CHAPTER - 3
MATERIALS AND METHODS

MATERIALS

3.1. Raw Material

Silk cotton hull was collected and used as the material for activated carbon preparation.

3.1.1. Preparation of Adsorbent

Silk cotton hull was collected from PSG College of Arts and Science, Coimbatore, TamilNadu, India. The collected material was sundried. The dried hull was chopped into pieces and acid treatment was carried out. To one part of the hull material 1.8 parts of concentrated sulphuric acid w/v was added and stirred and kept in hot air oven at 80 ± 5° C for 12 h. The carbonized material was washed with distilled water to remove the free acid. After washing the material it was soaked in 1% sodium bicarbonate solution and allowed to stand for 12 hrs to remove the acid. Then the material was washed with distilled water until the pH of the carbon reached 6.5 ± 0.2 and dried in hot air oven at 105° C. The dried material was ground and sieved to get different particle sizes ranging from 125-250μm, 250 - 500μm and 500 - 750μm. The adsorbent was stored in an air tight container and characterized. All the chemicals used was of analytical reagent grade obtained from B.D.H and E.Merck. Double distilled water was used for the whole of the experimental studies.

All pH measurements were made on systronics 120 pH meter and the spectrophotometric estimations were carried out on systronics 107 Spectrophotometer.
3.2. Preparation of Adsorbate

3.2.1. Nickel(II) stock solution.

A stock solution of 1000mg/l of Nickel (II) was prepared by dissolving 4.479g of nickel sulphate in double distilled water, 1ml of concentrated nitric acid to prevent hydrolysis and made up to 1000 ml.

3.2.2. Mercury (II) stock solution

A stock solution of 1000 mg/l of Mercury (II) was prepared by dissolving 1.3540 g of Mercury (II) chloride in double distilled water, acidified with 5ml of concentrated hydrochloric acid to prevent hydrolysis and made up to 1000 ml.

3.2.3. Chromium(VI) stock solution

A stock solution of 1000 mg/l of Chromium (VI) was prepared by dissolving 2.8300 g of dried potassium dichromate in double distilled water and made up to 1000 ml.

3.2.4. Lead (II) stock solution

A stock solution of 1000mg/l lead (II) was prepared by dissolving 1.5990 g of anhydrous lead nitrate in water, acidified with 1 ml of concentrated nitric acid and made up to 1000 ml.

3.3. Industrial Wastewater

Industrial wastewaters were collected from Electroplating industry for Cr(VI); Ni(II) and radiator manufacturing wastewater for Pb(II) from Coimbatore area, TamilNadu, India and was characterized and subjected for treatment studies.
3.3.1. Preparation of Synthetic Wastewater Containing Hg (II).

Hg (II) synthetic wastewater was prepared by dissolving HgCl₂, CaCO₃, NaCl, Fe₂SO₄, MgCl₂ and NaCO₃ in double distilled water and made up to 1000 ml.

3.4. Analytical Methods.

3.4.1. Characterization of the Adsorbent (Table - 1)

3.4.2. pH of the Adsorbent (Indian Standards Institute, 1997)

The carbon (adsorbent) was placed in a one litre beaker (5g carbon). 150 ml of freshly boiled and cooled water (pH 7.0) was added and heated to boiling point. After digesting for 10 minutes, the solution was filtered hot, rejecting the first 10 ml of the filtrate. The remaining filtrate was cooled at room temperature and the pH was measured using a pH meter.

3.4.3. Moisture Content of the Adsorbent (ISI, 1997)

About 5 g of the carbon was weighed in a petridish. The dish was placed in an electric oven maintained at 110 ± 5°C for about 5hrs. The dish was covered, cooled in a desiccator. Heating, cooling and weighing was repeated at 30 minutes interval until the difference between the two consecutive weighings was less than 5 mg.

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

where

\( M = \) Mass of the material taken for test (g)

\( X = \) Mass of the material taken for drying (g)
3.4.4. ASH Content: (Indian Standards Institute, 1997)

About 1g of carbon was weighed accurately into a crucible. The crucible and its contents were placed in an electric oven at 110±5°C and heated for about 5hrs. 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 2hrs. The process of heating and cooling was repeated until the difference between two consecutive weighings was less than 5 mg.

\[
\text{Ash (on dry basis) % by mass} = \frac{100 \times M_1}{M_2(100 - X)}
\]

where \( M_1 \) = Mass of ash (g)
\( M_2 \) = Mass of material taken for test (g)
\( X \) = % of moisture content present in the material taken.

3.4.5. Decolourising Power: (Indian Standards Institute, 1997)

About 0.5g of the carbon material was transferred to a 100ml conical flask. 1 ml of methylene blue solution (0.15% w/v) was added from a burette and shaken for 10 min. Addition of methylene blue solution and shaking was continued till the blue colour persisted for atleast 10 min.

Decolourising power of carbon is expressed in terms of milligrams of methylene blue adsorbed by 1g of carbon.

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

where \( V \) = Volume of methylene blue solution consumed (ml)
\( M \) = Mass of the material taken for the test (g).
3.4.6. Ion Exchange Capacity (Kinniburgh, et al., 1975)

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

250 ml of a solution of 0.25 M sodium sulphate was allowed to drip into the column at a rate of 2ml / min and the effluent was collected in a 500 ml in conical flasks. When all the solution has passed through the column, the effluent was titrated with standard 0.1N sodium hydroxide solution using phenolphthalein as indicator. The ion exchange capacity of the bed in milli equivalents / g is given by NV /W where N is the normality of the sodium hydroxide solution V is the volume in ml and W is the weight of the carbon.

3.4.7. Determination of Surface Area (p-nitrophenol method) (Giles and Silva, 1969).

A stock solution containing 1000 mg / l of p-nitrophenol (PNP) was suitably diluted to yield 100 mg /l solution. Aliquots ranging from 0.5 ml of this 100 mg /l solution was transferred to a series of 100 ml standard flasks, 20 ml of 0.1N sodium hydroxide was added and diluted to 100 ml. Absorbance of these solutions was measured at 400 nm using 1 cm cells against the reagent blank. A calibration graph was prepared using 1-5 mg/l of p-nitrophenol.
About 0.5g carbon samples was accurately weighed to the nearest mg and added to a series of 300 ml stoppered glass bottles. Para-nitrophenol solution in the range of 50-1000 mg/l was prepared separately and 100ml of these solutions were added to each of these bottles. The bottles were tightly stoppered and then shaken in a rotary mechanical shaker for 24h. At the end of an equilibration period, a suitable volume of supernatant was transferred to a 100 ml standard flask. Two ml of 0.1N sodium hydroxide was added and diluted to 100 ml. The absorbance of this solution was measured at 400 nm using 1 cm cells against a reagent blank. The concentration (c) PNP remaining in each instance was established by reference to the calibration graph. From the difference in initial and final concentrations of PNP, the number of millimoles of PNP adsorbed by 1g of carbon was calculated and designated as ‘N’.

The ratio of the concentration of PNP remaining in each instance (C) to millimole of PNP adsorbed per g (N) of the carbon (C/N) was plotted against the concentration of PNP remaining in the solution (L). The reciprocal of the slope of the linear plot gave the number of millimoles of PNP required per g of carbon to form a monolayer which was designated as Nm. Assuming that the molecular cross sectional area of PNP to be 52.5Å², the area available in m²/g of the carbon was calculated using the expression:

$$ A = Nm \times Nm \times \sigma \times 10^{-20} $$

where

- $Nm$ = Avagadro Number
- $Nm$ = The number of moles per g required to form a monolayer obtained from slope value.
3.4.8. Apparent Density (Indian Standards Institute, 1997)

A specific gravity bottle of 25 ml capacity was filled with the adsorbent and packed well by tapping with a rubber stopper. The weight of the adsorbent was determined. The ratio of weight (g/l) to the volume (g/ml) gave the apparent density (g/ml) of the adsorbent.

3.4.9. Matter soluble in Water (Indian Standards Institute, 1997)

Five gram of the carbon material of known moisture content was weighed accurately and transferred into a one litre beaker. About 300 ml of distilled water was added and heated to boiling point with continuous stirring. Stirring was continued for 5 minutes after the flame was removed.

The material was then allowed to settle and the supernatant was filtered through a gooch crucible fitted with an asbestos mat. The procedure was repeated thrice, the residue in the beaker was filtered with 300 ml of water each time. The combined filtrate was concentrated to less than 100 ml over a water bath, cooled and made up to 100 ml in a 100 ml volumetric flask. Exactly 50 ml of the concentrate was transferred to a china dish and evaporated to almost dryness on a boiling water bath and the residue was finally dried in an electric oven maintained at 110 ± 5°C, cooled in a desiccator and weighed. The procedure of drying and weighing was repeated at 30 minutes intervals, until the difference between two consecutive weightings was less than 5 mg.

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

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.
3.4.10. Matter soluble in Acid (Indian Standards Institute, 1997)

Five gm of the carbon under study was weighed accurately and transferred into one-liter beaker. 300 ml of 0.25 N HCl was added and heated to boiling point with continuous stirring. Stirring was continued for about 5 minutes after the flame was removed.

The material was then allowed to settle and the supernatant was filtered through a gooch crucible fitted with an asbestos mat into two litre. The procedure was repeated thrice with the residue in the beaker using 300 ml of acid each time. After the fourth treatment, the combined filtrate was concentrated to less than 100 ml over 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 and evaporated to almost dryness on a boiling water bath and finally dried in an electric oven maintained at 110 ± 5°C. The dish was then covered, cooled in a desiccator and weighed. The procedure of drying and weighing was repeated at 30 minutes intervals; until the difference between two consecutive weightings was less than 5 mg. Acid soluble matter was calculated using the same expression as in the case of matter soluble in water.

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

where

- \(A\) = Mass of the dried residue (g)
- \(M\) = Mass of the material taken for test (g)
- \(X\) = Percent of moisture content of the material taken for test.
3.4.11. *Estimation of Sodium, Potassium and Calcium in the Ashed Adsorbents (APHA, 1980).*

To 100 mg of ash, 10 ml of 6 N hydrochloric acid was added and digested on a hot plate. This was repeated twice and made up to 50 ml with water and centrifuged. The supernatant was used for the analysis of sodium, potassium using Elico flame photometer CL 220.

A series of standard solutions was prepared in the range of 4 to 24 mg/l of Na\(^+\) of k\(^+\) from a stock solution of 1000 mg/l of sodium and potassium. A calibration curve was prepared with emission reading vs concentration of sodium or potassium concentration of sodium and potassium in the sample was determined using the calibration graph.

A series of standard solutions was prepared in the range 20-100 mg/l of Ca (II) found a stock solution of 1000 mg/l Ca(II). A calibration curve was prepared between emission reading and concentration of calcium. Concentration of calcium in the sample was determined using the calibration graph.

3.5. *Analysis of Metal ions*

3.5.1. *Estimation of Mercury (II) (Ramakrishna, 1976).*

Mercury (II) was estimated spectrophotometrically using rhodamine 6G reagent. A suitable aliquot of the solution containing not more than 25\(\mu\)g of mercury(II) was transferred into a 25 ml volumetric flask. 5 ml each of 0.05m disodium salt of EDTA. 2% buffered potassium iodide (5g of Potassium iodide + 5g potassium hydrogen phthalate) made upto 250 ml and 0.005% rhodamine 6G solutions were added with mixing followed by 1 ml of 1% gelatin. The solution was diluted upto the mark with water and the
absorbance was measured at 575 nm against a reagent black of calibrations graph for 5-25 μg of mercury (II) prepared by following the above procedure and the concentration in the sample aliquot was established by referring to the calibration graph.

3.5.2. Estimation of Chromium (VI) (APHA, 1980)

Hexavalent chromium was determined spectrophotometrically by diphenyl carbazide method. To a series of standard solutions of chromium (VI) (5-50 μg) 10 ml of 1 MH$_2$SO$_4$, 2 drops of phosphoric acid and 1 ml of diphenyl Carbazide solution (0.5% in acetone) was added and made upto 50 ml with water. The absorbance was measured at 540 nm after 5 min against a reagent blank. A calibration graph with absorbance vs chromium (VI) concentration was prepared by following the above procedure. The concentration in the sample was established by referring to the calibration graph.

3.5.3 Estimation of Nickel (II) (Allen, 1982).

Nickel (II) was estimated spectrophotometrically using dimethyl glyoxime (DMG). To a series of standard solutions containing less than 200μg of Nickel(II) 10 ml of 20% sodium citrate solution and 2 ml of 0.05M iodine solution was added and mixed followed by the addition of 4 ml of DMG solution. The contents was made up to 50 ml with water. The absorbance was measured after 20 min at 470 nm against blank. A calibration graph with absorbance vs Nickel (II) concentration was prepared. The amount of Nickel (II) absorbed was obtained from the calibration curve.
3.5.4. Estimation of Lead (II) (Pollard, 1959)

Lead (II) was estimated spectrophotometrically using PAR reagent (4-(2 - pyridyldazo) resorcinol). A suitable aliquot of the sample containing not more than 50µg of lead (II) was transferred into a 25 ml volumetric flask. 10 ml of ammonia - ammonium chloride buffer solution (16.9g NH₄Cl + 123 ml liquor ammonia made up to 250 ml with water) was added to provide a pH of 10.0 followed by 1 ml of 0.01% solution of PAR reagent. The solution was diluted upto the mark with water. The absorbance was measured at 520 nm against a reagent blank. A calibration graph for 5-50µg of lead was prepared by the above procedure and the concentration in the sample aliquot was established by referring to the calibration graph.

3.5.5. Characterization of Industrial Wastewater (APHA, 1980)

The Industrial wastewater obtained from various industries were subjected to the analysis of parameters such as pH, turbidity, conductivity, total solids, chemical oxygen demand (COD), chlorides, sulphates, calcium, sodium, etc. The above parameters were determined using standard analytical procedure.

3.6. Batch Mode Adsorption Studies

Batch mode adsorption study was carried out by taking 50 ml of metal solution and required amount of carbon in 100 ml conical flask. Metal solutions were agitated at 120 rpm in mechanical shaker for different time intervals at room temperature. The adsorbate and adsorbent were separated by centrifugation at 3,000 rpm for 5 minutes.

Effect of agitation time and initial metal ion concentration, effect of pH, adsorbent dosage and particle size for metal removal was carried out.
with aqueous metal ion solution. With every experimental metal solution, control experiments were also carried out without adsorbent.

3.6.1. Effect of Agitation Time and Initial Metal ion Concentration

Experiments were carried out by using 50 ml of metal ion solution of desired concentration, adjusted the pH value, mixed with fixed amount of carbon concentration and agitated for different time intervals. After agitation time, the adsorbent and adsorbate were separated by centrifugation and centrifugate was estimated spectrophotometrically.

3.6.2. Effect of pH on Metal ion Adsorption

Experiments were carried out using 50 ml of metal ion solution of desired concentration, adjusted to different pH values and mixed with known concentration of carbon and agitated for a time interval. The pH adjustment was carried out using dilute nitric acid or dilute sodium hydroxide solution for Pb(II) and Ni(II) and dilute hydrochloric acid and sodium hydroxide in the case of Hg(II) and Cr(VI). After agitation time, the adsorbent and adsorbate were separated by centrifugation and estimated spectrophotometrically.

3.6.3. Effect of Adsorbent Dosage on Metal ion Concentration

Experiments were carried out using 50 ml of metal ion solution of desired concentration, adjusted to desired pH, varying the carbon concentration with fixed time interval were carried out. After agitation the adsorbent and adsorbate were separated by centrifugation and centrifugate was estimated spectrophotometrically.
3.6.4. Effect of Particle size on Adsorption

Experiments were carried with desired metal ion concentration of 50 ml, with fixed time, fixed adsorbent dosage but varying the particle size of carbon were carried out to know the effective particle size for adsorption. After agitation, the adsorbent and adsorbate were centrifuged and centrifugate were estimated spectrophotometrically.

3.7. Batch Mode Desorption Studies

Adsorption experiment with desired metal ion concentration with fixed carbon dosage were carried out after which the adsorbent and adsorbate were centrifuged and the supernatant was drained out. The remaining carbon was given gentle wash with double distilled water to remove unadsorbed metal ions. Several such samples were prepared and they were agitated with 50 ml of hydrochloric acid for Ni(II), Hg(II) and Pb(II) with NaOH for Cr(VI) of various strengths ranging from various concentration for desired time. The desorbed metal ion in the solution was separated by centrifugation and analysed.

3.8. Treatment of Industrial Wastewater Containing Metal Ion

Effect of adsorbent dosage for industrial wastewater containing metal ions was carried out. The wastewater collected from nickel plating (Ni(II)) chrom plating (Cr(VI)), radiator manufacturing (Pb(II)) industries was found to contain large quantities of respective ions and hence dilutions was carried out within the previous synthetic experimental concentrations. Synthetic wastewater was prepared for Mercury (II) solutions and experiments were carried.
Different amounts of adsorbent were added to 50 ml of respective metal ion wastewater and equilibrium time was considered from synthetic batch studies. After agitation the supernatant was centrifuged and analyzed spectrophotometrically.
### TABLE - 1
CHARACTERISTICS OF ACTIVATED CARBON

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 1 % solution</td>
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</tr>
<tr>
<td>Moisture content (%)</td>
<td>2.86</td>
</tr>
<tr>
<td>Ash content (%)</td>
<td>1.987</td>
</tr>
<tr>
<td>Decolorizing power (mg/g)</td>
<td>22.5</td>
</tr>
<tr>
<td>Ion – exchange capacity (equiv g)</td>
<td>0.0415</td>
</tr>
<tr>
<td>Determination of surface area (m²/g)</td>
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</tr>
<tr>
<td>Apparent density (g/l)</td>
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</tr>
<tr>
<td>Particle size (µm)</td>
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<tr>
<td>Volatile matter (%)</td>
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<tr>
<td>Fixed carbon (%)</td>
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<tr>
<td>Calcium (mg/g)</td>
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<tr>
<td>Sodium (mg/g)</td>
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<tr>
<td>Potassium (mg/g)</td>
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</tr>
<tr>
<td>Water – soluble matter (%)</td>
<td>2.0</td>
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<tr>
<td>HCl soluble matter (0.25 N) (%)</td>
<td>7.0</td>
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