

ZINC (II) RECOVERY FROM AQUEOUS SOLUTION USING CONTINUOUS FOAM FRACTIONATOR

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ABSTRACT

Process industries generate a large amount of waste materials during either production or down streaming operations. Among many methods available for their separation, 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. In the present investigation, recovery of zinc(II) ions from zinc plating effluent was carried out in a continuous foam column using sodium lauryl sulphate as surfactant. The effect of various experimental parameters such as air flow rate, liquid pool height, feed concentration, surfactant concentration, pH of the feed and feed flow rate on the enrichment of metal ions was investigated.

Enrichment ratios of 9.2 and 8.9 with a percentage removal of around 99% and 95% were obtained for the removal of zn(II) ions from synthetic aqueous solution and zinc plating effluent at the optimum operating parameters of 30 cm liquid pool height in column, 0.1 litre per minute (Lpm) of air flow rate, feed flow rate of 4 liters per hour (Lph), 0.1 % (w=v) of SLS concentration, pH of 6.0 and at feed concentrations of 10 ppm zinc(II) ions. Enrichment ratio was found to increase with an increase in feed flow rate. With a decrease in concentration of the bulk solution, the separation factor was found to increase. The study indicates the feasibility of continuous foam separation for treating industrial effluents.

Keywords: Zinc plating industrial effluent; metal ions; Foam fractionation; Enrichment ratio; sodium lauryl sulphate surfactant; adsorptive bubble separation technique

1. INTRODUCTION

Zinc is one of the essential metals but it becomes strongly toxic if present in a high concentration. The recommended limit for the maximum concentration of zinc in drinking water is 5 ppm. Zinc pollution is often associated with mining which causes pollution of air, water and soil. Zinc is also present in waste water streams from steel works, rayon, yarn and fibre manufacture, ground wood-pulp production, plating and metal processing industry and recirculating cooling water systems employing cathodic treatment. Though many new methods or modified old methods are being now investigated for removal of this metal ions and its re use before discharging them in to the environment, foam separation plays a major role in the removal of trace metals such as cadmium, chromium, copper, iron, zinc etc. with the aid of surface active substances called surfactants (Beheir, 1996).

During foam fractionation, gas bubbles are introduced into a liquid which contains surfactants. Foam formation occurs, when surface active molecules attach to the gas liquid interface of the introduced bubbles. The foam formation can be caused by dissolved substances or dispersed substances. The surface tension of the interface is decreased and the foam is stabilized. Thus, the formed bubbles create an emerging foam column above the liquid level (Burghoff, 2012).

The entrained liquid eventually drains back into the feed solution. This causes the foam to become dryer while rising. Coalescence and disproportionation inside the dry foam increase bubble size. Thus, the concentration of surface active substance between lamellae and Plateau borders increases. The emerging foam column can be diverted into a separate vessel, where the foam is collapsed, e.g. mechanically or by decreased pressure. The collapsed foam, called foamate, comprises an enriched solution of surface active components. Several advantages render foam fractionation as a desirable separation process, which also explains the recurrent interest in this technology. On the one hand, foam fractionation is suitable for processing dilute solutions (Uraizee and Narsimhan, 1990) with high enrichment (Backleh-Sohrt, 2005). On the other hand, there are no solvents necessary during this process, because only air or inert gases are involved (Stowers, 2009). In terms of sustainability, this process can thus be considered as 'green'.

In the present investigation, recovery of zinc (II) ions from zinc plating effluent was carried out in a continuous foam separation process using sodium lauryl sulphate as surfactant. As reported in our earlier

investigation (Arulmozhi, 2011), sodium lauryl sulphate is an anionic surfactant and it can be ionized into $C_{12}H_{25}OSO_3^-$ and Na^+ . The metal ion Zn^{2+} can be exchanged with Na^+ and combined with $C_{18}H_{29}SO_3$ to form complexes. These complexes are then adsorbed into the gas-liquid interface and then removed by concentrating the solute. Thus, the metal ion in the effluent is removed and concentrated. The effect of various experimental parameters on the enrichment of metal ions was investigated.

MATERIALS AND METHODS

Materials: Anionic surfactant, sodium lauryl sulfate (SLS) with a purity of 99% was obtained from Sigma Aldrich Chemicals Private Limited (Bangalore, India). Ethanol was AR grade purchased from BDH Chemicals Ltd. (Poole, England). Effluent from zinc plating industry was collected from nearby industrial unit. Distilled water was used in all experiments.

Equipment: Fig. 1 is a schematic of a simple continuous mode foam fractionation device (Arulmozhi et al., 2008). The column is a cylindrical glass tube (1000mm in height and 160 mm diameter) with a sintered glass sparger of pore size ranging from 15 to 40 microns, fixed at the bottom, functioning as a gas distributor. The length of the drainage section of the column is 760 mm. Airflow is metered using a rotameter and then passed through the distributor. The feed solution was continuously fed into the column through an inlet port and the residual solution was discharged from the bottom of the column. The outlet is provided above the gas sparger to ensure that the outflow of liquid from the column is not affected by the flow of gas and is similar to the one reported earlier (Maruyama et al., 2000 ; Suzuki et al., 2002). Further, due to the flow of gas in the upward direction, through the sparger, the liquid will not flow down through the sparger. Foamate was collected continuously at the top of the column and collapsed by heating. The liquid obtained by breaking the foam and the residual solution were then analyzed using atomic adsorption spectroscopy (Perkin-Elmer, Modle AAnalyst 700) for zinc (II) ions.

Calculations: The performance of foam fractionation is commonly expressed in two terms: enrichment ratio E; and removal fraction R (Yun-Huan Qu et al., 2007).

$$R (\%) = \frac{C_f - C_b}{C_f} \times 100 \quad (1)$$

$$E = \frac{C_p}{C_f} \quad (2)$$

where C_f and C_b are the surfactant or metal ion concentrations (ppm) in the feed and effluent streams, respectively and C_p is the surfactant or metal ion concentration in the collapsed foam solution (ppm). The percentage of removal is defined as above due to the fact that low concentrations are used in the present study and also the concentration changes involved are low, hence, the flow rates at outlet and inlet remain the same.

RESULTS AND DISCUSSION

Experimental studies in continuous foam fractionation column for various feed concentrations at different pH values of the solutions, liquid pool heights and flow rates of liquid and air were conducted using zinc plating effluent, collected from nearby industry, that contains zinc(II) metal ions to determine the enrichment ratio and the percentage recovery. The characteristic of the zinc plating effluent is given Table 1. The results obtained are discussed in detail.

Table.1.Characteristics of Zinc plating industrial effluent

Properties	Value
pH	6.5
Total dissolved solids(TDS),ppm	4800
Biological oxygen demand (BOD),ppm	295
Chemical oxygen demand, ppm	720
Zn(II) ion concentration, ppm	250

Effect of air flow rate: Experimental studies were conducted to find the effect of air flow rate on the enrichment ratio of metal ions and the results are shown in Fig. 2 for synthetic Zn (II) solution and zinc plating effluent at fixed operating conditions of 30 cm liquid pool height, feed concentration of 10 ppm, sodium lauryl sulphate (SLS) surfactant concentration of 0.1 % (w/v), pH of the feed at 6 and feed flow rate of 4 lph. The enrichment ratio decreased from 9.2 to 5.4 for synthetic solution of zinc and from 8.9 to 4.2 for zinc plating effluent.

An increase in air flow rate could cause changes in the following process conditions: (i) average bubble size, (ii) contact time of air in the liquid medium and (iii) liquid entrainment. With increase in air flow rate, both

enrichment ratio and percentage removal decreased. This is due to the fact that, at low flow rates, the larger bubble sizes are easily coalesced and more drainage occurs. Hence enrichment ratio and percentage removal increased initially. Subsequently on further increase in air flow rate, the foam bubble size decreased and coalescence as well as drainage decreased. This leads to decrease in both enrichment ratio and percentage removal. These results are in agreement with those reported in the literature (Boonyasawat et al., 2005). Hence low gas flow rate is generally beneficial for separation and for high enrichment.

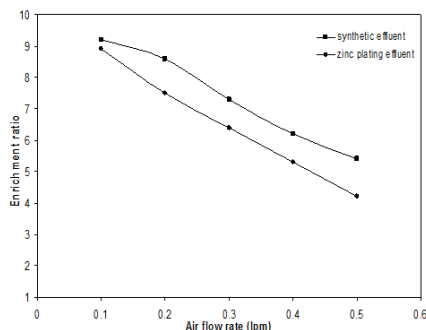


Fig.2. Effect of air flow rate on enrichment ratio of zinc (II)

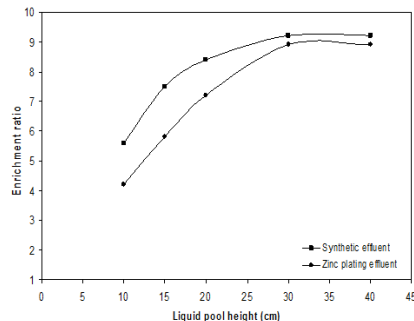


Fig.3. Effect of liquid pool height on enrichment ratio of zinc (II)

(liquid pool height=30 cm, feed concentration=10 ppm, SLS surfactant concentration = 0.1% (w/v), pH of the feed =6, feed flow rate = 4 lph)

Effect of liquid pool height: The effect of liquid pool height was studied on the enrichment ratio of zinc(II) ions and is presented in Fig.3 for synthetic Zn(II) solution and zinc plating effluent. The enrichment ratio increased from 5.6 to 9.2 for synthetic zinc solution and from 4.2 to 8.9 for zinc plating effluent. The residence time of bubbles in the liquid pool is high when the height of the liquid pool is more. This leads to a higher enrichment of metal ions on the bubble surface and it could reach an equilibrium beyond which enrichment may not increase. In the present study this equilibrium is reached at a pool height of around 30 cm. These results are in agreement with those reported in the literature (Yun-Huan Qu et al., 2008).

(air flow rate= 0.1 lpm, feed concentration = 10 ppm, SLS surfactant concentration = 0.1% (w/v), pH of the feed =6, feed flow rate = 4 lph)

Effect of feed concentration: Experiments were conducted to determine the effect of feed concentration on enrichment ratio by using the synthetic solution of zinc(II) and zinc plating effluent as shown in Fig.4. This figure indicates that with increase in feed concentration from 10 ppm to 40 ppm, the enrichment ratio decreased from 9.2 to 6.1 and 8.9 to 6.2 for synthetic zinc solution and zinc plating effluent respectively. This may be due to the fact that, as the feed concentration increases, the surface tension decreases. This generates more stable bubbles with lesser coalescence and drainage. Hence, the wetness of foam is higher at higher concentration which decreased the enrichment ratio and percentage removal.

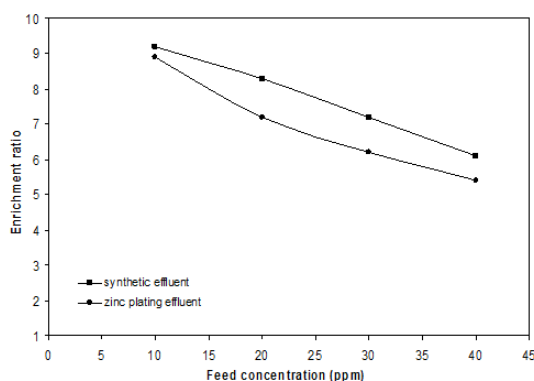


Fig.4. Effect of feed concentration on enrichment ratio of zinc (II)

(air flow rate= 0.1 lpm, liquid pool height=30 cm, SLS surfactant concentration = 0.1% (w/v), pH of the feed =6, feed flow rate = 4 lph)

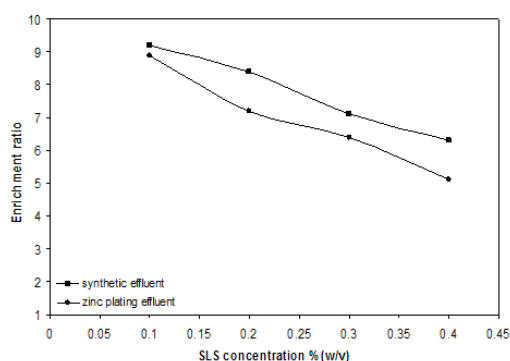


Fig.5. Effect of surfactant concentration on enrichment ratio of zinc (II)

Effect of surfactant concentration: The effect of sodium lauryl sulphate surfactant concentration on enrichment ratio for zinc(II) synthetic solution and zinc plating effluent is shown in Fig.5. The enrichment ratio decreased with

increase in surfactant concentration. The increase in surfactant concentration decreases the surface tension and increases the surface liquid viscosity which in turn decrease the rate of film drainage and the enrichment ratio.

(air flow rate= 0.1 lpm, liquid pool height=30 cm, feed concentration = 10 ppm, pH of the feed =6, feed flow rate = 4 lph)

A primary advantage of foam separation is the small volume of foamate necessary to perform separations which would otherwise require much larger volumes by other techniques. The production of a large amount of foam is both unnecessary and undesirable. An excess collector can reduce the separation by competing against the collector –colligen complex for the available surface. It can also reduce the separation by forming micelles in the bulk solution which adsorb some of the colligen, thus keeping the metal ions away from the surface.

Effect of pH of feed: Experiments were carried out to study the effect of pH on enrichment ratio using both synthetic solution as well as industrial effluents. The maximum enrichment ratios of 9.2 and 8.9 were achieved for zinc in synthetic solution and plating effluent respectively at an optimum pH of 6. In certain metal ions, the initial pH of the solution will determine whether the process to be performed by either foam fractionation or ion flotation. For example, the removal of zinc (II) ion with the anionic surfactant, sodium lauryl sulfate can be best accomplished below the value of pH 6, where the zinc exists primarily as the Zn^{2+} and $Zn(OH)^+$ ions and can be removed by foam fractionation. However, when the pH is above 6.0, the insoluble hydroxide is produced, which can easily be removed by ion flotation.

Therefore, when zinc is separated using an anionic surfactant such as sodium lauryl sulfate at low pH, the maximum removal can be expected because of the high concentration of Zn^{2+} and $ZnOH^+$. However, actual experimental results showed that the removal rate of Zn (II) at pH 4 was low and the results account for H^+ competition and instability of the Zn-lauryl sulfate complex in this pH region. Thus the rate of removal reached a maximum at pH 6 because the stoichiometry of collector to metal is more favorable in the presence of $ZnOH^+$ ion. Removal efficiency decreased above the value of pH 6 because of the formation of insoluble zinc hydroxide ($Zn(OH)_2$ and $HZnO_2$). These observations are in tune with those reported in literature (Kazimierz Jurkiewicz, 2006; Alan J.Rubin, 1969).

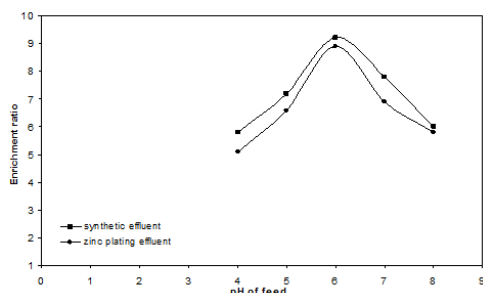


Fig.6. Effect of pH of feed on enrichment ratio of zinc (II)

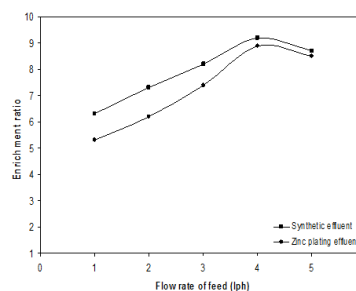


Fig.7. Effect of feed flow rate on enrichment ratio of zinc (II)

(air flow rate= 0.1 lpm, liquid pool height=30 cm, feed concentration = 10 ppm, sodium lauryl sulphate surfactant concentration= 0.1 % (w/v), feed flow rate = 4 lph)

Effect of feed flow rate: The effect of feed flow rate on enrichment ratio of zinc containing synthetic solution and industrial effluents is shown in Fig. 7. The figure indicates that with increase in feed flow rate from 1 to 4 lph, the enrichment ratio of zinc (II) ions increased from 6.3 up to a maximum value of 9.2 and then decreased to 8.7 for synthetic zinc(II) solution and from 5.3 up to a maximum value of 8.9 and then decreased to 8.5 for zinc plating effluent.

An increase in the feed flow rate from 1 to 4 lph results in a higher availability of metal ions leading to an increase in the enrichment ratio. However, further increase in feed flow rate leads to decrease in residence time for foam in the column causing a lesser drainage and thus decreasing the enrichment ratio.

(air flow rate= 0.1 lpm, liquid pool height=30 cm, feed concentration = 10 ppm, sodium lauryl sulphate surfactant concentration= 0.1 % (w/v), pH of feed = 6)

CONCLUSIONS

Foam fractionation is effective in the recovery of zinc(II) ions from synthetic aqueous solution and zinc plating effluent. The parameters include air and feed flow rate, liquid pool height, feed and surfactant concentrations and pH of the feed which were investigated in single stage continuous column. When the conditions were optimum such as concentrations of zinc (II) ions in the feed solution of 10ppm, liquid pool height and feed flow rate of 30 cm and 4 Lph, sparger pore size of 15-40 microns, and air flow rate, SLS concentration and pH of

0.1 Lpm, 0.1% and 6.0 respectively, an enrichment ratios of 9.2 and 8.9 with a percentage removal of around 99% and 95% were obtained. Enrichment ratio was found to increase with an increase in feed flow rate. With a decrease in concentration of the bulk solution, the separation factor was found to increase. Thus the study indicates the feasibility of continuous foam separation for treating industrial effluents.

Also, by experience from our earlier investigations (Arulmozhi, 2011), it was observed that chromium and copper has lower recovery both from synthetic and industrial effluent than zinc. This is due to the fact that bubbles consisting of anionic collector, to which metal ions are electrostatically bonded. This surface active system enriches on the gas liquid interface in such a way, an electrical double layer is formed around the surface of each bubble. Thus, each bubble brings some metal ions from the bulk to the surface. Metal cation- sodium lauryl sulphate anion pairs were collected by foam fractionation. In the meanwhile, the metal cation end of these pairs will be hydrated which should overcome a strong barrier of hydration energy from the aqueous phase into the hydrophobic froth phase. Since Cu(II) is a strong complex- forming metal, it will be very strongly hydrated (water is a Lewis base) and therefore least carried into the froth phase (Rubin,1969). Thus copper or chromium has lower enrichment ratio and percentage removal than that of zinc.

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