CHAPTER III

MATERIALS AND METHODS
3.1 MATERIALS AND METHODS

Kapok is the name of a tropical tree of the family Bombacaceae (Bombax family) and fiber (floss) is obtained from the seeds in the ripened pods. The floss has been commercially important since the 1890s and the chief source of such fibre is ceiba pentandra, the Kapok (or silk cotton) tree, cultivated in Java. Sri Lanka, Philippines, India and other parts of East Asia and Africa. It was introduced in these places from its native tropical America. The floss is removed by hand from the pods, dried, freed from seeds and dust, and baled for export. The lustrous, yellowish floss is light, fluffy, resilient and resistant to water and decay. It is used as a stuffing, especially for life preservers, bedding and upholstery, and for insulation against sound and heat. The seed kernel solid wastes that pose disposal problems are dried and totally used for burning purposes. This Kapok Hull or silk cotton hull (KHAC) collected from silk cotton processing units was used as the source for the preparation of the adsorbent.

3.2 Preparation of activated carbon from Kapok hull

The kapok hull was cut into small pieces, dried in sunlight until the moisture was partially evaporated and was further dried in a hot air oven at 60 C for 24 hours until the residual moisture was completely evaporated. This was confirmed by taking its initial and final weight. This dried material was kept in desiccators before it was used as a source material for the preparation of adsorbent.
The dried material was mixed with concentrated H$_2$SO$_4$ (ratio 1:1) and kept at room temperature overnight. Then it was washed with doubled distilled water for more than 5 times to remove the excess acid if any, and kept in hot air oven at 110°C for 12 hours. It was carefully taken in an iron vessel, covered with a tight fitting lid to avoid contact with atmospheric air, and that was placed in a muffle furnace and the temperature was gradually raised up to 550°C and the vessel kept at the same temperature for an hour. After cooling, the material was taken out and ground well by using ball mill. It was then sieved into particle size of 250, 150 and 100 BSS mesh numbers. These were preserved in airtight vessel for further studies on adsorption kinetics. The flow diagram of activation process is shown in the Fig.3.1.

3.3 Adsorbate

The dye stuffs predominantly employed in dye houses belong to acid, basic, direct, and reactive dyes. The prepared adsorbent was tested with these dyes for its adsorption kinetics studies. The dyes chosen for this adsorption kinetic study were as follows, 1.Acid Red -18 (New coccine), 2.Rhodamine-B 3.Malachite Green 4.Nile Blue 5.Congo-red 6.Direct Blue and 7.Reactive orange-16. The chemical structures of the dyestuffs were tabulated in the Table 3.1.

It is mandatory to know about the physicochemical characters of these dyes. These properties definitely play a vital role in the adsorption mechanism. Keeping this as a core concept, the adsorption kinetics could be understood.

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The acid dye chosen for this kinetic studies, Acid Red-18, contains SO$_3$ group and this makes the dye soluble in water. These dilute dye solutions exists in the forms like ions, simple molecules and micelles (Smith and Coackly, 1983) and show little affinity towards pure cotton and good affinity towards silk and synthetic yarns. The pH of the dye bath is preserved at 0 to 7.

The basic dyes Rhodamine-B, Malachite Green, and Nile blue were water soluble and dissociated into anions and colored cations. The electrostatic attraction builds up between the colored cations and acidic groups of acrylic fibres lead to form salts and develop the color fade upon the fabrics. The structural studies of basic dyes will open the door to know about the adsorption mechanism involved with these dyes. Xanthene class alkyl amino or aryl amino groups were present in its structure. Malachite green belongs to `Triphenyl methane' class and it contains 2-Amino group on the other hand; Nile Blue-A belongs to oxazin class which undergoes ionization to form basic ions and soluble in aqueous solutions. Congo red, Direct Blue -1 belong to Direct Dyes and water soluble substantive dyes. Finally, Reactive Orange-16 belongs to Dyazol dye of vinyl sulphone. The reactive site present in the dye covalently bonded with fibre to produce color.

The seven dyes each of 1000mg were accurately weighed and made up to 1000 ml with double distilled water. These dye solutions were taken for adsorption studies with KHAC.
Fig. 3.1 Flow diagram for the synthesis of activated carbon

1. KAPOK Hull
2. Dried in sunlight for three days
3. Mixed with Conc. $\text{H}_2\text{SO}_4$ (1:1)
4. Activated at 120°C in hot air oven for 12h
5. Washed with Deionized water (5 times)
6. Soaked in 2% $\text{Na}_2\text{CO}_3$ for over night
7. Washed with Distilled water (5 times)
8. Dried in hot air oven at 120°C for 6hr and in muffle furnace at 550°C
9. Separation of Particle size and stored in plastic containers
10. Used for treatment studies
Table 3.1 Structure of various dyestuffs used

<table>
<thead>
<tr>
<th>S.No</th>
<th>Name of the Dye</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Rhodamine-B</td>
<td><img src="image1" alt="Structure" /></td>
</tr>
<tr>
<td></td>
<td>$\lambda_{\text{max}} : 542.75$ nm</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Acid Red-18 (New Coccine)</td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td></td>
<td>$\lambda_{\text{max}} : 506$ nm</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Basic Nile blue (Nile blue-A)</td>
<td><img src="image3" alt="Structure" /></td>
</tr>
<tr>
<td></td>
<td>$\lambda_{\text{max}} : 635-645$ nm</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>Malachite Green</td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td></td>
<td>$\lambda_{\text{max}} : 616.5$ nm</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Direct Blue-1</td>
<td><img src="image5" alt="Structure" /></td>
</tr>
<tr>
<td></td>
<td>$\lambda_{\text{max}} : 618$ nm</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Reactive Orange-16</td>
<td><img src="image6" alt="Structure" /></td>
</tr>
<tr>
<td></td>
<td>$\lambda_{\text{max}} : 494$ nm</td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>Congo Red</td>
<td><img src="image7" alt="Structure" /></td>
</tr>
<tr>
<td></td>
<td>$\lambda_{\text{max}} : 497$ nm</td>
<td></td>
</tr>
</tbody>
</table>
3.4 Characterisation of Kapok Hull Activated Carbon (KHAC)

3.4.1 pH

One gram of activated carbon was agitated at 60 rpm for one hour in 50 ml of distilled water and equilibrated. The supernatant was analyzed for pH using digital pH meter.

3.4.2 Moisture content

About 1g of carbon was placed in a petriplate and heated in a hot air oven at 100±5°C for 1 hour. It was cooled in a desiccators and then weighed. The process of heating, cooling and weighing was repeated for 30min intervals. The loss in weight gives the moisture content.

\[
\text{Moisture content (\%) = 100 - \frac{(M-X)}{M}}
\]

Where,

- \( M \) = Amount of sample taken (g)
- \( X \) = Amount of sample after drying (g)

3.4.3 Ash Content

About 1 gram of carbon was weighed accurately in a sintered porcelain crucible that is placed in a hot air oven at 110±5°C for 5 hours. The crucible was removed from the oven and the contents were ignited in an electric muffle furnace at a temperature of 800°C for about 2 hours. The process of heating and cooling was repeated until the difference between two consecutive weighing was less than 5mg.

\[
\text{Ash content (\%) = \frac{(10000 \times M_1)}{M_2 (100 - X)}}
\]
Where,

\[ M_1 = \text{Amount of ash (g)} \]
\[ M_2 = \text{Amount of sample taken (g)} \]
\[ X = \% \text{ of moisture content present in the sample} \]

3.4.4 Decolorizing Power

About 0.5g of the carbon taken in the 100ml conical flask and 1ml of methylene blue solution (0.15%) was added and shaken well for 10 minutes. The addition of methylene blue solution and shaking was continued till the blue color persisted for at least 10 minutes.

\[
\text{Decolorizing power (mg/g)} = \frac{(1.5 \times V)}{M}
\]

Where,

\[ V = \text{Volume of methylene blue solution consumed (ml)} \]
\[ M = \text{Mass of the sample taken (g)} \]

3.4.5 Ion exchange Capacity

About 2g of carbon was taken in a beaker and a sufficient amount of distilled water was added to cover the carbon. The slurry was carefully transferred to a burette. The column was never allowed to drain completely and the water level was maintained at about 1cm above the carbon bed.

250ml of a solution of 0.25M sodium sulphate was allowed to drip into the column at a rate of 2ml/min and the effluent was collected in a 500ml conical...
flask, when all the solutions passed through the column. The effluent was titrated against 0.1N sodium hydroxide solution using phenolphthalein as (Wilde. S.A.. et al., 1992) indicator. The ion-exchange capacity of the bed (milli equiv/g) is.

\[
\text{IEC (milli equiv/g)} = \frac{NV}{W}
\]

Where,

\begin{align*}
N &= \text{Normality of sodium hydroxide solution} \\
V &= \text{Volume of solution (ml)} \\
W &= \text{Weight of carbon (g)}
\end{align*}

3.4.6 Determination of Surface Area -Acetic acid adsorption method

100ml acetic acid solution taken 300ml stoppered bottles in the range of 0.015M to 0.15M and 1g of KHAC was added to each bottle. To another bottle 100ml of 0.03M acetic acid alone was taken, which is served as control. The flasks were tightly stoppered and shaken well in a rotatory mechanical shaker for 60 minutes. At the end of equilibration period, the samples were filtered through Whatman filter paper (No.40). The first 10ml of filtrate was rejected and 25ml of the filtrate was titrated against 0.1N sodium hydroxide solution using phenolphthalein as an indicator. The final concentration of acetic acid was calculated. From the difference in initial and final concentrations of acetic acid, the number of moles of acetic acid adsorbed by the carbon was calculated (Shoemaker and Garland, 1967).
The concentration of acetic acid remaining in each instance (C) was divided by the number of moles of acid adsorbed per gram (N) of the carbon. A plot of C/N versus the concentration of acetic acid remaining in the containers after adsorption process (C) was made. A straight-line plot was obtained. The reciprocal of the slope of the straight line gives the number of moles of acetic acid required per gram to form a monolayer (N_m). The molecular cross sectional area of acetic acid is 21Å². The surface area (m²/g) available in the carbon was calculated from the following equation

\[ A \ (m^2/g) = N_m \times N_o \times \gamma \times 10^{-20} \]

Where,

N_m = Number of moles per gram required to form a monolayer
γ = Molecular cross sectional area given in square angstroms
N_o = Avagatro number (6.023 x 10²³)
A = Specific area (m²/g)

3.4.7 Apparent Density

For the determination of apparent density, a 50 ml graduated cylinder was weighed accurately. A trip balance was used to fill the carbon in the cylinder. Sufficient amount of carbon was poured with constant tapping and filled in the graduated cylinder at approximately 1ml/sec up to 50ml mark. After filling the graduated cylinder with the carbon, it was weighed accurately. The apparent density was calculated by dividing the weight of carbon by 50.
3.4.8 Water Soluble Matter

About 5g of carbon material was weighed accurately and transferred to one litre beaker, 300 ml of distilled water was added into it. This mixture was heated with continuous stirring up to its boiling temperature. The mixture was allowed to settle and the flame was removed. The supernatant liquor was filtered through a Gouch crucible fitted with an asbestos mat. The procedure was repeated thrice. The combined filtrate was concentrated to less than 100 ml over a water bath. It was cooled to room temperature and made up to 100ml. Exactly 50 ml of the concentrate was transferred to an already weighed china dish and evaporated to dryness on a water bath, and finally dried in a hot air oven, maintained at 110±5°C. Then it was cooled in a dessicator and weighed (ISI, 1997). The procedure of drying and weighing was repeated for a period of 30min intervals.

Material soluble in water (%) = \( \frac{20,000 \times M_1}{M_2 (100-X)} \)

Where,

\[ M_1 = \text{Mass of the residue (g)} \]
\[ M_2 = \text{Mass of the material taken for test (g)} \]
\[ X = \% \text{ of moisture present in the material} \]

3.4.9 Acid Soluble Matter

About 5g of the adsorbent was weighed accurately and transferred into a 500ml beaker. 150ml of 0.25N hydrochloric acid was added and heated to boiling point with continuous stirring for about 5 minutes. The material was then allowed
to settle. The supernatant was filtered through Gouch crucible fitted with asbestos mat. The procedure was repeated thrice with the residue in the beaker, using 150ml of acid each time. The combined filtrate was concentrated to less than 50ml over a water bath, cooled and the condensed were poured into a china dish and evaporated to dryness on a water bath, and finally dried in a hot air oven, maintained at 100±5°C. Then it was cooled in a desiccators and weighed (ISI, 1997). The procedure of drying and weighing was repeated for a period of 30 minutes interval.

\[
\text{Material soluble in acid (\%) = } \frac{20,000 \times A}{M (100-X)}
\]

Where,

\[
A = \text{Mass of the residue (g)}
\]

\[
M = \text{Mass of the sample taken (g)}
\]

\[
X = \% \text{ of moisture present in the material}
\]

3.4.10 Estimation of Sodium, Potassium and Calcium

About 100mg of ash obtained from the carbon, 10ml of 6N HCl was added and digested on a hot plate. This was repeated twice and made up to 50ml with water and centrifuged. The supernatant was used for the analysis of Na, K and Ca by Flame photometry. A series of standard solution were prepared in the range of 5-20mg/l of Na⁺ or K⁺ from a stock solution of 500mg/l of sodium or potassium. A calibration curve was prepared with emission reading versus concentration of
sodium or potassium. Concentration of sodium or potassium in the sample was determined using a calibration graph.

A series of standard solution was prepared in the range of 10-100mg/l of Ca(II) from a stock solution of 500mg/l Ca(II). A calibration curve was prepared with emission reading versus concentration of calcium. Concentration of calcium in the sample was determined using the calibration graph (APHA. 1980).

3.4.11 Phenol Adsorption Capacity

About 0.1 gm of carbon was accurately weight in a 100 ml conical flask and agitated for 3 hours with 25 mg/litre phenol. Absorbance was measured at 270 nm before and after the phenol (percent) removal was calculated (Economic and Lin, 1976).

\[
\text{Percentage Removal} = \frac{[B.T - A.T]}{B.T} \times 100
\]

Where,

B.T. = Absorbance before treatment

A.T = Absorbance after treatment

3.4.12 Determination of Iron

The iron content of the carbon was determined by 1,10-pheanthroline method. The ash obtained under ash content test was transferred to a 150 ml conical flask using 50 ml of 0.25N HCl, and heated to boiling. The contents were then cooled to room temperature and filtered through a Whatman 42 filter paper.
The contents of the filter paper were washed in to a conical flask and made up to 250ml with double distilled water. 10 ml of the made up sample was pipetted out into 125ml Erlenkeyer flask and 2ml of 0.25N HCl, 1ml of 10% Hydroxylamine hydrochloride solution were added and heated to boiling. Boiling was continued till the volume was reduced to about 10-15ml. The solution was then cooled and transferred to 100ml standard flask and 10 ml of ammonium acetate buffer (prepared by distorting 250g of ammonium acetate in 150ml of water followed by the addition of 700 ml of glacial acetic acid), followed by 2ml of 0.1% 1.10 phenanthroline solution were added and made up to the mark with double distilled water. The absorbance at the constant wavelength 525 nm was measured for the unknown and reagent blank using 1 cm quartz cells. A calibration graph was prepared using 10-20µg of Fe³⁺ by solution. Iron content was determined by referring to calibration curve. (ISI, 1977)

3.4.13 Matter soluble in water

About 5 gram of the carbon material of known moisture content was weighed accurately and transferred to a one-litre beaker. About 300ml of distilled water was added and heated (up to boiling) with continuous stirring. Stirring was continued for 5 minutes after the flame was removed. The material was then allowed to settle. The supernatant was filtered through a Gouch crucible fitted with an asbestos mat. The procedure was repeated thrice with the residue in the beaker using 300 ml of water each time. The combined filtrate was concentrated to
less than 100 ml of a water bath, cooled and made up to 100 ml mark in a volumetric flask. Exactly 50 ml of the concentrate was transferred to a china dish in an electric oven, maintained at 100± 5°C, cooled in a desiccators and weighed. The procedure of drying and weighing was repeated at 30 minutes interval.

\[
\text{Matter soluble in water (\%)} = 20,000 \times \frac{M_1}{M_2} \left(100 - X\right)
\]

Where

- \(M_1\) = mass of the residue (g)
- \(M_2\) = mass of the material taken for test (g)
- \(X\) = percent of moisture present in the material

### 3.4.14 Material soluble in Acid

About 5gm of the carbon material of known moisture of known content was weighed accurately and transferred into a one-litre beaker. Stirring was continued for 5 minutes after the flame was removed. The supernatant was filtered through a Gouch crucible fitted with an asbestos mat. The procedure was repeated thrice with the residue in the beaker using 300ml of acid each time. The combined filtrate was concentrated to less than 100ml over a water bath, cooled and the contents were transferred to a china dish and evaporated to almost dryness on a boiling water bath and finally dried in an electric oven, maintained at 100±5°C. cooled in a desiccators and weighed. The procedure of drying and weighing was
repeated at 30 minutes interval, until the difference between the consecutive weighing was less than 5 mg.

\[ \text{Acid soluble matter (\%) = 20,000 \times \frac{A}{M} \times (100 - X)} \]

Where,
- \(A\) = mass of the dried residue (g)
- \(M\) = mass of the material taken for test (g)
- \(X\) = percent of moisture present in the material.

3.5 Determination of dye concentration

The dye adsorbed after equilibrium time was separated by centrifugation and the quantity of dye adsorbed was determined by employing a UV-visible spectrophotometer, spectronic make, in respective \(\lambda_{\text{max}}\) of each dye. The percentage of dye adsorption was calculated from the absorbance value before and after treatment. The quantity of the dye adsorbed was determined by the following equation.

\[ Q = (C_0 - C) \times \frac{V}{W} \quad \ldots \ldots (1) \]

Where \(Q\) is the quantity of dye adsorbed (mg/g), \(C_0\) is the initial concentration of dye in the solution (mg/ml), \(C\) is the final concentration of the dye solution (mg/l), \(V\) is the volume of the solution in milliliters (ml) and \(W\) is the mass of the adsorbent in grams.

3.5.1 Measurement of pH

A digital pH meter Systronics make was used for the measurements of pH. The pH meter was calibrated by using potassium hydrogen phthalate pH 4 and sodium borate pH 9.2 as buffers.
3.5.2 Estimation of particle size of adsorbent

Large particles of adsorbent KHAC were grounded in a blender and sieved in electronic sieve machine (Chemae 640, Germany) to consistent particle sizes before use. The corresponding values in BSS mesh values / microns were noted against the sieve openings.

3.5.3 Isotherm studies

Batch experiments were so designed to cover equilibrium studies. 100 ml of dye solution at various concentrations like 50, 100, 250, 500, 1000 mg/l were prepared and each was treated with 1gm of the activated carbon and equilibrated for a period of 24 hours with stirring. The different parameters such as temperature and particle size were varied at a constant pH of 6.4.

3.5.4 Kinetic studies

A dye solution of 100ml of concentration 50mg/litre was agitated with one gram of the adsorbent namely activated carbon over a period of time with constant stirring. The following parameters were studied to elucidate the kinetics of adsorption.

3.5.5 Effect of carbon dosage

The carbon dosage of 100mg to 1000mg of particle size 250, 150, 100 BSS mesh was agitated with a known concentration of dye solution at constant pH (6.4) and at ambient temperature.
3.5.6 Effect of temperature

The kinetics studies were also performed at three temperatures of 300, 318 and 330K at constant pH and particle size 250, 150 and 100 BSS mesh numbers.

3.5.7 Effect of pH

The kinetics studies were performed at various pH levels at ambient temperature and at particle size 250 BSS mesh.

3.5.8 Effect of adsorbent particle size

The kinetic studies were performed with different adsorbent particle size ranging from 250 BSS mesh, 150 BSS mesh, 100 BSS mesh at the ambient temperature level and at pH 6.4.

3.5.9 Desorption studies

One gram of the dye adsorbed adsorbent was treated with 100 ml of double distilled water, desorbing agents like sulphuric acid, sodium hydroxide solutions (0.5, 1, 2N) and 50% acetic acid respectively and possible desorption was studied keeping all other parameters constant.

3.5.10 Application of mathematical tools

Some mathematical correlation between the variables (Temperatures, pH, Adsorbent particle size) and amount of dye adsorbed may be carried out.