CHAPTER 6

Summary and Conclusions

6.1 Introduction

Process industries generate large amount of heavy metals as waste materials during either production or down streaming operations thus interfering with the ecosystem. Heavy metals are considered as hazardous pollutants due to their toxicity even at low concentration and their nonbiodegradability. Increased industrialization and discharge of wastes has resulted in heavy metal influx into natural water bodies. The removal of toxic metal from waste water is an important step in water treatment.

Among many methods available for the separation of heavy metals from aqueous solutions, foam separation plays a major role, especially when the concentration of undesirable components involved is very low. The success of this technique depends on the stability and characteristics of the foam. This operation is simple with less maintenance as there are no moving parts.

This study investigates removal of metal ions zinc, cadmium and nickel from aqueous streams individually as well as in binary combinations of zinc-cadmium and nickel-cadmium and effect of polymer PVP on cadmium removal. The foaming behavior of surfactant sodium dodecyl sulfate (SDS) in absence and presence of metal ions zinc, cadmium and nickel were evaluated. The effect of surfactant-polymer association sodium dodecyl sulfate –poly (vinylpyrrolidone) (SDS-PVP) on foaming behavior, cadmium removal and sublate morphology was also studied.

The metal recovery in the foamate, identification of the outlet for optimal recovery, effect of gas flow rate, pH, interaction of metal ions with a polymer on metal recovery was also studied. Mechanism of metal recovery process was identified using species distribution diagram. For the case of metal recovery as precipitated solids the particles formed were appropriately characterized. Floatation rate constants were evaluated and the separation was scaled to larger column size.

6.2 Foam behavior in aqueous sodium dodecyl sulfate solutions

Ross-Miles method was used to evaluate liquid hold up and foam bed volumes in foams generated by aeration of aqueous SDS solutions. The presence of single metal ions such as zinc, cadmium, nickel on the foaming patterns of SDS solutions and in combinations of zinc-cadmium and nickel-cadmium were also investigated.

Liquid hold up in foam was determined for metal concentrations of 100 mg/l, 200 mg/l and varying SDS concentration in the range of 3.98 -7.97 mM/L. Liquid hold up of foam was also measured in the presence of 1% and 2% by wt PVP. Foam bed volume in presence of 100ppm, 200ppm metal with SDS concentration ranging between 3.98-7.97mM was also evaluated. Foam bed volume and percentage liquid hold up is more for 200 ppm metal concentration compared to 100ppm metal concentration.

It was observed that liquid hold up in foam was more in presence of 100 ppm metals Cd, Zn and Ni compared to same concentration of SDS alone. This is attributed to the formation of water bridge between the metal cation and the dodecyl sulfate anions. Liquid drains relatively slow from the foams in presence of metal, especially during the later stages of drainage. Due to this tendency larger foamate volume and moderately wet foam was obtained during metal recovery also. With increase of the surfactant concentration the drainage rate of foam decreases this can be attributed to the increasing immobilization of the surfaces by the adsorption monolayers resulting in an increase in liquid hold up in the foams.

6.3 Foam formation and associated metal recovery

Foam is a two-phase system in which gas bubbles are enclosed by liquid boundaries. 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 optimize sample outlet.

In order to get dry foam and maximum metal recovery, sample outlet O-3 at a distance of 157.7 cm from initial liquid surface was optimized with other parameters such as air flow rate 0.06 lpm, time 20 min., feed 450 ml for 100 ppm metal removal having metal:surfactant molar ratio of 1:2 were selected for all experimental runs.

6.4 Interfacial area and bubble size distribution

Interfacial areas of air-water system, in the foam column were determined by sulfite oxidation method at optimum conditions of pH. The interfacial areas obtained by sulfite oxidation technique did not show any significant change in the presence of metals such as Cd, Ni and Zn. In presence of surfactant with metal to surfactant molar ratio of 1:2 the interfacial area increased for Zn and Ni as metal concentration increased this was attributed to the presence of free surfactant in the aqueous system. The behavior of Cd was contrary to this behavior which is attributed to clustering tendency of Cd –SDS complexes.

Behavior of air bubbles in water and in dilute aqueous surfactant solutions was also observed**.** It was observed that clean bubble rises faster because its entire surface is mobile. However, for a bubble in surfactant contaminated water, the situation is very different. Gradient of surface tension has the important effect of decreasing surface mobility. Bubbles in contaminated water rise slower. As foaming continues and the surfactant is progressively removed from the liquid into the foam the foam interface becomes more distinct. It was observed that the density of bubbles has considerably reduced. Bubble size distribution was measured using Image J software. Confocal microscope was used to study the structure of foam.

6.5 Heavy Metals removal

Under identical operating conditions of feed containing 100 ppm zinc having Zn:SDS 1:2 molar ratio, air flowrate of 0.06 lpm and 20 minute operation duration the recovery of zinc was evaluated. Sodium dodecyl sulfate was used as surfactant for metal recovery. Foam is formed at the gas liquid interface and moves up.

Foamate was collected continuously at the top of the column and collapsed. The liquid was obtained by breaking the foam, and the residual solution was then analyzed using an atomic absorption spectrophotometer for estimating the concentration of metal ions.

Experiments were planned to study removal of Cd, Zn, Ni metal ions from aqueous feed solution having 100 ppm metal concentration with metal : surfactant molar ratio of 1:2. Selective removal of metals from binary mixtures of Zn-Cd and Ni-Cd and effect of PVP on cadmium removal was also investigated.

At 100 ppm zinc concentrations, the zinc ion, Zn^{2+}, is the dominant specie up to pH 9 while zinc hydroxide, $Zn(OH)_2$ is the dominant species from pH 9 to pH 11. Above pH 10, $Zn(OH)_3^-$ formation occurs and above pH 11, $Zn(OH)_4^{2-}$ formation takes place which was obtained by Visual Minteq 2.15. Zinc recovery begins at pH 4 and increases exponentially till pH 8 and then almost remain constant. Conditions ensuring ion floatation of Zn^{2+} ions almost ends by pH 9 and precipitate floatation begins and as a result the sensitivity of zinc recovery to pH ceases. At lower pH values the lower extent of zinc recovery can be attributed to competition of hydrogen ions with the metal cations for the available surfactant sites. Maximum zinc recovery 92% was obtained at pH 8.

Cadmium sulfate speciation was calculated as a function of pH for 100 ppm cadmium feed concentration. The fraction of cadmium species such as Cd^{2+} , $Cd(OH)^+$, $Cd(OH)_2$, $Cd(OH)_3^-$ and $Cd(OH)_4^{2-}$ in solution varies over a range of pH. Cd^{2+} is the main ion present in solution for pH < 8. Above pH 9 in basic conditions most Cd is present as $Cd(OH)_2$. Formation of $Cd(OH)_3^{2-}$ starts at pH 11, while at pH 12 or above, the main cadmium specie is $Cd(OH)_4^{2-}$. Polynuclear cadmium complex such as $Cd_2(OH)_3^+$ is also present.

Maximum cadmium recovery 54% was obtained at pH 2, which also corresponds to the maximum foamate volume observed. The profile of foamate volume and cadmium recovery follows the same pattern. This pattern of metal recovery is attributed to ion-adsorption, the adsorption of Cd^{2+} ions on SDS molecule leads to the transport of Cd-SDS complex with the ascending bubbles of the foam that tends to carry the Cd^{2+} ions from feed to foamate.

The speciation nature of nickel sulfate in water corresponding to the initial feed concentration of 100 ppm of Ni was also evaluated using Visual Minteq 2.15 software. The fraction of nickel species such as Ni^{2+}, $Ni(OH)^{+}$, $Ni(OH)_2$ and $Ni(OH)^{3-}$ in solution varies over a range of pH . The main ion present in solution till pH 8 was Ni^{2+}. Above pH 9 in basic conditions most Ni is present as $Ni(OH)_2$. At pH 9, $Ni(OH)_3^-$ formation begins and at pH 12 or above, the main nickel specie is $Ni(OH)_3^-$. Maximum nickel recovery was 31%, obtained at pH 8 which also corresponds to the higher foamate volume observed. This metal recovery is attributed to ion-adsorption.

The removal of metal ions from solutions of binary metal ion systems was investigated for the zinc-cadmium binary ionic system and the nickel-cadmium ionic system at varying pH with the objective to determine the selectivity of the separation. The selectivity of the separation process is mainly caused by the selective binding of metal ions to the surfactant ions.

For Zn-Cd binary system maximum zinc recovery of 34% was obtained at pH 4, cadmium recovery of 83% was obtained at pH 4. For Ni-Cd binary system maximum cadmium recovery 23.59% was obtained at pH 6. Nickel recovery 55.72% was obtained at pH 10. Competition between cadmium and zinc species is likely to occur for the available SDS sites. Cd^{+2} and Zn^{+2} concentrations are more till pH 8. Zinc hydroxide and cadmium hydroxide are dominant species between pH 8 to 10. Flotation rate constant for zinc at pH 4 is 0.00136 min^{-1} and 0.0151 min^{-1} for cadmium. Cadmium separation is more at pH 4 which is the favorable condition for cadmium removal. The fact that cadmium removal is much more at this pH compared to the similarly charged zinc species is an indication of a higher affinity of the cadmium species towards the SDS molecules till pH 4. For Ni-Cd binary system flotation rate constant is higher for nickel than cadmium at pH 8 and pH 10. For pH 8 and 10 nickel removal is also higher than cadmium. Cadmium recovery in presence of polymer PVP decreased to 17.5 % from 54 % at pH 2 due to SDS-PVP interaction. The size, shape and elemental analysis of the precipitate particles obtained in foamate were performed by different instruments like SEM-EDX, particle size analyzer etc.

6.7 Effect of column diameter on foam behavior and removal of metals

To investigate the foam behavior and metal recoveries and in larger diameter column a glass column (FC-3) having 0.10 m diameter and 1 m height with multiple sample outlets was fabricated.

Removal of metals such as cadmium, zinc, nickel, cadmium–PVP systems were 2%, 5.63%, 1.12%, 1.072 % respectively . Removal obtained from nickel-cadmium mixture were 6.26% Cd & 0.4% Ni , from zinc-cadmium mixtures 1.46% zinc and 1.8% cadmium respectively from 100 ppm feed metal concentration having metal: surfactant 1:2 molar ratio at their optimum pH. The poor recoveries observed is attributed to the fast foam decay in the large foam column due to the relatively large distance between the walls and the central regions of the foam which does not allow adequate mechanical support of these regions and so the foam structure disintegrates under its own weight.

6.8 Scope for future work

Foam separation has been investigated and found to be effective for heavy metals removal from dilute aqueous streams. Removal needs to be studied for other heavy metals as well. The effects of mixed surfactant and its role in heavy metals removal should also be investigated. Study of chemistry of metals and surfactant in solution, binding of heavy metals with surfactant, Selectivity of a metal while dealing with binary metal systems and calculations of distribution factors can help in detailed understanding of the separation system. Although much is known but still more focused investigations on the dynamics of foam drainage is needed and so is the need to study the effect of recycle on foam stability. Depletion studies due to influence of polymers in enhancing foam stability and ion removal and particle morphology should also be investigated.