

Chapter III

Experimental Section

3.1 Identification of Plant /Animal Based Raw Materials

Prosopis juliflora barks (plant based), generated as litter during timbering processes and goat dung which are invariably available had been chosen for the present study. The basis of these choices relied upon the prevalent availability of these materials.

Prosopis juliflora tree grows to a height of upto 12m (39 ft) and has a trunk with a diameter of upto 1.2 m. Its vegetation falls in dry lands and arid regions of India. It is one of the most tolerant species in saline, alkaline soils and also capable of growing in water logged areas. Being an aggressive intruder, it affects native vegetation grabbing rangelands⁹³. The basic components of PJB include hemicellulose, lignin, lipids, proteins, simple sugars, water, hydrocarbons and starch, containing variety of functional groups (acetamido, alcoholic, carbonyl, phenolic, amido, amino, sulphhydryl groups). These groups are reported to possess better ability to bind dyes and heavy metal ions⁹⁴.

Goats are one of the oldest domesticated animals, which have been reared for their milk, meat, hair and skins. Apart from the above advantages, goats produce manure daily, equal to about 5% of their body mass where the pelletized droppings have 60–70% moisture⁹⁵.

Both *Prosopis juliflora* Barks and Goat Dung were collected from Somanur, Coimbatore, Tamil Nadu, India for the sorption studies. The collected precursors were cleaned carefully and ground into small pieces and shade dried for a period of 12 days. Later, the materials were pulverized using electrical mixer. The collected raw and sieved materials are depicted in Figure 3.1 and 3.2.



Figure 3.1 *Prosopis juliflora* Bark (PJB)

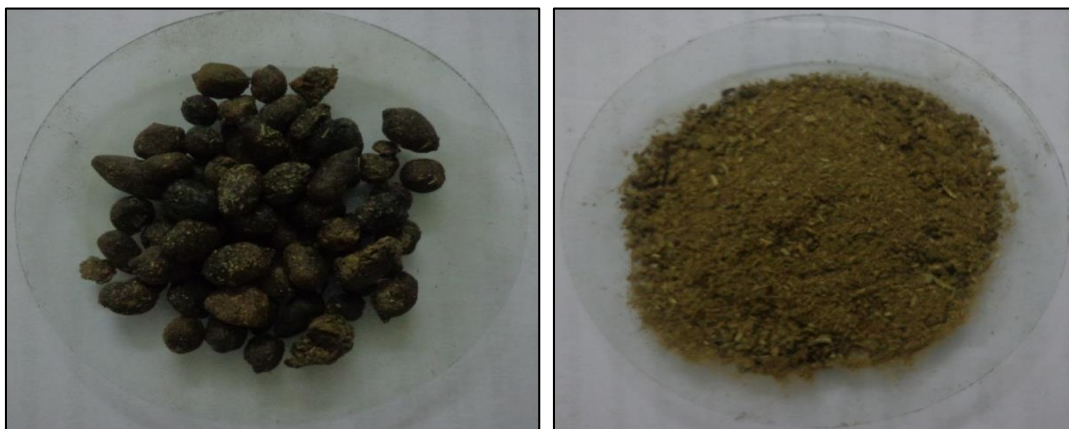


Figure 3.2 Goat Dung (GD)

3.2 Activation of Raw Materials

The common activating agents used for preparing activated carbon included sulphuric acid, phosphoric acid and potassium hydroxide. As the perusal of literature study indicated that the employment of aforesaid chemicals to enhance the sorption properties, *Prosopis juliflora* bark and Goat Dung were subjected to respective treatments.

Crushed *Prosopis juliflora* barks were boiled in 35% phosphoric acid for a period of 24 hours followed by decantation and the biomass was carbonised in a muffle furnace (YORCO) at 600°C for one hour in vacuum. Further activation at a higher temperature of 800°C for 10 minutes was ensured. The activated carbon thus obtained, was washed with

distilled water to remove residual acids present in it till the washed solution reached a neutral pH. Later, dried in a hot air oven at 110°C for a period of 4 hours. The drying was continued until a constant weight was reached.

Powdered goat dung were soaked in 1:1 sulphuric acid and kept for 24 hours at room temperature. Later, air dried and carbonized in muffle furnace at 500°C for one hour. The carbonized material was powdered and subjected to activation for about 10 minutes at 650°C. The prepared material was washed with distilled water several times to attain neutral pH and dried further.

The lumps of activated carbons derived from *Prosopis juliflora* Bark and Goat Dung were crushed and sieved using Scientific Test Molecular Sieves (manufactured by JAYANT Scientific Instruments Co., Mumbai) to 85 BSS mesh size and referred to as *Prosopis juliflora* bark activated carbon and goat dung activated carbon and labelled as PJBAC/GDAC respectively.

Few pilot experiments pertaining to the removal of the identified dye molecules/metal ion employing the modified carbons with specific chemicals were conducted under native conditions, where an order of sorption efficiency was exhibited as follows:

PJBAC - Phosphoric acid > Sulphuric acid > Potassium Hydroxide

GDAC- Sulphuric acid > Phosphoric acid > Potassium Hydroxide

Thenceforth, phosphoric acid activated PJBAC and sulphuric acid activated GDAC were subjected to batch equilibration studies and preparation of respective composites.

3.2.1 Preparation of Metal Nanocomposites

The composites of PJBAC and GDAC were prepared by an auto combustion method. A mixture of 2 moles of ferric nitrate and 1 mole of cobalt nitrate was prepared by dissolving appropriate doses of both the salts in 50 mL of distilled water each. 28 g of urea was dissolved in distilled water and added to the above solution to ensure the combustion process, followed by heating the contents in a magnetic hot plate with constant stirring using magnetic stirrer. The compound obtained is referred to as cobalt ferrite (CoFe_2O_4). Although other metal ferrites like MnFe_2O_4 and NiFe_2O_4 were reported in literature, cobalt ferrite was chosen for the present study due to its appreciable

saturation magnetization values. Being 86.1 emu/g against 78.4 emu/g, 58.1 emu/g for manganese and nickel respectively⁸⁴. 11g of both PJBAC/GDAC were added to the hot baths contains CoFe_2O_4 and the heating was further continued. Following that, the ignition of the mixture was ensured resulting in the formation of dried gel in a burnt state through self propagating combustion. The dry loose powder obtained was ground well using mortar/ pestle and stored. These synthesized materials were referred to as PJBAC- CFC and GDAC-CFC respectively.

3.2.2 Preparation of photocatalytic composite

Photocatalytic composites were prepared by dissolving 5 g of PJBAC/GDAC in 50 mL of H_3PO_4 (1M) in a beaker and agitated for 12 hours followed by the addition of 0.5 g of TiO_2 to the mixture. Then the mixtures were mechanically stirred at room temperature for 6 hours and filtered after centrifugation. The obtained masses were washed several times with distilled water until the attainment of pH 7, followed by ethanol wash and dried in a hot air oven at 105°C . These synthesized composite materials were referred to as PJBAC- TiO_2 and GDAC- TiO_2 .

3.3 Choice of Adsorbate Species

The systems under study of interest focus on removal of dyes and heavy metal ion include: Direct Brown 2, Reactive Red 152 and Copper [Cu(II)] were the adsorbate species chosen based on their frequent prevalences in textile discharges in and around Tirupur, Tamil Nadu, India

3.4 Characterization Studies

The physicochemical characteristic studies were carried out for PJBAC and GDAC.

3.4.1 pH and Conductivity

One gram each of the prepared activated carbons were transferred to 250 ml beakers and boiled with 300 mL double distilled water. The solutions were cooled and the supernatants were tested for pH and conductivity values⁹⁶ using ELICO (LI-120) pH meter and ELICO (CM 180) digital conductivity meter respectively.

3.4.2 Moisture

Moisture contents of the materials were determined by Xylene method⁹⁶ (ASTM D 2867-95). Approximately 0.25g of the activated materials were taken in 250 mL round bottom flasks. The flasks were connected with condensation tube and water receiving tube, followed by injection of 75 mL Xylene through condensation tube. The set up was regulated to constant heat, so as to ensure even collection of distillates.

Moisture contents of the distilled samples were calculated in accordance with the equation (1).

$$X = \frac{V}{m} \times 100 \quad (1)$$

where

X – Sample moisture content (mL/100 g)

(Mass calculation= water density (0.998) at 200C; 20 g/mL).

V – Volume of Water (Receiving tube) [mL]

M - Sample mass (g).

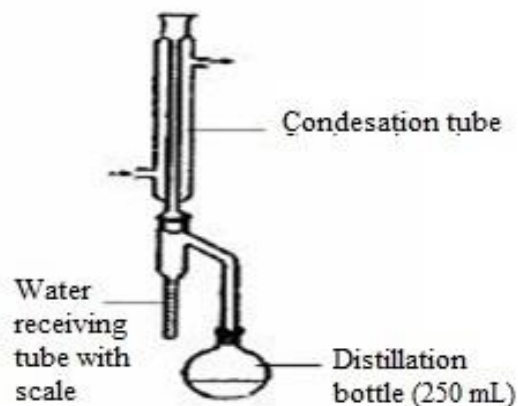


Figure 3.3 Moisture Determination Apparatus

3.4.3 Bulk Density

Specific gravity bottles of 10 mL capacity were closely packed with the materials of interest by constant tapping and stoppered with a rubber cork. The masses of the bottles along with the contents were weighed. Bulk densities were calculated by dividing the weighed masses (g) by bottle volumes (mL)⁹⁷.

3.4.4 Specific Gravity

5 g of PJBAC and GDAC were placed in small porcelain dishes, 50 ml of double distilled water was added to each and the contents were boiled gently (3 minutes) in order to expel the air. After cooling in a water bath, the suspensions were transferred to 100 ml pycnometers and weighed (W_c). Later, the pycnometers were emptied, washed well, filled with double distilled water and weighed (W_b). Calculations were done using equations (2) and (3)⁹⁷.

$$\text{Specific gravity} = \frac{\text{Weight of adsorbent (}W_a\text{)}}{\text{Volume of displaced water (}V\text{)}} \quad (2)$$

where

$$V = \frac{W_a + W_b + W_c}{\text{Density of water}} \quad (3)$$

W_a = Sample weight

W_b = Pycnometer mass filled with water

W_c = Pycnometer mass with material residue

3.4.5 Porosity

Porosities of all the chosen materials were determined from the calculated specific gravity (S) and bulk density (D) values as per equation (4)⁹⁶

$$\text{Porosity} = \frac{S-D}{S \times 100} \quad (4)$$

3.4.6 Ash Content

1 g each of carbons were kept in porcelain crucibles and placed in an electric oven at $110 \pm 5^\circ\text{C}$ for about 5 hours. Later, the crucibles were removed from the oven and the contents were ignited in an electric muffle furnace at a temperature of 530°C for 2 hours.

Later, the crucibles were cooled in desiccators and weighed. The above process of heating, cooling and weighing were repeated at 30 minutes intervals until the differences between any two consecutive weighings were less than 5 mg. The ash contents were calculated as percentages by weight⁹⁶.

3.4.7 Water Soluble Matter

0.5 g of the prepared materials were taken in 500 mL beakers, 60 ml of double distilled water was added and heated to boiling with continuous stirring (upto 30 minutes). The materials were then allowed to settle and the supernatants were filtered through gooch crucibles fitted with asbestos mats. This procedure was repeated thrice with residues in the beakers.

The combined filtrates were concentrated to less than 100 mL by heating over a water bath, later cooled and made upto 100 mL in volumetric flasks. Exactly, 50 mL of the concentrates were transferred to china dishes and evaporated almost to dryness on a boiling water bath, finally dried in an electric oven, maintained at $100 \pm 5^\circ\text{C}$, cooled in desiccators and weighed. The repeated procedures of drying, cooling and weighing were done as for ash content determined and the water soluble matter⁹⁶ was calculated using the following equation.

$$\text{Water soluble matter} = \frac{20000 X W_1}{W_2 X (100 - X)} \quad (5)$$

where

W_1 = Weight of the residue (g)

W_2 = Weight of the adsorbent (g)

X = Percentage of moisture in the adsorbent.

3.4.8 Acid Soluble Matter

Experimental and calculation procedures of acid soluble matter was carried out in a manner similar to that of studying Water Soluble Matter, the difference being the acid media i.e., 60 mL of 0.25N HCl was added in all beakers instead of double distilled water⁹⁶.

3.4.9 Ion Exchange Capacity

0.2 grams of the carbons were taken in 500 mL beakers and sufficient amounts of double distilled water were added, ensuring the complete soaking and stirring of the materials. The slurries were carefully transferred to burettes. The columns were never allowed to drain completely and the levels of the liquids were maintained at a height of about 1 cm above the materials' bed. 250 mL of 0.25 M sodium sulphate was dripped into the columns at a rate of 2 ml per minute and the out flows were collected in 500 mL conical flasks at the rate of 50 mL/5 minutes. After completion, the collected samples were titrated with standard 0.1 N sodium hydroxide solutions using phenolphthalein as indicator⁹⁸. The ion exchange capacity of the bed expressed as meq/g is given by NV/W . where,

N= Normality of NaOH solution;

V = Volume (ml) of NaOH and

W = Weight (gms).

3.4.10 Zero Point Charge (pH_{zpc})

The zero point charges were determined by solid addition method⁹⁹. To a series of 100 mL conical flasks, 45 mL each of 0.1 and 0.01 M KNO_3 were added. The acidic and basic pH values of the solutions were adjusted by adding 0.1M HCl or 0.1M NaOH. The total volumes in each flask were made exactly to 50 mL by adding 5 mL KNO_3 (0.1or 0.01 M as the case). The initial pH values were noted. Later, 1 g each of the carbons were added to the specified flasks. The suspensions were manually shaken and allowed to equilibrate for 48 hours. The pH values of the supernatant liquids were noted as pH_{zpc} .

3.4.11 Iodine Number

100 mL of 0.1N iodine solution was taken in a 250mL conical flask with 2 drops of starch was titrated against 0.05 N sodium thio sulphate solutions, the end point being blue to colourless. The burette solution value at the end point was noted as Blank (B). 0.2 g of carbons were taken in dried iodine flasks and 40 mL of 0.1 N iodine solution was added to them and shaken well for 5 minutes and filtered. 10 mL of the filtrates were titrated as before. The consumed volumes of sodium thio sulphate for the specified

carbons at the reach of end points were noted as (A) and the iodine values were calculated^{100, 101} as follows

$$\text{Iodine value} = C \times \text{Conversion Factor}$$

where $C = B - A$

$$\text{Conversion Factor} = \frac{\text{Molecular weight of the Iodine} \times \text{Normality} \times 40}{\text{Weight of the carbon} \times \text{blank}} \quad (6)$$

3.4.12 Methylene Blue Number

Methylene blue number is the milligrams of methylene blue adsorbed by 1 g of carbon. It indicates the pore diameter. To determine the methylene blue number, known weights of the activated carbons were transferred to 250 mL conical flasks. A few mL of methylene blue solution (1500 mg/L) was added to the flasks, shaken for 5 minutes, followed by further addition of methylene blue to the decolourized solutions in the flasks. The addition of the dye solution was continued by adding 1 mL at a time followed by shaking the flasks again until no colour changes were observed with the addition of 1 mL of methylene blue solution. The decolourizing capacities of the carbons were determined¹⁰² using the following equation (BIS 877-1977).

$$\text{Methylene Blue Number (mg/g)} = \frac{1.5 \times V}{M} \quad (7)$$

where, V is the volume of methylene blue (mL), M is the mass of the carbon taken (g).

3.4.13 Elemental Analysis

The percentage (by weight) of hydrogen, nitrogen, carbon, sulphur and oxygen (by difference) present in the materials were quantified by Elementary Vario EL III-Germany CHNS Analyser.

3.5 Characterization of Surface Functional Groups

The nature and concentration of surface functional groups modified through suitable thermal or chemical treatments have been determined by Boehm Method, BET, BJH, FTIR, SEM and EDAX analysis.

3.5.1 Active Sites' Determination

The amounts of oxygenated acid surface groups present in the activated carbons were determined using Boehm titration method¹⁰³. One gram of the carbon samples were placed in Erlenmeyer flasks followed by the addition of 50 mL 0.05 N basic solutions (NaOH, Na₂CO₃ and NaHCO₃). The flasks were sealed, shaken for 24 hours and filtered. 10 mL of each of the filtrates were pipetted out and to that 15 mL of 0.05 N HCl was added. The excess HCl was titrated against 0.05 N NaOH using phenolphthalein indicator. A blank titration was also performed. The amounts of acidic sites of various types were calculated on the basis that NaOH had neutralized carboxylic, phenolic and lactonic groups.

3.5.2 Bruner-Emmett-Teller and Barrett-Joyner-Halenda Analysis

Surface areas and pore characteristics of the prepared adsorbents were determined using the Bruner-Emmet-Teller (BET) and Barrett-Joyner-Halenda (BJH) plots respectively, employing nitrogen adsorption on an Accelerated Surface Area and Porosimetry System (Micromeritics, BEL, Japan, Inc), sophisticated with Belsorp Adsorption/ Desorption data Analysis software. Prior to analysis, portions of carbons were degassed for 5 hours at 120°C in N₂ environment using a Micromeritics degassing system. The pore size distribution and specific surface areas were determined via N₂ adsorption/desorption isotherms obtained at 77 K. Analyses were repeated twice, for attaining concordancy.

3.5.3 FT-IR Spectral Analysis

The carbon samples were subjected to spectral analyses (within the range of 400-4000 cm⁻¹) to determine the presence of main functional groups using Infrared Spectrophotometer (affinity-I). The spectra of both unloaded and dye loaded carbons were recorded.

3.5.4 SEM and EDAX Analyses

The surface morphologies of the prepared carbons before and after dyes and metal sorption was examined using the JEOL JFM- 6390 Scanning Electron Microscope (20 kV) under vacuum of 1.33×10^{-6} m Bar. The samples were covered with a thin layer

of platinum (10 nm) using a sputter coater (SCD 0050 – Baltec, Liechtenstein) and scanned to determine the chemical compositions. Energy dispersive X-Ray analyses were conducted.

3.5.5 TGA- DSC Analyses

TGA technique finds out selected characteristics of matter that demonstrates either mass loss or gain due to decomposition, oxidation, or loss of volatiles and assesses thermal stability at a desired temperature range. Thermal stability of the carbons was evaluated by TGA-DSC (NETZSCH JUPITOR STA 449F3) thermal analysis system. TGA curves were recorded under an N₂ atmosphere at a flow rate of 4 ml/min and a scanning rate of 20°C/min from 26°C to 1000°C.

3.6 Dyes and Chemicals Employed

Dye samples viz., Direct Brown 2 and Reactive Red 152 used as adsorbate solutions were procured from S.S. Brand colours, Tirupur, Tamilnadu, India. The details pertaining to the purchased dyes are listed in Table 3.1 and the structure of DB2 and RR152 are depicted in figures 3.4 and 3.5 respectively. All the reagents employed viz., Copper (II) chloride, TiO₂, Cobalt nitrate [Co(NO₃)₂.6H₂O], Ferric nitrate [Fe(NO₃)₃.9H₂O], urea, sodium hydroxide and sulphuric acid were of an Analytical grade and further used without purification.

Table 3.1 Properties of Dyes

Colour Index Name	Direct brown 2	Reactive Red 152
Molecular formula	C ₂₉ H ₁₉ N ₅ Na ₂ O ₇ S	C ₅₂ H ₃₀ Cl ₂ N ₁₄ Na ₆ O ₂₀ S ₆
Molecular weight	627.54	1752.11
λ_{\max}	540 nm	420nm
CI Number	22311	-
CAS Number	2429-82-5	71870-80-5
Class	Azo	Azo
Application	dyeing cotton fibres	dyeing cotton, wool, silk and nylon fibres

3.6.1 Preparation of Adsorbate Solutions

Stock solutions (1000 mg/L) of direct brown 2, reactive red 152 and Cu(II) was prepared by dissolving 1g of both the dyes and 2.6826 g of copper (II) chloride dihydrate in 1000 ml of doubly distilled water (Distillon 4DQ) separately. All weighings were taken using Shimadzu electronic balance. Aliquots of the adsorbate solutions of varying concentrations for dyes (25- 150 mg/L: 25 mg/L interval) and metal ion (4- 20 mg/L: 4 mg/L interval) were prepared by progressive dilutions of the stock solutions. Buffers pH 4 and 9 were prepared for the standardization of pH meter. HCl and NaOH were employed acidic and alkaline media to adjust pH values. pH values of prepared aliquots and carbons were noted.

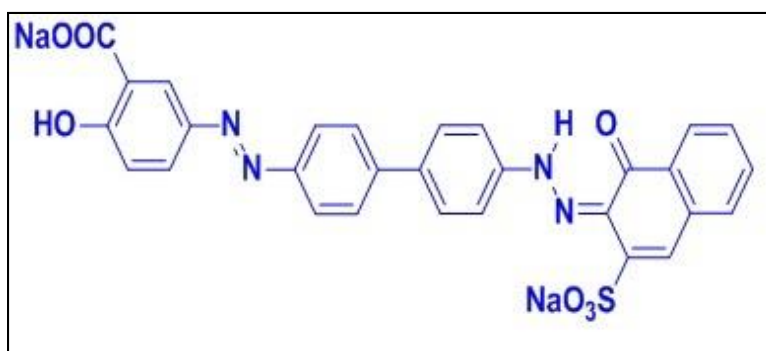


Figure 3.4 Structure of Direct Brown 2

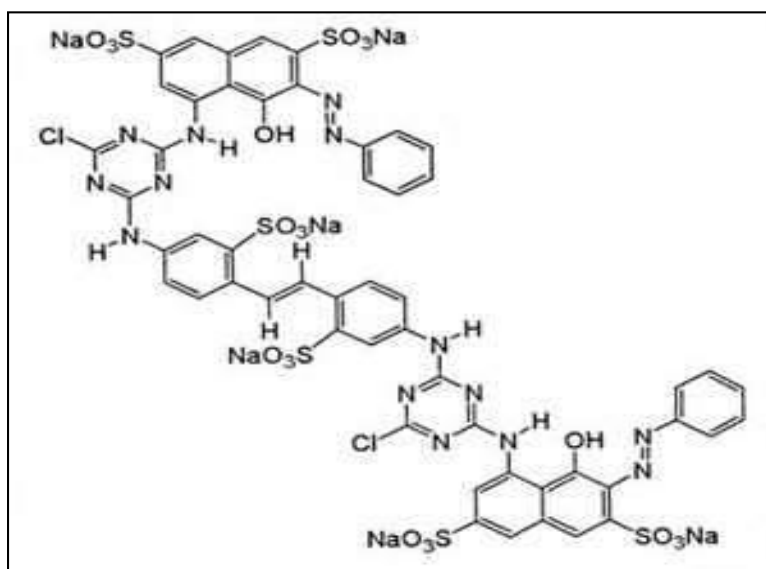


Figure 3.5 Structure of Reactive Red 152

3.7 Batch Equilibration Method

50 ml of DB2, RR152 and Cu(II) aqueous solutions were taken in Erlenmeyer flasks along with the specified treated sorbents and agitated in a mechanical shaker (KEMI) to define the role of variable parameters viz., dosages of the modified carbons (50-250 mg) for dyes and (20-100 mg) for metal ion, initial concentration of the aqueous dyes (25mg/L-150mg/L) and metal (4mg/L-20mg/L) solutions, predetermined time intervals between the sorbate and the sorbents species (10-120 minutes), pH of the medium (2-10), temperature environments (293K-333K) and influence of cations (Mg^{2+} , Na^+ & K^+), anions (Cl^- , NO_3^-), co-ions (Zn^{2+} , Cr^{6+}) to assess the sorption efficiencies. While studying the effect of one factor, the values of other parameters were ensured to be constant.

3.7.1 Analysis of the Samples

The initial and residual concentrations of DB2 and RR152 subjected to pilot studies were measured, using UV-Visible spectrophotometer (Lab India UV 3000+) (Figure 3.6). The initial and agitated samples of Cu(II) ions were analysed using Atomic Absorption Spectrophotometer: Shimadzu (AA 6200) (Figure 3.7) at a wavelength and slit width of 213.9 nm and 0.7 nm respectively by Acetylene method. Duplicate experiments were conducted to ensure the reproducibility of values within $\pm 2\%$.

The percentage of adsorption of sorbate species from aqueous solutions were estimated by the following equation¹⁰⁴

$$\% \text{ adsorption} = \frac{C_i - C_e}{C_i} \quad (8)$$

The amounts of adsorbed molecules (q) were calculated by the mass balance equation.

$$q = \frac{V(C_i - C_e)}{W} \quad (9)$$

where, V is the volume of the solution (l), W is the mass of the carbon (g), C_i and C_e are the initial and equilibrium concentrations (mg/L) of dyes and metal ion respectively.



Figure 3.6 UV-Visible Spectrophotometer (Lab India UV 3000 +)



Figure 3.7 Atomic Absorption Spectrophotometer (Shimadzu AA 6200)

3.8 Statistical Studies

Pearson Moment Coefficient Method was employed to correlate the relationship between adsorbed dyes/metal ion and optimized variable parameters. The extent of statistical fit was verified using the output variable tools viz., ANOVA, Pearson Correlation and descriptive analysis with significance based on 95% confidence level using IBM SPSS Statistics 20 software.

3.9 Column Studies

The results of batch equilibration experiments insist the feasibility and compatibility of the derived carbons, thence they were followed by column studies to quantify the sorbent characteristics and assess their efficiencies in the continuous column running¹⁰⁵.

Fixed-bed columns, made of cylindrical glass tube (6 cm inner diameter and 30 cm height) were packed with 40 gm of PJBAC between two supporting layers of glass wool, spreaded with the glass beads at the bottom layer of glass wool. The carbons were loaded from the top and allowed to settle by gravitational force.

Dye solutions of varying initial concentrations were poured into the columns and the flow rates were adjusted by collecting varying volumes of the residual concentrations at preset time intervals depending on the systems' frame work. Performance of a series of column running, based on trial and error method, led to the choice of carbons exhibiting maximum percentage removal of dyes and Cu(II) under optimized conditions for short term/ long term analyses.

3.9.1 Desorption Studies

Desorption experiments were carried out to investigate the possibilities of recycling the loaded carbons with 0.1N HCL as desorbing agent. Mixtures of 50 mL 0.1N HCL and 1g of loaded PJBAC and GDAC were shaken at 200 rpm in a mechanical shaker for 1 hour to attain equilibrium. After centrifugation, the supernatant solutions were tested for the presence of dye molecules and metal ions using UV-Visible spectrophotometer/Atomic Absorption Spectrophotometer in order to determine the percentage of desorption with the following equation¹⁰⁶.

$$\text{Desorption efficiency} = \frac{\text{Amount desorbed}}{\text{Amount adsorbed}} \times 100 \quad (10)$$

3.9.2 Regeneration Studies

Regeneration of the spent carbons was studied to explore the possibility of their reuse. Desorption of adsorbed dye using doubly distilled water imply weak bonding between dye-sorbent molecules. The present work had employed hydrochloric acid of varying molar concentrations (0.01 to 0.05M) as desorbing for DB2, RR152 and Cu(II) loaded PJBAC/GDAC at a contact period of one hour. The desorbed PJBAC and GDAC were washed several times with double distilled water until the pH values of the washings were almost neutral. The leached out PJBAC and GDAC were dried in an Air oven at 100±5°C after the proper filtration and reused for sorption studies. Repeated adsorption and desorption cycles were conducted at preset time intervals for three consecutive cycles.

3.10 Treatment of Industrial Wastewaters with PJBAC and GDAC

Textile effluents discharged from Texwell dyeing industry located at Tirupur, Tamil Nadu, India with the chosen sorbate species in their wastewaters were collected and subjected to treatment using PJBAC and GDAC. Based on the pilot batch results, agitations of effluent systems were experimentally verified at appropriate carbon dosages with specification to 100 mg/L initial concentration under the conditions of predetermined time intervals and pH 7. The agitated samples were analyzed for the residual concentrations against the initial concentration.

3.11 Adsorption Isotherms

Adsorption isotherms are the most important data that explain the nature of adsorption process. They describe the relation between the equilibrium concentration of adsorbate in solution and that adsorbed onto the sorbent material¹⁰⁷. The process of adsorption is usually expressed as graphical plots, plotted between the amounts of sorbate (x) adsorbed on the surface of adsorbent (m) at variables¹⁰⁸. A number of isotherm models are available that describe the equilibrium pattern of adsorption process. In this present study, the mathematical isotherm models developed by Langmuir, Freundlich, Tempkin and Dubinin- Kaganer- Radushkevich were applied to the systems in order to understand the sorption mechanism and dynamics.

3.11.1 Langmuir Isotherm

The Langmuir isotherm is based on the following assumptions¹⁰⁹

- Availability of fixed vacant sites
- Uniformity in the size of the sites
- Capability of the site to hold one sorbate molecule during adsorption process
- Lack of interaction between sorbate molecules and neighbouring sites
- Monolayer adsorption

The Langmuir isotherm equation is as follows

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \quad (11)$$

where, q_e is the equilibrium concentration of dyes/metal ion in solid phase (mg/g), C_e is the equilibrium concentration of dyes/metal ion in liquid phase (mg/L), q_m is the monolayer adsorption capacity of the adsorbent (mg/g) and b is the Langmuir constant (L/g) related to free energy of adsorption. The Langmuir constants q_m and b can be determined from the slope and intercept of the linear plot of C_e/q_e versus C_e , respectively.

3.11.2 Separation Factor (R_L)

Further analysis of Langmuir equation can be made on the basis of the dimensionless equilibrium parameter for the separation factor (R_L) which is given by¹¹⁰

$$R_L = \frac{1}{(1 + b C_i)} \quad (12)$$

Where, C_i is the initial concentration of the adsorbate. The isotherm type is indicated by R_L values as shown below:

• $0 < R_L < 1$ (favourable), • $R_L > 1$ (unfavourable), • $R_L > 1$ (linear) and • $R_L > 0$ (irreversible).

3.11.3 Freundlich Isotherm

In 1906, Freundlich proposed an isotherm called Freundlich isotherm based on the assumption that uptake of adsorbate takes place on a heterogeneous surface with multilayer adsorption and the amount of sorbate adsorbed increases infinitely with the increase in concentration. The Freundlich equation is given by,

$$q = K_F C_e^{1/n} \quad (13)$$

A linear form of above equation is used to calculate the constants 'K_F' and 'n'

$$\log q_e = \log K_F + 1/n \log C_e \quad (14)$$

Where, K_F is a constant related to adsorption capacity of the adsorbent (mg/g), $1/n$ and n is an empirical parameter related to intensity of adsorption. The value of n varies with the heterogeneity of adsorbent and n value of 1-10 indicates favourable adsorption¹¹¹.

The Freundlich constants K_F and n are evaluated from the intercept and slope of the linear plot of $\log q_e$ versus $\log C_e$ respectively.

3.11.4 Tempkin Isotherm

Tempkin isotherm is generally used for heterogeneous surface energy systems (non-uniform distribution of sorption heat). Tempkin and Pyzhey (1940) assumed that (i) occupation of surface active sites is inversely related to heat of adsorption indicated by a declining straight line at different initial concentrations and (ii) adsorption is characterized by an even distribution of binding energies, upto some maximum binding energy.

The linearized form of Tempkin isotherm equation is¹¹²

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (15)$$

where,

$$B_T = RT / b_T$$

T = Absolute temperature (K)

R = Universal gas constant (8.314 J/mol K).

The constant b_T and A_T is related to the heat of sorption and equilibrium binding constant corresponding to the maximum binding energy.

3.11.5 Dubinin- Kaganer-Radushkevich (DKR) Isotherm

DKR isotherm was applied to estimate the porosity apparent free energy of the studied systems and the characteristics of adsorption. The DKR isotherm can be used to describe adsorption on heterogeneous surfaces. It is a more generalized model when compared to other aforesaid models. This model assumes a monolayer adsorption, to evaluate the maximum sorption capacity and distinguish between physisorption and chemisorption of dyes/metal ions¹¹³. The linear form of the DKR isotherm equation is¹¹⁴

$$\ln q_e = \ln q_s - \beta_{DR} \varepsilon^2 \quad (16)$$

where, q_e (mol/g) is the amount of dye adsorbed per unit weight of the adsorbent, q_s (mol/g) is the theoretical saturation sorption capacity, β_{DR} (mol²/J²) is the constant related to mean free energy of sorption per mole of the sorbate and ε is Polanyi potential,

which is equal to $RT \ln(1+1/C_e)$. R is the gas constant expressed in $\text{J mol}^{-1} \text{ K}^{-1}$ units and T is the absolute temperature.

The values of q_s and β_{DR} are obtained from the linear plot of $\ln q_e$ versus ε^2 . The constant β_{DR} is related to the mean free energy E (kJ/mol) of sorption per molecule of the sorbate when it is transferred to the sorbent surface from the solution media. It is calculated using the relationship.

$$E = \frac{1}{\sqrt{2\beta_{DR}}} \quad (17)$$

The magnitude of E is useful for estimating the mechanism of the adsorption reaction. In the case of $E < 8 \text{ kJ mol}^{-1}$, the adsorption follows physical sorption. If E is in the range of $8\text{--}16 \text{ kJ mol}^{-1}$, adsorption is governed by ion exchange mechanism, while the values of $E > 16 \text{ kJ mol}^{-1}$ refer to the adsorption by particle diffusion¹¹⁵.

3.12 Adsorption Kinetics

Adsorption kinetic studies describe the uptake rate of sorbate molecules by adsorbent and the reaction pathways of adsorbate-adsorbent interaction until the attainment of equilibrium had occurred. In the present work, kinetic studies were determined by applying pseudo-first order, pseudo-second order, Elovich and Intraparticle models.

3.12.1 Pseudo-first order model

Lagergren (1898) presented a first-order rate equation to describe the kinetic process of liquid-solid phase adsorption. The pseudo-first-order equation is generally expressed as follows;

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (18)$$

where, q_e and q_t are the amount of dye molecules/metal ion adsorbed on adsorbent surface at equilibrium and at time t (mg/g) respectively and k_1 is the pseudo-first order rate constant (1/min). The values of k_1 and q_e are calculated from the slope and intercept of the linear plot of $\log (q_e - q_t)$ versus t respectively.

3.12.2 Pseudo-second order model

This model is based on the assumption that the rate of adsorption is proportional to the square of the number of unoccupied sites. A linear form of the pseudo-second-order adsorption kinetic rate equation (Ho and McKay, 2000) is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (19)$$

where k_2 (g/mg /min) is second order rate constant. A plot of t/q_t versus t (Figures 4.36-4.38) gives a straight line, and q_e and k_2 are calculated from gradient and intercept of the line, respectively

The best-fit among the kinetic models was assessed by the sum of squares of errors (SSE) values. It is assumed that the model which gives the lowest SSE values is the best model for the particular system. The SSE values were calculated by the equation:

$$SSE = \sqrt{\frac{\sum (q_{e, \text{exp}} - q_{e, \text{cal}})^2}{N}} \quad (20)$$

where, subscripts “exp” and “cal” are the experimental and calculated data respectively and N is the number of data points.

3.12.3 Elovich Model

Elovich equation has been applied satisfactorily to systems in which the adsorbing surface is heterogeneous. The Elovich model equation is generally expressed as¹¹⁶

$$qt = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (21)$$

where

α is an initial adsorption rate (mg/ g min)

β is the desorption constant (g/mg) related to external surface area and activation energy of adsorption. The kinetic constants α and β were calculated from the intercept and slope values of the linear plot of q_t vs $\ln t$.

3.12.4 Intraparticle diffusion model

Intra particle diffusion model gives an insight to predict the nature of the sorption process. As a solid-liquid adsorption process involve solute transfer from bulk solution to sorbent surface, it is said to be influenced by boundary layer diffusion/internal diffusion or both. An intraparticle diffusion coefficient (k_{id}) furnishes the information regarding driving force of sorbent species. It is calculated from the following equation¹¹⁷.

$$q_t = K_i t^{1/2} + C \quad (22)$$

where K_i (mg/g/min) is the intraparticle diffusion rate constant and C (mg/g) is the thickness of the boundary layer. The values of K_i (intra-particle diffusion rate constant) and C (boundary layer thickness) are obtained from the slopes and intercepts of the plot q_t vs $t^{1/2}$.

3.13 Activation Parameters

Activation energy terms are best regarded as temperature driven parameters involving the sensitivity of the reaction rates. Wherein the calculations of the changes in standard free energies (ΔG°), enthalpies (ΔH°) and entropies (ΔS°) of the adsorption systems are done to determine the possibility and feasibility of the reactions. The thermodynamic parameters of the adsorption process were determined from the experimental data obtained at various temperatures using the equations

$$\Delta G^\circ = -RT \ln K_c \quad (23)$$

where, K_c is the equilibrium constant, calculated using the equation $K_c = q_e / C_e$. q_e is the amount of dye molecule/metal ion adsorbed on the adsorbent per litre of the solution at equilibrium, C_e is the equilibrium concentration of the dye/metal solution, T is the absolute temperature(K), R is gas constant. The change in enthalpy and entropy of adsorption were calculated were calculated using Vant hoff's equation¹¹⁸:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (24)$$

The values of (ΔH°) and (ΔS°) are obtained from the slope and intercept of $\ln K_c$ versus $1/T$ plots. Finally, the ΔG° value is calculated by the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (25)$$