CHAPTER - III

EXPERIMENTAL PROCEDURE AND CHARACTERISATION

3.0 Introduction

This chapter deals with the reagents, materials, chemicals, sources of materials used, the methods of preparation of adsorbent materials and the procedure for the study. The experimental procedures for the characterization of adsorbents, instrumental studies, adsorption studies-carried out by employing the batch adsorption technique, equilibrium studies and desorption studies are presented. The procedure for adsorption of dyes from binary mixture is also given. The adsorption data were obtained under batch mode of operation for the adsorption of three different dyes viz., Malachite Green (MG), Rhodamine - B (RB) and Crystal Violet (CV) on six different adsorbent materials leaf carbon such as Casurina Equisetifolia (CE) Tectona Grandis (TG), Artocarpus Heterophyllus (AH), Pongamia Pinnata (PP), Madhuca Longifolia (ML) and Terminalia Catappa (TC). The adsorption data were compared with commercial activated carbon (CAC) at 30 ± 1 °C.

The removal of dyes by adsorption from single, binary mixtures and column studies were made at 30 ± 1 °C. All the experiment were replicated (error = ±1-2 %) and the average values were reported. Control experiments without adsorbents and dyes were also carried out in each case.

3.1 Reagents

The following reagents were prepared to carry out the experiments
3.1.1 Dye solution

Stock solutions of various dyes viz., MG., RB. and CV were prepared (concentration : 500 ppm) using AnalR grade (BDH, India) dye samples. They were suitably diluted to the required initial concentrations with double distilled (DD) water for carrying out the adsorption equilibrium and adsorption (removal) studies for adsorption studies from binary mixtures, solution of two dyes (dye-A and dye-B) were mixed in the required molar concentrations.

3.1.2 Acetic acid

About 10 mL of glacial acetic acid (AnalR; BDH, India) was dissolved in 500 mL of DD water. The exact strength of the acetic acid solution was established by titrating it against standardized sodium hydroxide solution using phenolphthalein as indicator [1]. The strength of the acetic acid solution was then corrected to 0.1 M.

3.1.3 Dilute sulphuric acid

Dilute sulphuric acid (4N) was prepared by diluting 250 mL of concentrated sulphuric acid (Fischer, India; Specific gravity = 1.30) to two litres with DD water and the strength of the acid solution was corrected to 4N, using a standard solution on sodium carbonate (AnalR; BDH, India).

3.1.4 Hydrochloric acid

Hydrochloric acid (1M) was obtained by diluting 100 mL of centered hydrochloric acid (Fischer, India; Specific gravity = 1.10) to one litre with DD water and the strength of the acid solution was corrected to 1.0 M, using a standard solution of sodium carbonate (AnalR; BDH, India).
3.1.5 Sodium hydroxide

Approximately 10.0 g of sodium hydroxide pellets (LR; Nice, India) were dissolved in 250 mL of DD water and the strength of the solution was corrected to 1 M using a standard solution of oxalic acid (AnalaR; BDH, India).

3.1.6 Indicator solution

Indicator solutions (phenolphthalein and methyl orange) were prepared freshly before carrying out the acid-base titration as per the method recommended by Vogel [1].

3.1.7 Phenol solution

Exactly 0.1 g of phenol (AnalaR; BDH, India) was dissolved in DD water containing small quantity of NaOH (0.005 g) and diluted to 100 mL to get 1% (w/v) phenol solution.

3.1.8 Sodium nitrate solution

Sodium nitrate solution (0.01N) was prepared by dissolving 8.5 g of sodium nitrate (Ranbaxy, India) in one litre of DD water.

3.1.9 Potassium dichromate solution

Exactly 1.226 g of potassium dichromate (AnalaR; BDH, India) was dissolved in DD water and made up to one litre in a standard flask (Strength = 0.025 N).

3.1.10 Sodium thiosulphate solution

About 6.2 g of sodium thiosulphate (LOBA Chemie, India) was dissolved to one litre in a brown coloured reagent bottle. The strength of the solution was estimated by iodometric method using starch as indicator and corrected to 0.025 N [1].
3.1.11 Starch solution

Approximately 0.4 g of soluble starch (AnalaR; BDH, India) was made paste with 10 mL of distilled water and poured into boiling water (250 mL) solution was prepared a fresh on the day of use.

3.1.12 Potassium iodide solution

Potassium iodide (10 g; LOBA Chemie, India) was dissolved in 100 mL of water and the 10% (w/v) KI solution was stored in a brown coloured reagent bottle.

3.1.13 Brominating mixture

About 3 g of potassium bromate and 15 g of potassium bromide (LR: N India) were dissolved in distilled water and diluted to one litre. Winkler brominating solution was stored in a brown coloured reagent bottle.

All the other chemicals and reagents used in the present investigation were either analytical grade or laboratory reagent grade, procured from BDH/SD chemicals/Nice/Ranbaxy, India and they were used as such without any further purification. DD water was used during the entire course of this work and used to prepare all the solutions and reagents

3.2 Materials and chemicals

Tree leaves from trees such as *Casurina Equisetifolia*, *Tectona Grandis*, *Artocarpus Heterophylius*, *Pongamia Pinnata*, *Madhuca Longifolia*, *Terminalia Catappa* were collected in Thiruchendur and nearby villages, Tamil Nadu, India.
The materials and chemicals used in the present study are listed below:

Commercial Activated Carbon - E Merck, (Guaranteed Reagent), India
Acetic acid, glacial - BDH (AnalaR), India
Malachite Green - BDH (LR), India
Rhodamine - B - BDH (AnalaR), India
Crystal Violet - BDH (AnalaR), India
Hydrochloric acid, concentrated - Fisher (LR), India
Nitric acid, concentrated - SD Fine Chemicals (LR), India
Phenol - BDH (LR), India
Phenolphthalein - BDH (LR), India
Potassium bromate - Nice (LR), India
Potassium bromide - Nice (LR), India
Potassium dichromate - BDH (AnalaR), India
Potassium iodide - Loba Chemie (LR), India
Sodium carbonate - BDH (AnalaR), India
Sodium hydroxide - Nice (LR), India
Sodium nitrate - Ranbaxy (CR), India
Sodium thiosulphate - BDH (AnalaR), India
Starch (soluble) - BDH (LR), India
Sulphuric acid, concentrated - Fisher (LR), India

3.2.1 Double distilled water

DD water was prepared in an all glass apparatus protected from carbon di oxide using soda lime guard tube. Distilled water was once distilled over alkaline potassium permanganate. DD water was stored in brown bottles [2]. All the solutions and reagents were prepared by using this DD water.

3.2.2 Calibrations

The burettes and sampling pipettes were calibrated at room temperature (30 ± 1 °C). The standard measuring flasks and graduated measuring jars were further
calibrated at room temperature (30 ± 1 °C). The calibrations were carried out by using pure, carbon di-oxide free distilled water, by adopting the method recommended by Vogel [1,2].

3.3 Adsorbents

3.3.1 Preparation of activated carbon

The tree leaves were collected from Tiruchendur and nearby villages, Tamil Nadu, India. The collected material was washed and air dried for one month. The dried material was cut into small pieces for further chemical modification. The preparation of carbon material was made according to the literature method [3]. The ground material was mixed with equal amount of sulphuric acid and stirred for 30 min. The acid tree leaf slurry was placed in a glass container and dried at 80 °C in a hot air oven. After 24h, the thermochemical reaction between acid and tree leaves was proceed by raising the oven temperature to 120 °C for 90 min. After cooling, the carbon material obtained was washed thoroughly with distilled water to remove residual acid. The wet carbon materials were dried at 110 °C until constant weight and preserved in a desiccator as adsorbents for further use.

3.4 Dye solution characteristics

Dyes used in the present study were of AnalR grade samples (BDH, India). The three dyes were studied (viz., MG, RB and CV) and characterized mainly by their absorption in the visible (λ<sub>max</sub> in nm) region. The measuring maximum absorbance of dyes in UV-visible double beam spectrophotometer (model no: UV-1700 Shimadzu, Japan). The UV-Spectrum of these dyes and λ<sub>max</sub> values are given in Figs. 3.1-3.3. The
molecular weight, $\lambda_{\text{max}}$, colour index (C.I.), commercial name and name of the dye samples used are listed in Table 3.1.

**Table 3.1. Characteristics of dye samples used in the study**

<table>
<thead>
<tr>
<th>Dye</th>
<th>Name</th>
<th>C.I. Number</th>
<th>Chemical Formula</th>
<th>Molecular weight</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MG</td>
<td>Malachite green</td>
<td>42,000</td>
<td>C$<em>{50}$H$</em>{52}$N$_4$O$_8$C$_2$H$_2$O$_4$</td>
<td>927.00</td>
<td>617</td>
</tr>
<tr>
<td>RB</td>
<td>Rhodamine-B</td>
<td>45,170</td>
<td>C$<em>{28}$H$</em>{31}$ClN$_2$O$_3$</td>
<td>479.02</td>
<td>554</td>
</tr>
<tr>
<td>CV</td>
<td>Crystal violet</td>
<td>42,555</td>
<td>C$<em>{25}$H$</em>{31}$N$_2$Cl</td>
<td>407.99</td>
<td>589</td>
</tr>
</tbody>
</table>

![Malachite Green](image1.png)

Malachite Green

![Rhodamine – B](image2.png)

Rhodamine – B

![Crystal Violet](image3.png)

Crystal Violet
The UV – Vis spectrum of dye solutions are given below

Figure 3.1  UV-Visible spectrum of Malachite green

Figure 3.2  UV-Visible spectrum of Rhodamine-B
Figure 3.3  UV-Visible spectrum of Crystal Violet

3.4.1 Preparation of standard curve

Exactly 50 mL of dye solutions of various initial concentrations were prepared in standard measuring flasks, separately by diluting the stock solution of dyes (1000 ppm). The optical density (O.D.) of each dye solution was determined spectrophotometrically by using Systronics spectrophotometer (India, model : 105) and ELICO UV - Visible Spectrophotometer (India, Model : SL 207) at the wavelength of maximum absorption ($\lambda_{\text{max}}$): 617.0, 554.0 and 589.0, respectively for the dyes, MG, RB and CV. The plots of O.D. vs concentration of dyes were made and found to be linear in the concentration range studied.

3.4.2 Estimation of dye concentration

Stock solution of dye (1000 ppm) was prepared (effluent concentration assumed 1000ppm) and suitably diluted to various concentrations. The dye concentrations of the
solutions of various dyes of different initial concentrations were estimated spectrophotometrically by measuring the O.D. values at their $\lambda_{\text{max}}$. The corresponding concentrations of dyes were obtained from the standard curves by interpolation technique (i.e., by interpolating the O.D. values in the standard curves). The concentrations of dyes after the adsorption were also determined by similar procedure. Wherever needed and necessary, the dye solutions were suitably diluted, before measuring the O.D. values, if the O.D. readings were not within the range (range of O.D. = 0.1 – 1.0).

3.5 Procedure for Instrumental Studies

The FT-IR spectra of the adsorbent materials before and after adsorption of dyes were recorded in KBr pellets by using a BIO-RAD WIN IR Spectrometer (Frequency range: 400 - 4000 cm$^{-1}$).

The scanning electron microscope (SEM) photographs of the adsorbent materials before and after adsorption of dyes were obtained [4], using a JEOL JSM - 5300 SEM (Current : 21.5 mA; pressure = 0.05 M bar; Inert gas atmosphere = Argon; Time = 1 min; Distance between cathode and sample = 30 mm).

The thermogravimetric traces of the adsorbent materials before and after adsorption of dyes (viz., AC, CR, MB and RB) were recorded in an UNIVERSAL V2.5H TA instrument, employing the method 20-1000 °C, under static nitrogen atmosphere at a heating rate of 20 °C per min., from 27 to 1000 °C. The sample weight used in TGA studies varied from 6.89 to 27.80 mg.
3.6 Characterisation procedure

The following physico-chemical characteristics of the adsorbent materials were determined. The experimental procedure employed is described below:

3.6.1 Apparent density

A preweighed ($W_1$) specific gravity bottle of 25 mL capacity was filled with the adsorbent materials (viz., CELC, TGLC, AHLC, PPLC, MLLC, TCLC and CAC) and packed well by tapping it with a rubber stopper. The weight of the specific gravity bottle, filled with the adsorbent material was weighed ($W_2$). The weight of the adsorbent material was determined from the difference in the weight ($W_2 - W_1$). The weight of adsorbents (g) divided by the volume (mL), resulted in the apparent density (gm L$^{-1}$) of the adsorbent [4].

3.6.2 Moisture content

One gram of the adsorbent material placed in a petridish was heated in an air-oven at 130 °C for 3h. After the heating was over, the dish was quickly covered and cooled in a desiccator and weighed. The loss in weight of the adsorbent material after heating, expressed in percentage, represented the mechanical or hydrosopic moisture content [4] of the adsorbent material.

3.6.3 Loss on ignition

One gram of the adsorbent material was placed in a pre-weighed silica crucible. It was ignited to 800-850 °C in a muffle furnace (Neolab, India, Model: AUS 101) for 4h. Then, it was kept in a desiccator for 30 min. The final weight of the silica crucible was determined. The weight loss (after ignition) was calculated in terms of percentage, as loss on ignition (LOI) of the adsorbent material [4].

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3.6.4 pH and conductivity

The adsorbent (100 mg) material was mixed with 50 mL, of DD water (pH = 6.46, conductivity = 0.05 μS cm⁻¹) and equilibrated for 1 h, by agitating it at 120 rpm in a thermostatic mechanical orbit shaker (NEOLAB, India). The supernatant liquid was analysed for pH and electrical conductivity (in ohm⁻¹ cm⁻¹), using pen type digital pH meter (Hanna Instrument, Portugal) and Systronics digital conductivity meter (Model: CM-335, India), respectively.

3.6.5 Zero point charge

The aqueous suspension of adsorbent material (100 mg in 50 mL) was prepared in 50 mL solution of sodium nitrate of concentration 0.001 N. Solution pH was adjusted to a required value by the addition of dilute solution of sodium hydroxide or nitric acid of strength 1.0 M. After 60 min., of equilibration at 30 ± 1 °C in a thermostatic mechanical orbit shaker (NEOLAB, India) the pH value (initial pH) was measured with a pen type digital pH meter (Hanna Instruments, Portugal). Then, one gram of sodium nitrate (LR, Ranbaxy, India) was added to each bottle, to bring a final electrolyte concentration to about 0.45 M. After an additional 60 min., agitation, the final pH was measured with pen type digital pH meter (Hanna Instruments, Portugal). The ΔpH (ΔpH = Final pH - Initial pH) was calculated and plotted against solution pH. The pH at which the ΔpH = 0, yielded pH value at zero point charge [5] i.e., pH_{zpc}.

3.6.6 Surface area

Surface area of the adsorbent material was determined by following the acetic acid adsorption method [6, 7]. The adsorbent material (0.5 g) was added to each one of
250 mL, reagent bottles containing 50 mL of 0.05, 0.10, 0.15, 0.20, 0.25 and 0.30 N acetic acid solution. A control experiment was also performed for each acid concentration without adsorbent. The bottles were tightly closed and kept for agitation at a speed of 200 rpm for a period of 60 min., in a thermostatic mechanical orbit shaker (NEOLAB, India) at 30 ± 1 °C. The solutions were filtered through Whatmann No. 42 filter paper. The filtrate (10 mL) was then titrated against standardised sodium hydroxide solution (0.10 N) to find out the equilibrium concentration (C_e) of acetic acid. The equilibrium concentration of acetic acid remaining after adsorption, in each bottle (C_e) was divided by the number of moles of acetic acid adsorbed per gram of the adsorbent to get the ratio (C_e/n). The (C_e/n) values are linearly related to C_e values. The slope of the linear correlation of (C_e/n) with C_e yielded N_m value (i.e., N_m value = 1 / slope). By substituting the value of N_m in the following equation, the surface area, A (m^2 g^-1) was calculated.

\[
A = N_m \times N_a \times \sigma
\]  

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

Where, \(N_a = \) Avogadro number \((6.023 \times 10^{23})\)

\(N_m = \) Number of moles of acetic acid per gram of adsorbent required to form mono-layer coverage and

\(\sigma = \) molecular cross sectional area of acetic acid \((21 \times 10^{-20} \text{ m}^2)\)

### 3.6.7 Decolourising power

Exactly 0.1 g of the adsorbent material was transferred into a 100 mL glass stoppered conical flask. One mL of methylene blue solution \([0.15 \% (w/v)]\) was added from a burette and shaken well for about five minutes. Addition of methylene blue solution and shaking was continued till the blue colour persisted for at least five minutes.
Decolourising power [8] of the adsorbent material expressed in terms of milligrams of methylene blue adsorbed by one gram of the material.

\[
\text{Decolourising power (mg g}^{-1}\text{)} = 1.5 \left( V / M \right)
\]

(3.2)

where, \( V \) = volume (mL) of the methylene blue [0.15 \% (w/v)] solution consumed and \( M \) = mass of the adsorbent material taken for the experiment in gram (\textit{i.e.}, 0.1 g).

### 3.6.8 Phenol number

Phenol number [9] of any adsorbent material is defined as the amount of adsorbent expressed in milligrams per litre required for decreasing 100 mg of phenol to 10 mg (90 \%). The initial concentration of phenol was first estimated by pipetting out 20 mL of phenol solution into a clean 250 mL conical flask and after adding 50 mL, of distilled water and 5-7 mL of concentrated HCl solution. A known volume of brominating mixture (40 mL) was then added from a burette with shaking, till a permanent pale yellow colour persisted in the solution. The flask was kept aside at room temperature (\(30 \pm 1\) °C) for about 10-20 min., in order to allow the bromination reaction to complete. Then, 20 mL of 10 \% (w/v) solution of KI was added and the liberated iodine was titrated against standardised solution of sodium thiosulphate (0.025 N) using starch as indicator. The strength of the brominating solution was also established.

<table>
<thead>
<tr>
<th>Phenol solution taken</th>
<th>= 20 mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 mL of brominating solution</td>
<td>= ( V_1 ) mL of sodium thiosulphate solution</td>
</tr>
<tr>
<td>40 mL of brominating solution</td>
<td>= ( 2V_1 ) mL of sodium thiosulphate solution</td>
</tr>
<tr>
<td>Volume of sodium thiosulphate solution, consumed after bromination reaction</td>
<td>= ( V_2 ) mL</td>
</tr>
</tbody>
</table>
Therefore, the amount of phenol present per litre of the solution (g L\(^{-1}\))

\[
= \left\{ \frac{2 \times (V_1 - V_2) \times N \times 15.66}{20} \right\}
\]

Where, \(N\) = normality of sodium sulphate solution and

\(15.66\) = equivalent weight of phenol.

Different weights of the adsorbent material ranging from 0.5 to 3.0 g were added to 250 mL reagent bottles containing 100 mL of phenol solution containing 100 mg of phenol per litre (100 ppm). The solutions were then mixed well and allowed to stand for 24 h. in order to allow the adsorption process to attain equilibrium. The phenol content was determined by taking suitable aliquots (20 or 40 mL), following the reported experimental procedure (as given above) for the estimation of phenol.

\[
\text{Percentage removal of phenol} = 100 \times \frac{(C_i - C_f)}{C_i}
\]

Where, \(C_i\) = initial concentration of phenol, in ppm and

\(C_f\) = final concentration of phenol, in ppm

The values of percentage removal of phenol were calculated and plotted against the dose of adsorbent added (mg L\(^{-1}\)). The dose of the adsorbent material (mg L\(^{-1}\)) required for the 90% removal of phenol (i.e., to a final concentration of 10 ppm) was obtained from the plot of percentage removal of phenol vs dose of adsorbent and reported as phenol number.
3.7 General procedure for adsorption studies

3.7.1 Batch type adsorption experiment

Stock solutions of dyes *viz.*, MG, RB and CV (500 mg L⁻¹) were prepared and suitably diluted to the required initial concentrations. Adsorption experiments were carried out at room temperature (30 ± 1 °C) under batch mode [10]. The initial concentrations (Cᵢ) of dyes were obtained by measuring OD at its λ_max values using Systronics spectrophotometer (Model: 105, India). Exactly, 100 mL of dye solution of known initial concentration (Cᵢ) was shaken at constant agitation speed (200 rpm) with a required dose of adsorbents of fixed particle size (range: 75-450 microns) for a specific period of contact time (range: 5-60 min.), in a thermostatic mechanical orbit shaker (NEOLAB, India), after noting down the pH of the solution using digital pen type pH meter (Hanna instruments, Portugal). The pH of the solution was adjusted to the required value by adding either 1 M HCl or 1 M NaOH solution only in the experiments to study the pH effect. After equilibration, the equilibrium concentration (Cₑ) of dye was determined by spectrophotometric method. The values of percentage removal of dye and amount adsorbed (mg g⁻¹) were calculated using the following relationships:

\[
\text{Percentage removal} = \frac{100}{C_i} \left( \frac{C_i - C_e}{C_i} \right) \quad \ldots \ldots \quad (3.5)
\]

\[
\text{Amount adsorbed (qₑ)} = \frac{(C_i - C_e)}{m} \quad \ldots \ldots \quad (3.6)
\]

Where, Cᵢ and Cₑ are the initial and equilibrium concentrations (mg L⁻¹ or ppm) of dye, respectively and m is the weight of adsorbents (g L⁻¹). Blanks, containing no dye and adsorbents were used for each series of experiments as controls. The error in the adsorption data is ± 1 -2 % in percentage removal and ± 0.02 - 0.1 mg g⁻¹ in amount
adsorbed. Replicates were performed and the average data were reported. The experimental conditions are given in the following chapters.

3.7.2 Effect of initial concentration

The dye solutions of various initial concentrations were prepared. Exactly 50 mL of each of the dye solution with different required initial concentration of dye was treated with a known dose of adsorbent of fixed particle size (75 microns) at solution pH and equilibrated for 30 min., with constant shaking at 200 rpm in a thermostatic mechanical orbit shaker (Neolab, India) at 30 ± 1 °C. The equilibrium concentrations (C_e) were determined using the filtrates. The percentage removal of dye and the amount of dye adsorbed (mg g⁻¹) were calculated.

3.7.3 Adsorption isotherms

In order to analyse the adsorption data, the Freundlich [11], Langmuir [12] adsorption isotherms were employed.

3.7.3.1 Freundlich isotherm

Freundlich adsorption isotherm [11] is given by the equation:

\[ \log q_e = \log K + (1/n) \log C_e \]  \hspace{1cm} (3.7)

Where, \( q_e \) = (x/m), is the amount of dye adsorbed (mg g⁻¹) per unit mass of the adsorbent at equilibrium; \( m \) is mass of the adsorbent (g L⁻¹), K and 1/n are the Freundlich constants, which are the measures of adsorption capacity (mg g⁻¹) and intensity of adsorption, respectively. The value of 1/n \([0 < (1 / n) < 1]\) is a fraction, so that, the value of n is a whole number (n > 1), which is the order of adsorption [12]. A plot of \( q_e \) vs \( C_e \) was found to be an exponential one. However, when the values of \( \log q_e \) were plotted
against log $C_e$ values, straight line plots were obtained, with log $K$, values as the intercept and $(1/n)$ value as the slope. Freundlich constants were calculated by employing linear regression analysis and reported.

### 3.7.3.2 Langmuir isotherm

Langmuir adsorption isotherm [13,14] is given by the expression

$$\left(\frac{C_e}{q_e}\right) = \left(\frac{1}{ab}\right) + \left(\frac{C_e}{a}\right)$$

............... (3.8)

Where, $q_e$ is the amount of dye adsorbed (mg g$^{-1}$) at equilibrium contact time ($i.e.$, time for maximum adsorption), $C_e$ is the equilibrium concentration (ppm) of dye; $(1/a)$ is the slope and $(1/ab)$ is the intercept and $a$ and $b$ are the Langmuir constants indicating respectively, the mono-layer adsorption capacity (mg g$^{-1}$) and adsorption energy (L mg$^{-1}$).

A plot of $(C_e/q_e)$ vs $C_e$ was found to be linear with $(1/ab)$ value as the intercept and $(1/a)$ value as the slope. This plot is known as Langmuir adsorption isotherm plot. The applicability of Langmuir isotherm indicates the formation of monolayer and also the nature of adsorption process [15].

Further, the essential characteristics of the Langmuir isotherm can be described in terms of dimensionless constant $viz.$, separation factor or equilibrium parameter, $RL$, which is defined by the equation [16, 17].

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

............... (3.9)

Where, $b$ is the Langmuir constant (L mg$^{-1}$) and $C_i$ is the optimum initial concentration of dye (ppm). The values of $R_L$ indicate the nature of adsorption process
and the shape of isotherm. The value of $R_L$ denotes an unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) and irreversible ($R_L = 0$) process of adsorption.

### 3.7.3.3 Redlich – Paterson isotherm

Redlich – Paterson (R – P) isotherm is a combination of the salient features of the Langmuir and Freundlich isotherms. The isotherm can be represented as [18] :

$$ q_e = \frac{(x/m)}{Q_0bC_e} = \frac{Q_0bC_e}{1 + (\alpha R\beta)C_e} $$

The linearised form of Redlich – Paterson (R – P) equation is expressed as :

$$ \log \left[(K_RC_e / q_e) - 1\right] = \beta \log C_e + \log(\alpha R) $$

where, $K_R = Q_0b(L^g)$

- $Q_0$ = Langmuir monolayer adsorption capacity (mg g$^{-1}$)
- $\beta$ = Langmuir constant (L mg$^{-1}$)
- $(\alpha R) = R - R$ isotherm constant
- $C_e$ = Equilibrium/liquid phase concentration of solute (mg L$^{-1}$)
- $m$ = Mass of adsorbent (g L$^{-1}$)
- $x$ = Amount of solute adsorbed by solid adsorbent (mg L$^{-1}$)
- $q_e$ = Equilibrium amount of solute adsorbed (mg g$^{-1}$)

By plotting the values of $\log \left[(K_C / q_e) - 1\right]$ against $\log C_e$, the values of $(\alpha R)$ and can be determined from the intercept $\log (\alpha R)$] and the slope $(\beta)$, respectively.

### 3.7.3.4 BET isotherm

The Brunauer, Emmett and Teller equation [19] is an extension of the Langmuir relationship that accounts for multilayer coverage. Here, multiple layers can form before
the monolayer is complete, with multiple layers forming as a “condensation” reaction.

The surface of solids has uniform and localized sites. Adsorption occurs successively on 2\textsuperscript{nd}, 3\textsuperscript{rd}, 4\textsuperscript{th} and n\textsuperscript{th} layers with the surface area available. There is a dynamic equilibrium between the successive layers. The multilayer form of BET equation is given as:

\[
\frac{C_e}{x} (C_0 - C_e) = \frac{1}{x_m k} + (k - 1) \frac{C_e}{C_0} \frac{1}{x_m k} C_0
\]

............... (3.12)

Where, \(C_0\) and \(C_e\) are the concentration (in mg L\(^{-1}\)) of solute (adsorbate) at initial time and at equilibrium time, respectively; \(k\) is a constant (in min\(^{-1}\)) related to the energy (enthalpy) of adsorption; \(x/m\) is the amount of solute adsorbed by solid adsorbent (mg L\(^{-1}\)) at time \(t\) and \(x\) is the amount adsorbed by solid adsorbent at equilibrium (mg L\(^{-1}\)).

3.7.4 Effect of contact time

In order to study the kinetics/dynamics of adsorption of dyes, the adsorption experiments were conducted by varying the contact time (range: 5 - 60 min.), at fixed optimum initial concentration of dyes with a fixed dose of adsorbent and particle size (75 microns) at 30 ± 1 °C and at the pH of the solution. The bottles were placed in a thermostatic mechanical orbit shaker (Neolab, India) at a constant agitation speed of 200 rpm. The bottles were withdrawn from the shaker at different time intervals viz., 5, 10, 20, 30, 40, 50 and 60 min., to find out the equilibrium concentration. The other procedures employed were similar to that of the general procedure employed for adsorption studies.
3.7.5 Kinetics of adsorption

In order to determine the mechanism, rate constants and also to confirm the first order nature of the adsorption process, various first order kinetic equations / models such as Natarajan – Khalaf [20], Lagergren [21] and Bhattacharya – Venkobachar [22] equations, intra – particle diffusion model proposed by Weber – Morris [23] and modified Elovich type equation [24], were applied. The mathematical form of the various first order kinetic equations and model used in the present study for the adsorption of dyes is given below.

**Natarajan – Khalaf equation**

\[
\log \left( \frac{C_i}{C_t} \right) = (k / 2.303)t \\
\text{......... (3.13)}
\]

**Lagergren equation (First order)**

\[
\log (q_e - q_t) = \log q_e - (k / 2.303)t \\
\text{......... (3.14)}
\]

**Lagergren equation (Pseudo second order)**

\[
1 / (q_e - q_t) = (1 / q_e) - k_2 t \\
\text{......... (3.15)}
\]

**Bhattacharya – Venkobachar equation**

\[
\log [1 - U(T)] = - (k / 2.303)t \\
\text{......... (3.16)}
\]

**Modified Elovich equation**

\[
(C_i - C_t) = (1/\beta) \ln (\alpha/\beta) + (1/\beta) \ln t \\
\text{......... (3.18)}
\]

**Intra – particle diffusion model**

\[
q_t = k_p t^{1/2} + c \\
\text{......... (3.19)}
\]

Where, \( C_i, C_t \) and \( C_e \) are the concentration (in mg L\(^{-1}\)) of solute (adsorbate) at initial time, at time ‘t’ and at equilibrium time, respectively; \( k \) is the first order rate constant (in min.\(^{-1}\)) for adsorption; \( q_e \) and \( q_t \) are amount adsorbed (in mg g\(^{-1}\)) at equilibrium time.
and at time ‘t’ respectively; $k_p$ is the intra – particle diffusion rate constant in mg g$^{-1}$ min.$^{-1/2}$, $c$ is a constant $k_a$ is related to the rate at which the system approaches equation (3.19) adsorption equilibrium.

The Elovich parameter $\beta$ was obtained from the negative inverse of the slope of the linear plot of values of $C_i$ against in $t$ (equation 3.18) and the ‘$\alpha$’ value can be obtained from the intercept [(1/$\beta$) ln ($\alpha/\beta$)] – C] of the plot by substituting the values of $C_i$ and $C_t$.

The first order rate constants ($k$ in min.$^{-1}$) for the adsorption process could be obtained by plotting the adsorption data with time or by carrying out the linear regression analysis of adsorption data with time according to the kinetic equations.

The applicability of intra – particle diffusion model proposed by Weber and Morris [23] indicate the presence of intra – particle diffusion as the rate limiting step. The applicability of linear relationship :

$$\log (\%R) = m \log \text{(time)} + C$$  

Where, $\%R$ is the percentage removal of dyes, $m$ is the slope and $c$ is constant. Moreover, the value of slope of the plot of log ($\%R$) against log (time), ranging around 0.5, confirm the occurrence of intra – particle diffusion as the rate determining step [134]. On the other hand, the divergence in the value of slope ($m$) from 0.5 indicates that, besides intra – particle diffusion, there may be other processes controlling the rate of adsorption and all of these steps may operate simultaneously. Thus, the test on the applicability of these kinetic equations and model, will give an insight into the dynamics and mechanism of
adsorption. In the present study, it is also proposed to apply these kinetic equations / models and the intra–particle diffusion model in order to test the applicability of these equations / models to the adsorption data for the removal of dyes by adsorption on ACs and the first order nature of adsorption.

3.7.6 Effect of dose of adsorbent

In this set of adsorption experiments, the values of percentage removal of dyes by adsorption and amount adsorbed on various adsorbents were obtained with different dose of adsorbent with optimum initial concentration of dyes and contact time (40 min., for all dyes), with fixed particle size (75 microns) at 30 ± 1 °C and at the solution pH.

The values of percentage removal of dye and the amount of dye adsorbed (q_e) per unit mass of the adsorbent (in mg g⁻¹) were plotted against the dose of adsorbent [9,25]. The plots were found to be exponential. The values of log q_e were linearly related to the value of log (dose) according to the following relationship:

\[
\log q_e = c - n \log (\text{dose})
\]

Where, c = intercept and n = slope

3.7.7 Effect of pH

The batch type adsorption experiments were carried out with optimum conditions of initial concentration of dye, contact time and dose of adsorbent with a fixed particle size (75 microns) at various solution pH (range: 2-8) by adding the required volumes of 1M HCl or NaOH solution. The pH of the dye solution was measured by using digital pen type pH meter (Hanna instruments, Portugal). The values of percentage removal and
amount of adsorbed (mg g⁻¹) were computed and plotted against the pH of the dye solution.

3.7.8 Effect of particle size

Adsorption studies of dyes were carried out at different particle size of adsorbent with the various indigenously prepared adsorbents (range: 75-450 microns) except CAC, under constant optimum initial concentration of dyes, contact time (40 min.), optimum dose of adsorbent and pH the dye solution at 30 ± 1 °C [10]. The values of percentage removal and amount of dye adsorbed (in mg g⁻¹) were calculated and plotted against the particle size of the adsorbents.

3.7.9 Equilibrium studies

The equilibrium studies were carried at 30, 35 and 40°C with the optimum experimental conditions viz., initial concentration of dyes (MG, RB and CV), dose of adsorbents (viz., CELC, TGLC, AHLC, PPLC, MLLC, TCLC and CAC), contact time (60 min.), at fixed particle size (75 microns) and pH of the solution itself. Thermodynamic parameters were calculated from the equilibrium constant (Keq). The values of standard free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) at standard state have been calculated using the following relationships [26]:

\[ K_{eq} = \frac{C_{ad \ (solid)}}{C_e \ (solution)} \]  \hspace{1cm} ............ (3.22)

\[ \Delta G^° = -2.303 \ RT \ \log K_{eq} \]  \hspace{1cm} ............ (3.23)

\[ \log K_{eq} = -\frac{\Delta H^°}{2.303 \ RT} + \frac{\Delta S^°}{2.303R} \]  \hspace{1cm} ............ (3.24)

Where, \( K_{eq} \) = equilibrium constant

\( C_{ad \ (solid)} \) = concentration of dye adsorbed (in mg L⁻¹) on an adsorbent in solid phase, at equilibrium.
C_e (solution) = concentration of dye in aqueous solution (in mg L^{-1}) at equilibrium.

R = Universal gas constant (8.314 J mol^{-1} deg^{-1}),

T = temperature (in K)

\Delta G^0 = standard free energy change (in kJ mol^{-1})

\Delta H^0 = standard enthalpy change (in kJ mol^{-1}) and

\Delta S^0 = standard entropy change (in J mol^{-1} K^{-1})

The log K_{eqm} values at 30, 35, 45 and 50 °C were plotted against l/T and linear plots were obtained. The \Delta S^0 and \Delta H^0 values were calculated from the intercept and slope of the linear correlations of log K_{eqm} with l/T.

3.7.10 Desorption studies

After the adsorption experiments, the adsorbent samples loaded with dyes were filtered (Whatmann No. 42) separated and gently washed with distilled water to remove any un-adsorbed dye or loosely held dye molecules and dried. The dye loaded adsorbent samples (1 g) were treated with 100 mL of DD water in 250 ml reagent bottles and shaken in a thermostatic mechanical orbit shaker (Neolab, India) at 30 ± 1 °C at the pH of the solution itself. The bottles were taken out after agitating it for 60 min. The concentration of the dye was estimated spectrophotometrically. The extent of dye desorbed (%) was calculated [26] and reported (Error = 0.05 ± 0.1%). The desorption studies were also carried out as per the above procedure with 1 M aqueous solutions of acid, HCl, HNO_3, H_2SO_4, CH_3COOH and base NaOH.
3.7.11 Dye removal from binary mixtures

Batch adsorption equilibrium experiments have been carried out at room temperature, 30 ± 1 °C. A mixture of dye solution of two different dyes (dye-i and dye-j) was obtained by mixing required volume of dyes (stock solution) to get a fixed initial concentration in different mole fraction ratio (mole fraction ratio of dye i and j; \(x_i : x_j = 0: 1.0, 0.2:0.8, 0.4:0.6, 0.6:0.4, 0.8:0.2\) and 1.0:0). The mixed dye solution (100 mL) was then treated with a constant dose of adsorbent at its solution pH with a fixed particle size (75 microns) of adsorbent and equilibrated for 1 h at 30 ± 1 °C. The solutions were then filtered through Whatmann No. 42 filter paper. The equilibrium concentration of the two dyes (i and j) was obtained by measuring their OD values at the corresponding \(\lambda_{\text{max}}\) values of each dye. Suitable dilutions were made wherever necessary. Systronics spectrophotometer (Model: 105, India) was used to measure OD values. From the equilibrium concentration of dyes, the values of total amount of dye adsorbed and the percentage removal were calculated by the usual method [1].

The mixed dye solutions were then employed in batch adsorption equilibrium studies. From the equilibrium concentration of each dye, the differential percentage removal of dye and amount adsorbed \((q_i \) or \(q_j)\) were calculated using the following relationships:

Differential percentage removal of dye:

\[
\text{Dye i} = 100 \left\{ \frac{(C_i - C_e)}{C_i} \right\} \quad \text{............ (3.25)}
\]

\[
\text{Dye j} = 100 \left\{ \frac{(C_i - C_e)}{C_i} \right\} \quad \text{............ (3.26)}
\]

Differential amount of dye adsorbed:
\[ q_i = \left[ \left( C_i - C_{i,e} \right) \right] \frac{M_i}{m} \]  \hspace{1cm} \text{........... (3.27)}

\[ q_j = \left[ \left( C_j - C_{j,e} \right) \right] \frac{M_j}{m} \]  \hspace{1cm} \text{........... (3.28)}

Where, \( C_i \) and \( C_e \) are the respective initial and equilibrium concentration (mM) of dyes i and j; \( q_i \) and \( q_j \) are the respective amount of dye i and j adsorbed (mg g\(^{-1}\)), \( M_i \) and \( M_j \) are the molecular mass of i and j and m is mass of adsorbent (g L\(^{-1}\)).

### 3.7.12 Column studies

A stock solution of MG, RB and CV (500 mg L\(^{-1}\)) was prepared and suitably diluted to the various required initial concentrations. Column adsorption experiments were carried out in a glass column with an inner diameter of 10 mm and various column heights at room temperature (30 ± 1 °C). The adsorbents with known weight of fixed particle size (250 micron) were placed into the column in the form of slurry and packed uniformly. The column was safe-guarded with glass wool. The influent/feed solution of dyes (MG, RB and CV) of known initial concentration, at specified pH was fed from the glass bottle container (5 L capacity). The initial pH of the solutions were adjusted by adding 1 M HCl or 1 M NaOH solution. Initial pH values of dye solutions were noted with digital pen pH meter (Hanna instruments, Portugal). Auto flow meter (MeClins, India) was used to adjust the required flow rate (mL min\(^{-1}\)). The effluent from the column was collected at desired intervals of time to study effect of contact time. The concentrations of the dye solutions before and after adsorption were estimated by measuring OD at corresponding \( \lambda_{\text{max}} \) value of dyes with the help of Systronics spectrophotometer (Model: 105, India) and then interpolated into the standard curve.

The equilibrium isotherm data for the adsorption of dyes from binary mixture
were analysed using binary component Sheindroff-Rebhun-Sheintuch (SRS) isotherm model [28] to evaluate the competitive co-efficient for binary system. SRS isotherm is a multi-component Freundlich-type equation and so it is based on the assumption that there is an exponential distribution of adsorption energies avail for each solute. SRS equation may be written as follows:

\[
(q_e)_i = K_{Fi} C_{ei} \left( \sum a_{ij} C_{ej} \right)^{1/n_i} i
\]

\[
............. (3.29)
\]

where, \((q_e)_i\) is the amount of solute adsorbed per unit weight of adsorbent in the presence of solute \(j\); \(K_{Fi}\) and \((1/n_i)\) are the single component Freundlich constant and Freundlich exponential term for solute \(i\); \(C_{ei}\) and \(C_{ej}\) are the equilibrium concentrations of solute \(i\) and \(j\), respectively and \(a_{ij}\) is the competitive co-efficients indicating the interaction of solute \(j\) on the adsorption of solute \(i\).

The general form of SRS equation for a two component/binary mixture of dyes \((i = \text{Dye A and } j = \text{Dye B})\) may be rewritten as follow:

\[
(q_e)_i = K_{Fi} C_{ei} \left( C_{ej} + a_{ij} C_{ej} \right)^{1/n_i} i
\]

\[
............. (3.30)
\]

The linearised form of SRS equation is convenient to construct competitive adsorption isotherm that measure the amount of solute \((i)\) adsorbed in the presence of a competing solute \((j)\). In order to represent the batch isothermal data, the following linear forms of the SRS equation for binary solute system is used.

\[
\frac{(C_{ei} / C_{ej})}{(B_i / C_{el})} = a_{ij}
\]

\[
............. (3.31)
\]

\[
(C_{ei} / C_{el}) = (B_i / C_{ei}) - a_{ji}
\]

\[
............. (3.32)
\]
Where, $B = \left[ \left( K_{ij} C_{ei} \right) / \left( q_{ei} \right) \right]^{[n_i/n_j]}$ and $a_{ij}$ or $a_{ji}$ are the competitive co-efficient having negative numerical value of the y-intercept, computed as the slope of the plot $(C_e / C_{ei})$ vs $(B_i / C_{ei})$ or $(C_e / C_{ei})$ vs $(B_j / C_{ei})$.

### 3.7.13 Column adsorption kinetics

The experimental data of adsorption kinetics indicated that the adsorption process was very fast at the beginning and then slowed down as equilibrium approached. The column adsorption kinetics was specified by determining the mass transfer co-efficient according to Adams-Bohart equation [29,30]:

$$\ln \left( \frac{C_i}{C_i} \right) = k C_i t - k q \left( Z / u_i \right) \quad \text{............ (3.33)}$$

Where, $C_i$ is the concentration of dye in the effluent (mg L$^{-1}$) at time $t$ (min.), $C_i$ is the initial or inlet dye concentration (mg L$^{-1}$), $q$ is the amount of dye solution uptaken by adsorbent (mg L$^{-1}$), $Z$ is the height of column (m), $u$ is the linear flow rate of solution (mL min.$^{-1}$) and $k$ is the mass transfer co-efficient (mg$^{-1}$ min.$^{-1}$). A straight line was attained for this system by plotting $\ln \left( \frac{C_i}{C_i} \right)$ against $t$, which gives the value of $k$ from the slope of the line.

### 3.8 Physico – chemical properties

The physico – chemical properties such as bulk density, moisture content, loss on ignition (LOI); residue after ignition, pH, electrical conductivity, zeropoint charge ($pH_{zpc}$), surface area (by acetic acid method), decolourising power (methylene blue number) and phenol number CAC and indigenous prepared ACs have been determined.
The physico – chemical properties of CAC and indigenously prepared ACs are given in Table 3.2.

Table 3.2  Physico - chemical properties of adsorbents

<table>
<thead>
<tr>
<th>Characteristic parameter</th>
<th>*CAC</th>
<th>CELC</th>
<th>TGLC</th>
<th>AHLC</th>
<th>PPLC</th>
<th>MLLC</th>
<th>TCLC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density (g m⁻²)</td>
<td>0.966</td>
<td>0.852</td>
<td>0.824</td>
<td>0.761</td>
<td>0.723</td>
<td>0.790</td>
<td>0.823</td>
</tr>
<tr>
<td>Moisture content (%)</td>
<td>10.1</td>
<td>5.2</td>
<td>8.2</td>
<td>6.7</td>
<td>7.9</td>
<td>9.3</td>
<td>8.4</td>
</tr>
<tr>
<td>Loss on ignition (%)</td>
<td>95.0</td>
<td>76.3</td>
<td>63.8</td>
<td>70.4</td>
<td>73.2</td>
<td>89.2</td>
<td>68.5</td>
</tr>
<tr>
<td>Residue after ignition (%)</td>
<td>5.0</td>
<td>23.7</td>
<td>36.2</td>
<td>29.6</td>
<td>26.8</td>
<td>10.8</td>
<td>31.5</td>
</tr>
<tr>
<td>pH</td>
<td>8.4</td>
<td>7.2</td>
<td>7.6</td>
<td>7.3</td>
<td>7.6</td>
<td>7.8</td>
<td>7.1</td>
</tr>
<tr>
<td>Electrical conductivity × 10⁴ (ohm⁻¹ cm⁻¹)</td>
<td>5.3</td>
<td>11.2</td>
<td>13.0</td>
<td>12.1</td>
<td>12.8</td>
<td>7.9</td>
<td>9.2</td>
</tr>
<tr>
<td>Zero point charge (pHₑₒ₂)</td>
<td>6.21</td>
<td>6.35</td>
<td>6.86</td>
<td>4.31</td>
<td>4.89</td>
<td>5.31</td>
<td>7.2</td>
</tr>
<tr>
<td>Surface area (m² g⁻¹)</td>
<td>872</td>
<td>512</td>
<td>386</td>
<td>483</td>
<td>350</td>
<td>544</td>
<td>212</td>
</tr>
<tr>
<td>Decolourising power (mg g⁻¹)</td>
<td>72.6</td>
<td>60.5</td>
<td>52.8</td>
<td>54.0</td>
<td>48.1</td>
<td>66.8</td>
<td>416</td>
</tr>
<tr>
<td>Phenol number × 10³ (mg L⁻¹)</td>
<td>8.89</td>
<td>12.32</td>
<td>16.18</td>
<td>14.35</td>
<td>18.72</td>
<td>11.85</td>
<td>19.21</td>
</tr>
</tbody>
</table>

*Data given by E.Merck, India are close to the experimental observations.

The range of bulk density and moisture content of ACs are 0.723 – 0.966 and 1.68 - 10.1 %, respectively. CAC has the high moisture content indicating that it is highly porous in nature. The low moisture content of IPACs is due to the method of preparation and activation.

The moisture content does not affect the adsorption capacity / power directly, but it dilutes the adsorbent dose and therefore necessitates the use of additional quantity of adsorbent for the effluent treatment process [30]. The loss on ignition and ash content were observed to be in the range of 63.8 – 95.0 and 5.0 – 36.2, respectively.
The high ash content of IPACs may be due to the presence of mineral content in it, as evidenced from thermal degradation studies also. The order of carbon content is:

\[ \text{TGLC} < \text{TCLC} < \text{AHLC} < \text{PPLC} < \text{CELC} < \text{MLLC} << \text{CAC} \]

IPACs are found to abstract protons from water and the resultant aqueous slurry or solution is found to be alkaline (basic) as evidenced from the pH value (range: 7.1 – 8.4). The range of electrical conductivity is \(5.3 – 12.8 \times 10^{-4} \text{ohm}^{-1} \text{cm}^{-1}\).

The pH_{zpc} zero point charge of CAC is 6.21, while the range of pH_{zpc} for IPACs is 4.31 – 6.86. The pH_{zpc} values are noted to be in the acidic range. This may due to the presence of surface functional groups like \(-\text{COOH}, -\text{OH} \text{etc.}\), which are slightly acidic in nature. This is also evidenced from the FT – IR spectral data. The surface area of ACs is of the order of 212 – 872 mg g\(^{-1}\). The order of surface area is found to be:

\[ \text{TCLC} < \text{PPLC} < \text{TGLC} < \text{AHLC} < \text{CELC} < \text{MLLC} << \text{CAC} \]

The surface area is found to be linearly related to the decoloursing power the range of phenol number is 8.89 – 19.21 mg and the order is found to be exactly reversed and inversely related to the surface area. The high value of phenol number makes all the IPACs as very good adsorbent for the removal of cationic dyes.

3.9 Instrumental studies

3.9.1 FT – IR spectra

FT – IR spectra were recorded for the AC samples with and without dye leading. The characteristic group frequencies (\(\tilde{v}\), in cm\(^{-1}\)) observed for various surface functional groups are shown in table 3.3. The FT-IR spectra of various carbons and dye loaded ACs are almost similar with slight shift in frequencies (Figs. 3.4 - 3.9).
The surface functional groups are almost common as revealed by some common peaks, which appeared at 3400 – 3550, 2850 – 2950, 1635 – 1822, 1500 – 1600 and 1240 – 1504 cm\(^{-1}\), depending upon the nature and type of raw materials. The characteristic peaks are slightly varying in their position for different IPACs. A peak ranges 2850 – 2950 cm\(^{-1}\) in all the ACs confirm the C – H stretching. The peaks around 1800 cm\(^{-1}\) in all the ACs confirm the presence of carbonyl group. This was further evidenced by another peak around 1631 – 1745 cm\(^{-1}\), which reveals the keto nature. The peak around 3400 – 3558 cm\(^{-1}\) confirm the presence of –OH group (Table 3.3). The functional group may be –COOH or –OH. The nature of –CH group is revealed by another peak around 2804 – 2950 cm\(^{-1}\). The IR peaks around 1200 – 1500 cm\(^{-1}\) may be due to the stretching vibrations of lactone (\(\gamma\) and / or \(\delta\)) =C–O, –CH= and –CH\(_2\)= functional groups (Figs. 3.4-3.9). In dye loaded carbons, some of the peaks are shifted to 5-30 cm\(^{-1}\) and some of them are disappeared indicating the involvement of the surface functional groups in binding the dye. The IR spectra indicates the presence of surface functional groups like, >C=O, -CH, -COOH, -OH, etc., [31, 32] and their involvement in the adsorption process.
<table>
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<td>1654</td>
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<td>--</td>
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<td>MLLC</td>
<td>3495</td>
<td>2934</td>
<td>1678</td>
<td>1520</td>
<td>1389</td>
<td>1420</td>
<td>1045</td>
<td>990</td>
<td>634</td>
</tr>
<tr>
<td>18</td>
<td>MLLC-MG</td>
<td>3492</td>
<td>2890</td>
<td>1640</td>
<td>-</td>
<td>--</td>
<td>--</td>
<td>1042</td>
<td>--</td>
<td>638</td>
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<td>19</td>
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<td>2912</td>
<td>1643</td>
<td>-</td>
<td>--</td>
<td>--</td>
<td>1044</td>
<td>--</td>
<td>636</td>
</tr>
<tr>
<td>20</td>
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<td>3499</td>
<td>2896</td>
<td>-</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>1043</td>
<td>--</td>
<td>637</td>
</tr>
<tr>
<td>21</td>
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<td>2892</td>
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<td>1528</td>
<td>1365</td>
<td>1375</td>
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<td>1057</td>
<td>630</td>
</tr>
<tr>
<td>22</td>
<td>TCLC-MG</td>
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<td>2892</td>
<td>1680</td>
<td>1515</td>
<td>1369</td>
<td>1378</td>
<td>1105</td>
<td>1060</td>
<td>626</td>
</tr>
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<td>23</td>
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<td>3458</td>
<td>2892</td>
<td>1672</td>
<td>-</td>
<td>1371</td>
<td>1373</td>
<td>1107</td>
<td>1061</td>
<td>628</td>
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<tr>
<td>24</td>
<td>TCLC-CV</td>
<td>3461</td>
<td>2892</td>
<td>1696</td>
<td>-</td>
<td>1365</td>
<td>1377</td>
<td>1104</td>
<td>1063</td>
<td>631</td>
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</table>
Figure 3.4 FT-IR spectra of CELC and CELC-dye samples

Figure 3.5 FT-IR spectra of TGLC and TGLC-dye samples
Figure 3.6  FT-IR spectra of AHLC and AHLC-dye samples

Figure 3.7  FT-IR spectra of PPLC and PPLC-dye samples
Figure 3.8   FT-IR spectra of MLLC and MLLC-dye samples

Figure 3.9   FT-IR spectra of TCLC and TCLC-dye samples
3.9.2 Thermogravimetric studies

TGA studies have been made only with MLLC and AHLC before and after adsorption of dyes (Figs. 3.10 and 3.11). It has been found that the samples undergo two stages of thermal degradation in the temperature ranges of 110 – 150 °C and 650 – 750 °C, respectively. The peak temperature (T in °C) and weight loss (Δm, in %) for the two stages of degradation of the AC and AC - dye samples are listed in Table 3.4.

<table>
<thead>
<tr>
<th>AC/AC - Dye</th>
<th>Weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I Stage</td>
</tr>
<tr>
<td>CELC</td>
<td>10.8</td>
</tr>
<tr>
<td>CELC-MG</td>
<td>6.2</td>
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<tr>
<td>CELC-RB</td>
<td>6.0</td>
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<tr>
<td>CELC-CV</td>
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</tr>
<tr>
<td>MLLC</td>
<td>6.5</td>
</tr>
<tr>
<td>MLLC-MG</td>
<td>5.6</td>
</tr>
<tr>
<td>MLLC-RB</td>
<td>3.8</td>
</tr>
<tr>
<td>MLLC-CV</td>
<td>5.6</td>
</tr>
</tbody>
</table>

About 60% of the total weight losses were observed in indigenously prepared AC and AC - dye samples. It has been reported by E Merck, India that the loss on ignition (LOI) of CAC sample is 95 % and hence the residue left after ignition of CAC at 600 °C is approximately only 5 %. The LOI for CELC is 76.3 % and 63.8 % for MLLC at 850 °C. The dye loading on CELC and MLLC leads to increase in thermal stability of these ACs. This observation is similar to the one reported earlier [33].
Figure 3.10  TGA of CELC before and after adsorption

Figure 3.11  TGA of MLLC before and after adsorption
van Kreveleven [34] proposed the following expression to calculate the oxygen index [O.I] of a material from the char residue obtained by thermo gravimetric methods in static air or nitrogen atmosphere by employing a heating rate of 10 or 20 °C min⁻¹.

\[
\text{Oxygen index (O.I)} = 17.5 + 0.4 \left( \% \right. \text{ char residue at 850 °C} \quad \ldots \ldots \ (3.34)
\]

When the O.I. is < 36 %, the material is classified as ‘flammable’ whereas, if the O.I. is ≥ 26 %, the material is considered as ‘inflammable’. It is observed that in all the thermograms of AC and AC - dye samples the increase in weight loss above 850 °C is insignificant. Employing the percentage of char residue left at 850 °C, the O.I. values for the AC and AC - dye samples have been calculated using the relationship (eqn. 3.1) proposed by van Kreveleven [34] and in the values are given in Table 3.4.

The O.I. values are in the range of 28.72 – 33.40 % for the AC and AC dye samples, indicating that these samples are ‘flammable’ and possess high thermal stability. The thermal stability of indigenously prepared ACs is very high compared to that of CAC (LOI = 95 %; char residue left at 600 °C = 5 % according to the analysis report of E Merck, India; hence O.I = 19.5). This is very interesting to note that thermal stability characteristics of these ACs are unique. This may be due to greater extent of char formation in AC (and also in AC - dye) samples and high content of refractories and minerals in the ACs. This indicates that these AC - dye samples undergo poor thermal degradation and hence the thermal regeneration of dye loaded ACs is difficult. One could employ the other chemical, photochemical and biological oxidation methods for the removal of dyes and regeneration of dye loaded ACs.
Table 3.4  Percentage char residue and oxygen index of ACs and AC-dye samples

<table>
<thead>
<tr>
<th>S.No</th>
<th>AC-Dye</th>
<th>% Char residue</th>
<th>O.I (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>CELC</td>
<td>33.0</td>
<td>30.7</td>
</tr>
<tr>
<td>2.</td>
<td>CELC-MG</td>
<td>39.4</td>
<td>33.2</td>
</tr>
<tr>
<td>3.</td>
<td>CELC-RB</td>
<td>39.2</td>
<td>33.2</td>
</tr>
<tr>
<td>4.</td>
<td>CELC-CV</td>
<td>39.8</td>
<td>33.4</td>
</tr>
<tr>
<td>5.</td>
<td>MLLC</td>
<td>27.9</td>
<td>28.7</td>
</tr>
<tr>
<td>6.</td>
<td>MLLC-MG</td>
<td>28.5</td>
<td>28.9</td>
</tr>
<tr>
<td>7.</td>
<td>MLLC-RB</td>
<td>30.2</td>
<td>29.6</td>
</tr>
<tr>
<td>8.</td>
<td>MLLC-CV</td>
<td>31.2</td>
<td>30.0</td>
</tr>
</tbody>
</table>

3.9.3  SEM studies

Scanning electron microscope (SEM) studies provide useful information regarding the textural morphological characteristics of the surface of the adsorbents. The SEM photos of the adsorbents before and after adsorption of dyes were recorded. The typical SEM photographs of adsorbent samples, before and after adsorption of dyes are shown in Figs. 3.12-3.17.

SEM photographs clearly reveal the surface texture and porosity of the samples. SEM photographs also show that the particles can be roughly approximate as spheres or globules, if the roughness factor is included to account for the irregularities. At higher magnification (viz., 1 x 3000), the globules are distinct visible and they appear to be quite uniform with internal pores (porous structures) or holes of the adsorbents. SEM photographs also depict the porosity nature of the carbonaceous materials and the presence of grains in it. The adsorb dye molecules are either engulfed or surrounded by the porous adsorbent particle [33,35].
The colour of ACs was found to be black and blackish-gray and when view under powerful microscope, the presence of the spherical particles was also know the results of the SEM studies indicate that the dye molecules are adsorbed on surface of the adsorbents. Hence, it is concluded that all the IPACs could be employed as adsorbent materials for the removal of dyes from water and wastewater.

Figure 3.12 SEM photographs of CELC and CELC-dye samples
Figure 3.13  SEM photographs of TGLC and TGLC-dye samples
Figure 3.14  SEM photographs of AHLC and AHLC-dye samples
Figure 3.15 SEM photographs of PPLC and PPLC-dye samples
Figure 3.16  SEM photographs of MLLC and MLLC-dye samples
Figure 3.17  SEM photographs of TCLC and TCLC-dye samples
3.10 Conclusions

The details of materials, reagents used and their sources, or the method of preparation of adsorbent materials along with the experimental procedure for the characterisation, adsorption studies employing batch adsorption technique, equilibrium and desorption studies and adsorption of dyes from binary mixtures are given in this chapter. The analytical methods and various physico-chemical techniques employed are also furnished.

The physico-chemical characteristics of ACs have been determined. The results revealed that these ACs could be employed as adsorbent materials for dyes. The parameters such as bulk density, moisture content, pH, electrical conductivity, loss on ignition, residue after ignition, zero point charge (pH\(_{ZPC}\)), surface area (by acetic acid method), decolourising power and phenol number were determined by following the standard procedure. FT-IR spectra and SEM photographs of unloaded and loaded adsorbents with dyes were also recorded. TGA traces of ACs and ACs loaded with dyes were recorded in order to get an idea about the thermal degradation characteristics of unloaded and dye loaded materials.
3.11 References


10. (a) N. Kannan, Indian J. Environ. Prot., 11 (1991) 514;


