboxylic acid</td>
</tr>
<tr>
<td>Lactone, lactol</td>
</tr>
<tr>
<td>Phenolic</td>
</tr>
<tr>
<td>Basic (pyrones and chromenes)</td>
</tr>
</tbody>
</table>
4.3. Materials

All the chemicals employed in the present study were commercially available high purity Analar grade (Merck, India or SRL, India) and were used as received. Double distilled water was used throughout the work and the second distillation was made over alkaline permanganate. The glasswares used in the present study were of Borosil grade.

4.4. Preparation of metal ion solutions

The metal ions chosen for the adsorption studies in the present work are Fe (II) and Cu (II). Stock solutions (1000 mg/L) of Fe (II) and Cu (II) were prepared by dissolving required amount of metal salt in one litre of distilled water. The weights of the respective salts taken are listed in Table.4.2.

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Metal salt</th>
<th>Weight to be dissolved for one litre(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(II)</td>
<td>FeSO$_4$.7H$_2$O</td>
<td>4.9785</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>CuSO$_4$.5H$_2$O</td>
<td>3.9294</td>
</tr>
</tbody>
</table>

4.5. Preparations of dye solutions

The dyes employed for the adsorption studies, in the present work are MG and RDB. All the dyes for the study were commercially available high purity Analar grade (Merck, India) and used without further purification. Stock solution (500 mg/L) of the dyes was prepared by dissolving required amount of the respective dye in one litre of distilled water.
4.6. Methodology

The concentration of the metal ions and dyes before and after adsorption was measured using a double UV-Visible spectrophotometer (Shimadzu UV 240 Graphicord). Standards for the establishment of calibration curve for UV-Visible spectrophotometer analysis was prepared by diluting the stock solutions to have 5 to 100 mg/L of the metal ions or dyes and the absorbance of the solution at the respective wavelength was recorded. The wavelength of maximum absorbance for Fe (II), Cu (II), MG and RDB are given in Table 4.3.

Table - 4.3
Wavelength for the estimation of metal ions/dyes

<table>
<thead>
<tr>
<th>Metal ion/Dye</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(II)</td>
<td>530</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>620</td>
</tr>
<tr>
<td>MG</td>
<td>614</td>
</tr>
<tr>
<td>RDB</td>
<td>543</td>
</tr>
</tbody>
</table>

4.7. Adsorption studies
4.7.1. Batch equilibration method

All experiments were carried out at 30 to 65°C temperature in batch mode. Batch mode was selected because of its simplicity and reliability. The batch experiments were done in different Erlenmeyer glass flasks of 100 ml capacity. Prior to each experiment, a predetermined amount of absorbent was added to each flask. The stirring was kept constant (120 rpm) for each run throughout the experiment to ensure equal mixing. Each flask was filled with a
known volume of sample before commencing stirring such as metal ion and dye solution with an initial concentration of 5 mg/L to 100 mg/L, the flask containing the sample was withdrawn from the shaker at the predetermined time interval, filtered and the residual concentration of the metal ion and dye was measured. The amount of dye adsorbed at time $t$, $q_t$, and at equilibrium, $q_e$, was calculated from the mass balance equation:

$$t = \frac{(C_0 - C_t) V}{m}$$  \hspace{1cm} ... (4.2)

where, $q_t$ was the amount of dye adsorbed (mg/g) at time $t$,

- $C_0$ was the initial dye concentration (mg/L),
- $C_t$ was the dye adsorbent (mg/L) at time $t$,
- $V$ was the volume of solution (mL),
- $m$ was the mass of the adsorbent (g).

where, $t$ was equal to the equilibrium contact time, $C_t = C_e$, $q_t = q_e$, then, the amount of dye ion adsorbed at equilibrium, $q_e$, was calculated using the above equation.

### 4.7.2. Effect of variable parameters

#### i. Concentration of adsorbents

Different concentrations consisting of 10 to 250 mg/50 ml of the two adsorbents were taken and they mixed with the metal ion and dye solutions and the mixture was mixed thoroughly by using a mechanical shaker. The
percentage of adsorption for different concentrations was determined by keeping all other factors constant.

**ii. Initial concentration**

The experiments were conducted with different initial concentrations of dyes ranging from 10 to 100 mg/L and metal ions ranging from 10 to 60 mg/L to determine the rate of adsorption by keeping all other factors constant.

**iii. Contant time**

Particle size, initial concentration, dosage, pH and temperature, these parameters were keeping constant, the effect of period of contact between the adsorbent and adsorbate on the removal of the metal ions and dyes was determined in a single cycle.

**iv. Initial pH**

At a wide range of pH of the solution i.e. 3-9, adsorption experiments were carried out. Required amount of hydrochloric acid and sodium hydroxide solution was added by maintaining of the acidic and alkaline pH of the medium. While carrying out the experiments, the parameters like particle size of the adsorbents, metal ion or dye concentration, dosage of the adsorbents, and temperature were kept constant.

**v. Other Ions**

A specific metal ions and dye in the presence of calcium and chloride ions were experimentally verified using the adsorbents in adsorption studies.
Keeping all other factors constant, the determination of the percentage of metal ion or dye adsorbed from particular initial concentration of the metal ion/dye solution with varying concentration of the added ion.

vi. Temperature

The adsorption experiments were performed in between 30-65°C in a thermostated shaker machine (Remi, India). The constancy of the temperature was maintained with an accuracy of ± 0.5°C.

4.8. Adsorption isotherms

The sorption isotherm was highly significant in the removal of metal ions and dyes by the adsorption technique, as it provides an approximate estimation of the sorption capacity of the adsorbents. The equilibrium data for the removal of metal ions and dyes by sorption on the two adsorbents at different temperature have been used in Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1906) isotherms.

Langmuir isotherm: \[ \frac{C_e}{Q_e}=\frac{1}{Q_m b} + \frac{C_e}{Q_m} \] ... (4.3)

Freundlich isotherm: \[ \log Q_e = \log K + \frac{1}{n} \log C_e \] ... (4.4)

Where, \( C_e \) was the equilibrium concentration of the adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g); \( Q_m \) and \( b \) are Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. The values of \( Q_m \) and \( b \) have been obtained from the linear correlation of \( C_e/Q_e \) against \( C_e \). The Freundlich constants \( K_f \) and \( n \) are the measures of adsorption.
capacity and intensity of adsorption respectively and these values have been calculated from the linear correlations of log $Q_e$ versus log $C_e$.

The essential characteristics of the Langmuir isotherm can be described by a separation factor $R_L$, which was defined as

$$R_L = \frac{1}{1+bc_0}$$

... (4.5)

where, $b$ was the Langmuir constant and $C_0$ was the initial concentration of the metal ion/dye. The values of $R_L$ indicated the types of the isotherm as follows (Table 4.4).

<table>
<thead>
<tr>
<th>$R_L$ value</th>
<th>Types of Isotherms</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_L &gt; 1$</td>
<td>Unfavourable</td>
</tr>
<tr>
<td>$R_L = 1$</td>
<td>Linear</td>
</tr>
<tr>
<td>$0 &lt; R_L &lt; 1$</td>
<td>Favourable</td>
</tr>
<tr>
<td>$R_L = 0$</td>
<td>Irreversible</td>
</tr>
</tbody>
</table>

4.9. Kinetics of adsorption

The kinetics of sorption describes the solute uptake rate, which in turn governs the residence time of sorption reaction. It was one of the important characteristics in defining the efficiency of sorption. In the present study, the kinetics of the metal ion and dye removal was carried out to understand the behaviour of these low cost carbon adsorbents. The adsorption of metal ion and dye from an aqueous solution follows reversible first order kinetics, when a single species are considered on a heterogeneous surface. The heterogeneous
equilibrium between the metal ion or dye solutions and the activated carbon are expressed as

$$A \xleftrightarrow[k_1/k_2]{\text{B}}$$ ... (4.6)

where, $k_1$ was the forward rate constant and $k_2$ was the backward rate constant.

A represents metal ions or dyes remaining in the aqueous solution and

B represents metal ions or dyes adsorbed on the surface of activated carbon.

The equilibrium constant ($K_0$) was the ratio of the concentration of adsorbate in adsorbent and in aqueous solution ($K_0 = k_1/k_2$).

In order to study the kinetics of the adsorption process under consideration the following kinetic equation proposed by Natarajan and Khalaf as cited in literature (Prasad, 2003) has been employed.

$$\log \frac{C_0}{C_t} = \left(\frac{k_{ad}}{2.303}\right) / t$$ ... (4.7)

Where, $C_0$ and $C_t$ are the concentration of the metal ion or dye (in mg/L) at “0” and “t” time, respectively. The rate constants ($k_{ad}$) for the adsorption processes have been calculated from the slope of the linear plots of $\log C_0/C_t$ versus $t$ for different concentrations and temperatures, the forward and backward rate constants are calculated using the following equation, as described in literature (Rengaraj et al., 1999).

$$k_{ad} = k_1 + k_2 = k_1 + (k_1/K_0) = k_1[1 + 1/K_0]$$ ... (4.8)
4.10. Intraparticle diffusion

The sorption process was an overall conjunction of several mechanisms with a preponderant part played by intraparticle diffusion (Gopal and Elango, 2006). Hence, the sorption performances of the adsorbents have been determined by the influence of the diffusion mechanism on metal ions or dyes uptake. Pore diffusion in the fluid phase within the particles represents the diffusion in the adsorbed state. When pore diffusion limits the adsorption process, the relationship between the initial adsorbate concentration and the rate reaction will not be linear. It seems that pore diffusion limits the overall rate adsorption by the adsorbents.

As the metal ions are vigorously agitated during the adsorption period, it was probably reasonable to assume that mass transfer from the bulk solution to the external surface of the adsorbent does not at all limit the rate of the reaction. A functional relationship common to majority of intraparticle diffusion treatments was that uptake varies almost proportionally with the half power of time was explained (Aravind and Elango, 2006). The influence of intraparticle diffusion was estimated by evaluation of initial sorption rate. The intraparticle diffusion rate constant was given by the following equation.

\[ Q = K_p t^{1/2} + C \]  \hspace{1cm} (4.9)

In the present study the possibility of existence of intraparticle diffusion has been tested by plotting the graph between amount of metal ions or dyes adsorbed and square root of time. The rate constant for intra-particle diffusion
co-efficient $K_p$ for metal ions and dyes was determined from the linear portion of the respective plots.

### 4.11. Activation parameters

The standard free energy change ($\Delta G^\circ$), enthalpy change ($\Delta H^\circ$) and entropy change ($\Delta S^\circ$) were calculated from the variation of the thermodynamic equilibrium constant $K_0$. The values of $K_0$ for the adsorption process were determined by the reported method (Muthulakshmi Andal, 2003).

The thermodynamic parameters were calculated using the following equations.

\[
K_0 = \frac{C_{\text{solid}}}{C_{\text{liquid}}} \quad \ldots (4.10)
\]

\[
\Delta G^\circ = -RT \ln K_0 \quad \ldots (4.11)
\]

\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \ldots (4.12)
\]

\[
\ln K_0 = \frac{\Delta G^\circ}{RT} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \ldots (4.13)
\]

\[
\log K_0 = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad \ldots (4.14)
\]

$\Delta H^\circ$ and $\Delta S^\circ$ were determined from the slope and intercept of the plot of $\ln K_0$ versus $1/T$.

### 4.12. Desorption studies

Desorption studies help to elucidate the nature of adsorption and recycling of the spent adsorbent and the metal ions and dyes. If the adsorbed metal ions or dyes can be desorbed using water, then the attachment of the metal ion or dye on the adsorbent by weak bonds. If sulphuric acid or alkaline
water desorp the metal ion or dye, then the adsorption was by ion exchange. If organic acids, like acetic acid can desorp the metal ion or dye, then the metal ion or dye was held by the adsorbent through chemisorption (Stephen Inbaraj and Sulochana, 2002). The effect of various regents used for desorption studies are carried out by using 0.2 M hydrochloric acid, sulphuric acid, nitric acid, sodium chloride and water.

4.13. Analytical Measurements

The activated carbons before and after adsorption have been recorded by using JASCO FT-IR 460 plus spectrometer, (St. Joseph’s College, Trichy, Tamil Nadu) and (PANalytical X’ per PRO XRD Instrument) and (HITACHI S-3000H Scanning Electron Microscope), (CECRI, Karaikudi, Tamil Nadu).

4.14. Data Analysis

The experimental data were analyzed using Microcal Origin Software (version 6.0). The goodness of fit was discussed with using correlation coefficient r.