Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Recovery of Zn(II), Mn(II) and Cu(II) in Aqueous Solutions by Foam Fractionation with Sodium Dodecyl Sulphate in Combination with Chelating Agents

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To cite this Article Yenidünya, Melek Doğutan(2006) 'Recovery of Zn(II), Mn(II) and Cu(II) in Aqueous Solutions by Foam Fractionation with Sodium Dodecyl Sulphate in Combination with Chelating Agents', Separation Science and Technology, 41: 8, 1741 — 1756

To link to this Article: DOI: 10.1080/01496390600636959

URL: http://dx.doi.org/10.1080/01496390600636959

Separation Science and Technology, 41: 1741–1756, 2006

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390600636959

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Abstract: Adsorptive bubble separation was used to remove polyvalent ion colligends Zn(II), Mn(II) and Cu(II) from aqueous solutions, for which optimum parametrical values that influenced the recovery of these ions were scrutinized. Additionally, the effect of some auxiliary ligands (malic acid, maleic acid, and EDTA) on the recovery was investigated. Sodiumdodecylsulphate (SDS) was used as a collector. The pH was measured as 5.5 and 4.0 for the solutions, which include metal : SDS and metal : SDS : auxiliary ligand, respectively. In the metal : SDS mixtures, SDS has retained metal ions at pH 5.5, which was exactly the value of the membrane filtered water. Therefore, no further pH adjustment was necessary throughout the experiments. The metal ions were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). The optimum experimental conditions (run time, SDS concentration, and the concentration of feed solution) on the recovery and enrichment of metal ions were also discussed. The maximum recovery rate was reached within 60 min. The optimum molar ratio between metal and SDS was found to be 1 : 5, and it was shown that the recovery of metal ions increased with increasing concentration of SDS. The most suitable initial concentration of metal ions was 2×10^{-5} M. The recovery rates for Zn(II), Mn(II) and Cu(II) in the presence of SDS was found to be 90.5, 99.8 and 73.4%, respectively. By adding malic acid, and maleic acid as auxiliary ligands, higher recovery rates were achieved, even in a shorter foaming

Received 15 May 2005, Accepted 1 January 2006

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time. For optimal recovery, the best molar ratio between metal:SDS:auxiliary ligand was 1 : 5 : 5.

Keywords: Foam fractionation, zinc, manganese, copper, malic acid, maleic acid, EDTA

INTRODUCTION

Known industrial processes for removing precious metals generally consist of multiple steps such as dissolution (leaching), conditioning and precipitation. However, these processes are labor-intensive and time-consuming, and therefore, much work has been carried out to develop alternative methods as solvent extraction and ion-exchange.

Adsorptive Bubble Separation (ABS) techniques are applied as bubble and foam separation methods. In ABS techniques an amount of water is removed together with the surfactant-counterions species adsorbed at the gas/aqueous solution interface. This occurs due to hydration of counterions and surfactant polar groups with water molecules being a structural part of the adsorption layer on gas bubbles (1, 2). ABS techniques can be effectively applied for both trace analysis and removing of undesired analysis products (3). There are two important types of foam separation:

1. foam fractionation, which is effective in removing soluble matter, and
2. froth flotation, capable of removing insoluble matter (4).

Foam fractionation is a promising surfactant-based separation process. This method is attractive not only because of low energy consumption and operational costs but also due to its advantage in recovering substances from high diluted solutions. Ion flotation is a method for the removal of dissolved valuable ions from aqueous solution by using air bubbles (5). Much fundamental work in this field has been done by applying ion flotation to the recovery of trace amounts of metal ions from solution (6). Kinoshita et. al has carried out to separate Au(III) from solution with nonionic surfactant (7). Liu investigated for the removal of metal ions from dilute solutions by ion flotation (8) and Liu and Doyle proposed a thermodynamic approach to ion flotation (9). Jacobelli-Turi et. al floated both zinc and copper by the complexing surfactant dodecylimminodipropionic acid (10).

During the process, foam is produced by leading in different kinds of gases (mostly nitrogen). Surface active solutes to be removed or recovered are adsorbed onto the surface of bubbles and, therefore, concentrate in the foam. While the foam rises up the column, drainage of the interstitial water between the foam takes place, enhancing in turn the adsorption effect. The foam, thereafter, desintegrates back to liquid, the so-called "foamate."

A foam producing agent, i.e. a surface active reagent such as SDS etc., can be added to the feed solution (depending on the substance under investigation) to stabilize the foam, while a collector is introduced to the system to make targeted solutes surface active and collectable. A great deal of research was done to combine such additives and solutes under various conditions (1, 11–13).

So far, a variety of applications have been reported for mineral ores (14–16), hazardous metal ions (14, 15), proteins (17, 18) and surfactants (19). Adsorptive bubble purification/separation methods are generally applied as bubble and foam separation techniques. Foam separation has become important for wastewater treatment, in particular for the removal of trace metals such as cadmium, chromium, copper, iron, lead, manganese, mercury, nickel and zinc, in the presence of surfactants (20).

As surfactants have electron-donating oxygen atoms, they can form complexes with various metal ions (21) in the same manner as solvating extractants. Thus, ABS techniques are suitable for the recovery of metal ions with the help of specific surfactants (22). For example, a study with a tapered column simple-mode apparatus was carried out by St. Eloi (23), reporting on the foam fractionation of zinc with dodecyl benzene sulfonate (NaDBS) as a collector along with excess sodium chloride. The author observed that zinc recovery level in the foamate increased with decreasing concentration of the surfactant. Konduru (1) employed foam fractionation to separate and remove zinc ions using SDS as a surfactant.

However, not much information about the application of auxiliary ligands on the efficiency of metal ions recovery exist in the literature. Doyle and Liu report the effect of a neutral chelating ligand, triethylenetetraamine (Trien), on the ion flotation of cations with dodecylsulphate, DS-, introduced as sodium dodecylsulphate, SDS (24). N-Monodecanoyl Diethylenetriamine was synthesized for removing heavy metal ions by foam treatment (25). Schulz and Warr investigated the effect of macrocyclic ligands on the selective flotation of metal ions (26). Several surfactants with hydrophilic headgroups containing macrocyclic ligands were also reported in the literature (27). Many studies have been done on the role of auxiliary ligands in micellar-enhanced ultrafiltration, and such ligands are central to liquid-membrane separation processes (28, 29).

The recovery of various heavy metals by using surface active substances have also been explained in the review prepared by M. Doyle (30).

In this study, the effects of auxiliary ligands, malic and maleic acid as well as EDTA, on the recovery rates of zinc, copper, and manganese were studied by foam fractionation in the presence of SDS. The reason why we have chosen these substances as auxiliary ligands is that they are very cheap and can be obtained easily and also they have complexing ability with heavy metals. For our purpose, which is the enrichment/recovery of metal ions from highly diluted solutions, adsorption bubble separation method is very effective. Furthermore, several experimental parameters influencing the recovery and enrichment of the metals were investigated.

EXPERIMENTAL

Reagents

All reagents used were of analytical reagent grade.

A stock solution of Zn(II) was prepared from its sulphate salt. $ZnSO_4 \cdot 7H_2O$ was obtained from Fluka, Germany. Those of Mn(II) and Cu(II) were prepared from their chlorides, and these were purchased from VWR International, Germany. Malic acid, maleic acid, EDTA, and SDS were obtained from VWR as well. Aqueous solutions of metal ions, SDS, malic acid, maleic acid, and EDTA were prepared with membrane filtered water, which was purified by a Milli-Q system. For all feed solutions, the pH values were kept at 5.5, which was exactly that of membrane filtered water. ICP standards (high purity and Y standards) were purchased from ATSC, Germany. Nitric acid (suprapur) was obtained from VWR.

Foam Fractionation

The column used for foam fractionating experiments consisted of a cyclindrical glass flask (30 cm height, 1,5 cm ID) with a bottom-mounted porous glass frit (porosity 4) as a gas distributor. The solution (50 ml) was charged into the flask. In order to prepare a feed-solution, the exact amounts of stock metal solution were transferred into a 50 ml volumetric flask. Thereafter, the required amount of SDS was added. The solution was made up to the mark with membrane filtered water and then transferred into a conical flask, which was finally connected to the column used for foaming. The pH of the solution was measured as 5.5.

Nitrogen was used to create the foam and its flow rate was adjusted with a fine metering needle valve to control both the height of the foam (25 cm) and steady counter-current conditions in the column during the foaming period. Finally, foam fractions were transferred by slightly increasing the flow rate into a foam receiver. For creating the foam, nitrogen was led in with an appropriate flow rate of about 20 ml min^{-1} (Doyle: poorer mass transport is not attractive for ion flotation equipment because transport is driven by rising). The foamate was collected into a graduated cyclinder, installed at the top of the column. Nitrogen flow was stopped after 60 min, unless otherwise stated. In each experiment, 5 ml of foamate was collected, for which the nitrogen flow rate was adjusted to appropriate values to keep the volume constant. All experiments were carried out at room temperature. Metal ion concentrations in the foamate and residual (retentate) were determined by ICP-OES according to EN ISO 11885 E 22.

Analytical Instruments

The concentration of metal ions was determined by a Perkin Elmer Optima 3200 ICP-OES. The concentrations of the dicarboxylic acids were analyzed using a Gynkotek 480 HPLC system equipped with a SP-6 UV-Vis detector and a Perkin Elmer Lambda 16 UV/Vis spectrometer. The pH value of the feed-solutions were measured with an wtw inoLab pH-meter equipped with pH electrode SenTix 41, having the full range of 0–14.

RESULTS AND DISCUSSION

The Selection of Optimal Foaming Parameters

SDS Concentration

The concentration of SDS was optimized for metal recovery. Therefore, the molar ratio between metal and SDS were chosen as 1 : 5, 1 : 10, and 1 : 15. Initial metal concentration was kept as 2×10^{-5} M through the experiments. According to the results, the 5-times excess of SDS was sufficient for the recovery of almost all the metal ions in the foamate (Table 1). The molar ratio between metal : SDS was kept constant (1 : 5) in further experiments.

Bubbles consisting of anionic collector, to which metal ions are electrostatically bounded, are formed. This surface active system enriches on the gas liquid interface (1). 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.

The reason why copper has the lowest recovery (Table 1) can be explained as follows: metal cation-dodecylsulphate anion pairs were collected by froth flotation. In the meantime, the metal cation end of these

Table 1. The recovery of Zn(II) as a function of SDS concentration

The molar ratio of SDS/metal ion	Percentage recovery of Zn(II), (%)	Percentage recovery of Mn(II), (%)	Percentage recovery of Cu(II), (%)
5	90.5	99.8	73.4
10	95.1	99.8	75.5
15	95.4	100.0	76.7

pairs will be hydrated. The ion pairs have to pass a strong barrier of hydration energy from the aqueous phase into the hydrophobic froth phase. Since Cu(II) is the strongest complex-forming metal among the 1st row transition metals according to Irving-Williams order, it will be very strongly hydrated (water is a Lewis base) and therefore least carried into the froth phase. On the other hand, for two ions with different charges the same sign, the higher the valence of a counterion, the higher is the selectively for that species over other counterion with lower valence. In contrast, the rules for selectivity between ions with the same valence are not so well understood. Jorne and Rubin (31) modelled the selectivity between ions with different effective aqueous radius using the Gouy-Chapman electric double layer theory. According to this theory, the order of increasing selectivity related to the different effective ionic radius and equilibrium constants of the metal dodecylsulfonate compounds. Ionic radius of Mn(II), Zn(II), and Cu(II) ions are reported as 0.96, 0.89, and 0.72 Å, respectively in literature (32). The order of increasing selectivity is found to be Cu(II) $<$ Zn(II) $<$ Mn(II) in our study. For this reason, our data confirm the selective foam fractionation model proposed by Jorne and Rubin, which is based on the Gouy-Chapman diffused double layer theory with the restriction that the closest approach to the surface is determined by the size of the hydrated ions (30, 32).

Comparing the SDS concentrations in terms of the recovery of the metal ions, no significant increase of recovery could be achieved with higher SDS concentrations. However, as the results were almost similar, we chose the lowest concentration because of environmental and economical reasons (it is cheaper to use lower amounts of SDS). This ratio was kept constant for all other experiments when optimizing the other parameters.

Foaming Time

The optimal foaming time was selected in order to recover the whole amount of metal ions from the initial solution. By keeping the concentration of metal ions and SDS constant, only the foaming time was changed. For this aim, the experiment was repeated in different foaming time periods (10, 20, 30, 40, 50, and 60 min). During bubbling, a stable foam was produced and the generation of foam continued 60 min until the surfactant became insufficient in the bulk solution. It was possible to recover the entire amount of metal ions from the initial solution within 60 min (Fig. 1). Therefore, 60 min was chosen for further experiments. As the bubbling proceeds, metal ions accumulate in the foamate phase in high amounts, implying the strong interaction between the metal and the surfactant. On the other hand, by increasing foaming time, not only the recovery percentage of metal ions but also enrichment ratio was increased.

When the solution stays longer in the column, it has more time to flow back. Thus, the concentration of metal ions and surfactant increases. This

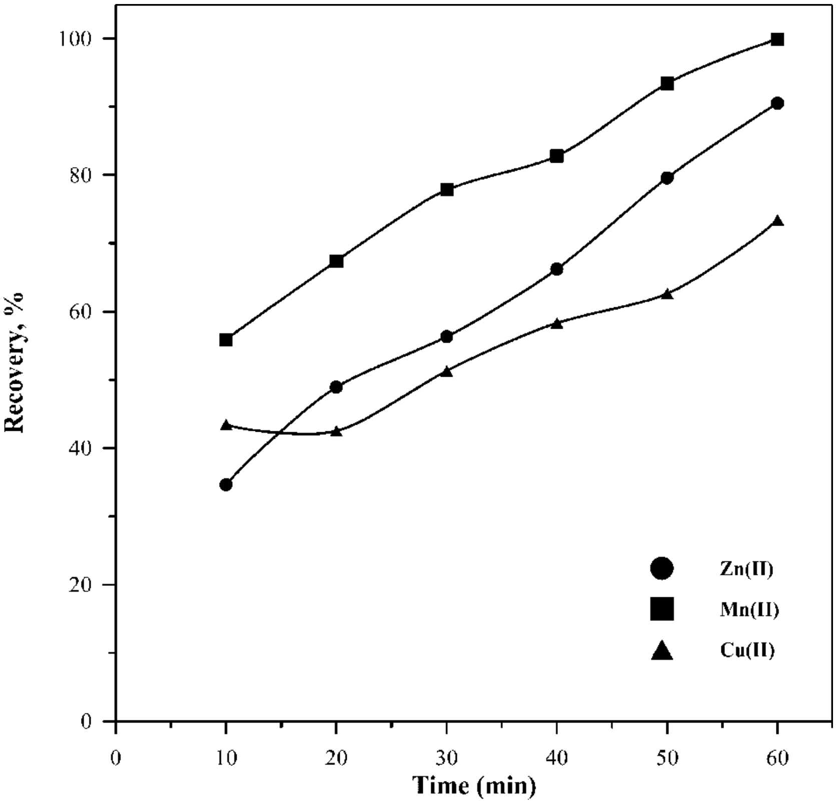

Figure 1. The recovery of metal ions in different foaming time periods.

in turn increases the enrichment in foamate. A longer foaming time is a consequence of a lower flow rate, wherein a dry foam occurs. The mass transport of collector and colligend is higher. It should be mentioned as well that the smaller foams are wet and therefore the enrichment of collector and colligend becomes lower. This however can be compensated for by providing a longer time for foam drainage. Therefore, it is imperative to choose the correct interaction values of foaming time and gas flow rate.

Initial Metal Concentration

The influence of the initial concentration of metals on the recovery was examined, for which 4.5×10^{-6}, 1.0×10^{-5}, 2.0×10^{-5}, and 3.0×10^{-5} M of metal ions in the initial solution were chosen.

The recovery of the entire amount of metals could not be achieved with low initial metal concentrations (Table 2). However, starting with 2.0×10^{-5} M, the recovery efficiency increased to above 90% for Zn(II)

Table 2. The recovery of metals in different concentrations

The concentration of metal, mol/l	Percentage recoveryof Zn(II), %	Percentage recovery of Mn(II), %	Percentage recovery of Cu(II), %
4.5×10^{-6}	74.0	54.9	36.0
1.0×10^{-5}	86.6	91.5	55.7
2.0×10^{-5}	90.5	99.8	73.4
3.0×10^{-5}	92.7	100.0	75.2

and Mn(II), and therefore, 2.0×10^{-5} M was selected as a working concentration of metals for further experiments.

When the ratio between metal and SDS concentration is elevated to almost 1 : 20 (for diluted metal solutions, e.g., 4.5×10^{-6} M), there is a stronger tendency for SDS to form micelles. Jurkiewicz observed a higher removal of cadmium with smaller concentrations of sodium sulphate, which was used as surfactant (2). Micellar chemistry is not easy to predict, and metal recoveries by flotation may show significant drops in the micellar phase. Another possibility is that micelles with an extra negative charge due to the high concentration of SDS may be more strongly aquated due to ion-dipole interactions between the SDS anion and water dipoles, and consequently less transfered to the froth phase.

The Effect of Auxiliary Ligand

The chelating behaviors of the auxiliary ligands malic acid, maleic acid, and EDTA were investigated under identical conditions with those of zinc, manganese, and copper uptake. The molar ratio between metal : SDS : auxiliary ligand was kept as 1 : 5 : 5 (30, 33) and the pH of the working solution was measured as 4.0. In each experiment, the collecting time was between 10 to 60 minutes. When comparing the results, it was observed that the recovery rates by adding malic and maleic acid were higher than without. In the presence of EDTA the higher recovery rates of metal ions could not be reached (Figs. 2, 3, 4).

In the presence of auxiliary ligands the mechanism of metal retention can be explained as follows:

a. Positively charged metal-auxiliary ligand complexes can be more strongly attached to the bubble surface by a negatively charged surface-active agent than only positively charged metal ion. Cationic chelates will form a stronger ion-association complex with the SDS anion, and consequently, it will be carried much more easily into the froth phase. Froth flotation

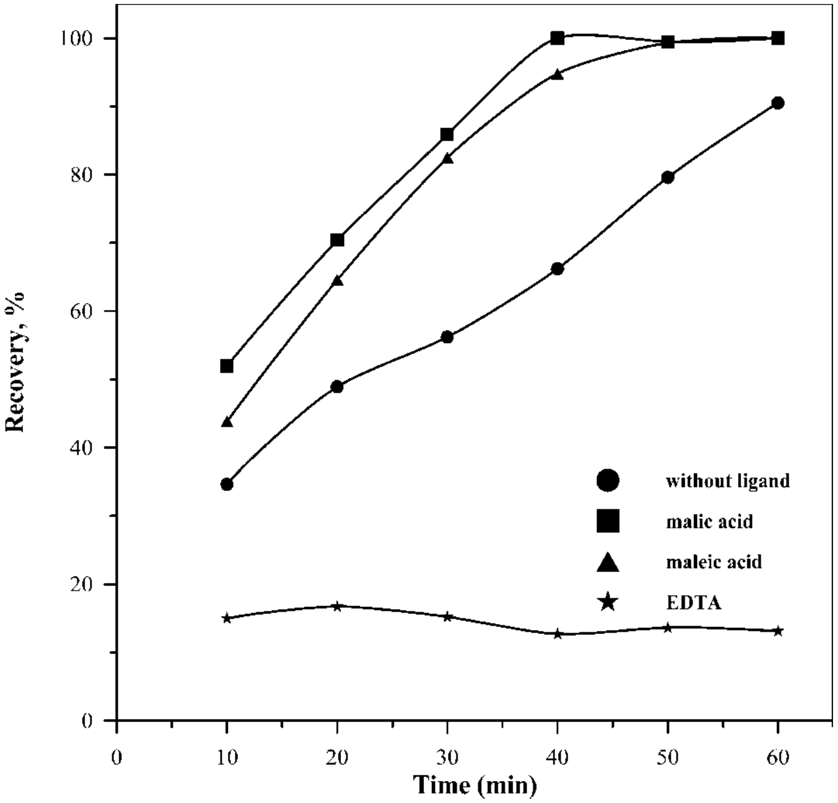

Figure 2. The recovery of zinc as a function of foaming time, in the presence of various ligands: malic acid, maleic acid and EDTA.

is like solvent extraction; the more neutral and hydrophobic the resultant species are, the better they will be carried to the froth phase.

b. On the other hand, in the experiments the Na^+-dodecylsulphate and Me^{2+}-dodecylsulphate combinations at the gas/solution interface can be expressed in the form of hydrated ion pairs. This expression of the hydrated ion pairs results from the competition for metal cations between water molecules and surfactant anions as all functional groups possessing a free pair of electrons at the oxygen atom that is capable of forming the donor-acceptor bonds can compete effectively with water molecules. On the basis of analysis of intermolecular interaction in aqueous solutions it can be supposed that dodecylsulphate hydration results from two kinds of hydrogen bonds, namely among water molecules as well as between dodecylsulphate anion and water molecules. Also, hydration can result from the formation of a donor-acceptor bond between a metal cation and a water oxygen (2).

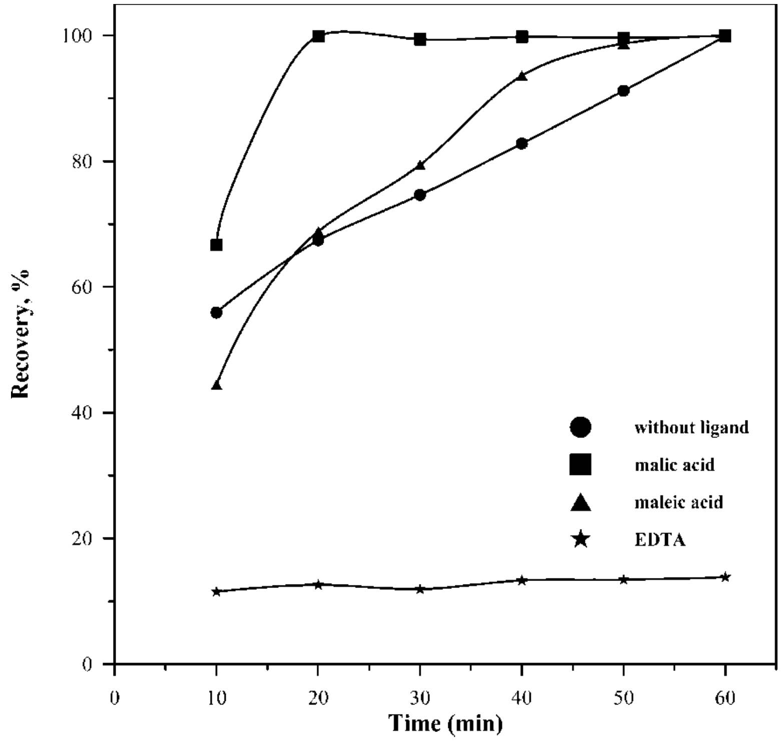

Figure 3. The recovery of manganese as a function of foaming time, in the presence of various ligands: malic acid, maleic acid and EDTA.

As a principle, a large hydrophobic cation forming an ion pair with a large anion is devoid of a primary hydration sphere, and therefore is much more hydrophobic. Solvent extraction and adsorptive bubble separation techniques are very similar to each other. In literature, the recovery of Ni(II) was examined in the presence of versatic acid (a dicarboxylic acid) using both of these separation techniques (33). In that work, the authors disclose possible complex formation mechanisms during Ni(II) removal by these methods. This approach has also been confirmed in our work by measuring maleic acid concentrations in the absence and presence of metal ions in solution. In the absence of metal ion, e.g, Zn^{2+}, maleic acid concentration has not increased in the foam after foaming procedure. This result indicates that, negatively charged maleic acid (i.e., pH > pKa_1) cannot be recovered by negatively charged SDS. However, in the presence of such a metal ion, maleic acid concentration has decreased in the aqueous retentate after foaming procedure. This has been observed by both HPLC and UV-Vis spectrophotometry. This result obtained for maleic acid cannot be observed for malic acid, since the concentrations of malic acid in the initial solution and in the residue were below the detection limit.

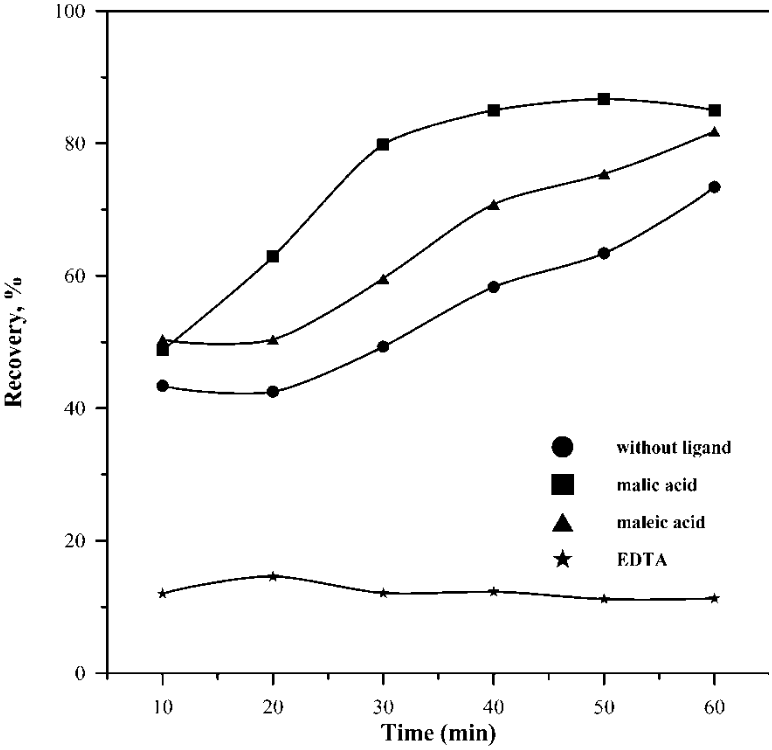

Figure 4. The recovery of copper as a function of foaming time, in the presence of various ligands: malic acid, maleic acid and EDTA.

This phenomena can be explained as follows: equilibrium analysis (species distribution diagrams of weak polyprotic acids, together with their conjugate bases) reveals that at the working pH of 4.0 (in the presence of metal, SDS, and polyprotic acid at 1 : 5 : 5 molar ratio), both malic and maleic acids are predominantly in their HL^- forms, and therefore should not be floated alone with the anionic surfactant due to electrostatic repulsion. However, when they co-exist with Zn(II), the Zn(II) recovery increases, and the same amount of Zn(II) is recovered in a shorter time than that of the absence of maleic acid. This shows that some kind of complexation occurs between Zn(II) and HL^-.

If respective metal-malic and metal-maleic acid first stability constants are compared, it can be seen that the first metal-malic acid stability constants are higher than the first metal-maleic acid stability constants. It means that Zn(II)- and Mn(II)-malic acid chelates are stronger than the corresponding maleic acid chelates: $\log K_1 = 2.80$ for Zn(II)-malic acid, $\log K_1 = 2.24$ for Mn(II)-malic acid, $\log K_1 = 2.0$ for Zn(II)-maleic acid, and $\log K_1 = 1.68$ for Mn(II)-maleic acid. Experimental results which are obtained in this study confirm this explanation. Because, the recovery rates using malic acid were higher than those in the presence of maleic acid under the same experimental conditions. Figures 2–4 show that the recovery rate of Zn(II) and Mn(II) were higher in the presence of malic acid than that of maleic acid. Equilibrium analysis at the working concentrations of Zn(II) and HL^- at $pH = 4$ reveals that the percentage of Zn-malate is less than the percentage of Zn-maleate in such a system. In the literature, both Zn(II) and Mn(II) are also reported to show fast kinetics of metal chelation through sp^3-tetrahedral chelate formation, which can be confirmed by our results (Figure 2 and 3). The stronger complexation of Zn(II) with malate is reflected in the sooner recovery of Zn(II) than in the presence of malic acid in preference to maleic acid. However it should be borne in mind that froth flotation of Zn(II) is not an equilibrium process, meaning that Zn-malate/maleate is removed from the solution (incorporated in a foam) as soon as it is formed. This shifts the equilibrium to the direction of Zn-malate/maleate formation according to Le Chatelier's principle. Thus, even though Zn-malate/maleate is not a predominant species at equilibrium, it can be effectively removed as a kinetic intermediate as incorporated in the foam, and it can, result in forming the basic species more hydrophobic than the aqua-metal cation which is simultaneously removed in the foam structure (similar reasoning also applies for solvent extraction or adsorption recovery of metals, where minor species in solution may be major species in the separated phase) (24).

Although Cu(II) has higher stability constants with malic and maleic acids ($\log K_1 = 3.40$ for Cu(II)-malic acid, $\log K_1 = 3.90$ for Cu(II)-maleic acid) than Zn(II) and Mn(II) with the same ligands, experimental results indicate that the recovery efficiencies of Cu(II) is lowest (Fig. 4). This apparent inconsistency can be explained as follows: as Cu(II) probably forms 1 : 2 complexes with malate and maleate under identical conditions, which are neutral, i.e., 2 carboxylate ligand ions (L^-)-neutralize the divalent charge of Cu^{2+} to form CuL_2. In that case, this neutral chelate may be only associated with the SDS anion through hydrophobic interactions, and electrostatic interaction will not be exploited (Fig. 4). Furthermore, Cu(II) will be least transfered to the froth phase in the presence of malic or maleic acid and SDS, because the copper end of CuL_2 chelate will still be moderately aquated. Besides, malic or maleic acids are not hydrophobic enough to make the final chelate sufficiently hydrophobic.

Another confirmation for complex formation between metal ion-malic/maleic acid is the FT-IR spectra (Fig. 5). When the foam was separated, dried, and subjected to IR spectroscopy, the carbonyl band appearing at $1704\,cm^{-1}$ and the (C=O) band for coordinated carboxylate group appearing at $1432\,cm^{-1}$ is a direct confirmation of malate/maleate incorporation to the floated Zn(II). In literature (34) the vibration bands, which are responsible for (C–H) group on the Cu(II), Ni(II), and Co(II)-maleate complexes have been detected between $2730–2866\,cm^{-1}$. Had Zn(II) not

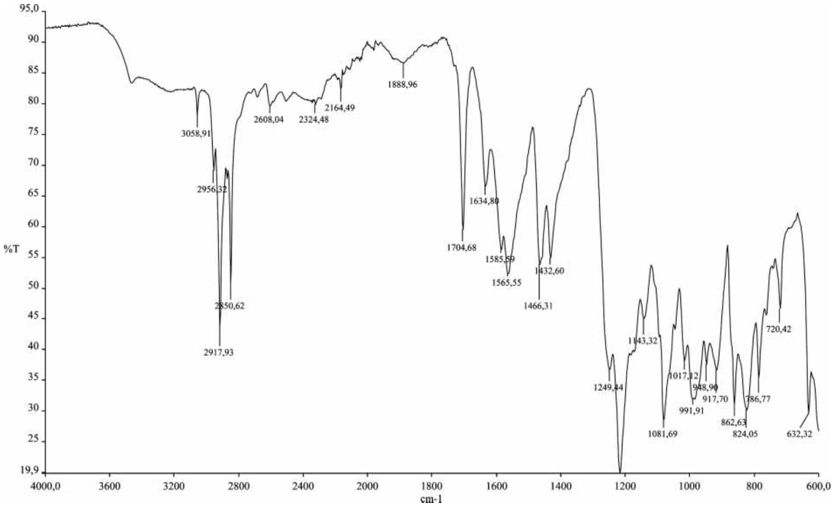

Figure 5. IR spectra of Zn(II)-maleate.

complexed with malate/maleate to some extent, the negatively charged HL^- could not have been floated with anionic surfactant. In this case the strongest possibility is that $Zn(HL)^+$, Zn(II), and ZnL species are co-floated with SDS forming a mixed product.

It is also worth mentioning that in our experiment, Zn(II) could not be recovered by using Cetyltrimetylammonium bromide (CTAB), which is a cationic surfactant (2). This is due to electrostatic repulsion between existing $Zn(HL)^+$ complexes and the CTA^+ cation.

When comparing our results, it was also seen that the lowest percentage recovery of metals was obtained with EDTA, because in the presence of it, stronger anionic metal(II)-EDTA complexes (MY^{2-}) are formed. These anionic complexes repel the anionic SDS surfactant. Due to these repulsive forces, copper may not be transfered to the froth phase in the presence of EDTA: H_2Y^{2-} (30), and prefer to remain in the aqueous phase.

CONCLUSIONS

Adsorptive bubble separation is a group of ecologically friendly methods that are very effective for highly diluted solutions such those in this work. The other advantages are the use of a simple apparatus as well as low energy, investment, and maintenance costs. This technique offers possibilities for application in several different spheres. These can be summarized as follows:

- As a method for the preparation of new compounds, or opening up new methods for the preparation of known compounds

- As a tool for academic studies into the behaviour and properties of ions in solution
- As a analytical technique
- As a concentrating technique in industry
- As a separating technique in industry.

This method can be used to remove of Zn(II), Mn(II), and Cu(II) from dilute solutions efficiently. In the presence of some auxiliary ligands (malic acid, maleic acid) the recovery efficiency for all metal ions could be increased and the process could be completed in a shorter time. This is very important and advantageous for industrial applications. It should also be mentioned that these ligands are quite cheap, and because of that, this separation method is economic. Furthermore, the pH-value did not need to be adjusted, the process became not only feasible for the praxis but also time-saving. In industrial applications, it would not be economic to have to make too many adjustments to the solution before floating.

Because ion flotation can concentrate from solutions where the solute is of a concentration that is of the order of tenths of a millimole per litre or even less, it would seem that it would find application simply as a concentrating technique. So, one of the most useful characteristics of ion flotation is its ability to concentrate from extremely dilute solutions.

In a world of expanding population and limited mineral resources the need to eliminate waste will increase in importance. In considering treatment of waste solutions, the emphasis here will be on inorganic constituents because some of these are not only potentially worth recovering, but also because their entry into sewage plants is often undesirable. Wastes from aqueous solutions could be purified using ion flotation. For these reasons, ion flotation is an ecologically alternative method (5).

The role of electrostatic and hydrophobic interactions of auxiliary ligands in the froth flotation/separation of metal cations has been interpreted.

ACKNOWLEDGMENT

The author expresses her thanks to Prof. Dr. Harun Parlar, Technical University of Munich, Department of Chemical-Technical Analysis and Chemical Food Technology, for his support and contributions.

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