

Chapter III

Experimental Section

3.1 Selection of Plant/ Animal Based Raw Materials

Apparently as from the literature review, the main factors focusing on selection of the adsorbent materials include affordability, local availability and abundant quantity. Therefore, *Prosopis juliflora* Bark (timber industry waste), *Tamarindus indica* Hull (agricultural waste) and Goat Hoofs (slaughter house waste) have been chosen for the present study. The barks, hulls and goat hoofs were identified on the basis of their bulk availability of being thrown as litter after appropriate domestic purposes. Also, least or no reports are available in the literature regarding their sorptive abilities. Employment of these materials was focuses on the preventive measures of burning off in dumpsites and abattoirs.

Prosopis juliflora is a small tree belonging to *Fabaceae* family, a kind of mesquite. This tree grows to a height of upto 12 m (39 ft) and one of the most tolerant species for saline, alkaline soils, also capable of growing in water logged areas. Being an aggressive invader, it affects the native vegetation and takes over rangelands⁸⁴.

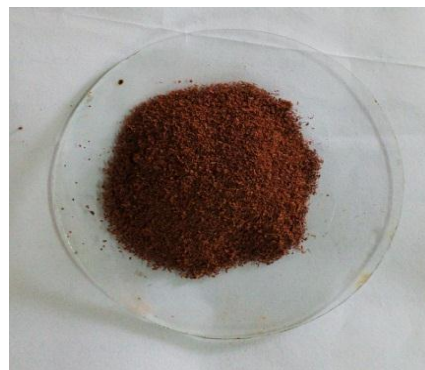
Tamarind (*Tamarindus indica*) belonging to the family *Fabaceae* indigenous is a semi-evergreen tree with large alternately arranged and reach a height of about 10 to 20 m. The hard pod shell is removed (deshelled) from the ripened fruit⁸⁵, which is used as the chief acidulate in the preparation of foods.

Goat Hoofs is composed of a bone core covered by a thick keratin layer. Hoof tissue contains keratin molecules having different biomechanical properties, molecular weights with varied degrees of hardness and sulphur concentration. Moreover, many polarizable and ionisable groups present in keratin proteins capable of bind metal ions⁸⁶, shall promote the material as sorbent for heavy metals from water and wastewaters.

3.2 Collection and Categorization of Raw Materials

Prosopis juliflora Barks (PJB), *Tamarindus indica* Hulls (TIH) were collected from various localities in Coimbatore and the slaughterhouse (Goat Hoofs - GH) wastes were gathered from butcher shops in markets of Ukkadam, Coimbatore, Tamil Nadu, India.

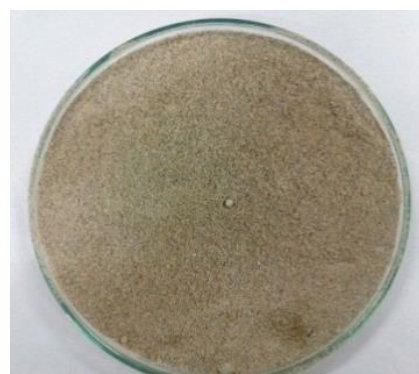
The collected materials were cleaned carefully and broken into small pieces, washed well with doubly distilled water and dried under sun for a period of 10 days. Later, the materials were pulverized in an electrical mixer, sieved into various mesh sizes (85 BSS, 72 BSS, 52 BSS, 36 BSS and 22 BSS) with Scientifically Tested Molecular Sieves (*JAYANT Scientific Instruments Co., Mumbai*). Raw and categorized materials are depicted below:



PJB



TIH



GH

3.2.1 Microscopic Analysis

Particle Size determination of the sieved materials (PJB, TIH and GH) were carried out by microscopic studies for the five mesh sizes. An Ocular micrometer with a dimension of 10X was attached to the Binocular Microscope (*OLYMPUS* make, *Model- CX21I*). Each division in the micrometer scale is 0.01 mm which facilitated the measurements of length and breadth of fifteen granular particles, as no two single particles are alike.

3.3 Choice of Heavy Metals

Lead [Pb(II)], Cadmium [Cd(II)] and Nickel [Ni(II)]. Heavy metals were identified as the adsorbate species based on their prevalence in the metal discharges of various paint industries located in and around Coimbatore, Tamil Nadu, India.

3.4 Pilot Studies

Batch Equilibration studies were performed to assess the sorption characteristics of raw materials in trapping 100 mg/L initial concentration of Pb(II), Cd(II) and Ni(II) ions, with a dose of 1g under native pH conditions. The percentage removal of metal ions with the categorized raw PJB, TIH and GH are listed in table 3.1 at a contact time of 30 min, supporting their reveal appreciable sorptive nature.

Table 3.1 Sorption of Heavy Metal Ions by Raw Materials

S. No	Metal Ions	Percentage Removal (%)		
		PJB	TIH	GH
1	Pb(II)	38.51	27.83	47.37
2	Cd(II)	34.82	23.15	42.36
3	Ni(II)	26.74	21.87	32.12

3.5 Modifications of the Adsorbents

Based on the literature review,^{87, 88} varied chemicals viz., Hydrochloric acid (HCl), Citric acid, Phosphoric acid and Sodium Hydroxide were employed to modify the raw materials. The collected plant and animal residues got charred and found immiscible

in alkaline and acid media respectively. Acid treatment of plant wastes is supported by Isabel Vellaescusa et al., for the pre-treatment of grape stalk wastes in the removal of Cu(II) and Ni(II) ions from aqueous solution⁸⁹. Pretreatments of PJB and TIIH favour the removal of lignin, hemicellulose, cellulose crystallinity and rise in the porosity/ surface area. Alkaline treatment is expected to break down the disulfide bond in the keratinous materials, in turn, inclining the sorption capacity. Thence, the materials are subjected to hydrochloric acid and Sodium Hydroxide corresponding to maximum their sorptive nature.

The sieved plant materials were boiled with 0.1 N HCl for three hours, washed thoroughly with double distilled water and soaked for sufficient time, to ensure swelling. This would make more sites to enhance their surface area for sorption. The prepared materials were dried and stored in air tight containers.

The dried hoofs were soaked in 0.2 N NaOH for 3 hours, later washed for many times using doubly distilled water, dried and kept in labeled bottles. Thenceforth, the treated materials are referred to as TPJB, TTIH and TGH in the forthcoming chapters.

3.6 Characterization Studies

3.6.1 pH and Conductivity⁹⁰

The modified materials (1g each) were transferred into 500 mL beakers. The contents were boiled for min with the addition of 300 mL of freshly boiled and cooled doubly distilled water. Later, after discarding first 15 mL of the hot filtrate, the remaining was cooled and pH/ conductivity were measured using *ELICO* pH meter (*LI-120*) and *ELICO* digital conductivity meter (*CM 180*) respectively.

3.6.2 Moisture⁹⁰

Moisture contents of the materials were determined by Xylene-extraction test method (*ASTM D 2867-95*) using the moisture determination apparatus. 0.25g of TPJB, TTIH, and TGH were added to Round Bottom flasks, followed by addition of 75 mL of Xylene. The flasks with the mixtures were heated slowly, collected the distillate and determined for moisture content. Calculations were done in accordance with the equation.

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

where, X - Moisture content [mL/100 g] V – Aqueous volume (Receiving tube) [mL], m - Sorbent mass (g).

3.6.3 Ash Content⁹⁰

After proper pre-heating in a muffle furnace to about 500°C porcelain crucibles were cooled in a desiccator and the empty weights were noted. One gram of adsorbent materials were transferred into the crucibles and reweighed. Later, the crucibles were heated in an electric oven at 383 K (5 hours), followed by ignition in a muffle furnace (800 K) for 2 hours. Weighings of the crucibles were repeated at 30 min intervals after cooling to room temperature until the difference between two consecutive weighings recorded a values (< 5 mg) and the ash contents was calculated as percentage by weight.

3.6.4 Bulk Density⁹¹

10 mL volume specific gravity bottles were packed with the three materials and tapped using a rubber stopper. Measured weights (g) divided by volume (mL) gave the bulk density (g/mL) of the adsorbents.

3.6.5 Specific Gravity⁹¹

The treated sorbents (5 g), along with 50 mL of double distilled water were placed in small porcelain dishes and boiled gently for 3 min to expel the air. The sorbent suspensions were transferred to 100 mL pycnometers after cooling in a water bath (288 K) and weighed (W_c). Later, the pycnometers were emptied and refilled with double distilled water and weighed (W_b)

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

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

W_a = Mass of adsorbent

W_b = Mass of pycnometer with water

W_c = Mass of pycnometer with sorbent residues

3.6.6 Porosity⁹⁰

The difference between specific gravity (S) and bulk density (D) measurements of the prepared materials resulted in the porosity values.

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

3.6.7 Water Soluble Matter⁹⁰

Sorbents of 0.5 grams weighings were suspended in 60 mL of doubly distilled water and heated to boiling with continuous stirring. The stirrings were continued for 5 min, even after the heating was stopped. The materials were later settled down and clear solutions were filtered using crucibles matted with asbestos. The procedure was experimentally verified thrice for concordance and the combined filtrates were concentrated to less than 100 mL by heating on a water bath, cooled and made up to 100 mL in volumetric flasks. 50 mL of the concentrates were transferred to china dishes and evaporated to almost dryness on a boiling water bath, heated in an electric oven (373±5 K), cooled in a desiccator and weighed as similar to ash content determination and calculated as follows.

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

where, W_1 = Mass of the residue (g)

W_2 = Mass of the adsorbent (g)

X = % of moisture in the adsorbent

3.6.8 Acid Soluble Matter⁹⁰

Acid soluble matter values of the materials were calculated as per the procedure of water soluble matter, for the addition of 60 mL of 0.25 N HCl, instead of doubly distilled water.

3.6.9 Zero Point Charge (pH_{zpc})⁹²

Solid addition method was involved in the determination of the zero point charges. 0.1/ 0.01 M concentration of each 45 mL of KNO_3 solution were poured into

three conical flasks and their pH values were adjusted employing 0.1 M HCl / NaOH solutions followed by further addition of the former upto 50 mL. The initial pH (pH_i) of the solutions was noted after the second addition of respective KNO_3 solutions. 1 g of the adsorbents were added to appropriate labeled flasks and shaken manually for 5 min, allowed to equilibrate for 48 h and the pH values were recorded after the stipulated time interval. The differences between the initial (pH_i) and final pH (pH_f) values ($\Delta \text{pH} = \text{pH}_i - \text{pH}_f$) were plotted against pH_i . The zero point charge values were interpreted from the point of intersection of the resulting curves.

3.6.10 Ion Exchange Capacity⁹³

The contents with 0.2 grams of materials suspended in double distilled water were carefully transferred to burettes with the column maintaining the liquid levels at a height of about 1 cm above the materials' bed. 250 mL of 0.25 M Na_2SO_4 were dripped into the columns (2 mL per min) and the solutions were collected. Followed by titration against standard 0.1 N NaOH solution with phenolphthalein indicator. The ion exchange capacity of the bed is expressed as $\text{m}_{\text{eq}}/\text{g}$ and represented as NV/W where N is the normality of the NaOH solution; V is the volume of NaOH in mL and W is the weight of the sorbent dose.

3.6.11 Elemental Analysis and Surface Area Determination

The percentage (% by mass) of hydrogen, nitrogen, carbon, and sulphur (by difference) present in the chosen adsorbents were quantified using *Elementary Vario EL III-Germany CHNS Analyzer*, as per the procedures.

3.7 Characterization Methods

The nature and concentrations of surface functional groups present in the sorbents may be subjected to modification by suitable thermal or chemical post treatments. Presence of functional groups in raw and treated materials was characterized by varied chemical titration, spectral and BET/ BJH Analyses.

3.7.1 SEM and EDAX Analyses

Segregated raw materials, their corresponding treated and metal laden counter parts were examined using the *JEOL JFM- 6390 Scanning Electron Microscope* (20 kV) in order to determine the native changes in the surface morphologies. The samples covered

with a thin layer of platinum (10 nm) with a sputter coater (*SCD 0050 – Baltec, Liechtenstein*) were scanned under a vacuum of 1.33×10^{-6} m Bar. The generated *Energy dispersive X-Ray Analysis Spectra* furnished information regarding the chemical composition, their shifts band appearance of metal peaks. SEM and EDAX spectral data are dealt in result and discussions chapters.

3.7.2 Determination of Acidic Groups Analyses

The amounts of oxygenated acid surface groups were determined by Boehm titration method⁹⁴. 50 mL each of 0.05 N NaOH, Na₂CO₃ and NaHCO₃ were added to 1 g of the respective sorbents and the flasks were sealed, shaken for 24 h and filtered. 10 mL of the filtrates were pipetted out and 15 mL of 0.05 N HCl was added to the flasks. Excess HCl were titrated against 0.05 N NaOH using phenolphthalein indicator. Blank experiment was conducted. The acidic groups masses were calculated based on NaOH neutralization of carboxylic, phenolic and lactonic groups against Na₂CO₃ neutralization for carboxylic and lactonic groups and NaHCO₃ neutralization for carboxylic acid groups.

3.7.3 FT-IR Spectral Analysis

FT-IR analyses of unloaded and metal loaded sorbents were determined in *Shimadzu Infrared Spectrophotometer* and the corresponding spectra were recorded within the range of 400-4000 cm⁻¹. The spectral discussions are dealt in chapters IV, V, VI and VIII.

3.7.4 Bruner-Emmett-Teller and Barrett-Joyner-Halenda Analyses

Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) plots furnished information regarding surface areas and pore characteristics of the adsorbents. Nitrogen adsorption technique available in the BET surface area analyzer (*Micrometrics, BEL, Japan, Inc*) on an accelerated surface area and a system to determine porosity is sophisticated by Belsorp data analysis software. Sorbents masses were degassed for 5 hours at 120°C in N₂ environment before the exact method of analysis. The pore size distribution and specific surface area values were calculated from the isothermal plots of adsorption/desorption (77 K).

3.8 Preparation of Adsorbate Solutions

3.8.1 Stock/ Aliquots Solutions

1.5985 g of Lead Nitrate, 2.5666 g of Cadmium Acetate and 4.9546 g of Nickel Nitrate were weighed and made upto 1000 mL using doubly distilled water (*Distillon 4DQ*) for Pb(II), Cd(II) and Ni(II) stock solutions respectively. Adsorbate species of predetermined concentrations (50 - 500 mg/ L: 50 mg/ L) were made up into required standards from the bulk solutions.

3.8.2 Chemicals Employed

AnalaR, GR purity grade chemicals were utilized for the experiments. Lead Nitrate, Cadmium Acetate and Nickel Nitrate salts were employed to prepare the metal solutions of interest. Magnesium Nitrate, Potassium Sulphate, Sodium Chloride, Sodium Sulphate and Sodium Nitrate were employed for the ionic studies using pH-4 and pH-9 buffers standards. pH meter was standardized. *Shimadzu APX 200* electronic balance was used to record the weighings of the various chemicals.

3.9 Batch Mode Adsorption Studies

Identical batch experimental conditions were performed for the removal of the chosen divalent ions (lead, cadmium and nickel) for the plant based modified materials (TPJB, TTIH), the parametric ranges being: 50 mL initial concentration (50 – 250 mg/ L: 50 mg/ L); material dosage (100 – 500 mg: 100 mg) and preset time frames (10 –60 min: 10 min). The range of initial concentration extended upto 300 mg/ L and contact time reduced to 30 min for the sorption experiments with TGH against 250 mg/L and 60 min respectively for the former, based on the sorption characteristics of the latter. Agitations of the solutions in a thermostat controlled mechanical shaker (*TECHNICO*) were maintained at 120 rpm. As far as the influence of pH, cations, anions, temperature studies were concerned, the procedures adopted were: pH (3, 5, 7, 9, 11); Mg^{2+} , K^{+} ; Cl^{-} , SO_4^{2-} (50 – 250 mg/ L: 50 mg/ L); temperature (293 K-333 K: 10 K). Effect of selected co-ions viz., Cr^{6+} and Zn^{2+} were verified for the nine systems at varying concentrations of 50 – 250 mg/ L: 50 mg/ L, where 25 mL volume of these metal solutions were mixed with equal volume of the divalent ions and subjected to batch studies. Performances of duplicate experiments supported the reproducibility of the systems to be within $\pm 2\%$.

3.9.1 Sample Analysis

The initial and final metal ion concentrations after batch and column trials were measured using *Shimadzu (AA 6200) Atomic Absorption Spectrophotometer* (Figure 3.1) at respective wavelengths and slit widths as indicated in the following table.

S.No	Metal Ions	Wavelength (nm)	Slit Width (nm)
1.	Pb(II)	283.3	0.7
2.	Cd(II)	228.8	0.7
3.	Ni(II)	232.0	0.2



Figure 3.1 Atomic Absorption Spectrophotometer Shimadzu (AA 6200)

3.9.2 Data Analysis

The adsorption percentage and amount of metal ions adsorbed were calculated as per the following equations (6 and 7)⁹⁵

$$\% \text{ adsorption} = \frac{(C_i - C_e)}{C_i} \times 100 \quad \dots (6)$$

$$q = \frac{V(C_i - C_e)}{W} \quad \dots (7)$$

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.

3.10 SPSS Software Analysis

Experimentally optimized parametric values were systematically subjected to data analysis using **SPSS 20 Software**. Studies on Descriptive, Pearson correlation and analysis of variance (ANOVA) were calculated to validate the experimental data for the influence of optimized particle size, contact time, initial concentration, dosage and pH during the adsorption process. The relationship and variability of the parametric data whose the significance is based on 95% confidence level can be derived.

3.11 Column Experiments

The results of Batch experiments were quantified through column analysis in the fixed bed continuous columns⁹⁶, made up of cylindrical glass tubes with inner diameter and height of 4.5 cm and 50 cm respectively. Maximum specific metal ion removal against the corresponding sorbents were registered through trial and error method (short and long term analysis), wherein the parameter viz., initial concentration of the former, dosage of the latter and flow rate of the studies were taken into account. Based on this, the columns were packed an appropriate grams of adsorbents of 0.71 mm particle size between the two supporting layers of glass wool, topped up with glass beads, where the sorbents down by gravity. The aqueous Pb(II) solution at optimized initial concentration were poured from top of the column slowly, to be in contact with the packed materials for 30 minutes, after which the elements were collected at specific rates through the adjustable knob fixed at the column bottom.

3.11.1 Desorption

Desorption studies were performed with varying concentrations of dilute HCl (0.01 -0.05 M) for loaded sorbents. Mixture of 50 mL HCl and spent sorbents (2 g) were agitated at 180 rpm in a mechanical shaker for 30 min, filtered and supernatant solutions analyzed using AAS to determine the desorption efficiency as per equation⁹⁷

$$\text{Desorption efficiency} = \frac{\text{Amount desorbed}}{\text{Amount adsorbed}} \times 100 \quad \dots (8)$$

3.11.2 Regeneration

The adsorption process can be made more economical, through regeneration of the spent sorbent. Sorbents were confirmed of metal free active sites, washed with double

distilled water till neutral pH was attained. Further, were oven dried for many a time (378 ± 5 K) and after agitation with desorbing medium retested for metal sorption capacity. Five consecutive sorption and desorption cycles were repeated by AAS determination and the consequent decline in the regeneration capacities were measured.

3.12 Effluent Analysis

3.12.1 Pb(II)

Prevalence of Pb(II) ions in discharges from paint industry formed the basis of the effluent collection from the identified location at Kariyampalayam, Coimbatore, Tamil Nadu, India. The samples were agitated with native initial concentration at appropriate dosages, pH environments and time frames for the chosen systems. The filtered samples were digested with HNO_3 at a ratio of 1:1 and analyzed for their residual Pb(II) concentrations against the initial effluent concentration.

3.12.2 Cd(II) and Ni(II)

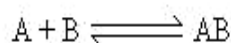
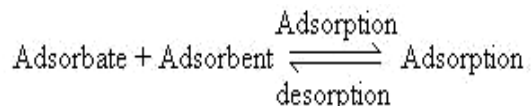
Minimal prevalence of Cd(II) and Ni(II) in effluent samples has led to the preparation of their corresponding synthetic solutions in the laboratory. 100 mg/ L concentrations of the respective ions were prepared, maintaining the pH as 5.5 and other elemental concentrations as mentioned in table 3.2.

Table 3.2 Composition of Synthetic Solutions [Cd(II) and Ni(II)]

Components (mg/ L)	Conc. (mg/ L)
Cd(II)/ Ni(II)	100.00
Sodium	50.00
Magnesium	50.00
Potassium	50.00
Chloride	152.00
Sulphate	135.00
Nitrate	463.00
Zinc	50.00
Chromium	50.00

3.13 Adsorption Isotherms

Adsorption isotherms indicate the distribution of molecules between the liquid phase and solid phase when the adsorption process reaches an equilibrium state⁹⁸. The isotherm models developed by Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich were applied to the equilibrium data in order to understand the sorption mechanism and surface characteristics.



3.13.1 Langmuir Isotherm

This model is based on the adsorption occurring at specific homogeneous active sites and equation can be written^{99, 100} as

$$C_e / Q_e = C_e / Q_m + 1 / bQ_m \quad \dots (9)$$

where, C_e = the equilibrium metal ion concentration in solution (mg/L),

Q_e = the equilibrium metal ion concentration on the sorbent (mg/g),

Q_m = the maximum monolayer adsorption capacity of the sorbent (mg/g)

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

The Langmuir constants Q_m and b were calculated from the linear slopes $1/Q_m$ and intercepts $1/bQ_m$. Higher the value of b indicates the greater affinity of the adsorbent in the metal sorption¹⁰¹.

(i). Separation Factor (R_L)

The essential characteristics of Langmuir equation can be expressed in terms of a dimensionless separation factor (R_L). The R_L values less than unity refer to unfavourable adsorption conditions, whereas equal to unity, between zero and unity, zero correspond to linear, favourable and irreversible nature. Equilibrium parameter R_L , is defined by the following relationship^{102, 103}.

$$R_L = \frac{1}{(1 + b C_i)} \quad \dots (10)$$

where, C_i is the initial metal ion concentration (mg/ L).

3.13.2 Freundlich Isotherm

The linear form of the Freundlich isotherm extended to multilayer adsorption is mathematically described by the equation,

$$\log q_e = \log k + 1/n \log C_e \quad \dots (11)$$

where, q_e = amount of metal ions sorbed per unit weight of the sorbent (mg/g)

C_e = equilibrium metal ion concentration (mg/L) of the metal ions in the solution

The constant K_f refers to an approximate indicator of adsorption capacity and $1/n$ to heterogeneity parameter¹⁰⁴ (function of the strength of adsorption). Adsorption intensity value (n) implies favorable sorption process.

3.13.3 Tempkin Isotherm

Heat of sorption factor derived from Tempkin isotherm equation explains the adsorbent –adsorbate interactions. The linearized form of isotherm¹⁰⁵ is

$$q_e = B_T \ln A_T + B_T \ln C_e \quad \dots (12)$$

where, $B_T = RT/b_T$

T is the absolute temperature in Kelvin

R is the universal gas constant, 8.314 J/ mol K.

The constants b_T (heat of sorption) and A_T (equilibrium binding constant) which corresponds to the maximum binding energy. Tempkin constants A_T and b_T were obtained from the intercept and slope of the linear plots of q_e vs $\ln C_e$.

3.13.4 Dubinin- Kaganer-Radushkevich Isotherm

DKR model assumes a monolayer adsorption in the process of evaluating the maximum sorption capacity of the sorbent and distinguish between the process of

physisorption and chemisorption of metal ions¹⁰⁶. The linear form of the DKR isotherm equation¹⁰⁷ is expressed as

$$\ln q_e = \ln q_s - \beta_{DR} \varepsilon^2 \quad \dots (13)$$

where, q_e = the amount of metal ions adsorbed per unit weight of the adsorbent (mol/g)

q_s = the theoretical saturation sorption capacity (mol/g)

β_{DR} = constant related to mean free energy per mole of the sorbate (mol^2/J^2)

ε = Polanyi potential, which is equal to $RT \ln (1+1/C_e)$

R = gas constant expressed in J/ mol K units

T = the absolute temperature.

The values of q_s and β_{DR} are obtained from the linear plot of $\ln q_e$ vs ε^2 . The constant β_{DR} provides an idea about mean free energy E (kJ/ mol) per molecule of the sorbate species when it is transferred to the solid surface and can be intended using the relationship.

$$E = \frac{1}{(2 \beta_{DR})^{1/2}} \quad \dots (14)$$

The parameter (E) provides information about sorption mechanism, which may be physical or chemical ion exchange sorption. If the magnitude of E lies in between 8 and 16 kJ/ mol, the sorption process said to follow chemical ion exchange, and if less than 8 kJ/ mol, the sorption process is of physical nature¹⁰⁸.

3.14 Adsorption Kinetics

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

3.14.1 Pseudo-First-Order Model

The model is based on the statement that the sorption rate is proportionate to the number of unoccupied sites and the equation is generally expressed as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad \dots (15)$$

where, q_e and q_t are the adsorption capacity at equilibrium and at time t , respectively (mg/ g) and k_1 denotes the rate constant for pseudo-first-order adsorption (min^{-1}). After integration by applying the conditions: $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the equation becomes

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad \dots (16)$$

The above equation is employed to verify the experimental data. The slopes and intercepts of plots of $\log (q_e - q_t)$ vs t were used to determine the first- order rate constant k_1 and equilibrium adsorption capacity q_e .

3.14.2 Pseudo-Second-Order Model

The sorption rate is proportional to the square of the number of unoccupied sites. The pseudo-second-order adsorption kinetic rate equation is expressed as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad \dots (17)$$

where, k_2 is the rate constant for pseudo-second-order adsorption (g/mg min). After integration, as in the case of pseudo first order, the equation (18) becomes

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad \dots (18)$$

Equation (19) is the integrated rate law for pseudo-second-order reaction and it can be rearranged to a linear form

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

The slopes and intercepts of plots of t/q_t vs t were used to calculate the q_e and pseudo-second-order rate constant k_2 . The sum of squares of errors is stated by

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

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

3.14.3 Elovich Model

The Elovich equation has been applied satisfactorily to systems in which the adsorbing surface is heterogeneous. The Elovich model equation is expressed¹⁰⁹ as

$$q_t = 1/\beta \ln(\alpha \beta) + 1/\beta \ln(t) \quad \dots (21)$$

where, α (mg/g min) is the initial adsorption rate and β (g/mg) represents the adsorption constant related to the extent of the surface coverage. The kinetic constants α and β were calculated from the intercepts and slopes of the plot of q_t vs $\ln t$.

3.14.4 Intraparticle Diffusion Model

In order to determine the mechanisms and rate controlling steps affecting the adsorption dynamics, the kinetic experimental results were applied to the Weber and Morris intraparticle diffusion model. Adsorption of metal ions from aqueous phase onto solid phase is a multi-step process involving metal ion transport to the sorbent surface followed by diffusion of metal ions through boundary layer to solid surface and later, the transfer of sorbed metal ions to its interior pores, which may be a slow process (rate determining step) in adsorption studies¹¹⁰. The possibility of intraparticle diffusion is explored by the following equation¹¹¹,

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

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

3.15 Activation Parameters

The activation energy terms from the Arrhenius equation indicate the sensitivity of the reaction rate to the temperature. Thermodynamic parameters: free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) change of adsorption can be evaluated from equations,

$$K_d = q_e / C_e \quad \dots (23)$$

where K_d is the sorption distribution coefficient. The K_d values are used to determine the ΔG° , ΔH° and ΔS° ,

$$\Delta G^\circ = -RT \ln K_d \quad \dots (24)$$

where ΔG° (cal mol^{-1}) is the free energy of adsorption, T (Kelvin) is the absolute temperature and R is the universal gas constant (J/mol K).

The K_d may be expressed in terms of the ΔH° (Kcal/ mol) and ΔS° (cal/ mol/ K) as a function of temperature:

$$\ln K_d = -\Delta H^\circ / (RT) + \Delta S^\circ / R \quad \dots (25)$$

where, ΔH° and ΔS° were derived from the slopes and intercepts of Van't Hoff plots.