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Heavy metal removal from waste waters by ion flotation

H. Polat [a,*], D. Erdogan [b]

[a] *Faculty of Science, Department of Chemistry, Izmir Institute of Technology, Urla-Izmir, Turkey*
[b] *Environmental Engineering Program, Izmir Institute of Technology, Urla-Izmir, Turkey*

Abstract

Flotation studies were carried out to investigate the removal of heavy metals such as copper (II), zinc (II), chromium (III) and silver (I) from waste waters. Various parameters such as pH, collector and frother concentrations and airflow rate were tested to determine the optimum flotation conditions. Sodium dodecyl sulfate and hexadecyltrimethyl ammonium bromide were used as collectors. Ethanol and methyl isobutyl carbinol (MIBC) were used as frothers. Metal removal reached about 74% under optimum conditions at low pH. At basic pH it became as high as 90%, probably due to the contribution from the flotation of metal precipitates.
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1. Introduction

An increasing demand for fresh water along with the larger amounts of waste water generation due to increase in the world population and development of industrial applications make the recycling of the waste waters an imperative issue. Presence of heavy metals which display high and long term toxicity create limitations on the recyclability of these waters. The amount of heavy metals is especially high in industrial waste waters and endanger public health and the environment if discharged without adequate treatment (Table 1). Methods such as chemical precipitation, solvent extraction, reverse osmosis, ultrafiltration, electrodialysis, ion exchange and adsorption are commonly used for this purpose [1–9].

Ion flotation may be an alternative method to remove heavy metal ions from waste waters. The process of ion flotation is based on imparting the ionic metal species in waste waters hydrophobic by use of surface active agents (surfactants) and subsequent removal of these hydrophobic species by air bubbles.

A typical surfactant molecule such as those used in this study consists of a polar ionic head and non-polar hydrocarbon chain.

Attachment of the polar head group to a metal ion exposes the non-polar, hydrophobic section of the surfactant into the solution. When air bubbles are introduced into the flotation cell, the metal ion-surfactant assemblies are collected by the air bubbles due to the favoured interactions between the exposed hydrocarbon chains and the air bubbles. Therefore, these surfactant molecules are also called collectors in the flotation terminology. The air bubbles laden with the metal ions float to the surface and are removed as a froth which is rich in metal content.

The size of the air bubbles in a flotation cell should be fine (in the order of a few hundred micrometers) to present sufficient surface area for collection. The reagents which control the size of the bubbles by reducing the air/water interfacial tension are called frothers. Some common flotation frothers are MIBC (methyl isobutyl carbinol), ethanol, methyl ethers (e.g., Dowfroth 250), polypropylene glycol. Some commercial frothers may have both frothing and collecting properties [19].

As opposed to the classical flotation process where the valuable mineral species are floated and removed with the froth, the species which are floated in ion flotation are the metal ions. In other terms, ion flotation is about selectively concentrating the metal ions in the froth phase. However, the degree of this concentration process will be determined not only by the metal content of the froth, but also the amount of water in the froth by definition. A successful removal of metal ions should correspond to a large metal ion/water ratio in the froth phase. It follows that the

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* Corresponding author. Tel.: +90 232 750 7531; fax: +90 232 750 7509.
 E-mail address: hurriyetpolat@iyte.edu.tr (H. Polat).

Table 1
Cu, Zn, Cr, Ag levels reported in industrial waste waters [8]

Source	Cu (mg/L)
Paint-pigment manufacturing	0.04–100
Motor plating	0.5–33
Copper plating baths	2.2–183
Acid mine drainage	0.12–128
Petroleum refining	0.0–1.4
Copper ore extraction	0.28–20
Leather industries	1.7–55
	Zn (mg/L)
Paint manufacturing	0.3–77.4
Zinc plating	2–1050
Pigment manufacturing	0–1702
Metal processing	0.2–1.0
Textile dying	2–6
Steel works	2.1–1210
	Cr (mg/L)
Chemical industries	1.1–17.7
Leather industries	1.7–55
Paint industries	2.5–30
	Ag (mg/L)
Photographic manufacturing	100–260,000
Steam wells	100–300,000
Oil well brines	10–100

Maximum allowable limits are—copper: 1 mg/L, zinc: 5 mg/L, chromium: 0.5 mg/L, silver: 0.2–2.0 μg/L.

selectivity of the ion flotation process must be evaluated based on the relative recoveries of both the metal ions and water from the flotation cell.

Though there are several studies on ion flotation [10–18, 20–24], they lack information on the relative amounts of metal and water removals from the flotation cell. Therefore, the scope of this study was to investigate the optimum conditions for the removal of such highly toxic heavy metals as copper, zinc, silver and chromium from simulated industrial waste waters using ion flotation with special emphasis on the relative rates of metal and water removal from the flotation cell.

2. Experimental work

2.1. Materials

Anionic sodium dodecyl sulfate (SDS; MW = 288 g/mol and CMC = 8.25×10^{-3} M) and cationic hexadecyltrimethyl ammonium bromide (HATB; MW = 364.5 g/mol and CMC = 9.2×10^{-2} M) from Sigma were used as collectors.

Ethanol from Carlo Erba was used as the frother in all tests except in silver flotation where it did not produce a stable froth. For silver flotation methyisobutyl carbinol (MIBC) from Merck had to be employed as the frother.

Copper nitrate ($Cu(NO_3)_2$, 99.3%) from Sigma, zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 98%) from Aldrich, chromium (III) chloride hexahydrate ($CrCl_3 \cdot 6H_2O$, 99%) from Sigma and silver nitrate ($AgNO_3$, 99.5%) from Carlo Erba were used to prepare the simulated waste water solutions.

The solution pH was adjusted using NaOH and HCl when necessary. Double distilled water which was passed

through Barnstead Easypure UV-Compact ultrapure water system (18.3 Ω) was used to prepare the stock solutions.

2.2. Method

A Denver type flotation machine was used in the experiments. The impeller speed was kept constant at 750 rpm. The concentrations of Cu(II), Zn(II), Ag(I) and Cr(III) in the flotation cell were each 10 mg/L unless otherwise stated. The flotation solution was conditioned for 1 min and pH of the solution was adjusted to a desired value. Following the addition of the required amount of the collector, the solution was conditioned for an additional 2 min. Ethanol or MIBC was added as the frother and the solution was conditioned for an additional 1 min prior to the introduction of air into the flotation cell. The froth developed at the surface of the flotation cell was removed by hand using a rubber paddle at preset time-intervals for up to 16 min. The froth products were analyzed by atomic absorption spectrometry (AAS) to determine the amount of metal ions in the froth phase.

2.3. Calculation of metal recoveries

An example calculation of the metal recoveries is presented in Table 2. It should be noted that the weight of the water removed from the flotation cell is essentially the same as the weight of the froth removed. Therefore, the froth weights directly give the water recoveries.

3. Results and discussion

3.1. Dominant species in simulated waste waters

Solution pH is a significant factor for determining the form and the charge of the metal present in solution. Fig. 1 gives the graphs of the thermodynamic distributions of the Cu(II), Zn(II), Ag(I) and Cr(III) in aqueous solutions as a function of pH. The salts employed preparing these solutions and the stochiometric concentrations of the metals and their associated anions are shown in the inset boxes in these graphs. Note that the amount of salt used in preparing the simulated waste water solutions was selected such that the total metal concentration in solution was always equal to 10 mg/L for each metal. The calculations were carried out using Visual Minteq ver.2.15.

The graphs in Fig. 1 show that the salts dissociate to produce metal species with various degrees of hydrolysis and charging. For example, the dominant species for copper are the positively charged Cu^{2+}, $CuOH^+$ and at pH values less than 10 whereas they are negatively charged $Cu(OH)_3{}^-$ and $Cu(OH)_4{}^{2-}$ at pH values greater than 10. At and around pH 10, precipitation of neutral $Cu(OH)_2$ takes place. Similar observations can also be made for Zn(II), Ag(I) and Cr(III). It is apparent that the pH of the solution is extremely important in ion flotation since it dictates the type and the charge of the species present in solution and therefore the structure of the surfactant (an anionic or a cationic collector) to be employed.

The dashed lines in the figures give the concentration of the free anion in solution and demonstrate that the salts used to pre-

Table 2
Example calculation for determining the water and metal recoveries in the froth products

Flotation time (min) (1)	Water recovery (g) (2)	Water recovery (%) (3)	Cumulative water recovery (%) (4)	Metal conc. in froth (mg/L) (5)	Metal units in froth (6)	Metal recovery (%) (7)	Cumulative metal recovery (%) (8)
0–2	45	4.5	4.5	37.9	170.4	18.6	18.6
2–4	51	5.1	9.6	28.2	143.7	15.6	34.2
4–8	135	13.5	23.1	19.4	261.6	28.5	62.7
8–16	250	25.0	48.1	9.8	245.8	26.8	89.5
Remaining in cell	519	51.9	100.0	1.9	96.0	10.5	100.0
Total	1000	100.0			917.5	100.0	

Weight of the froth removed from the cell (determined by weighing the froth). Note that froth weight is essentially equal to the weight of the water removed from the cell. Percent weight of the froth in each froth product, $(2) \times 100/\sum(2)$. Cumulative percent weight of froth, $\sum(3)$. Metal ion concentration in froth product (determined by AAS). Weighed metal ion concentration in froth product, $(3) \times (5)$. Metal recovery in froth product, $(6) \times 100/\sum(6)$. Cumulative metal recovery, $\sum(7)$.

pare the solutions completely dissociate since all the NO_3^- or Cl^- originating from the salts are present in free ionic form. Though presence of such species as $CrOHCl_2$, $MeNO_3^+$ or $Me(NO_3)_2$ were observed based on our calculations, their concentrations in solution are completely negligible (in the order of 10^{-8} mg/L or less) and were not shown here for sake of clarity. Hence, it is clear that the form of the salt used (a nitrate or a chloride salt) is immaterial for the purpose of this study.

Also, it was observed that co-existence of these metal ions in solution (such as a solution prepared by dissolving both zinc

and copper salts together) did not change the distributions given in Fig. 1 appreciably. The very small, negligible shifts of the curves observed in the pH scale in these cases were due to the slight increase in the ionic strength due to the presence of both salts in solution simultaneously.

3.2. Flotation of metal ions

The initial flotation tests were conducted as a function of frother (ethanol) and collector (SDS) concentrations at pH 4. The
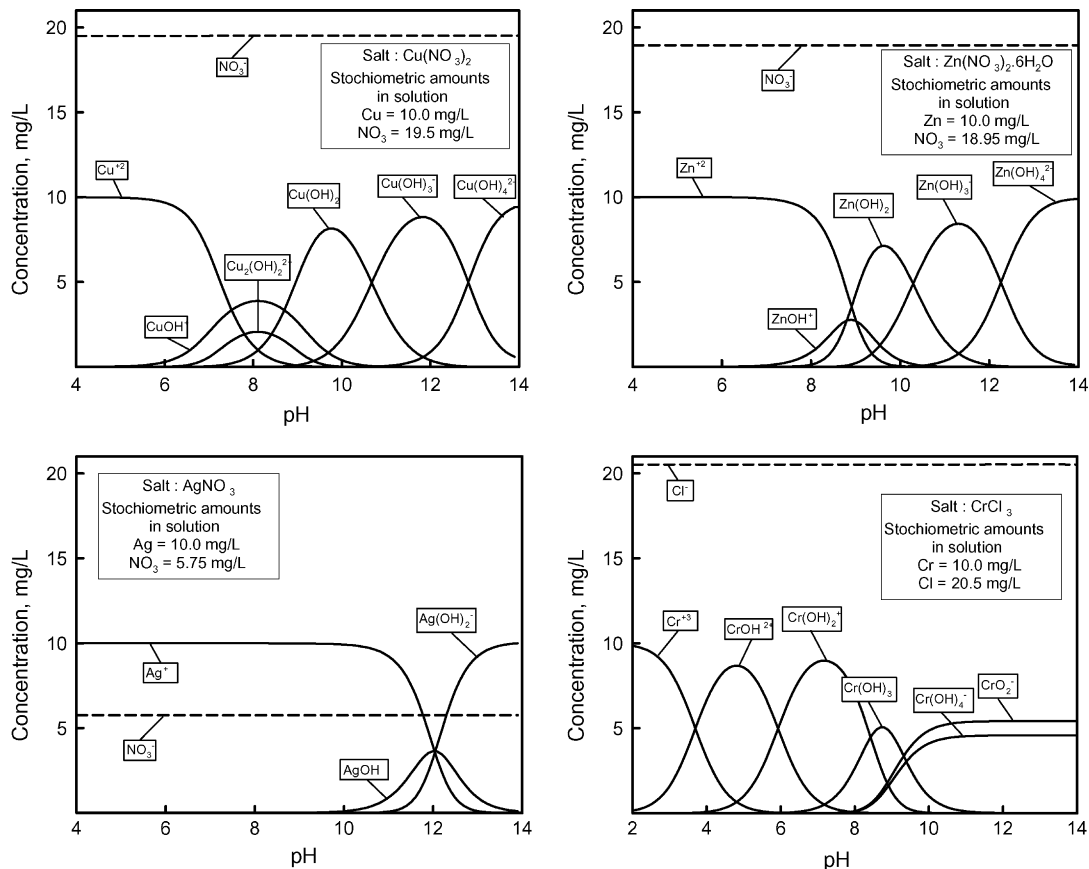

Fig. 1. Thermodynamic distribution of the prevalent species available in simulated waste waters used in this study as a function of solution pH. The total solution concentrations shown in the boxes for the metals and their associated anions were calculated stochiometrically from the amount of salt used in preparing the simulated waste waters. The dashed lines in the figures show that the salts dissolve completely and nearly all the NO_3 or Cl is in free ionic form. Though such species as $CrOHCl_2$, $MeNO_3^+$ or $Me(NO_3)_2$ are thermodynamically possible, their concentrations in solution are completely negligible and were not shown here for the clarity of the figures. The calculations were carried out using Minteq ver 2.15.
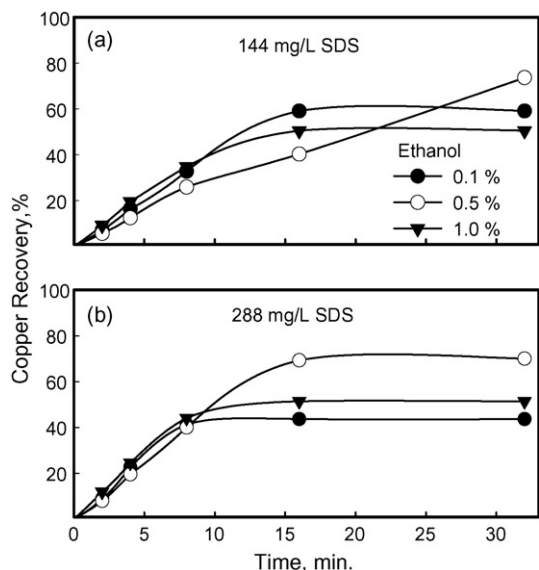
Fig. 2. Copper recovery as a function of time for different SDS and ethanol concentrations.

results of the Cu(II) system are presented in Fig. 2 as a function of time. There was no flotation at low concentrations of surfactant (28.8 mg/L SDS) most probably due to insufficient collector-metal ion Cu(II) pairing. At higher concentrations, however, respectable recoveries were obtained which varied with frother concentration. At an SDS concentration of 288 mg/L, the final copper recoveries were 44%, 70% and 52% for 0.1%, 0.5%, and 1.0% of ethanol concentrations, respectively. At an SDS concentration of 144 mg/L, the copper recoveries were 59%, 74% and 51% for 0.1%, 0.5%, and 1.0% of ethanol concentrations, respectively. As it can be seen that there is an optimum around 0.5% of ethanol.

Similar flotation tests were also conducted as a function of air flow rate at fixed ethanol and SDS concentrations. The results were presented in Fig. 3a as a function of time. However, these figures are not enough to analyze efficiency of the ion flotation since there is no information about the amount of water removed from the cell along with the metal ions. Though several researchers who studied ion flotation reported satisfactory metal recoveries, they provided no information on the water recovery [4,11,13,16,21]. Therefore, the copper recoveries obtained for different air flow rates were also plotted as a function of the water recovery and presented in Fig. 3b. In this figure, the diagonal line is the 50/50 split line, which corresponds to no enrichment of the metal either in the solution or in the froth. The recoveries which remain above this line mean that the metal is concentrated in the froth phase whereas those which remain below mean that the metal is concentrated in solution remaining in the flotation cell.

When the initial copper concentration was increased to 50 mg/L in the presence of 144 mg/L SDS and 0.5% ethanol at pH 4, the recovery decreased to 42%. This might be due to the presence of higher number of Cu(II) ions in the system compared to the surfactant molecules present. This supports the hypothesis that metal ions attach to the oppositely charged surfactant molecules for flotation.
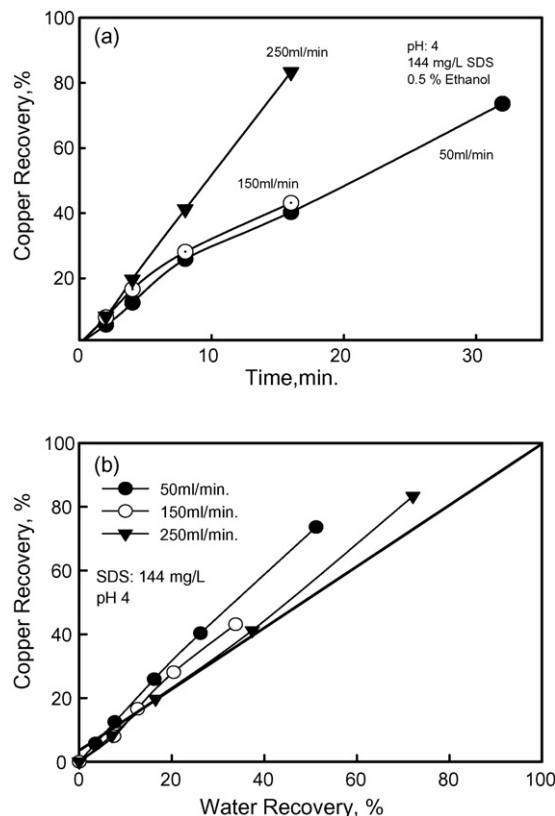

Fig. 3. (a) Copper recovery as a function of time for different air flow rates. (b) Copper recovery vs. water recovery plot as a function of air flow rate.

The effect of solution pH was also tested. The reason was to observe the response of the various copper species towards the collectors used. The experiments with the anionic SDS (144 mg/L) were carried out at pH values of 4, 6, 8 and 10 since the copper species prevalent in solution were mainly positively charged below pH 10 (see Fig. 1). On the other hand, the cationic HTAB (182 mg/L) was used for pH values 10 and 12 since the appearance of negatively charged copper species in solution could take place at pH values greater than 10.

The results of these experiments are presented in Fig. 4 in terms of copper recovery as a function water recovery. In the experiments with the SDS, the figure shows that copper
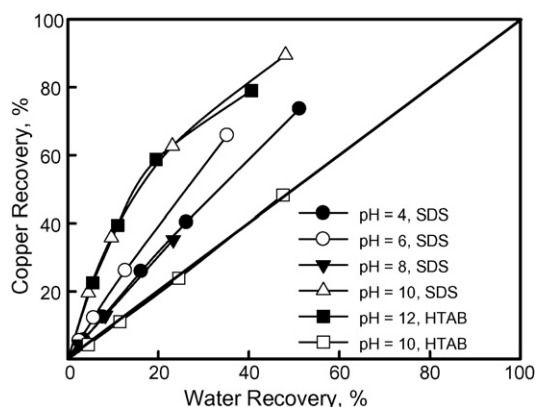

Fig. 4. Copper recovery vs. water recovery plot as a function of pH (initial copper concentration: 10 mg/L).

is selectively floated at pH 4 and 6 where doubly charged Cu(II) species are prevalent. When the pH is increased to 8, however, selectivity decrease probably due to the appearance of mono-charged copper species which show smaller affinity towards the SDS most probably due to a smaller charge density. If the pH is further increased to 10, the selectivity of copper increases once again. This seems somewhat surprising since the amount of positively charged copper species should be lower at pH 10 where the dominant copper form is the neutral $Cu(OH)_2$ precipitate. The high recovery at pH 10 (actually the highest recovery within this set of tests) implies that the precipitated copper must be floating. Actually, a visual inspection at this pH clearly showed precipitated copper in the froth products.

The flotation of copper at pH 10 with the cationic HTAB, however, shows no selectivity. The copper–water recovery data falls squarely on the 50/50 split line which means that flotation shows no preference between copper and water. When the pH is raised to 12, where negatively charged copper species begin to form, the copper selectivity with the HTAB improves drastically as expected and equals the best results obtained with the SDS at pH 10.

The observed floatability of the precipitated copper forms at pH 10 with the anionic SDS, but not with the cationic HTAB, certainly points out to a favoured interaction between the $Cu(OH)_2$ species and the SDS, but the form of this interaction needs to be investigated further.

In order to determine the relative selectivities of the metals Cu(II), Zn(II), Ag(I) and Cr(III) with respect to each other, flotation tests were carried out at a fixed pH of 4 where these metals were known to be completely positively charged (see Fig. 1). The differences in flotation recoveries of metal ions can be seen in Fig. 5. It had to be noted that MIBC was used as the frother for silver flotation since a stable froth could not be obtained in case of silver, significantly decreasing the froth recovery from the cell and leading to a no flotation condition. Even though the reason why ethanol did not produce a stable froth phase while there were no problems with other metals is not known, this work shows that the froth properties may differ in the presence of different metal ions and that frother selection has to be done with care in any future studies.
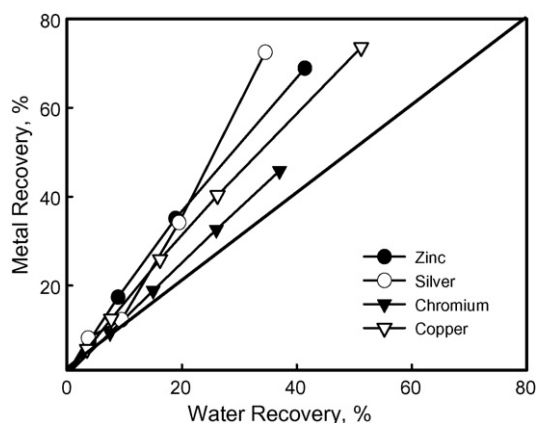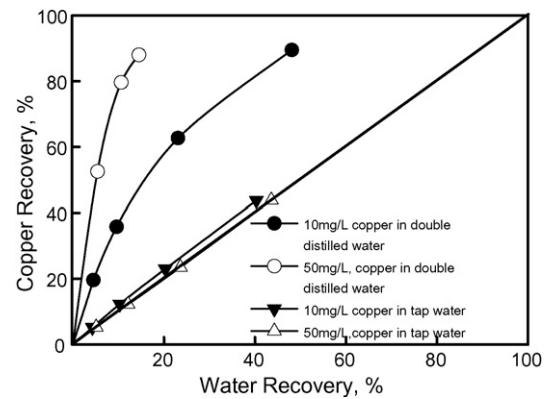

Fig. 6. Effect of ionic strength on copper recovery (SDS: 144 mg/L, ethanol: 0.5%, pH:10, airflow rate: 50 mL/min).

The effect of ionic strength on ion flotation was also studied since industrial ion flotation studies may have to be carried out with tap water. For this purpose a simulated tap water was used along with the double distilled water in preparing the waste water solutions. The composition of the simulated tap water was Na (18 mg/L), Mg (200 mg/L) and Ca (26 mg/L). The results and the conditions of this study are presented in Fig. 6 for copper concentrations of 10 and 50 mg/L. It is clearly obvious that use of simulated tap water decreases the flotation selectivity for both copper concentrations. For example, for 50 mg/L, the double distilled water test shows nearly perfect separation whereas the test with the simulated tap water is almost on the 50/50 split line. This drastic decrease can be explained by the consumption of the SDS molecules by the excess Na, Mg and Ca ions, rendering the SDS unavailable for the flotation of copper. The fact that analysis of the froth for the Ca, Mg and Na shows that almost all of these ions (>98%) reported to the froth phase is a strong proof of this point. This data also indirectly backs the above argument that SDS strongly interacts with and floats the available copper species at pH 10.

In pH 4, where copper is present in ionic form, recovery at 50 mg/L copper is lower compared to 10 mg/L copper, most probably because there are not enough SDS molecules for flotation (surfactant molecule pairs with individual ions). On the other hand, at pH 10 where copper clearly precipitates, there is no such constraint on the number of surfactant molecules where they float aggregation of precipitated copper ions. In this case, recovery for 50 mg/L copper is actually higher as a function of water recovery.

3.3. Selective flotation of copper from silver and zinc

In this part of the study, some preliminary tests were carried out to demonstrate if selective flotation of one metal was possible from another in a waste water solution. For this work, only separation of copper from silver and zinc in separate tests was studied. Though several conditions were tested, those where the best separation was observed are reported in the following paragraphs. The metal concentrations in solution was set to be 10 mg/L in solution for each metal in these tests. The SDS and ethanol concentrations were 144 mg/L and 0.5%, respectively.

Fig. 5. Metal recovery vs. water recovery plot as a function of metal type at pH 4 (SDS: 144 mg/L, ethanol: 0.5%, $MIBC_{Ag}$: 0.1%, airflow rate: 50 mL/min).
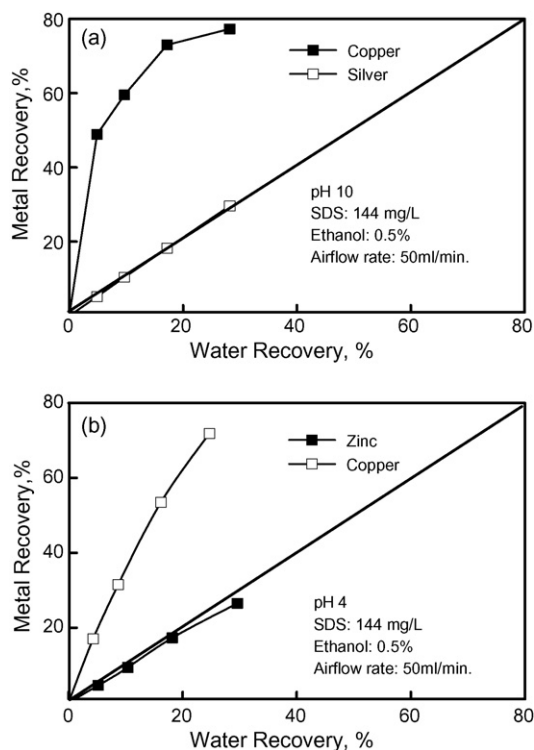
Fig. 7. (a) Selective flotation of copper and silver (initial metal concentrations (Cu, Ag): 10 mg/L each). (b) Selective flotation of copper and zinc (initial metal concentrations (Cu, Zn): 10 mg/L each).

For the copper–silver system, the best separation was achieved at pH 10 where the copper is in $Cu(OH)_2$ precipitate form whereas silver is in Ag^+ form. The results are presented in Fig. 7a. They clearly demonstrate that copper can be very successfully separated from silver which does not respond to flotation at all and remain on the 50/50 split line. These results simply show that SDS has much more affinity towards the available copper species at this pH than it has towards the silver species.

For the copper–zinc system, the best separation between the two was observed at pH 4 where both metals must be present in their cationic forms (Fig. 7b). The data shows that there must be a competition between the copper and zinc species in the favor of copper since zinc was observed previously to float under similar conditions when it was the only metal in solution (see Fig. 5). The fact that copper floats much more readily at this pH compared to the similarly charged zinc species is an indication of a higher affinity of the copper species towards the SDS molecules. However, the reasons for the observed selectivity must be investigated further.

4. Conclusions

Ion flotation studies were conducted to investigate the selectively removing several metals from waste waters. Various parameters such as airflow rate, surfactant and frother concentrations and water chemistry were tested to determine the optimum flotation conditions. Anionic sodium dodecyl sulfate (SDS) and cationic hexadecyltrimethyl ammonium bromide (HTAB) were used as collectors.

It was observed that it was possible to find conditions to concentrate these metals with recoveries as high as 90% in a froth phase which contain less than about 20% of the original water. Considering the ease of application, low cost and very high capacities achievable in the flotation process, such results are very promising.

Preliminary tests demonstrated that it was also possible under suitable conditions to remove the metals from each other. In the selected cases of copper–silver and copper–zinc systems, copper could be selectively concentrated in the froth phase, leaving the other metal in solution.

Acknowledgment

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