

3.1 Adsorbent Materials

3.1.1 Collection of *Terminalia catappa* nut shell

The tropical Almond *Terminalia catappa* (Indian almond) belongs to the family Combrataceae. It is a large spreading tree distributed throughout the tropics in coastal environment²⁰¹. The tree is a native of Australia, Thailand and Vietnam. Typically one to five fruits develop on the basal part of the flower spike. The fruit is a sessile, laterally compressed, ovoid to ovate and smooth skinned drupe. The oil containing seeds are encased in a tough fibrous husk with a fleshy pericarp. This shell helps the fruits to float as the seed is dispersed by water. The corky fibrous endocarps (Fig 3.1a) of the fruits were collected from various localities in Coimbatore, Tamilnadu, India.

3.1.2 Collection of *Azadirachta indica* nut shell

Neem tree botanically known as *Azadirachta indica* belongs to the family Meliaceae and is a native of India which is widely grown in almost 30 countries including USA. The tree is tall, fast growing and is known for its drought resistance²⁰². It has potential value in the field of medicine and culture. The fruits are green and yellow when ripe and are yielded around 37-55 kg per tree. It is a smooth olive-like drupe which varies in shape from elongate oval to nearly roundish. The white, hard inner core of the fruit (fig 3.1b) known as the nut shell (endocarp) were collected from fertilizer manufacturing units in Coimbatore, Tamilnadu, India.



Fig 3.1a *Terminalia catappa* nut shell



Fig 3.1b *Azadirachta indica* nut shell

3.1.3 Preparation and treatment of the adsorbents

The common agents used for the preparation and treatment of adsorbents are hydrochloric acid, phosphoric acid, sodium hydroxide and zinc chloride. In the present study, hydrochloric acid was used for the acid treatment of the adsorbent, since it is an inexpensive and non volatile agent compared to phosphoric acid. Zinc chloride is not preferred due to problems of additional environmental contamination by zinc. For the alkali treatment of the adsorbent materials, sodium hydroxide is utilized. Perusal of literature study indicates that hydrochloric acid had been used for the preparation of acid treated adsorbent obtained from agricultural wastes such as *Lemna minar*²⁰³. Isabel Vellaescusa et al., had also mentioned the use of hydrochloric acid for the acid pre-treatment of grapestalk wastes in the removal of Cu (II) and Ni (II) ions from aqueous solutions²⁰⁴. The use of hydrochloric acid and sodium hydroxide for the pretreatment process had also been reported by A.L.Ahmad et al., in the adsorption of residue oil from palm oil mill effluent using powder and flake chitosan²⁰⁵.

Terminalia catappa nut shells and *Azadirachta indica* nut shells were thoroughly washed with double distilled water and dried in air. The dried shells were then powdered and sieved to various sizes viz., 85BSS, 72BSS, 52BSS, 36BSS and 22BSS. The powdered, sieved adsorbents were treated with 0.1 N HCl and boiled for three hours. After decanting the solution, the residues were allowed to boil with 0.1 N NaOH for three hours. The treated sorbents of varying sieve sizes were washed well several times with double distilled water. Later, they were soaked in the same for sufficient time, to ensure swelling, as it would make more sorption sites available and finally the sorbent materials were dried in sunlight. The chemically treated *Terminalia catappa* nut shell powder and *Azadirachta indica* nut shell powder were used for further experiments and shall be denoted as TTCNS (Fig 3.2a) and TAINS (Fig 3.2b) respectively in the forthcoming discussions.

**Fig. 3.2a TTCNS****Fig. 3.2b TAINS**

3.1.4 Microscopic Analysis

Microscopic study was carried out in order to determine the particle sizes of the employed adsorbents viz., TTCNS and TAINS, each of five different mesh sizes, using Nikon Diaphot light Microscope. The ocular micrometer with dimension of 10X was attached. Each division in the scale of the micrometer is 0.01 mm. The length and breadth of each granular particle size was measured using the micrometer scale. Fifteen different granular particles of each mesh sizes were chosen for the measurement of lengths and breadths to arrive at an average, as no two single particles are alike. By applying multiplication factors, the particle sizes were calculated. The plates of the microscopic structure of five different calculated particle sizes corresponding to the mesh sizes of 85BSS, 72BSS, 52BSS, 36BSS and 22BSS are 0.18mm, 0.21mm, 0.30mm, 0.42mm and 0.71mm respectively.

3.1.5 Preparation of modified adsorbents

The modification process was carried out using disodium hydrogen phosphate for both *Terminalia catappa* nut shells and *Azadirachta indica* nut shells. The adsorbents were soaked separately in 0.1M solution of disodium hydrogen phosphate for a period of 24 hours at room temperature. The aged adsorbents were later washed several times with double

Distilled water, until the supernatant solutions did not produce yellow colouration with ammonium molybdate solution ensuring the absence of free phosphate in the modified sorbents and then air dried. The phosphate modified adsorbents thus prepared from *Terminalia catappa* nut shells and *Azadirachta indica* nut shells are represented as MTCNS (fig 3.3a) and MAINS (Fig 3.3b) in their respective discussions.



Fig. 3.3a MTCNS



Fig. 3.3b MAINS

3.1.6 Preparation of Nano hydroxyapatite-adsorbent composite

Nano hydroxyapatite composites are widely applied in the field of adsorption of heavy metal ions from aqueous solutions and industrial effluents. A one-step co-precipitation method²⁰⁶ was adopted to prepare the nano hydroxyapatite, by adding 15g of Ammonium dihydrogen phosphate with 15g of Calcium nitrate (1:1ratio) in the presence of ammonia (pH-9). The white nano hydroxyapatite powder thus obtained was washed well with double distilled water several times to bring the pH to 7 and later dried under normal conditions. The dried nano powder was then mixed with 0.18 mm of AINS in the ratio of 1:1 by adopting the one step co-precipitation method. pH adjustments were done using acetic acid and NaOH solutions. The obtained nano hydroxyapatite-adsorbent composite was then dried well and

utilized for the specific studies. The Nano hydroxyapatite – *Azadirachta indica* nut shell composite is mentioned as NAINSC (fig 3.4) in the forthcoming discussions.



Fig 3.4 NAINSC

3.2 Characterization of Treated adsorbents

The physicochemical characteristics of the treated adsorbents are compiled in table 3.1

3.2.1 pH and Conductivity²⁰⁷

One gram of each of the adsorbents were transferred to 250 ml beakers. 300 ml of freshly boiled and cooled double distilled water (adjusted to pH 7.0) was added and heated to boiling. After 10 minutes, the solutions were filtered and the first 15 ml of the hot filtrate was discarded. The remaining filtrate solutions were cooled to room temperature. The pH and conductivity were determined using *ELICO (LI-120)* pH meter and *ELICO (CM 180)* digital conductivity meter.

3.2.2 Moisture²⁰⁷

Approximately 0.25g of the adsorbents were taken in petri dishes and placed in an electric oven maintained at 383 ± 5 K for about 2 h. The dishes were covered and cooled in desiccators and then weighed. Heating, cooling and weighing were repeated at 30 min intervals until the difference between two consecutive weighings was less than 5 mg.

$$\text{Moisture Content (\%)} = \frac{(W-X)}{W} \times 100 \quad \dots (1)$$

where W = Weight of the material (g)

X = Weight of the material after drying (g)

3.2.3 Bulk density²⁰⁸

Specific gravity bottles of 10 ml capacity were filled with the adsorbents and packed well by tapping with a rubber stopper. The weights of the adsorbents were determined. The weight (g) divided by volume (ml) resulted in the bulk density (g/ml) of the adsorbents.

3.2.4 Specific gravity²⁰⁸

Five grams of the adsorbents were placed in small porcelain dishes, 50 ml of double distilled water was added and the contents were heated to boil gently for 3 min to expel the air. After cooling in a water bath to 288 K, the sorbent suspensions were transferred to 100 ml pycnometers and weighed (W_c). Later, the pycnometers were filled with double distilled water and weighed (W_b)

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

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

W_a = Weight of adsorbent

W_b = Weight of pycnometer with water

W_c = Weight of pycnometer with adsorbent residue

3.2.5 Porosity²⁰⁷

Porosity was determined from the specific gravity (S) and bulk density (D) values of carbon.

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

3.2.6 Ash content²⁰⁷

One gram of the adsorbents was placed in porcelain crucibles. The crucibles and its contents were placed in an electric oven at 383 ± 5 K for about 5 h. The crucibles were removed from the oven and the contents were ignited in an electric muffle furnace at a temperature of 800 K for about 2 h. The crucible was removed and cooled in desiccators and then weighed. Heating, cooling and weighing was repeated at 30 min intervals until the difference between two consecutive weighings was less than 5 mg. The ash content was calculated as percentage by weight.

3.2.7 Water soluble matter²⁰⁷

0.5 grams of the adsorbents were taken in 500 ml beakers, 60 ml of double distilled water was added and heated to boiling with continuous stirring. Stirring was continued for 5 minutes even after the burner was removed. The materials were then allowed to settle and the supernatants were filtered through gooch crucibles fitted with asbestos mats. The procedure was repeated thrice for the remaining residues in the beakers using 60 ml of double distilled water every time.

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. Exactly 50 ml of the concentrates were transferred to china dishes and evaporated to almost dryness on a boiling water bath and finally dried in an electric oven, maintained at 373 ± 5 K, cooled in desiccators and weighed. The procedure of drying and weighing was repeated at 30 min interval, until the difference between two consecutive weighings was less than 5 mg.

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

Where W_1 = Weight of the residue (g)

W_2 = Weight of the adsorbent (g)

X = Percentage of moisture in the adsorbent

3.2.8 Acid soluble matter²⁰⁷

0.5 grams of the adsorbents were taken in 500 ml beakers, 60 ml of 0.25 N HCl were added and heated to boiling with continuous stirring. Stirring was continued for 5 min even after the burner was removed. The materials were then allowed to settle and the supernatant was filtered through gooch crucibles fitted with asbestos mats. The procedure was repeated thrice for the remaining residue in the beakers using 60 ml of HCl each time.

The combined filtrates were concentrated to less than 100 ml by heating over a water bath, cooled and made upto 100 ml in volumetric flasks. Exactly 50 ml of the concentrate was transferred to china dishes and evaporated to almost dryness on a boiling water bath and finally dried in an electric oven, maintained at 373 ± 5 K, cooled in desiccators and weighed. The procedure of drying and weighing was repeated at 30 min interval, until the difference between two consecutive weighings were less than 5 mg. Acid soluble matter was calculated using the same expression as in the case of water soluble matter.

$$\text{Acid soluble matter} = \frac{20000 \times A}{W (100 - X)} \quad \dots (6)$$

where A = Weight of the dried residue (g)

 W = Weight of the adsorbent (g)

 X = Percentage of moisture in the adsorbent

3.2.9 Ion exchange capacity²⁰⁹

0.2 grams of the adsorbents were taken in beakers and sufficient amount of double distilled water was added to cover the adsorbents. 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 material bed. 250 ml of the solutions of 0.25 M sodium sulphate were allowed to drip into the columns at a rate of 2 ml per minute and the samples were collected in 500 ml conical flasks. When all the solutions have passed through the columns, the collected samples were titrated with standard 0.1 N sodium

hydroxide solutions using phenolphthalein as indicator. The ion exchange capacity of the bed in m eq/g is given by NV/W where N is the normality of sodium hydroxide solution; V is the volume in ml and W is the weight of the adsorbent.

3.2.10 Zero point charge (pH_{ZPC})²¹⁰

The zero point charges of the adsorbent were determined by the solid addition method. To a series of 100 mL conical flasks 45 ml of KNO_3 solution (0.1 and 0.01 M) was transferred. The pH values (viz., 2, 4, 6, 8, 10) of the two different solutions were adjusted by adding 0.1 M HCl or 0.1 M NaOH solutions respectively. The total volume of the solution in each flask was made exactly to 50 ml by adding excess KNO_3 solution (0.1 or 0.01 M as the case may be). The pH values of these solutions were noted (pH_i). 1 g of the adsorbents were added to each flask. The suspensions were manually shaken for 5 minutes and allowed to stand undisturbed for 48 h. The pH values of the supernatant liquid were noted after the stipulated time interval. The difference between the initial (pH_i) and final pH (pH_f) values ($\Delta\text{pH} = \text{pH}_i - \text{pH}_f$) was plotted against pH_i . The zero point charges were interpreted from the point of intersection of the resulting curve.

3.2.11 Elemental analysis and Surface area

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

3.3 Characterization of Surface Functional Groups

The nature and concentration of surface functional groups may be modified by suitable thermal or chemical post treatments. Carboxyl, carbonyl, phenol, quinine and lactone groups have been identified on the adsorbents surfaces^{186,187}. Varieties of experimental techniques have been used to characterize these functional groups such as chemical titration methods, spectral and BET analysis etc.,

3.3.1 Determination of active sites

The amount of oxygenated acid surface groups was determined using Boehm titration method²¹¹. 1 gm of adsorbent samples were placed separately in 50 ml of the following 0.05 N solutions: NaOH, Na₂CO₃, and NaHCO₃. The flasks were sealed and shaken for 24 h 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 of HCl was titrated against 0.05 N NaOH using phenolphthalein indicator. A blank titration was also conducted for each titration. The amounts of acidic sites of various types were calculated under the assumption that NaOH neutralizes carboxylic, phenolic and lactonic groups; Na₂CO₃ neutralizes carboxylic and lactonic groups; NaHCO₃ neutralizes only carboxylic acid groups.

3.3.2 FT-IR Spectral Analysis

Fourier transform infrared spectral analysis of adsorbent samples was performed by using *Thermo Nicolet Infrared Spectrophotometer*. FT-IR analysis were carried out as a preliminary and qualitative analysis to determine the main functional groups present in the sorbent that might have involved in the metal uptake. The spectra of the adsorbents before and after metal ion sorption process were recorded. For the sorption process, adsorbent samples were loaded with a 50 mg/L of metal solution at a suitable pH adopting the batch procedure. The adsorbents were blended with IR-grade KBr in an agate mortar and pressed into pellets. The spectra were recorded within the range of 400-4000 cm⁻¹. The spectral discussions are dealt in chapters IV, V, VI and VII.

3.3.3 SEM and EDAX analysis

The surface morphology of the treated adsorbents before and after metal sorption was examined using the *JEOL JFM- 6390* Scanning Electron Microscope. After drying, the samples were covered with a thin layer of platinum (10 nm) using a sputter coater (SCD 0050 – Baltec, Liechtenstein) and observed using the scanning electron microscope (20 kV) under

vacuum of 1.33×10^{-6} m Bar (*Jeol, Japan*)., Energy dispersive X-Ray analysis spectra was performed for unloaded and loaded adsorbent materials to determine their chemical composition. The observations based on SEM pictures and EDAX spectra are discussed in chapters IV, V and VI.

3.3.4 Bruner-Emmett-Teller and Barrett-Joyner-Halenda analysis

Surface areas and pore characteristics of the treated adsorbents were determined using the Bruner-Emmet-Teller (BET) and Barrett-Joyner-Halenda (BJH) plots respectively. The instrument (*Micromeritics, BEL, Japan, Inc*) employs nitrogen adsorption on an accelerated surface area and porosimetry system. This is supported by sophisticated Belsorp adsorption/desorption data analysis software. Prior to analysis, portions of adsorbents were degassed for 5 hours at 120°C in N₂ environment using a Micromeritics degassing system. The pore size distribution and specific surface areas (Table 3.1) were determined via N₂ adsorption/desorption isotherms obtained at 77 K. Analysis were repeated, at least twice, for both the adsorbents.

Table 3.1 Physicochemical Characteristics of the Adsorbents

Properties	TTCNS	TAINS
pH of 1 % solution	6.80	6.15
Conductivity	41.40	35.50
Yield (%)	68.06	63.08
Moisture (%)	8.51	8.75
Bulk density (g/L)	0.25	0.36
Specific gravity	4.41	1.16
Porosity	94.95	68.89
Ash content (%)	9.09	3.29
Water soluble matter (%)	2.93	2.09
Acid soluble matter (%)	1.70	1.85
Ion exchange capacity (meq/g)	0.40	0.59
pH _{zpc}	6.20	5.10
Sodium (mg/g)	1.8	1.3
Calcium (mg/g)	8.0	8.4
Surface area (m ² /g)	83.14	28.81
Mean Pore diameter (nm)	38.69	14.76
Carbon (%)	48.24	42.97
Hydrogen (%)	5.95	6.09
Nitrogen (%)	0.45	0.48
Sulphur (%)	0.67	0.44
Oxygen (%)	44.69	50.02
Surface acidic groups		
Phenolic	0.23	0.79
Carboxylic	0.94	1.13
Lactonic	0.17	0.32

3.4 Preparation of Adsorbate Solutions

The metal ions chosen for the adsorption studies were Ni(II), Co(II) and Cr(VI). All the chemicals employed for the analysis were either analaR or other high purity grade and were used without further purification. Nickel ammonium sulphate, Potassium dichromate, Cobaltous chloride, Potassium nitrate, Magnesium nitrate, Sodium chloride, Sodium sulphate and Sodium nitrate were purchased from Ranbaxy and Qualigens companies. Water was deionized and doubly distilled, using an all glass distillation still (*Distillon4DQ*). All weighings were taken using a *Shimadzu APX 200* electronic balance.

3.4.1 Ni(II) solution

A stock of Ni(II) solution of 1000 mg/L was prepared by dissolving 6.7303 g of anhydrous Nickel ammonium sulphate in 1000 ml of double distilled water.

3.4.2 Co(II) solution

A stock of Co(II) solution of 1000 mg/L was prepared by dissolving 4.037 g of Cobaltous chloride in 200 ml of double distilled water, then acidified with 5 ml of concentrated hydrochloric acid to prevent hydrolysis and diluted to 1000 ml with double distilled water.

3.4.3 Cr(VI) solution

A stock of Cr(VI) solution of 1000 mg/L was prepared by dissolving 2.828 g of Potassium dichromate in 1000 ml of double distilled water.

3.4.4 Collection of Industrial effluents

Industrial effluent samples were collected from an electroplating industry in Coimbatore also from chemical, fertiliser industries and Madras Aluminium Company (MALCO) in Salem were subjected to testing, for the analysis of Cr(VI) and Ni(II).

3.5 Batch Mode Adsorption Studies

Adsorption experiments were carried out in batch mode at ambient temperature. In order to investigate the nature of metal- adsorbent interaction, initially the effect of pH on the percentage removal was carried out and then further experiments on the influence of particle size, contact time, initial concentration of adsorbates, adsorbent dosage, cations, anions, co-ions and temperature were conducted using optimized pH. Only one of the parameters was changed at a time while others were maintained constant. The influential ions chosen for the study were chloride, nitrate, sulphate, sodium, potassium, magnesium and calcium ions and metal adsorption was determined to ensure the nature of the employed materials in presence of these ions. The impact of the co-ions on individual metal ions adsorption was studied. The effect of temperature on the adsorption was determined in the range of 293-323 K.

Batch mode adsorption studies was carried out by taking 50 ml of the metal solution of fixed initial concentration and required amount of adsorbent in 100 ml conical flask. Metal solutions were agitated in a thermostat controlled mechanical shaker (*TECHNO*) at different time intervals at 303 K. The adsorbent and the adsorbate were separated by simple filtration. The pH values of the solutions were measured using *ELICO (LI-120)* pH meter. Duplicate experiments were conducted to ensure the reproducibility of the experimental set-up to be within $\pm 1\%$. Control experiments were carried out to check the occurrence of adsorption by the container walls. The residual metal ion concentrations after adsorption were measured using a UV-Visible double beam spectrophotometer (*LAB INDIA*). The metal ion concentrations in the collected samples pertaining to the specific metal ions under study were also measured using *Shimadzu (AA 6200) Atomic Absorption Spectrophotometer*.

The percentage of adsorption of metal ions from aqueous solutions were estimated using the following equation¹³³

$$\% \text{ adsorption} = \frac{(C_i - C_e)}{C_i} \times 100 \quad \dots (7)$$

The amount of metal ions sorbed by adsorbents (q) in the sorption system were calculated using the mass balance

$$q = \frac{V(C_i - C_e)}{W} \quad \dots (8)$$

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

3.6 Metal ions Estimation

3.6.1 Estimation of Ni(II)

Ni(II) was determined spectrophotometrically as Ni-DMG complex. To about 10 ml of the filtered sample solution containing Ni(II), 0.5ml of 0.5N HCl, 0.2ml of 0.25N Sodium citrate, 1 drop of 0.05N iodine and 0.8ml of 0.5% DMG were added. The absorbance of rosy red Ni-DMG complex was measured at 445 nm.

3.6.2 Estimation of Co(II)

Co(II) was determined spectrophotometrically employing alcoholic potassium thiocyanate solution to complex the metal ion. To about 5ml of the filtered sample solution containing Co(II), 7ml of ethyl alcohol and 1g of potassium thiocyanate were added, the developed greenish blue coloured complex were estimated in the spectrophotometer and their absorbance values were recorded at 630 nm.

3.6.3 Estimation of Cr(VI)

Cr(VI) was determined spectrophotometrically using diphenyl carbazide. 2.5ml of the filtered sample solution containing Cr(VI) was transferred to 25ml standard flask. 3ml of 2N H_2SO_4 and 0.5ml of diphenyl carbazide solution (0.5% in acetone) were added and made upto 25ml with double distilled water. The absorbance of red-orange Cr(VI)-diphenyl carbazone complex was measured at 540 nm.

Desorption and regeneration studies were also carried out to assess the reusability and reproducibility of the adsorbents. The thermodynamic constants for the adsorption processes of each system were calculated. The results of all experiments conducted at 303 K are presented in detail in the forthcoming chapters accompanied by detailed discussions.

3.7 Effect of Variable parameters

3.7.1 Particle size

Adsorption experiments were performed at different particle sizes (viz., 0.18mm, 0.21mm, 0.30mm, 0.42mm and 0.71mm) of the adsorbent materials employed at desired pH values and agitated at preset time intervals.

3.7.2 Contact time and Initial metal ion concentration

Batch experiments were carried out at different initial concentrations ranging from 3 to 11 mg/L, adjusted to desired pH values while the other factors were kept constant.

3.7.3 Adsorbent dosage

Batch adsorption experiments were carried out at varying adsorbent doses (viz., 50mg, 100mg, 150mg, 200mg and 250mg) and filtered at regular time intervals.

3.7.4 pH

The experimental solutions were adjusted to different pH values (1-8) for chosen metal ion concentrations under study and agitated at predetermined time intervals.

3.7.5 Cations and Anions

The adsorption efficiencies of the adsorbent materials in the presence of cations and anions were evaluated for 11 mg/L of metal ions. The concentrations of cations and anions ranging from 25 to 100 mg/L were mixed up in equal volumes with the adsorbate solutions. In all these cases, the absence of other ions was ensured.

3.7.6 Co-ions

Adsorption studies of a specific metal ion in the presence of other metal ions were experimentally verified for 11 mg/L concentration of respective metal ion, at optimum pH and dosage of the adsorbent. This involved the determination of the residual Ni(II) in the mixture containing equal amounts of co- ions. Similarly, the analysis of Co(II) and Cr(VI) from the solutions containing equal amounts of the other metal ions were also carried out.

3.7.7 Temperature

Adsorption experiments were performed at four different temperatures viz., 293, 303, 313 and 323 K for 11 mg/L of metal ions in a thermostat controlled shaker. The constancy of the temperature was maintained with an accuracy of $\pm 0.5\text{K}$.

3.7.8 Desorption

Desorption studies are helpful to explore the possibility of recycling the adsorbents and the recovery of the metal resource. Sorption of a solute on any adsorbent can either be physical bonding or ion exchange or combination of both. If the adsorption is by physical bonding, then the loosely bound solute can be easily desorbed with distilled water in most cases. However, if the mode of adsorption is by ion exchange mechanism, then desorption can be effected by stronger desorbing agents like acid or alkali solutions. Adsorption experiments with 11 mg/L metal ion concentration with fixed adsorbent dosage were carried out, later the contents were centrifuged and the supernatant was drained out. The remaining adsorbent was given gentle wash with double distilled water to remove unadsorbed metal ions. Several such samples were prepared and agitated for 120 min, with 50 ml of HCl for Ni(II) and Co(II) and with NaOH for Cr(VI) of various strengths. The desorbed metal ions in the solution was separated by filtration and analysed for the metal ion concentration.

The desorption efficiencies of the adsorbents were calculated as per equation²¹²

$$\text{Desorption efficiency} = \frac{\text{Amount desorbed}}{\text{Amount adsorbed}} \times 100 \quad \dots (9)$$

3.7.9 Regeneration

To make the adsorption process more economical it is necessary to regenerate the spent adsorbent materials. The metal loaded adsorbents (200 mg) were agitated with 50 ml of HCl as desorbing medium. The desorbed adsorbents were separated by filtration, washed several times with double distilled water until the pH of the solution was almost neutral. The regenerated adsorbent was dried in an oven at 378 ± 5 K and was employed to adsorb the metal ions again. Each sorption and desorption cycles were allowed with required amount of contact time and consecutive sorption-desorption cycles were repeated three times.

Various criteria adopted in batch mode studies of TTCNS, TAINS, MTCNS, MAINS and NAINSC are tabulated in 3.2, 3.3, 3.4, 3.5 and 3.6 respectively.

Table 3.2 Batch mode studies of Ni(II) onto Treated Adsorbents

Nature of study	Metal ion Conc. (mg/L)	Agitation Time (min)		Adsorbent dose (mg)	
		TTCNS	TAINS	TTCNS	TAINS
Particle size	11	30	14	150	50
Contact time and Initial conc.	3-11	30	14	150	50
Dose	11	30	14	50-200	50-200
pH	11 and 13	30	14	150	50
Cations and Anions	11	30	14	150	50
Co-ions	11	30	14	150	50
Temperature	11	30	14	150	50
Desorption	11	60	60	500	500
Regeneration	11	60	120	200	200
Nickel effluent	2.86	30	14	50-500	50-500

Table 3.3 Batch mode studies of Co(II) onto Treated Adsorbents

Nature of study	Metal ion Conc. (mg/L)	Agitation Time (min)		Adsorbent dose (mg)	
		TTCNS	TAINS	TTCNS	TAINS
Particle size	11	30	30	100	150
Contact time and Initial conc.	3-11	30	30	100	150
Dose	11	30	30	50-200	50-200
pH	11 and 13	30	30	100	150
Cations and Anions	11	30	30	100	150
Co-ions	11	30	30	100	150
Temperature	11	30	30	100	150
Desorption	11	60	60	100	150
Regeneration	11	60	60	200	150

Table 3.4 Batch mode studies of Cr(VI) and effluent onto Treated Adsorbents

Nature of study	Metal ion Conc. (mg/L)	Agitation Time (min)		Adsorbent dose (mg)	
		TTCNS	TAINS	TTCNS	TAINS
Particle size	11	60	60	150	150
Contact time and Initial conc.	3-11	60	60	150	200
Dose	11	60	60	50-250	50-250
pH	11 and 13	60	60	150	150
Cations and Anions	11	60	60	150	150
Co-ions	11	60	60	150	150
Temperature	11	60	60	150	150
Desorption	11	120	120	200	200
Chromium effluent	12.3	30	15	50-500	50-500

Table 3.5 Batch mode studies of Ni(II), Co(II), Cr(VI) onto Modified Adsorbents

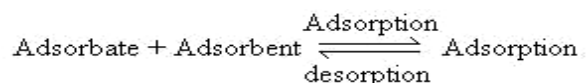
Metal ion	Nature of study	Metal ion Conc. (mg/L)	Adsorbent dose (mg)	
			MTCNS	MAINS
Ni(II)	Contact time and Initial conc.	3-13	50	150
Co(II)	Contact time and Initial conc.	3-13	100	150
Cr(VI)	Contact time and Initial conc	3-13	200	150
Nickel effluent	Dosage	2.86	50-500	50-500
Chromium effluent	Dosage	12.3	50-500	50-500

Table 3.6 Batch mode studies of Ni(II) and Cr(VI) onto Nanocomposited Adsorbent

Metal ion	Nature of study	Metal ion Conc. (mg/L)	Adsorbent dose (mg)
			NAINSC
Ni(II)	Dosage	11	10-50
Cr(VI)	Dosage	11	10-50
Nickel effluent	Dosage	2.86	10-50
Chromium effluent	Dosage	12.3	10-50

3.8 Adsorption Isotherm and Kinetics

The process of adsorption is usually studied through graphs known as adsorption isotherms. It is the graph between the amounts of adsorbate (x) adsorbed onto the surface of adsorbent (m) and pressure at constant temperature. In the process of adsorption, adsorbate gets adsorbed on the adsorbent.



According to Le-Chatelier principle, the direction of equilibrium would shift in that direction where the stress can be relieved. The equilibrium established between the adsorbate component on the sorbent and the unabsorbed component in the solution can be represented by adsorption isotherms. To understand the sorption mechanism and surface characteristics of the adsorbent, the mathematical isotherm models developed by Langmuir, Freundlich, Tempkin and Dubinin-Kaganer-Radushkevich were applied to the equilibrium data.

Adsorption kinetics describes the solute uptake rate which in turn controls the resident time of sorbate uptake at the solid-solution interface. Therefore, it is important to be able to predict the rate at which pollutant is removed from aqueous solutions in order to design appropriate sorption treatment plants. The rate at which dissolved heavy metal ions are removed from dilute aqueous solutions by solid sorbents is a significant factor for application in water quality control.

The adsorption kinetics of metal transport onto an adsorbent can be controlled by several independent processes. These are (i) Bulk diffusion (ii) External mass transfer (film diffusion) (iii) Chemical reaction (Chemisorption) and (iv) Intra-particle diffusion. These processes can act in series or parallel to account for the surface transport of a metal into an

adsorbent. The efficiencies of the adsorbents were evaluated by following adsorption kinetics viz., pseudo- first-order, pseudo-second-order, Intra-particle and Elovich models.

3.9 Activation parameters

The activation energy term from the Arrhenius equation is best regarded as an experimentally determined parameter that indicates the sensitivity of the reaction rate to temperature. The kinetic data obtained from temperature studies were employed to calculate the change in standard free energy, enthalpy and entropy of adsorption to determine the possibility and feasibility of the reaction.