2 MATERIALS AND METHODS

2.1 Apparatus
Systronics UV-Visible spectrophotometer.
Systronics pH meter with combined glass electrode for pH measurements.
Orbitek temperature controllable mechanical shaker for equilibrium studies.

2.2 Reagents
Unless otherwise specified all reagents are of analytical grade and double distilled water was used for dilution purposes.

2.2.1 Reagents for batch adsorption experiments
o-Nitrophenol, p-Nitrophenol, Eosin Yellow, Rose Bengal, Rhodamine B and Malachite Green (1000mg/L) solutions:
Prepared by dissolving 1.0000g of each substance in water and diluting to 1000mL.

2.2.2 Reagents for adsorbents characterization
2.2.2.1 Determination of the total surface reactive- site number:\(^{267}\)
Preparation of cobalthexamminetricloride:\(^{268}\): A mixture of 240g CoCl\(_2\)\(_6\)H\(_2\)O, 160g of NH\(_4\)Cl and 240 mL of water is shaken until solution is almost complete. Then, 4-5g of activated charcoal and 500 mL of con.NH\(_3\) are added and a fast stream of air is passed through the mixture until the red solution becomes yellow brown. The precipitated [Co(NH\(_3\))\(_6\)]Cl\(_3\) and the charcoal are filtered off and the residue is dissolved in hot 2% HCl. The solution is filtered hot and the pure product is collected, washed first with 60% alcohol, then with 95% alcohol and finally dried at 100°C.
Stock cobalthexamminetrichloride solution (0.1 M): Prepared by dissolving 2.6740g salt in water and diluting to 100 mL.

Standard cobalthexamminetrichloride solution (0.02 M): Appropriate volume of stock solution was diluted to get a concentration of 0.02 M.

2.2.2.2 Boehm Titrations

The following solutions were used: Sodium hydroxide (0.05N), hydrochloric acid (0.05N), sodium carbonate (0.05N) and sodium bicarbonate (0.05N). All the solutions were standardized before use.

2.2.2.3 Iron content determination

Iron(III) solution (1000 mg/L): Prepared by dissolving 7.2337g Fe(NO₃)₃·6H₂O in water and diluting to 1000 mL.

Standard Iron(III) solution: Appropriate volume of stock Fe(III) solution (1000 mg/L) was diluted with water to obtain a concentration of 25 mg/L.

Ammonium thiocyanate solution (7.6%): Prepared by dissolving 38g ammonium thiocyanate in water and diluting to 500mL.

2.2.2.4 Iodine number determination

Sodium thiosulphate solution (0.1N): 24.820g was dissolved in water and diluted to 100mL. Exact strength was established by titrating against standard KIO₃ solution.

Iodine solution (0.1N): About 12.7g I₂ crystals were mixed with 19.1g KI, dissolved with small amounts of water and the solution is finally made up to 1L in a standard flask. Exact strength was established by titrating against the standardized thiosulphate solution.
KI\textsubscript{3} solution (0.1N): Exactly 3.5667 \pm 0.1 \text{mg} of previously dried (at 383 K) KI\textsubscript{3} crystals were dissolved in water and made up to 1L.

Starch solution: About 0.1 \text{g} of starch powder was mixed with 25mL water; the resulting paste was poured into 100mL of boiling water and the boiling was continued for 4 - 5 minutes. The solution was freshly prepared every day.

2.2.2.5 Phenol value determination

Standard Phenol solution

Prepared by dissolving 1.000g of distilled phenol in water and making up the resulting solution to 1L.

2.2.2.6 Methylene Blue number determination

Stock methylene blue solution (100mg/L): Prepared by dissolving accurately 0.1000g of the dyestuff in water and diluting to 1L.

Standard methylene blue solutions: Appropriate volumes of the stock solutions were diluted to get solutions of concentrations: 10, 20, 30, 40, 50, and 60mg/L.

2.2.2.7 Tannin value determination

Stock tannic acid solution (1000mg/L): Prepared by dissolving accurately 1.0000 g tannic acid in water and diluting to 1L.

Standard tannic acid solution (100mg/L): Appropriate volume of stock tannic acid solution was diluted to get a concentration of 100mg/L.
2.3 Methods

2.3.1 Analytical procedure

2.3.1.1 Determination of \( p \)-nitrophenol by visible absorption

An aliquot containing not more than 10 mg/L \( p \)-nitrophenol is taken and made up to 100 mL with water after the addition of 2 mL of 0.1 N NaOH solution to develop yellow colour. Absorbance is then measured at 400 nm against a reagent blank. A calibration graph for 1-10 mg/L \( p \)-nitrophenol was plotted (figure 2.1).

2.3.1.2 Determination of \( o \)-nitrophenol by ultraviolet absorption

An aliquot containing not more than 30 mg/L \( o \)-nitrophenol was taken and its absorbance is directly measured at 277 nm against a reagent blank. A calibration graph for 5-30 mg/L was plotted (figure 2.2)
2.3.1.3 Determination of Eosin Yellow, Rose Bengal, Malachite Green and Rhodamine B by visible absorption

All the above mentioned dyes were analyzed by monitoring their absorption in the visible region, 516 nm for Eosin Yellow, 544 nm for Rose Bengal, 620 nm for malachite green and 555 nm for Rhodamine B. Calibration graphs were prepared (1-8 mg/L for Eosin Yellow, 1 to 10 mg/L for Rose Bengal, 1-9 mg/L for malachite green and 1 to 8 mg/L for Rhodamine B, figures 2.3-2.6) and concentrations of sample aliquots were established by referring to the respective calibration graph.
Figure 2.3 Calibration Graph for EY

Figure 2.4 Calibration Graph for RBL
Figure 2.5 Calibration Graph for MG

Figure 2.6 Calibration Graph for RB
2.3.1.4 Determination of methylene blue

Methylene blue was estimated by monitoring its absorption at 613 nm. A calibration graph was prepared for the concentration range 0.5-5.0 mg/L (figure 2.7).

![Figure 2.7 Calibration Graph for MB](image)

2.3.1.5 Determination of tannic acid and phenol

The concentration of tannic acid and phenol were measured at 275 nm and 270 nm, respectively. Calibration graphs for 5-30 mg/L tannic acid (figure 2.8) and 5 to 150 mg/L phenol (figure 2.9) were used.
Figure 2.8 Calibration Graph for TA

![Graph of Absorbance vs Amount of TA, ppm]

Figure 2.9 Calibration Graph for phenol

![Graph of Absorbance vs Amount of phenol, ppm]
2.3.1.6 Cobalthexamminetrichloride estimation by UV absorption

Cobalthexamminetrichloride was estimated by directly noting the visible absorption of Co$^{3+}$ ions at 470 nm. A calibration graph constructed for the concentration range 0-0.02 M was used (figure 2.10).

![Figure 2.10 Calibration Graph for cobalthexamminetrichloride](image)

2.3.1.7 Determination of Iron(III) by spectrophotometry

An aliquot from standard Fe solution was transferred to a 50 mL volumetric flask. 10 mL of 7.6% NH$_4$CNS solution was added, the solution was diluted to the mark and the absorbance was read as soon as possible at 480nm. A calibration graph for 0.2-5 mg/L was prepared (figure 2.11).
2.3.2 Methods for physicochemical characterization

2.3.2.1 Moisture content

A crucible is dried in an oven at 150 ± 5°C for an hour, cooled and weighed. 5-10g of the representative sample is placed in the cooled crucible, kept in the oven at 150 ± 5°C for an hour, cooled and weighed.

Moisture, weight % = [(C-D)/(C-B)] × 100

where,

B = weight of empty crucible, g
C = weight of crucible with the original sample, g
D = weight of crucible with the dried sample, g
2.3.2.2 Apparent density and dry apparent density

A 100mL-graduated cylinder (previously calibrated) is taken and the sample is added carefully and slowly up to the mark. The contents were then transferred quantitatively and weighed to the nearest 0.1mg.

Apparent density, as-received, g/mL = mass in grams / volume in mL

Dry apparent density, g/mL = as-received apparent density $\times \frac{1 - \% \text{ moisture}}{100}$

2.3.2.3 Volatile matter content

A crucible with a lid is placed in a preheated muffle furnace at 950°C for 30 minutes, cooled and weighed. Approximately 1g of the as-received sample is placed in it and immediately weighed. The contents were then kept at 950 ± 25°C for 7 minutes cooled and weighed.

Weight loss, % (E) = $\frac{(C-D)}{(C-B)} \times 100$

where,

B = weight of the crucible with cover, g
C = weight of the crucible with cover and sample, g
D = weight of crucible with cover and the devolatalized sample, g

Volatile matter, % = E - F

where,

E = weight loss, %
F = moisture, %
2.3.2.4 Total ash content

A crucible is ignited in the muffle furnace at 650 ± 25°C for an hour, cooled and weighed. An adequate sample is dried at 150 ± 5°C to constant weight. Sufficient dried activated carbon is added to the ignited crucible so that the estimated amount of ash will be 0.1g, the contents were kept in the muffle furnace at 650 ± 25°C for an hour, cooled and weighed. Ashing is considered complete when constant weight is achieved.

\[
\text{Total ash, } \% = \left(\frac{D-B}{C-B}\right) \times 100
\]

where,

\[
B = \text{weight of empty (dried) crucible, g}
\]

\[
C = \text{weight of crucible with the original sample, g}
\]

\[
D = \text{weight of crucible with the ashed sample, g}
\]

2.3.2.5 Fixed carbon

Fixed carbon is a hypothetical parameter, which is determined by

\[
\text{Fixed carbon} = 100 - [\% \text{ moisture} + \% \text{ volatile matter} + \% \text{ ash}]
\]

2.3.2.6 Water solubles

10.0 ± 0.01g of carbon samples were weighed, 100mL of boiled water is added and the contents were boiled gently for 900 ± 10 sec, cooled and filtered. Using a pipette 50mL aliquot of the filtrate is transferred to a previously dried porcelain-evaporating dish and is dried on a steam bath until the liquid disappeared. The residue is dried at 150 ± 5°C for a period of one hour to a constant weight.

\[
\text{Water solubles, } \% = \left(\frac{B-A}{D} \times \frac{100}{C\times E}\right)
\]
where,

\[ A = \text{mass of the evaporating dish, g} \]
\[ B = \text{mass of dish with residue, g} \]
\[ C = \text{mass of carbon, g} \]
\[ D = \text{volume of water used in the extraction, mL} \]
\[ E = \text{volume of aliquot used, mL} \]

2.3.2.7 Acid extractable content

Sufficient dried activated carbon is weighed to the nearest 0.1mg so that the estimated amount of ash will be at least 0.1g. The samples were quantitatively transferred to a 250mL beaker and reagents in the following order were slowly added, 100mL water, then 25mL concentrated HCl and swirled. The contents were covered with a watch-glass; brought to a boil on a hot plate, maintaining boiling for 5 minutes; cooled and filtered. The carbons retained on the filter paper were washed with several portions of water to thoroughly remove the entire acid residue. The carbon contents were then transferred to a silica crucible and ashed in a muffle furnace at 650°C and its ash content is evaluated.

2.3.2.8 pH

pH is measured on a portion of the filterate obtained in the water solubles determination experiment (section 2.3.2.7).

2.3.2.9 Iron content

The iron contents of the adsorbents were determined by spectrophotometric method. The ash obtained under ash content test was transferred to a 150 mL conical
flask after dissolving in 50 mL dilute hydrochloric acid and the contents were heated to boiling, cooled to room temperature and filtered through a Whatmann No. 41 filter paper. The contents of the filter paper were washed with distilled water and the filtrate and entire washings were made up to 250 mL. Iron present in the made up solution was established by the thiocyanate method (section 2.3.1.7).

2.3.2.10 Surface area by BET method
The BET surface areas of the samples were measured using nitrogen adsorption isotherms in an instrument based at Central Electrochemical Research Institute (CECRI), Karaikudi.

2.3.3 Chemical characterization

2.3.3.1 Cation Exchange Capacity (CEC) or the total surface reactive site number, $S_{\text{tot}}$
One gram of the solid is equilibrated with 10mL of 0.02 M cobalthexamminetrichloride solution for 3 hours. After centrifugation of the suspension, the concentration of cobalthexamminetrichloride ions remaining in the solution is measured at 470 nm with the spectrophotometer. A calibration graph constructed with a maximum concentration of 0.02 M hexamminetrichloride was used for this purpose (figure 2.10, section 2.3.1.6). Experiments were carried out in triplicate.

2.3.3.2 Boehm titrations$^{278, 279}$
One gram of solid sample was placed in 50mL each of the following 0.05N solutions: sodium hydroxide, sodium carbonate, sodium bicarbonate and hydrochloric
acid. The vials were air tightly closed and shaken for 24 hours; then 10mL of each filtrate was pipetted out, and the excess of base or acid was titrated with standard HCl or NaOH. The numbers of acidic sites of various types were calculated under the assumption that NaOH neutralizes carboxyl, phenolic and lactonic groups; sodium carbonate, carboxyl and lactonic; and sodium bicarbonate, only carboxyl groups. The number of surface basic sites was calculated from the amount of HCl that reacted with the carbon. Neutralization with HCl characterizes the amounts of surface basic groups, such as pyrones and chromenes. The basic properties are ascribed to surface basic groups and the π-electron system of the carbon basal planes.

2.3.3.3 Mass titration\textsuperscript{280,281}

Three solutions of different ionic strengths of NaNO\textsubscript{3} were used: 0.1, 0.01, 0.001 M. For each ionic strength, six bottles were filled with 20mL of the solution and different amounts of carbon samples were added (0.05%, 0.1%, 0.5%, 1%, 5% and 10% by weight). Following this the samples were agitated for 24 hours, and the equilibrium pHs were measured with the help of a pH meter.

2.3.4 Adsorbents characterization by standard testing of adsorption from solution\textsuperscript{283}

The adsorption properties of the adsorbents were estimated by adsorption from liquid phase of four standard test substances: iodine, phenol, methylene blue and tannic acid.

In order to determine the adsorption capacity, 100 mL of the standard compound solutions were added to varying amounts of adsorbents (0.1-2g) and the
resultant slurries agitated for 24 hours at room temperature. The liquid fractions were then separated from the carbon by filtration through Whatmann No.41 filter paper, prior to analysis by a method suitable for each type of compound, described below.

Multiple data points were collected for each adsorbent-adsorbate system and correlated by the Freundlich model:

\[ q_e = \frac{x}{m} = K_F C_e^{(1/n)} \]

where,

- \( x \) = amount of solute adsorbed, mg/L
- \( m \) = adsorbent concentration, g/L
- \( q_e \) = amount of solute adsorbed per g of adsorbent, mg/g

\( n \) and \( K_F \) = constants

From the adsorption isotherms, the following parameters were calculated to characterize the adsorbents:

**Iodine Number (IN):** the amount (mg) of iodine adsorbed by 1g of adsorbent in a solution of iodine with a residual concentration of 2500 mg/L.

**Phenol Value (PhV):** the carbon dose required (g/L) to reduce the concentration of the standard phenol solution from 100 to 10 mg/L.

**Methylene Blue Number (MBN):** the amount (mg) of methylene blue adsorbed by 1g of adsorbent in solution of methylene blue with a residual concentration of 1mg/L.

**Tannin Value (TV):** the carbon dose (mg/L) required to reduce the concentration of the standard tannic acid solution from 20 to 2 mg/L.
The concentration of phenol, methylene blue and tannic acid were measured using a systronics UV-Visible spectrophotometer at 270, 613 and 275 nm, respectively (sections 2.3.1.4 and 2.3.1.5). Iodine concentration was determined by titration with sodium thiosulphate using starch as indicator.

2.3.5 Adsorbent dose variation studies

In order to find out the optimum adsorbent dose for the maximum removal of adsorbates, experiments were carried out with solutions of same concentration by varying the dose of adsorbent. Adsorbent doses ranging from 0.01 to 2.00 g were considered for all types of adsorbents.

2.3.6 Isotherm Procedure

Four adsorbents were used: BDC, RHC, WC and CAC. For isotherm studies, the adsorbents were used in a pulverized form (150-250\(\mu\)m), dried at 100°C up to 10 hours before use.

Prior to isotherm studies, minimum contact times for adsorption equilibria to become established were estimated for each adsorbent. Each experiment comprised three replicate 100 mL glass-stoppered bottles containing appropriate amount of adsorbent and 50 mL of adsorbate solutions of selected concentrations. Control flasks without the adsorbents also prepared simultaneously. Mixtures were maintained in a rotary shaker (orbitek) at constant temperature (30, 45 or 60°C). After the attainment of equilibrium the contents of each flask were filtered through a Whatmann No.41 filter paper, with the first 10mL discarded. The filtered samples were then analysed for unadsorbed solutes.
The results are presented as plots of solid phase equilibrium solute concentration expressed as milligrams of adsorbate per gram adsorbent (ordinate) versus the liquid phase equilibrium solute concentration expressed as milligrams of solute per L of solution (abscissa). These data were then represented mathematically by Freundlich, Langmuir and Redlich-Peterson isotherm equations:

- **Freundlich**
  \[ q_e = \frac{x}{m} = K_F \frac{C_e^{1/n}}{ } \]

- **Langmuir**
  \[ q_e = \frac{K_L C_e}{(1 + b C_e)} = q_m b C_e / (1 + b C_e) \]

- **Redlich-Peterson**
  \[ q_e = \frac{K_R C_e}{(1 + b_R C_e)^{\beta}} \]

### 2.3.7 Kinetic Studies

Each experiment comprised triplicate glass bottles containing selected adsorbent (0.01-2.00g) and adsorbate doses (50 mL) at a fixed pH. The bottles were kept in the mechanical shaker at a constant temperature of 30 ± 2°C. At time intervals (in minutes) of 0, 10, 20, 30, 40, 50, 60, 90, 120, ... etc, one triplicate was sacrificed for measurement of the non-adsorbed solutes. The slurries were filtered through a Whatmann No. 41 filter paper, with the first 5 mL discarded. The filtered samples were then analyzed.

### 2.3.8 pH Variation Studies

In order to find out the optimum pH for maximum removal of adsorbates experiments were carried out with solutions of same concentration but adjusted to different pH values (with 0.1M HCl or 0.1M NaOH). pH values ranging from 2-10 were considered for all types of adsorbates.
2.3.9 Desorption Experiments

Some desorption experiments were also conducted in order to explore the feasibility of recovering both the adsorbed species and the adsorbent and to elucidate the nature of adsorption processes. They were carried out as follows. After adsorption experiments using the selected adsorbent and adsorbate doses, the adsorbate loaded adsorbents were separated and washed gently with several portions of distilled water to remove any unadsorbed species. The samples were then air-dried and agitated with 0.1M solutions of HCl, AcOH, NaOH and water for a period of 10 hours and the amounts of desorbed species were determined in the usual way.