CHAPTER 2
MATERIALS AND METHODS

2.1. Materials

2.1.1. Adsorbent

The adsorbent ‘photofilm waste’ was collected from Hindustan Photofilm Industry, Udagamandalam, Tamil Nadu, India. It was ground and washed with dilute sulphuric acid to remove acid soluble impurities and soaked in 2% sodium bicarbonate solution until effervescence ceased and allowed to stand overnight in contact with 2% sodium bicarbonate solution to remove residual acid if any. The material was washed with distilled water and dried at 105 ± 5°C. The dried material was screened to get different geometrical sizes such as 0.100-0.200 mm, 0.150-0.250 mm and 0.250-0.500 mm. Adsorbent of the particle size, 0.100-0.200 mm was used for characterisation.

All the chemicals used were of analytical reagent grade, obtained from B.D.H. and E.Merck. Double distilled water was used for the preparation of solutions.

All pH measurements were made on Elico pH meter and the colorimetric estimations were carried out on ECL spectrophotometer.

2.1.2. Preparation of metal ion solutions

a) Mercury(II) chloride solution

A stock solution of 1000 mg/L of mercury(II) was prepared by dissolving 1.3540 g of mercury(II) chloride in water, acidified with 5 mL of concentrated hydrochloric acid to prevent hydrolysis and made upto 1000 mL.
b) Potassium dichromate solution

A stock solution of 1000 mg/L of chromium(VI) was prepared by dissolving 2.8300 g of dried potassium dichromate in water and made upto 1000 mL.

c) Nickel sulphate solution

A stock solution of 500 mg/L of nickel(II) was prepared by dissolving 2.2395 g of nickel sulphate (NiSO₄·6H₂O) in water, acidified with 1 mL of concentrated nitric acid to prevent hydrolysis and made upto 1000 mL.

d) Lead nitrate solution

A stock solution of 1000 mg/L of 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 upto 1000 mL.

2.1.3. Industrial wastewaters

Industrial wastewaters were collected from chloralkali industry [for Hg(II)] at Mettur, chromium and nickel plating industries [for Cr(VI) and Ni(II)] and radiator manufacturing industry [for Pb(II)] at Coimbatore area of Tamil Nadu, India and were immediately subjected to characterisation and treatment.

2.2. Analytical procedures

2.2.1. Characterisation of the adsorbent

a) Apparent density[103]

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 weight (g) divided by the volume (mL) gave the apparent density (g/mL) of the adsorbent.
b) Mechanical moisture content[103]

Five gram of the adsorbent placed in a petriplate was heated in a ventilated drying oven at 120°C for 2h. After heating the plate was quickly covered, cooled in a desiccator and weighed. The loss in weight of the adsorbent gave the mechanical or hygroscopic moisture.

c) Loss on ignition[103]

The adsorbent of one gram weight was placed in a weighed silica crucible. It was ignited at 1000°C for 4h. Then it was kept in a desiccator for 1h. The final weight was measured. The weight difference corresponds to loss on ignition.

d) pH of the adsorbent

The adsorbent (5.0g) was placed in a one litre beaker. 150 mL of freshly boiled and cooled water (adjusted to pH 7.0) was added and heated to boiling. After digesting for 10 min, the solution was filtered while hot, rejecting the first 10 mL of the filtrate. The remaining filtrate was cooled to room temperature and the pH was measured using a pH meter.

e) Zero point charge (pH_{spc}) [104]

The adsorbent (100 mg) suspension (particle size 0.100-0.200 mm) was prepared in 50 mL solution of NaNO₃ electrolyte of concentration, approximately 10⁻³ M. Aliquots of suspension were adjusted to various pH values with dilute sodium hydroxide and nitric acid solutions. After 60 min of equilibration the initial pH values were measured. Then 1.0 g of NaNO₃ was added to each aliquot to bring final electrolyte concentration to about 0.45M. After an additional 60 min equilibration, the final pH was measured. The results were plotted with ΔpH (final pH - initial pH) against final pH. The pH at which ΔpH = 0 yielded pH_{spc}. 
f) Surface area

The surface area of the adsorbent was measured at liquid nitrogen temperature using direct reading CARLO EBA SORPTOMATIC - 1800, by assuming that the adsorbed nitrogen forms a monolayer and possess a molecular cross sectional area of $16 \text{ A}^2$.

2.2.2. Analysis of adsorbent

a) Estimation of aluminium and iron

The concentrations of aluminium and iron in the adsorbent were determined using Atomic Absorption Spectrophotometer (Perkin Elmer 403 Spectrophotometer).

b) Estimation of cellulose [105]

To a known amount of adsorbent (1.0g) in a test tube, 3 mL of acetic/nitric reagent (Prepared by mixing 150 mL of 80% acetic acid and 15 mL of concentrated nitric acid) was added and mixed well in a vortex mixture. It was then heated in a waterbath at 100°C for 30 min, cooled and centrifuged for 15-20 min. The residue was washed with distilled water and mixed with 10 mL of 67% sulphuric acid and allowed to stand for 1h. One mL of the above solution was diluted to 100 mL and 1 mL of this diluted solution was mixed with 10 mL of anthrone reagent (200 mg of anthrone in 100 mL of concentrated sulphuric acid). It was then heated on a waterbath for 10 min, cooled and absorbance was measured at 630 nm against a reagent blank. A calibration graph for 40-200 µg of cellulose was prepared by following the above procedure and the concentration in the sample aliquot was established by referring to the calibration graph.
c) Estimation of lignin [105]

A known amount of adsorbent (1.0g) was treated with distilled water and heated at 100°C for 3 h. The process was repeated thrice. The residue obtained was heated with 1:2 Ethanol - benzene (v/v) at 70°C for 6 h. The residue was then washed with dilute sulphuric acid and water. The final residue obtained was dried and weighed which gave the amount of lignin present in the adsorbent.

2.2.3. Analysis of adsorbate metal ions

a) Estimation of mercury [106]

Mercury(II) was estimated spectrophotometrically using rhodamine 6G reagent. A suitable aliquot of the solution containing not more than 25 µg 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 KI + 5g of potassium hydrogen phthalate made upto 250 mL with water) 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 blank. A calibration graph for 5-25 µg of mercury(II) was prepared by following the above procedure and the concentration in the sample aliquot was established by referring to the calibration graph.

b) Estimation of chromium(VI)[107]

Hexavalent chromium was determined spectrophotometrically by diphenyl carbazide method. To a series of standard solutions of chromium(VI) (5-50 µg), 10 mL of 1M H₂SO₄,2 drops of phosphoric acid and 1 mL of diphenyl carbazide solution (0.5% in acetone) were added and made up to 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 aliquot was established by referring to the calibration graph.

c) Estimation of nickel [108]

Nickel(II) was estimated spectrophotometrically using dimethyl glyoxime (DMG). To a series of standard solutions containing less than 200 µg of nickel(II), 10 mL of 20% sodium citrate solution and 2 mL of 0.05M iodine solution were added and mixed followed by the addition of 4 mL of DMG solution. The contents were made upto 50 mL with water. 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) adsorbed was obtained from the calibration curve.

d) Estimation of lead [109]

Lead (II) was estimated spectrophotometrically using PAR reagent [4-(2-Pyridylazo) resorcinol]. A suitable aliquot of the sample solution containing not more than 50 µg of lead(II) was transferred into a 25 mL volumetric flask. 10 mL of ammonia-ammonium chloride buffer solution (16.9 g NH₄ Cl + 123 mL liquor ammonia made up to 25 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 5-50 µg of lead was prepared by the above procedure and the concentration in the sample aliquot was established by referring to the calibration graph.

2.2.4. Characterisation of industrial wastewaters

The industrial wastewaters obtained from various industries were subjected to the analysis of parameters such as pH, turbidity, conductivity, total solids,
chemical oxygen demand (COD), chlorides, sulphate, calcium, sodium and iron. The amount of the above parameters were determined using standard analytical procedures[107].

2.3. Batch mode studies

The batch experiments were carried out by taking 50 mL of the respective metal ion solution/effluent and known amount of adsorbent in reagent bottles of 100 mL capacity. The bottles were agitated at 120 rpm using a mechanical shaker at room temperature (27 ± 2°C). The adsorbent and adsorbate solutions were separated by centrifugation at 3000 rpm for 5 min.

The studies such as effect of pH on metal ion removal, effect of agitation time and initial metal ion concentration, effect of adsorbent dosage and effect of particle size of adsorbent were conducted using aqueous metal ion solutions. Control experiments were carried out without adsorbent in order to give correction for metal ion adsorption on the walls of the container. It was found that there was negligible adsorption of metal ions on the container walls.

2.4. Desorption studies

The metal loaded adsorbent present in the adsorption experiment was separated by centrifugation and the supernatant was drained out. The adsorbent was given a gentle rinsing with water and the rinsed water was quickly removed by suction filtration to remove any unadsorbed metal ion. 50 mL water was added to the metal loaded adsorbent and pH was adjusted using dilute nitric acid or sodium hydroxide solution. Then they were agitated for the equilibrium time of the respective metal ion. The desorbed metal ion in the solution was separated from the adsorbent by centrifugation and analysed for the respective metal ion concentration.
2.5. Treatment of industrial wastewaters

The study of effect of adsorbent dose was carried out to remove the respective metal ions from the wastewaters collected from the respective industries. The concentration of metal ions present in the wastewaters were adjusted. In the case of chloralkali wastewater the concentration of mercury was found to be very low and hence it was spiked with mercury(II) chloride. The study was carried out with same concentration of chromium(VI) present in the chromium plating wastewater. The wastewaters collected from nickel plating and radiator manufacturing industries were found to contain large quantities of the respective ions and hence appropriate dilutions were made in the case of nickel and lead. In each case different amounts of adsorbent were added to 50mL of wastewater and equilibrated for the effective equilibrium time found in the batch study. Then the supernatant was centrifuged and analysed for the respective metal ion concentrations.
2.6. Fixed-bed adsorption studies

Fixed-bed column experiments were carried out using an experimental arrangement as shown in the figure.

Schematic representation of the column

[Diagram of a fixed-bed adsorption column with labeled parts: Polythene reservoir, Polythene tube, Flow regulating valve, Glass column, Glass wool, Adsorbent, Container for collecting effluent, Iron stand, Test solution containing metal ion under study]
The adsorbent of particle size 0.250-0.500 mm was used for the removal of mercury(II), chromium(VI), nickel(II) and lead(II) in glass column of internal diameter 1.4 cm. Clean glass wool was placed at the bottom and top of the column to retain the adsorbent and prevent disturbance of the bed by high flow rates. The adsorbent was slowly transferred into the column in the form of slurry with distilled water. After complete transfer, the bed was washed five times with water. Solution of metal ions under study was placed in a polythene reservoir as shown in the figure and the flow rate was adjusted with a flow regulating valve. Frequent checks were made at regular intervals to correct any change in flow rate. The pH of the metal ion solution was maintained at a value where maximum adsorption was observed in the batch studies.

In the column study the effect of flowrate, bed height and metal ion concentrations were studied. In each case 50 mL of effluent from the column were collected in a series of volumetric flasks and individually analysed for respective metal ion under study.

All the experiments in batch mode and fixed-bed studies were conducted in duplicate and the mean values are presented. The maximum deviations in the experiments were within 5%.