CHAPTER 3

Materials and methods

The various materials required, the experimental methods as well as the analytical tools used in this study on the removal of heavy metals from aqueous solution using foam separation techniques is described in this chapter.

3.1 Materials & Reagents

The metal salts the ancillary reagents and chemicals used in this study are listed below:

3.1.1 Metallic precursors:

Nickel sulphate ($NiSO_4.6H_2O$) having assay of 23% nickel, supplied by Ranbaxy laboratories Ltd., was used as the nickel source.

Zinc Sulphate ($ZnSO_4.7H_2O$) of excelar grade having minimum 99.5% purity, supplied by Merck Specialities Pvt. Ltd., was the zinc source.

Cadmium sulphate ($CdSO_4.8H_2O$) having assay of 98% supplied by Thomas Baker was the source for cadmium.

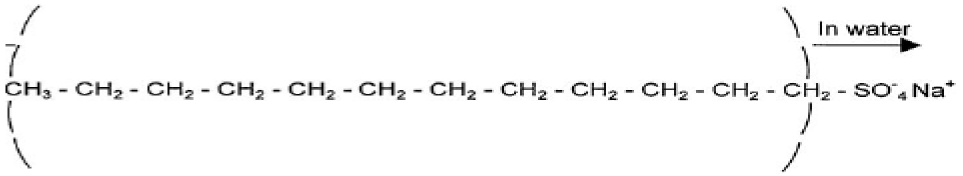
3.1.2 Surfactant

Sodium dodecyl sulphate (SDS) of LR grade having assay of 94% supplied by S.D. Fine Chemicals Limited was used as the surfactant for metal removal. (Rosen 1989)

Table 3.1: Selected properties of the surfactant used in this study

Commercial Name	Hydrophobic Group	Hydrophilic Group	Molecular Weight g/mol	C.M.C. x10^{-3} Moles/l
Anionic surfactant				
Na-Dodecyl Sulfate	Dodecyl	Sulfate	288	8.25

Structural formula of SDS



$$\left(CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 \right) \xrightarrow{\text{In water}} - SO^{-}_{4} Na^{+}$$

3.1.3 Polymer additives:

Polyvinyl pyrrolidone (PVP) having assay of 94.1%, supplied by Loba Chemie Pvt. Ltd., was used to investigate the polymer-surfactant interaction.

3.1.4 Indicators:

Bromophenol blue was used as indicator in analyzing surfactant concentration by two phase titration. Starch solution was used as indicator for interfacial area determination.

3.1.5 Miscellaneous chemicals:

- Chloroform of AR grade having assay of 99.4% supplied by S. D. Fine Chem. Ltd., Sodium Hydroxide with assay 98% of Ranbaxy make, Benzothonium chloride as cationic surfactant were used for two phase titration to determine surfactant concentration in feed, foamate and residue.

- Sodium sulphite (Na_2SO_3) LR grade with assay 96% supplied by S.D. Fine Chem. Ltd., Cobalt Sulphate heptahydrate ($CoSo_4$ $7H_2O$) of AR grade supplied by S. D. Fine Chem. Ltd. and Iodine solution were used in sulphite oxidation method for Interfacial area determination. Rhodamine B dye was used for confocal microscopy.

3.1.6 Ancillary reagents and chemicals

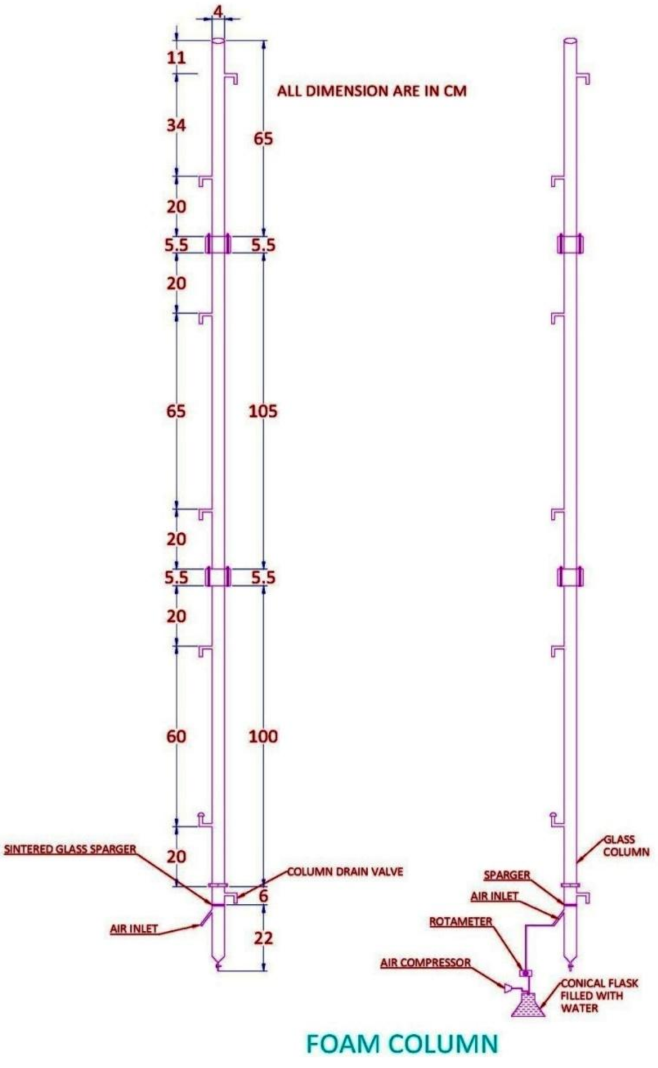
- Sulfuric acid of AR grade with assay 98% was of Ranbaxy make.
- Standard pH buffer of 4 pH, 7 pH and 9.2 pH of Qualigens make were used.

Certified Atomic absorption spectroscopy standards of SRL make for zinc, nickel and cadmium were used to generate standard curves for metal analysis.

3.2 Experimental setup

Foam separation was studied in three different columns.

i. Glass column having 0.04 m diameter and 2.5 m height with a sparger provided at the bottom (FC-1). This glass column was fabricated with multiple sample outlets as shown in Fig.3.1. at a distance of 0.8, 1.15, 1.85 m from sparger of column.



(a) **(b)**

Fig. 3.1**:** (a) Foam Column with dimensions (b) line diagram of foam column

Sparger and cylindrical glass column under operation are shown in Fig. 3.2, Major part of the work was done in this column.

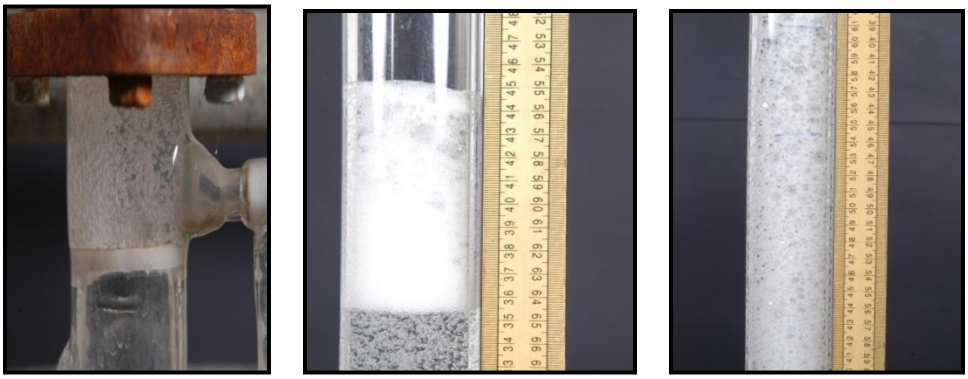


Fig. 3.2**:** Sparger and cylindrical foam column under operation

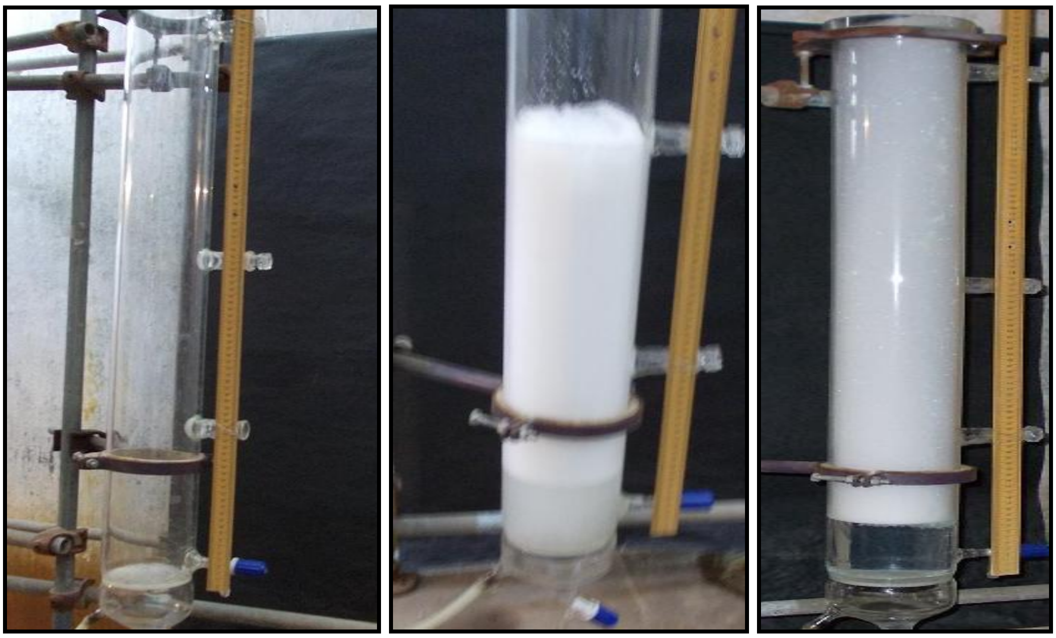
ii. To study behavior of air bubbles in dilute aqueous solutions rectangular shaped perspex column (FC-2) having area identical to the glass column of 0.04 m i.d with same effective height was fabricated. Since the 4 cm diameter cylindrical glass column has an area of 12.56 cm^2 therefore to have the same c.s. area the rectangular perspex column having base area of 8cm x 1.6 cm and height of 1.9m was fabricated as shown in Fig.3.3. Column has sample outlets also at a distance 0.69,0.118 & 0.168 m from sparger.

(a) **(b)**

Fig. 3.3: Experimental rectangular column with (a) surfactant solution (b) water

iii. A larger diameter cylindrical glass column (FC-3) having 0.10m diameter and 1 m height with multiple sample outlets at a distance of 0.04, 0.24, 0.50 and 0.86 m was fabricated to study scale up effects and recoveries in larger columns. Fig. 3.4 shows sparger and Fig. 3.5 shows larger diameter column.

Fig. 3.4**:** Sparger of large cylindrical glass column



(a) **(b)** **(c)**

Fig. 3.5: Cylindrical glass column of 0.10 m dia. (a) empty (b) and (c) under operation

3.3 Experimental Technique:

Determination of Surface Tension

The surface tension of SDS solutions were measured at 25 ^{O}C with a DuNuoy model using the ring type surface tension method. All glasswares for the measurement were thoroughly cleaned and rinsed with distilled water. Between measurements, the ring was rinsed many times in distilled water and then burned in a flame. Different concentrations of SDS solutions were prepared. Then a fixed amount of sample (50 ml) was taken for the measurement in each case.

pH measurement

Metal extractions studied in this work are extremely pH sensitive, particularly so with the proprietary carrier/ surfactant that were used in this study. The pH measurements were made using a *Systronics* make digital pH meter that was calibrated at pH values of 4 and 7 and 9.2 for extraction of metal solutes.

Evaluation of liquid hold up by Ross-Miles pour test method (ASTM D1173-63)

Liquid hold up in foam was determined using Ross Miles pour test method at varying metal concentration and varying SDS concentration in the range of 3.88-7.97 mM/L. Liquid hold up of foam was also measured in the presence of PVP.

The Ross-Miles pour test method is a standard test method developed by ASTM since the type and amount of generated foam depends on the height of pouring, the volume of liquid poured, the initial volume of liquid on which it is poured, and the construction of the experimental apparatus.

In this standard test a surfactant solution of 200 ml was placed in a pipette of specified dimensions with an orifice of internal diameter (i.d.) 0.0029 m and length 0.010 m. The solution in the pipette was allowed to fall from a height of 0.90 m on to 50 ml of the same solution present in a cylindrical vessel (i.d. 0.05 m). The foam height in the receiver was measured immediately after the last drop of the solution fell from the foam pipette and again five minutes later. The first reading is a measure of the foaming power of the surfactant while the second indicates the stability of the foam. All measurements were performed at 25^0 C. The foam produced is not homogenously dispersed but has a coarser foam upper layer, which is less stable than the bulk foam. (Milwidsky 1982)

Foam formation in columns and associated metal recovery

Aqueous solutions of sodium dodecyl sulfate were taken in a glass column and air was passed through it in a controlled manner this led to formation of foam bed inside the column. The foam was allowed to rise in the column and allowed out from a particular outlet.

The foam was collected and disintegrated and the foamate volume was noted at different time intervals ranging from 5 min to 30 min. This procedure was adopted for SDS as well as for SDS with 100 mg/L zinc ions. Experiments were performed at varying gas rates to ascertain the effect of gas flow rates. The foamate volumes obtained in presence and absence of metals were compared.

To investigate the extent of metal recovery by foam separations a known aqueous solution of metal ions containing known amount of surfactant was loaded in the column and air was bubbled in it to form the foam. The foam was allowed to rise in the column and was collected from specific outlet. The collected foam was broken and analyzed for surfactant and metal content and the recoveries were calculated.

Effect of pH, surfactant concentration, feed concentration, gas flow rate etc. on metal recovery was investigated for zinc, cadmium and nickel removal from aqueous streams. Surfactant-polymer association using PVP as the polymer was also investigated at various pH conditions for cadmium removal.

3.4 Analysis of surfactant and metals

Anionic surfactant SDS is used in present work. Surfactant determination is done by two phase titration. Metals cadmium, zinc and nickel were analyzed by Atomic Absorption Spectrophotometer.

3.4.1 Surfactant analysis by two phase titration

Quantitative analysis of ionic surfactants is quite precise and achieved by two phase titration. Analysis of anionic surfactant such as SDS is achieved using benzethonium chloride and is very widely used method for total anion active content. The detailed procedure is listed below.

Weigh a sample containing about 1.5 gm of anionic active. Dissolve in water. Dilute to 1 litre and mix. Pipette 20 or 25 ml into a 100ml stoppered measuring cylinder, a stoppered flask. Add 10 ml water, 15 ml chloroform and 10 ml acid mixed indicator (disulphine blue VN and dimidium bromide).Titrate with 0.004M benzethonium chloride with thorough shaking or stirring after each addition until the pink color is just discharged from the chloroform layer. If the chloroform layer becomes blue the endpoint has been overshot.

The acid mixed indicator can be replaced with 1 ml 0.04% bromophenol blue and 10 ml 0.1M sodium hydroxide. Titrate with 0.004M benzethounium chloride with thorough shaking or stirring after each addition until the water layer is clear and colourless. (Cullum 1994)

All the glass wares for measurement were thoroughly cleaned using distilled water. The surface tension of SDS solutions were measured at 25^{o}C with a Du Nouy’s ring apparatus. Between measurements, the ring was rinsed many times using double distilled water and then burned in a flame. Different concentrations of SDS solutions were prepared. Then a fixed amount of sample (50 ml) was taken for the measurement in each case.

3.4.2 Metal analysis

The metal ion concentrations were measured using an atomic absorption spectrophotometer (AAS) (Chemito Make Model AA- 203) equipped with Photon make hollow cathode lamps for cadmium, nickel and zinc. The instrument was fully computer controlled using software AA203 data station version 3.2.

The optimized instrument parameters for measurement of targeted metal ions are given in Table 3.2. Ratio method was preferred for curve fitting. The samples of the experimental runs were appropriately diluted so that they were in the specified working range for the corresponding metals .The concentrations were reported in ppm.

Table 3.2: Optimized instrument parameters for measurement of targeted metal ions

Parameter	Nickel	Zinc	Cadmium
Wavelength (nm)	232.10	212.5	228.7
Current (mA)	9.0	5.0	5.0
Slit Width (nm)	0.3	1.0	0.5
Pmt (V)	370.7	333	278.2
Burner height (mm)	1.0	0.5	1.6
Fuel (liter/min)	3.55	3.5	3.5
Working range (ppm)	2 – 10	0 – 2	0 – 2

3.5 Determination of Interfacial areas in foam column

Interfacial areas of air-water system, in the foam column were determined by sulfite oxidation method. Absorption of oxygen (even air oxygen) in an aqueous sodium sulfite solution is commonly used as a model reaction of known kinetics in determining mass transfer characteristics in gas-liquid contactors such as bubble columns, draft tube bubble columns, loop reactors, packed absorption columns and stirred tank reactors etc.

Sulfite Oxidation Method

The sulfite oxidation method was originally developed by Cooper et al. (1944) to evaluate performance of gas-liquid contactors. This method employs the catalytic oxidation of sodium sulfite to sulfate by dissolved oxygen.

$$2Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4 \qquad 3.1$$

This irreversible reaction has very complex kinetics, for instance, according to Astarita et. al (1964), the reaction when catalyzed by $CoSO_4$ is zero order in O_2 when sulfite concentration is up to 0.06 M; first order when it is 0.25 M and second order when it is 0.25 – 1 M. Some experimental results by Alper et. al (1988) confirm that the reaction is second order with respect to oxygen at the oxygen partial pressure range of 0.2 atmosphere., Since, this would corresponds to interfacial area determination experiments at about atmospheric pressure with air. The oxidation rate depends on the type of catalyst, its concentration, partial pressure of oxygen, temperature, ionic strength of solution, the presence of catalytic impurities and pH of the solution etc.

In the present work, the initial concentration of sodium sulfite [B_0] and $CoSO_4$ concentration were 0.5 M and 5×10^{-4} M respectively. The source of oxygen was air at1 atm. total pressure and 30° ± 2 temperature. pH of the system was adjusted to 8.5 by alkali addition. Under these conditions, the reaction is zero order (n=0) with respect to sulfite and second order (m=2) with respect to oxygen and the rate of mass-transfer is given by

3.2

$$R_A a = aC_A^* \sqrt{\frac{2}{m+1} D_A k_{mn} C_A^{*m-1} [B_0}$$

3.3

$$R_A a = a \sqrt{\frac{2}{3} D_A k_2 C_A^{*3}}$$

Where C_A solubility of oxygen mol/cc, D_A Diffusivity of oxygen cm^2/sec, K_2 second order rate constant cc/mol-sec, a = interfacial area m^{-1}

The average oxygen transfer rate (OTR), R_A (left side of above equation) based on the liquid volume was obtained as one half of the rate of decrease of sulfite concentration, which was determined experimentally by iodometric titration. The iodometeric titration method for sulfite concentration determination is discussed in Appendix A.

3.6 Characterization of particles formed in foam and foam morphology

Foamate collected was collapsed and centrifuged at 5000 rpm for 15 min. Upper liquid layer was decanted and the solid particles (sublate) settled at the bottom of test tube were washed repeatedly with water in order to remove SDS . Water washed particles were kept in petridish in oven at 150^0 C for drying and then in a dessicator for one day.

Dried particles were characterized using Fourier transform infrared (FT-IR) spectrophotometry using PerkinElmer FT-IR and Shimadzu FT-IR (model no. 6400s). X-ray Diffraction analysis of the particles was done using Particle XRD BRUKER AXS Gmbh, German, Model D8 Advance, at scanning rate of 0.15^0 / min with 2θ angles ranging from 5 to 80^0 using CuKα radiation having wave length $\lambda = 1.54$ A^0 operating at 40 KV and 40 mA.

Morphology of particles were determined using Scanning electron microscopy (SEM) using model JOEL JSM- 6380LV and Elemental analysis was done by EDX (Energy dispersive X-ray Spectroscopy). Particle size analysis of particles obtained in foamate at optimum conditions was determined using particle size analyzer Malvern Mastersizer Hydro 2000 MU (A) of Malvern Instruments.

The liquid in foam forms an interconnected network, which is composed of Plateau borders, nodes and films. One of the dominant pathways for foam drainage is flow through Plateau borders leading to dry foam. Confocal Microscope LSM-710, Carl Zeiss Germany was used to study structure of foam.

Confocal microscopes possess several advantages over conventional microscopy. It produces images of improved resolution, up to 1.4 times greater than standard microscopy, by eliminating out-of-focus light. Confocal microscopes also have a higher level of sensitivity compared to conventional microscopes, due to highly sensitive light detectors and the ability to accumulate images captured over time. Another key advantage of confocal microscopy is the ability to produce 3-dimensional reconstructions of specimens.

Computer software is then used to digitally reconstruct 3D representations of the sample. It allows one to visualize not only into foams but to also create images in three dimensions. The advantage of fluorescence for microscopy is that we can attach fluorescent dye molecules to specific parts of sample, so that only those parts are the ones seen in the microscope.

Confocal Microscope LSM-710, Carl Zeiss Germany was used to study structure of foam. Laser accessory mounted on 630 M microscope was used for this study. This instrument was equipped with HeNe gas laser, operating at wavelength 534 nm (for excitation of Rhodamine B). Rhodamine B dye 1 mg was dissolved in 10 ml of aqueous foamate to give a 0.1 wt% dye solution. The diluted sample was placed on a glass slide and imaged directly by confocal microscopy.