

Chapter III

Experimental Section

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3.1 Identification and Collection of Raw Materials

Eco based green materials are biocompatible, biodegradable, nontoxic, economically viable, abundant, indigenous, safe to handle with appreciable regeneration capacity. On the basis of thorough investigation of the literature studies, three plant and one animal origin a total of four eco-friendly materials were identified. *Camellia Sinensis* stem (tea stem), *Elaeocarpus tectorius* seed (agricultural waste), *Vicia faba* husk (agricultural waste) and *Gallus gallus domesticus* beaks (poultry farm waste) have been chosen for the present study. The stem, seed, husk and hen beaks had been selected on the basis of their bulk availability of being thrown as litter. Seldom work had been reported regarding their sorption capacities. The identified plant materials had been collected from a place called Balacola in Ootacamund, Tamil Nadu, India.

3.1.1 *Camellia sinensis* Stem (CSS)

Camellia sinensis is an evergreen shrub / small tree, usually trimmed to 2 m (6.6 ft), being cultivated for its leaves (fig 3.1). The flowers are yellow-white, 2.5 – 4 (0.98–1.57 inch) in diameter, approximately with 7 to 8 petals¹. The stem material, discarded as litter, during winter seasons were employed as the sorbent material.

3.1.2 Scientific Classification:

Family	: Theacea
Genus	: <i>Camellia</i>
Species	: <i>sinensis</i>
Kingdom	: Plantae
Clade	: Angiosperms, Eudicots, Asterids
Order	: Ericales



Figure 3.1 *Camellia sinensis* shrub

3.1.3 *Elaeocarpus tectorius* Seed (ETS)

Elaeocarpus is a tropical evergreen tribal tree of Nilgiris, *Elaeocarpus tectorius* is a wild edible fruit (fig 3.2) broadly employed for therapeutic purpose, mostly used by various ancient tribes for the treatments of leprosy, pneumonia, rheumatism, ulcers, piles, and dropsy². Its roots contain alkaloids, terpenoids, flavonoids possessing curative properties against tuberculosis, headache, arthritis, heart disease, asthma, back pain and diarrhoea. The seeds of these fruits thrown as litter, had been utilized in the present work.

3.1.4 Scientific Classification

Family	: <i>Elaeocarpaceae</i>
Genus	: <i>Elaeocarpus</i>
Species	: <i>tectorius</i>
Kingdom	: Plantae
Clade	: Angiosperms, Eudicots, Rosids
Order	: Oxalidales



Figure 3.2 *Elaeocarpus tectorius* fruit

3.1.5 *Vicia Faba* Husk (VFH)

Vicia faba, known as broad bean, is a stiff / erect plant of 0.5 to 1.8 metres (1.6 to 5.9 ft) tall, with stems that are square in cross-section. The leaves are 10 to 25 centimetres (3.9 to 9.8 inch) long. These broad beans have a long tradition of cultivation in old agriculture as pulses. The beans are deseeded from their pods for consumption³ (fig 3.3a). These pods thrown as litter had been employed for the current study (fig 3.3b).

3.1.6 Scientific Classification

Family	: <i>Fabaceae</i>
Genus	: <i>Vicia</i>
Species	: <i>faba</i>
Kingdom	: Plantae
Clade	: Angiosperms, Eudicots, Rosids, Tracheophytes
Order	: Fabales



Figure 3.3 (a) *Vicia Faba* Bean



Figure 3.3 (b) *Vicia Faba* Husk

3.1.7 *Gallus gallus domesticus* Beaks (GGDB)

Hen (*Gallus gallus domesticus*) is a type of domesticated fowl, a subspecies of the red jungle fowl. It is one of the most common and widespread domestic animals. The beaks of *Gallus gallus domesticus* (GGDB) usually discarded as litter material had been chosen for the investigation. Hen beaks were collected from poultry farm located at Namakkal, Tamil Nadu, India.

3.1.8 Scientific Classification:

Kingdom	: Animalia
Phylum	: Chordata
Class	: Aves
Order	: Galliformes
Family	: Phasianidae
Genus	: <i>Gallus</i>
Species	: <i>G. gallus</i>
Subspecies	: <i>G.g. domesticus</i>

3.2 Categorization of Raw Materials

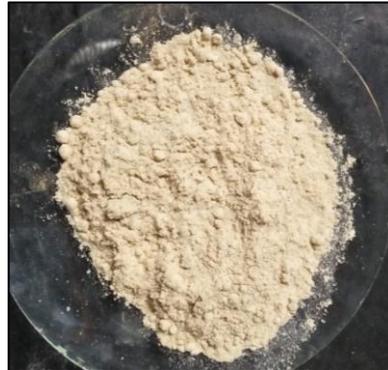
The collected materials [(CSS), (ETS), (VFH), (GGDB)] were cleaned, crushed into small pieces, washed well with doubly distilled water and completely sun dried. Later, the materials were pulverized in an electrical mixer, sieved into various mesh sizes (85 BSS, 72 BSS, 52 BSS, 36 BSS and 22 BSS) using Scientifically Tested Molecular Sieves (JAYANT Scientific Instruments Co., Mumbai). The pictorial representations of collected raw materials and their categorized counterparts (0.18 mm) are shown below.



CSS



ETS



GGDB



VFH

3.3 Microscopic Analysis

Particle sizes of the sieved materials (CSS, ETS, VFH and GGDB) were determined through microscopic studies. An Ocular micrometre with a dimension of 10 X was attached to the Binocular Microscope (Optica make, Model- CX21I), where each division in the micrometre scale is 0.01 mm. Measurements of length and breadth of fifteen granular particles had been recorded as no two single particles were alike. Among which 0.18mm particle size is chosen for the Batch Equilibration studies.

3.4 Choice of Adsorbate Species

Anions like Phosphate [PO_4^{3-}], Nitrate [NO_3^-] and Sulphate [SO_4^{2-}] were chosen for the present research work, based on their prevalent discharges in laundry units located in and around Coimbatore/Ootacamund, Nilgiris, Tamil Nadu, India.

3.5 Materials' Modifications

Crystallinity reduction and inclination in porosity / surface areas can be brought by adopting suitable modifications of the identified materials. Generally, chemically modified adsorbents exhibited higher adsorption capacities on anions than their counterparts. Hydrochloric acid, Sulphuric acid, Phosphoric acid, Formaldehyde and Sodium hydroxide were employed as modifying agents⁴.

Sieved CSS, ETS, VFH and GGDB were boiled for three hours with 1L of 0.1N prepared solution to enhance the sorption properties. Several washings with double distilled water was ensured to maintained at neutral pH. The modified material was soaked in double distilled water for 3 hours to ensure swelling which would make extensive availability of active sites air dried and stored in air tight containers.

Pilot studies were conducted to test the sorption abilities of raw and modified selected Eco based materials against the chosen anionic species under native conditions, where the later exhibited marked sorption capacity.

The employed modifying agents registered better anion trapping nature as follows:
Hydrochloric acid > Sodium Hydroxide > Sulphuric acid > Phosphoric acid > Formaldehyde

From the observations made, it is understood that the materials modified using hydrochloric acid⁵ and sodium hydroxide exhibited better chelating ability due to enhanced

surface area brought about by the conversion of macropores into micropores. Thence, HCL modified materials were fixed as the finalized sorbents in the forthcoming batch equilibration studies. The treated materials are referred to as TCSS, TETS, TVFH and TGGDB.

3.6 Physio- Chemical Characterization

The prepared sorbents of 0.18 mm particle size were subjected to characterization studies.

3.6.1 pH and Conductivity

One-gram of the modified sorbents' and 300 mL double distilled water were added to 500 mL beakers, boiled for 10 minutes, filtered, where first 15 mL of the hot filtrates were discarded. The remaining solutions were cooled, the supernatants were tested for their pH and conductivity values⁶ using ELICO (LI-120) pH meter and ELICO (CM 180) digital conductivity meter respectively, after standardizing the instruments.

3.6.2 Moisture (Bidwel- Sterling Method)

Modified materials' moisture contents were determined by Xylene method⁷ (ASTM D 2867-95). Approximately 0.25g of biomaterial was taken in 250 mL Round Bottom flask and 75 mL of Xylene was added, the flask was connected with condensation tube and water receiving tube, followed by injection of Xylene from the top of condensation tube, filling the water in water receiving tube. The set up (fig 3.4) was heated in such a manner to collect two drops of the distillate per second until all water had apparently been distilled. Finally, distilled for a moment until no water drop adhered onto the upper part of the receiving tube as well as the wall of the condensation tube. Moisture content of the samples were calculated in accordance with the equation (1).

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

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)

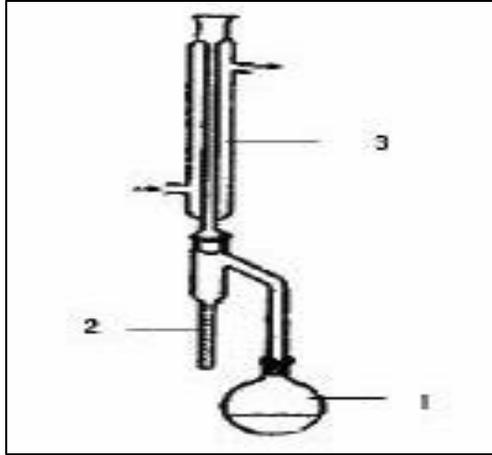


Figure 3.4 Moisture Determination Apparatus

(1) 250 mL Round Bottom flask; (2) Bidwell- Sterling Moisture Trap; (3) Condense

3.6.3 Bulk Density

10 mL capacity of specific gravity bottles were tapped continuously with the prepared materials to ensure maximum complete filling and later stoppered with a rubber cork. The loaded bottles were weighed. The measured weighings (g) divided by volumes of specific gravity bottles (10 mL) registered the bulk density⁸.

3.6.4 Specific Gravity

Porcelain dishes (3 inch) were laden with 5 g of sorbent material and 50 mL double distilled water, boiled gently for 3 min to expel the air. The suspensions were cooled in water bath, later transferred to 100 mL pycnometers and weighed (W_c). Followingly, the pycnometers were emptied thoroughly refilled with doubly distilled water and reweighed (W_b)⁹. The difference between these weighings were calculated as follows,

$$\text{Specific Gravity} = \text{Weight of Suspension } (W_a) / \text{Volume of displaced water}(V) \dots\dots\dots (2)$$

where,

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

W_a = Sample weight

W_b = Pycnometer mass filled with water

W_c = Pycnometer mass with material residue

3.6.5 Porosity

Porosities of all the chosen materials were determined from the calculated values of specific gravity (S) and bulk density (D) using the following equation¹⁰ (4)

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

3.6.6 Ash Content

One gram of the eco-friendly material was transferred to porcelain crucibles and these crucibles were electrically heated in an oven (383±5) K for a period of 5 hours. Followingly, they were ignited in muffle furnace (800 K), for 2 hours. The ignited crucibles were cooled in desiccators and weighed. The aforesaid processes were repeated periodically for 30 min till a variation less than 5 mg was observed between any two continuous weighings¹¹. Ash contents were calculated as weight percentage.

$$\% \text{ Ash} = \frac{M_{\text{ash}}}{M_{\text{dry}}} \times 100 \quad \dots\dots\dots (5)$$

3.6.7 Water Soluble Matter

0.5 g of the prepared materials were boiled in 500 mL beakers along with 60 mL double distilled water with continuous stirring for 30 minutes. Later, the supernatants were filtered through gooch crucibles fitted with asbestos mats. This procedure was repeated thrice with residues in the beakers and the filtrates were combined.

The combined filtrates were concentrated, cooled and made upto 100 mL in volumetric flasks. 50 mL of the flask solutions were transferred to china dishes, evaporated almost to dryness on a boiling water bath, dried in an electric oven (100 ± 5°C) cooled and weighed. Water soluble matter¹² was calculated as per the following equation.

$$\text{Water soluble matter} = \frac{20000 \times W_1}{W_2 \times (100 - X)} \quad \dots\dots\dots (6)$$

where,

W_1 = Weight of the residue (g)

W_2 = Weight of the adsorbent (g)

X = Percentage of moisture in the adsorbent.

3.6.8 Acid Soluble Matter

Experimental set up and calculation for acid soluble matter were similar to that designed for water-soluble matter, 60 mL of 0.25 N HCl was added, instead of double distilled water¹³.

3.6.9 Ion Exchange Capacity

Slurries of the modified sorbents (0.2 g) after proper soaking and stirring were carefully transferred to burettes. 250 mL of 0.25 M sodium sulphate was dripped into the burettes 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. Later, the collected samples were titrated against standardized 0.1 N sodium hydroxide solutions using phenolphthalein as indicator¹⁴. The ion exchange capacity of the bed expressed as m_{eq}/g is given by the following equation:

$$NV/W \dots\dots\dots (7)$$

where,

N= Normality of NaOH solution

V = Volume (ml) of NaOH and

W = Weight (gms)

3.6.10 Zero Point Charge (pHzpc)

The zero point charges were determined by solid addition method¹⁵. To a series of 100 mL conical flasks, 50 mL of 0.1 and 0.01 M KNO₃ solutions were added. The acidic and basic pH conditions of these solutions were maintained using 0.1M HCl or 0.1M NaOH as required. The initial pH values were noted. Later, 1 g of modified materials were added to the specified flasks, manually shaken and the suspensions were allowed to equilibrate for 2 days. The pH values of the supernatant liquids were recorded implying the zero point charge values of the respective materials.

3.7 Elemental Characterization

3.7.1 CHNS Analysis

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

3.7.2 Active Sites' Determination

The amounts of oxygenated acid surface groups present in the treated sorbents were determined using Boehm titration method¹⁶. One gram of the modified samples were placed in 250 mL 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 filtrate were pipetted out and 15 mL of 0.05 N HCl was added. The excess HCl was titrated against 0.05 N NaOH using phenolphthalein indicator followed by blank experiments. The amounts of organic acidic sites were calculated from the neutralization of NaOH with carboxylic, phenolic and lactonic groups, which may be present in the modified materials.

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

Surface areas and pore characteristics of the materials 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, carbon contents in the materials 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.

3.7.4 FT-IR Spectral Analysis

FT-IR analyses of unloaded and anion loaded sorbents were determined using Shimadzu Infrared Spectrophotometer. The spectral runs were recorded within the range of 400-4000 cm⁻¹.

3.7.5 SEM and EDAX Analyses

Scanning Electron Microscopy (SEM) has been a primary tool for characterizing the surface morphology and the fundamental physical properties of the material surface. The elemental identification and quantitative compositional information of the treated materials was carried out using an Energy Dispersive X-ray spectrometer (*ZEISS*) attached to a Scanning Electron Microscope (20 kV) under a vacuum of 1.33×10^{-6} m Bar. A thin layer of platinum (10 nm) with a sputter coater was used to cover the materials and subjected to scan.

3.8 Chemicals Employed

Potassium dihydrogen phosphate, potassium nitrate, sodium sulphate, ammonium molybdate, sulphuric acid, hydrochloric acid, sodium hydroxide, sodium nitrate, potassium chloride, magnesium sulphate, zinc sulphate, pH-4 and pH-9 buffers were purchased from Sigma – Aldrich Company. All chemicals employed were of AnalaR, GR purity grade. Shimadzu APX 200 electronic balance was used to record the weighing's of the various chemicals.

3.8.1 Stock/ Aliquots Solutions

1.4329 g of potassium dihydrogen phosphate, 1.630 g of potassium nitrate and 1.9546 g of sodium sulphate were weighed and made upto 1000 mL using doubly distilled water (Distillon 4DQ) to prepare stock solutions of PO_4^{3-} , NO_3^- and SO_4^{2-} respectively. Aliquots of adsorbate solutions of varying concentrations were prepared through progressive dilutions of the stock solutions.

3.9 Batch Equilibration Method

Adsorption studies were performed by Batch mode at room temperature in the process of determining the nature of sorbate – sorbent interactions. The operating parameters viz., particle size and dosage of the adsorbents, contact time, initial concentration of adsorbate, cation, anion, co-ion was experimentally validated at varying pH and temperatures since they play the role of controlling factors in many adsorption systems. Constancy of other parameters was ensured, while studying the impact of a particular variable.

50 mL of PO_4^{3-} , NO_3^- , and SO_4^{2-} aqueous solutions along with the appropriate doses of modified sorbents were taken in Erlenmeyer flasks and agitated in a mechanical shaker (KEMI model) at 120 rpm. At predetermined time frames, the sorbate species were separated through filtration and analysed. pH values of the experimental solutions were recorded using ELICO (LI-120) pH meter.

3.10 Operating Parameters

3.10.1 Particle Dimension

Impact of particle dimensions (0.18 mm, 0.24 mm, 0.30 mm, 0.52 mm and 0.71 mm) on the anionic sorbate species was evaluated containing 50 mL of the chosen anions. The contents of the flasks were agitated in a mechanical shaker at preset time factors, filtered and the samples were analysed for their concentration. The experiment was ensured in keeping other factors constant.

3.10.2 Initial Anion Concentration, Agitation time, Dose and pH

The influence of time frames (3-30 minutes: 5 min) between the sorbate and sorbent species, initial anionic concentrations (50 - 300 mg/L: 50 mg/L) under variable doses of identified eco based materials (50 – 300 mg: 50 mg) and pH environments (3,5,7,9 and 11) were determined, keeping other factors viz., particle size and temperature static.

3.10.3 Other Ions

Apart from the prime anions of interest, laundry discharges possess other toxic chemicals which contributes to the inhibition of the specific anion removal. Therefore, the sorption efficiencies of the sorbents in presence of other ions (Mg^+ , Na^+ , Cl^- , F^-) were examined under different concentrations (100 to 500 mg/L: 100 mg/L). Equal volumes of influencing ions and sorbate anions were mixed then the experiment was run under optimized conditions.

3.10.4 Temperature

The sorption process was done at five different temperature environments (293K-333K: 10 K), to describe an optimum temperature. Experimental set up was carried out in TECHNO thermostat-controlled incubator shaker by keeping other fixed parameters viz., particle size, agitation time, initial anion concentration, dose and pH.

3.11 Sample Analysis

Initial and residual concentrations of the experimental anionic solutions were analysed using UV – Visible Spectrophotometer (Lab India – 3000⁺). Complexation methods pertaining to studied anions, the specific wavelengths of recording the absorbance values are listed in the following table. Figure 3.5 shows the image of the spectrophotometer employed for the analyses purpose.

S.No	Anions	Wavelength (nm)	Complexation method
1	PO ₄ ³⁻	660	Molybdenum Blue
2	NO ₃ ⁻	550	Azo Dye
3	SO ₄ ²⁻	420	Barium Chloride



Figure 3.5 UV- Visible Spectrophotometer (Lab India UV 3000⁺)

3.11.1 PO₄³⁻ - Molybdenum blue Method

Reagents

Ammonium molybdate [(NH₄)₆MO₇O₂₄.4.H₂O] – 1.5 L of 2 N conc. H₂SO₄ solution was prepared and cooled until room temperature was attained. 10.4g of (NH₄)₆MO₇O₂₄.4.H₂O was weighed, dissolved in 250 mL of the prepared acid solution and

diluted to 2 L in a standard flask. The prepared complexing agent was later stored in a brown bottle in order to prevent photolytic decomposition.

Stannous chloride [SnCl₂.2H₂O] – Conc. HCl and distilled water were mixed in 1:3 ratio slowly stirred and boiled for one hour. SnCl₂ solution was prepared by adding 7 g of stannous chloride to the boiling solution. The mixture was heated further until a clear solution was obtained then cooled and made upto 250 mL. A few drops of mineral oil (paraffin oil) was added and stored in a brown bottle¹⁸.

Complexation Procedure

2mL of Ammonium molybdate and 4 drops of Stannous chloride solutions were added to phosphate sample to be analysed. The mixture was thoroughly shaken to develop a blue coloured MO⁴⁺-P complex, the absorbance values of which was registered at 660 nm against a blank solution¹⁹.

3.11.2 NO₃⁻-Azo dye Method

Reagents:

HCl – Conc. HCl and distilled water were mixed in 1:4 ratio, stirred well and stored in a reagent bottle.

Sulfanilic acid –1N of sulfanilic acid was prepared by dissolving 0.6 g of the former in 70 mL hot distilled water, cooled and diluted to 100 mL²⁰.

Zn/NaCl mixture – 1g Zn and 20 g NaCl were ground in a mortar and pestle to obtain a uniform granular mixture.

Sodium acetate solution (NaC₂H₃O₂) – 69.5 g of sodium acetate was dissolved in 800 mL distilled water to prepare 2 N solution of the salt. The prepared solution was neutralized by adding dilute acetic acid and made upto 1 L.

NEDD solution - 0.60g of N- (1- naphthyl) - ethylenediamine dihydrochloride (NEDD) was dissolved in 1 mL Conc. HCl and made upto 100 mL.

Complexation Procedure

1mL each of HCl/sulfanilic acid reagents and 0.1 g of Zn/NaCl mixture was added to 50 mL of nitrate sample, swirled for 7 minutes and filtered. 1mL each of NEDD/ sodium

acetate solution were added to the filtrate, where a development of pink colour was observed after 5 mins due to the formation of azo dye complex²¹. The absorbance reading was measured spectrophotometrically at 550 nm.

3.11.3 SO₄²⁻ - Barium Chloride Method

Reagents:

Buffer Solution A: 30 g magnesium chloride, 5 g sodium acetate, 1 g potassium nitrate were transferred to a beaker containing 20 mL acetic acid. The contents were stirred well and diluted to 500 mL with double distilled water. The solution was further made upto 1000 mL.

Buffer Solution B: This buffer solution was prepared as per the procedure followed for Buffer solution A, but with 0.1 g sodium sulphate against 1g potassium nitrate²².

Complexation Procedure

10 mL of filtered sulphate solution was taken in 25 mL standard flask, to which 5 mL of the buffer solutions and 0.15g BaCl₂ crystals were added. The contents of the flask were made upto the mark, after ensuring thorough mixing. The solution turned turbid after 10 minutes indicating the presence of sulphate anions, being estimated at λ_{\max} value of 420 nm²³.

3.12 Data Analysis

The removal percentage and amounts of anions chelated were calculated as per equations 8 and 9.

$$(C - C_e) \% \text{ adsorption} = C_i - C_e / C_i * 100 \quad \dots\dots\dots (8)$$

$$q = V(C - C_e) / W \quad \dots\dots\dots (9)$$

where, V is the volume of the solution (L), W is the weight of the adsorbent (g), C_i and C_e are the initial and equilibrium metal ions concentrations (mg/ L) respectively.

3.13 SPSS Software Analysis

The relationship between adsorbed anions and variable parameters (particle size, contact time, initial concentration, dosage and pH) was correlated by Pearson Moment

Coefficient Method with SPSS 20 Software studies. The extent of statistical fit was validated by means of descriptive analysis, Pearson Correlation and analysis of variance (ANOVA) with 95 % significant confidence level values²⁴.

3.14 Adsorption Isotherm

The adsorption isotherm describes the relation between the equilibrium concentration of adsorbate in solution and that adsorbed onto the sorbent material. A number of isotherm models are available to describe the equilibrium pattern of adsorption process. Mathematical isotherm models developed by Langmuir, Freundlich, Tempkin and Dubinin- Kaganer- Radushkevich were applied to the experimentally verified systems in order to understand the sorption mechanism and dynamics of the sorbent – sorbate species.

3.14.1 Langmuir Isotherm

Langmuir sorption occurs at specific homogeneous sites each of which can hold only one molecule²⁵. The adsorption is limited to monolayer which is expressed as follows:

$$C_e / q_e = C_e / q_m + 1/ b q_m \quad \dots\dots\dots (10)$$

where,

q_e - equilibrium anion concentration on the sorbent (mg/g)

C_e - equilibrium anion concentration in solution (mg/L)

q_m - maximum monolayer adsorption capacity of the sorbent (mg/g)

b - Langmuir sorption constant (L/mg) related to the free energy of sorption

The Langmuir constants q_m and b were determined from the slope and intercept of the linear plot C_e/q_e vs C_e . Higher the value of q_m , greater is the affinity of adsorbent for the anion to be sorbed.

3.14.2 Separation Factor (R_L)

The linearity of Langmuir isotherm predicts the favourability of the studied system. The essential characteristics of this model is expressed in terms of a dimensionless parameter called the separation factor or equilibrium parameter R_L , which is defined by the following relationship²⁶.

$$R_L = 1 / 1 + bC_i \quad \dots\dots\dots (11)$$

where,

C_i is the initial anion concentration (mg/L)

The parameter R_L indicates the isothermal linearity and the nature of the sorption process given as,

$R_L > 1$ Unfavourable isotherm

$R_L = 1$ Linear isotherm

$R_L = 0$ Irreversible isotherm

$0 < R_L < 1$ Favourable isotherm

3.14.3 Freundlich Isotherm

Freundlich isotherm is focussed on the assumption that adsorbate uptake occurs in a heterogeneous surface with multilayer driven sorption and the amount of sorbate adsorbed increases infinitely with concentration²⁷. The Freundlich equation is given by,

$$q = K C_e^{1/n}$$

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

$$\log q_e = \log K + 1/n \log C_e \quad \dots\dots\dots (12)$$

K and 1/n are empirical constants correspondingly indicating sorption capacity and adsorption intensity, whose values are calculated from the slopes and intercepts of Freundlich plots (log q_e vs log C_e).

3.14.4 Temkin Isotherm

Temkin and Pyzhev considered the effects of some indirect sorbate/sorbent interactions on desorption isotherms and suggested that the heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to the physiochemical interactions²⁸.

The linearized form of Tempkin isotherm equation is,

$$q_e = B_T \ln A_T + B_T \ln C_e \quad \dots\dots\dots (13)$$

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 correspond to the heat of sorption and equilibrium binding constant with respect to maximum binding energy.

3.14.5 Dubinin- Kaganer-Radushkevich (DKR) Isotherm

DKR isotherm is generally applied to express the adsorption mechanism with Gaussian energy distribution onto the heterogenous surface²⁹.

The linear form of DKR isotherm expressed as,

$$\ln q_e = \ln q_s - \beta_{DR} \epsilon^2 \quad \dots\dots\dots (14)$$

where,

q_e - Amount of anions adsorbed per unit weight of the adsorbent (mol/g)

q_s - Theoretical saturation capacity (mol/g)

β_{DR} - Mean free energy Constant (mol²/J²)

ϵ - Polanyi potential [RT ln (1+1/Ce)]

R- Gas constant (J/mol K)

T- Absolute Temperature

The values of q_s and β_{DR} constants are derived from the linear plot of $\ln q_e$ vs ϵ^2 . Mean free energy E (kJ/ mol) per molecule of the sorbate species is calculated using β_{DR} values as follows:

$$E = 1/ (2 \beta_{DR})^{1/2} \quad \dots\dots\dots (15)$$

The magnitude of E provides estimating the mechanism of the adsorption reaction. In the case of $E < 8$ kJ/mol, the adsorption follows physical sorption. If E is in the range of 8–16 kJ/mol, adsorption is governed by ion exchange mechanism, while the values of $E > 16$ kJ/mol refer to the adsorption by particle diffusion³⁰.

3.15 Adsorption Kinetics

Adsorption kinetics describes the solute uptake rate which in turn controls the resident time of the solid-solution interface. Adsorption kinetics of anion transport onto an adsorbent is influenced by the following properties: (i) External mass transfer (film diffusion) (ii) Chemical reaction (Chemisorption) (iii) Bulk diffusion (iv) Intra-particle diffusion³¹. The efficiencies of the sorbents were evaluated by Lagergren pseudo first-order and pseudo-second-order, Elovich and Intraparticle diffusion models were applied to the Batch results to study the sorption kinetics.

3.15.1 Pseudo First Order Model

Lagergren presented a first order rate equation to describe the kinetic process of liquid-solid phase adsorption³². The pseudo-first-order equation is generally expressed as follows,

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303 \quad \dots\dots\dots(16)$$

where,

q_e and q_t - adsorption capacity at equilibrium and at time t , respectively (mg/g)

k_1 - rate constant for pseudo-first-order adsorption (min^{-1}) [q_t vs t].

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.

3.15.2 Pseudo Second Order model

The sorption rate is proportional to the square of the number of unoccupied sites³³. The second order kinetic rate equation is expressed as,

$$t / q_t = 1 / k_2 q_e^2 + t / q_e \quad \dots\dots\dots (17)$$

where,

Rate constant K_2 is derived from plot t/q_t vs t .

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 system³⁴. The SSE values were calculated by the equation:

$$SSE = \sum q_{e,exp} - q_{e,cal} / N \quad \dots\dots\dots (18)$$

where,

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

3.15.3 Elovich Model

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

$$qt = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t) \quad \dots\dots\dots (19)$$

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 qt vs $\ln t$ ³⁵.

3.15.4 Intra particle Diffusion Model

Intra particle diffusion model gives an insight to predict the nature of the sorption process. Adsorption of any anions from aqueous phase onto solid phase is a multi-step process (bulk diffusion) and then, diffusion of anions via the boundary layer to the surface of the solid particles (film diffusion), followed by transport of anions from the solid particle surfaces to its interior pores (pore diffusion or intra particle diffusion), which is likely to be a slow process, which may be the rate determining step in many adsorption process³⁶. The possibility of intraparticle diffusion is explored by the following equation,

$$qt = K_i t^{1/2} + C \quad \dots\dots\dots (20)$$

where, K_i (mg/g min^{1/2}) is the intraparticle diffusion rate constant and C (mg/g) is related to the boundary layer thickness, calculated from the slope and intercept of qt versus $t^{1/2}$ plots respectively.

3.16 Thermodynamic Parameters

Thermodynamic considerations of biosorption process are necessary to conclude whether the process is spontaneous or not. The free energy change (ΔG^0) is a critical factor for determining the degree of spontaneity of the biosorption process; a higher negative value of ΔG^0 indicates a more energetically favourable biosorption³⁷. The adsorptive process will occur favourably and spontaneously at a given temperature when ΔG^0 exhibits a negative quantity; in contrast, it will be non-feasible and non-spontaneous. In the biosorption study, it is essential to establish the biosorption mechanisms (i.e., either chemical or physical). Physical biosorption (also known as physisorption) arises from relatively weak interactions such as van der Waals force, while chemisorption involves stronger chemical interactions (chemical bonding) with attendant transfer of electrons between the biosorbent and adsorbate³⁸. It has to be noted that the differentiation between physisorption and chemisorption is widely arbitrary and the boundaries are fluid.

At equilibrium conditions, free energy of biosorption process is defined as follows:

$$\Delta G^0 = - RT \ln K_C \quad \dots\dots\dots (21)$$

where,

ΔG^0 - Standard free energy change (kJ/mol),

R - Ideal gas constant (8.314 J/mol.K)

T – Absolute temperature (K)

K and K_C - Equilibrium constant ($K_C = q_e / C_e$.)

q_e - Amount adsorbed

C_e - Equilibrium concentration

The change in enthalpy and entropy of adsorption were calculated using Van't Hoff's equation as follows:

$$\ln K_C = \Delta S^0 / R - \Delta H^0 / RT \quad \dots\dots\dots (22)$$

The values of (ΔH^0) and (ΔS^0) are obtained from the slope and intercept of $\ln K_C$ versus $1/T$ plots. The ΔG^0 value is calculated by the following equation:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \dots\dots\dots (23)$$

3.17 Synthesis of Bio-beads

The synergistic nature of composite materials exhibited as beads have sought much attention in recent times due to their remarkable properties. In view of this, bioencapsulated beads of TCSS/ TETS were synthesized using alginate/goethite/magnetite dopants as precursors. The sorption property of these beads were tested under previously optimized conditions.

3.18 Column Studies

Column studies were planned to quantify the sorbents' nature through continuous line performance. This was conducted as short term and long term analyses.

3.18.1 Short term Analysis

Cylindrical glass columns of 3.5 cm inner diameter and 30 cm height were packed with glass wool, glass beads, at the bottom, followed by appropriate doses of TETS/M@TETSB, layer of glass wool and glass beads. The purpose of packing the material in between the layer of glass wool and glass bead is to prevent the seepage of materials during the experimental run and also to ensure the constant flow of adsorbate species. The materials packed in the columns settle down by gravity. 100 mg/L (PO_4^{3-} , NO_3^-) and 250 mg/L (SO_4^{2-}) concentration solutions were streamed down the prepared column. The contact time between the column bed and the anionic solutions were prolonged for 30 minutes prior to collection of the outlet samples. The flow rate was fixed as 20 mL/5mins. After 5 minutes the effluent samples were collected through the adjustable knob fixed at the column bottom.

3.18.2 Long term Analysis

Columns with 5 cm inner diameter and 50 cm height were packed with required doses of the modified materials/magnetite beads, sandwiched between glass wool/glass beads as supporting layers. The conditions for this analysis is similar to short term analysis, but for the change in flow rate fixed as 50 mL/5 mins.

3.18.3 Modelling of Column Operations

Many mathematical models have been proposed for evaluating the efficiency and applicability of the column models at large scale (industrial) operations. In the current study, Bohart – Adams, Thomas and Yoon – Nelson models have been tested to assess adsorption breakthrough behaviour of the studied systems with a high degree of accuracy.

The ratio between influent (C_0) and effluent (C_t) concentrations of the adsorbate species is expressed as normalized concentration. A plot of this normalized concentration as a function of time required for the effluent flow rate at fixed bed depth is derived, wherein a breakthrough curve is observed³⁸.

Time quadrants and shape of breakthrough curve are the important characteristics in the determination of column operations.

3.18.4 Thomas Model

Adsorption rate constant and concentration of sorbate anions on sorbent medium is determined by this model³⁹. The linearized form of Thomas model can be expressed as:

$$\ln [C_0/C - 1] = K_T q_T M / Q - K_T C_0 t \quad \dots\dots\dots (24)$$

where,

K_T – Thomas Constant (L/mg min)

q_t - Adsorption capacity (mg/g)

Q - Volumetric flow rate (mL/min)

M – Mass of the adsorbent (g)

C_0 – Initial Concentration (mg/L)

C - Effluent Concentration (mg/L)

The curvature graph is obtained by plotting $\ln (C_0/C_t - 1)$ vs t from which K_T and q_t (slope & intercept) values are derived.

3.18.5 Adams – Bohart Model

The Adams – Bohart model assumes that the adsorption rate is proportional to both the residual capacity of the adsorbent and the concentration of the adsorbing species.

This model applied to the experimental data describes the initial part of the breakthrough curve⁴⁰. Maximum adsorption capacity (N_0) and kinetic constant (K_{AB}) values are derived as the intercept and slope of the linear plot $\ln (C_i/C_0)$ vs time.

The linear expression for the Adams – Bohart model is,

$$\ln [C_i/C] = K_{AB} C_0 t - K_{AB} N_0 Z/F \dots\dots\dots (25)$$

where,

K_{AB} – Kinetic Constant (L / mg min)

F - Flow rate (mL / min)

Z - Bed depth (m)

N_0 – Saturation constant (mg/L)

t - time

C_0 – Influent concentration (mg/L)

C_i - Effluent concentration (mg/L)

3.18.6 Yoon – Nelson Model

Rate constant for the flow of sorbate ions through the column at specific time frames can be recorded through Yoon - Nelson model⁴¹.

The linear equation for Yoon – Nelson model is,

$$\ln [C_t / C_0 - C_t] = K_{YN} * t - \tau * K_{YN} \dots\dots\dots (26)$$

where,

K_{YN} – Velocity constant (L / min)

τ - Time required for 50 % of adsorbate breakthrough

t - Sampling time

Time required for 50% sorbate breakthrough can be calculated from the slope (K_{YN}) and intercept (τ) values of the plot between $\ln [C/-C_t]$ and time.

3.19 Desorption and Regeneration Experiments

Recycling, recovery and reusability of the loaded sorbents can be achieved through desorption experiments. 50 mL of phosphate, nitrate and sulphate solutions were agitated with 200 mg dose of respective bio-sorbents at pH 5 in a mechanical shaker for 10 mins as per the conditions optimized. The contents were filtered through Whatman 42 filter paper and the spent materials were oven dried (378 ± 5 K)⁴².

50 mL of dil. HCl (0.01 - 0.05 M) was added as desorbing agent to these used up materials and the contents were agitated for a contact time of 30 minutes in excess to their equilibrium time frame, supernatant solutions analysed by the usual procedure. The efficiency of the species achieved in batch results is derived from the following equation,

$$\text{Desorbing efficiency (\%)} = \text{Amount adsorbed} / \text{Amount desorbed} * 100$$

In addition to efficient sorption capacity, maximum reusability of the exhausted material with insignificant loss of its chelating property is an essential criteria for any adsorbent. Keeping this in view, the desorbed materials with acidic pH was stirred with double distilled water and allowed to settle. The supernatant solution was decanted and the procedure was repeated several times until the solution displayed neutral pH⁴³. The regenerated sorbents were dried and reused in successive adsorption-desorption cycles, so as to determine the regenerating efficacy of the spent material.

3.20 Effluent Analysis

Laundry discharges classified under greywater category is enriched with anions exceeding the permissible limits. Also, these wastewaters are alkaline in nature, the reason being that use of highly concentrated alkalis in soaps and detergents⁴⁴.

Effluent samples were collected in 2 L capacity PET bottles from seven laundry units located in and around Coimbatore and Ootacamund, Nilgiris, Tamil Nadu, India. The collected samples after proper dilutions were subjected to the analyses of physico-chemical parameters viz., pH, Alkalinity, Total Nitrogen, Phosphate, Sulphate, Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), Total solids (TS), Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Chloride, Calcium, Magnesium and Total

Hardness. The values obtained for all studied factors exhibited a threefold increase than their respective permissible limits (BIS Standards – pH 5.5-9, Alkalinity – 600 mg/L, Total Nitrogen – 100 mg/L, Phosphate – 100 mg/L, Sulphate – 120 mg/L, COD – 250 mg/L, BOD – 100 mg/L, TS – 2300mg/L, TDS – 2200 mg/L, TSS – 200 mg/L, chloride – 1000 mg/L, calcium – 200 mg/L, magnesium – 100 mg/L)

Pilot scale experiments using diluted effluent samples were carried out with approximately required dosages of the functionalized sorbent materials, to minimize the concentration of studied anions and limit the alarming parametric values within the tolerant levels. Further, continuous column runs had been organized for the effluent system, mimicking the column studies with aqueous solutions.

Based on the column results, the laboratory set up was upscaled to a laundry unit located at Ootacamund, Tamil Nadu, India. This was achieved through successful fabrication and installation of a prototype device, made up of FRP material. Column packing and execution of the experiments were followed as already reported for pilot studies.

3.21 Nutrient Application

Thoroughly exhausted column packed materials will pose toxic threat while being disposed therefore, these exhausted sorbents, with immobilized anions within the sorbent matrix, are sorted out as nutrients for promoting bacteria for plant growth. This in turn favours the conversion of waste biomass into quality nutrients. This had been achieved by conducting pot trials with seeds meant for growing greens. These pots with the seeds were nurtured with the spent material as an added nutrient against the control as reference without nutrient addition. Germination of seeds were monitored by measuring the shoot growth at specific time intervals through continuous watering of pots.

3.22 References

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