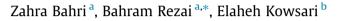Contents lists available at ScienceDirect

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Evaluation of cupferron on the selective separation of gallium from aluminum by flotation: The separation mechanism

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ABSTRACT

Aluminum is an impure element in acidic solutions obtained from gallium sources. Therefore, the selective separation of gallium from aluminum, using cupferron as a ligand (chelating agent) and sodium dodecyl sulfate as an anionic collector was investigated by flotation. The effect of the solution pH, the molar ratio of cupferron to gallium, the collector concentration, the impeller speed, the conditioning time and the flotation time on the selective separation of Ga(III) from Al(III) were studied. The results indicate that the chelating agent cupferron, efficiently separated gallium from aluminum, owing to the higher chelating strength of the interaction between Ga(III) and cupferron. The Ga(III)-cupferron complexes, formed in the presence and absence of SDS, were spectroscopically confirmed and characterized by Fourier transform infrared (FTIR), UV–visible spectroscopy and scanning electron microscopy coupled with energy dispersive X-ray (SEM/EDX). The bonding of cupferron with Ga(III) was considered to be as a bidentate ligand, and gallium formed 1:1.5 complexes with cupferron in aqueous solution. The separation mechanism of flotation was proposed owing to the formation of a physical interaction between the Ga(III)-cupferron complex and SDS.

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1. Introduction

Gallium is mainly obtained as a byproduct from Bayer solutions of aluminum, and from acidic solutions in the manufacture of zinc (Flamini et al., 2007; Xu et al., 2007; Dumortier et al., 2005). It is widely used in the electronic industry and medicine. The release of gallium from mining wastes and industrial scrap may result to environmental pollution and may cause hazardous effects on human health (Chang et al., 2003). Therefore, the development of a gallium-extraction method is necessary, not only to increase the efficiency of gallium, but also to reduce environmental pollution. In this study, because aluminum is an impure element in acidic solutions obtained from gallium sources, the selective separation of gallium from aluminum was investigated by ion flotation.

Ion flotation was introduced by Sebba, and has been employed as a separation process since 1960 (Sebba, 1962). This technique has a great number of advantages, such as the selective removal of non-surface active ions from dilute (10^{-6}–10^{-3} M) aqueous solutions, low energy requirements and minimal environmental impact (Stoica et al., 1998; Shakir et al., 2007). Although all of these factors make ion flotation an effective method for the recovery of

valuable metals from industrial wastewater, the selective separation of the target ion greatly depends on the composition and ionic strength of the solution (Scorzelli et al., 1999; Polat and Erdogan, 2007; Doyle, 2003). As a result, further studies on the mechanism and selective separation of the target ion from mixed solutions, are necessary. The selectivity and recovery of the target ion is low, when the aqueous solution of flotation includes ions with the same charge (Ulewicz et al., 2001). In ion flotation technique, ions with charges of the same sign and same valence compete for adsorption to the collector; therefore, the separation efficiency of the metal values is reduced (Sebba, 1962; Lemlich and Arod, 1972).

Only a few studies are available in the literature to the selective separation of ions using ion flotation. Reviews of published works on the selective separation in ion flotation are presented in Table 1.

Although the selective separation of mono- and divalent ions has been studied, no studies have been published on the selective separation of two trivalent ions by ion flotation. Thus, the selective separation of gallium from aluminum was studied using cupferron as a chelating agent to form complexes with gallium and SDS as an anionic surfactant to separate the complexes from the bulk liquid. The objective of this work was to examine the optimal conditions for the removal of Ga(III) from Al(III) by flotation. To this end, the effect of the process parameters, i.e., pH (0–4), molar ratio of

Table 1
The summaries of the literature reviews on the selective separation in the ion flotation.

Purpose of the study	Ligand type	Surfactant type	Selectivity sequence	Reference
Selective separation of the alkali-metal ions over sodium	2.2.2-Cryptand	Bis (2-ethylhexyl) sulfosuccinate (AOT)	$Rb^{+1} > K^{+1} > Na^{+1} > Cs^{+1} > Li^{+1}$	Schulz and Warr (1998)
Selective separation of Zn and Cd ions	Diphosphaza PNP16C6 crown ethers	Rokafenol N-8	$Cd^{2+} > Zn^{2+}$	Ulewicz et al. (2001)
Selective separation of Zn(II)/Cd(II)	4-Thiazolidinone derivatives	Sodium dodecylbenzenesulfonate	$Cd^{2+} > Zn^{2+}$	Kozlowski et al. (2002)
Competitive flotation of Cs, Sr and Ba ions from dilute aqueous solutions	Proton-ionizable lariat ethers	Triton X-100	$Sr^{2+} < Cs^{+} < Ba^{2+}$	Maciejewski and Walkowiak (2004)
Competitive ion flotation of Cu, Zn and Cd ions from diluted aqueous solutions	B-cyclodextrin (b-CD) polymers	Rokafenol N-8	$Zn^{2+} > Cd^{2+} > Cu^{2+}$	Girek et al. (2005)
Selective separation of Cd(II) from solutions of Cd(II)-Pb(II), Cd(II)-Ca(II), Cd(II)-Cu(II), and Cd(II)-Zn(II)	–	Sodium dodecyl sulfate and ethanol	$Pb^{2+} > Ca^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+}$	Ehrampoush et al. (2011)
Removal of Cd(II) from clean and Zn(II)- and Cu(II)-contaminated solutions	–	Rhamnolipid biosurfactant	$Cd^{2+} > Zn^{2+}$, $Cd^{2+} > Cu^{2+}$, and $Zn^{2+} > Cu^{2+}$	Bodagh et al. (2013)
Selective separation of Ga(III) from Zn(II)	–	Sodium dodecyl sulfate	$Ga^{3+} > Zn^{2+}$	Bahri et al. (2016)

cupferron to gallium and the collector concentration on the selective separation of Ga(III) from Al(III) is discussed.

2. Materials and methods

2.1. Reagents and sample preparation

Gallium nitrate hydrate 98+ [Ga(NO₃)₃·xH₂O], aluminum chloride [AlCl₃], cupferron [C₆H₉N₃O₂] and SDS [NaC₁₂H₂₅SO₄] were purchased from Merck. Caustic soda (NaOH) and hydrochloric acid (HCl), obtained from Merck, were used to adjust the pH solution. In the flotation tests, the initial concentration of Ga(III) was the same and constant at 1.5×10^{-4} M. Flotation experiments were carried out in a Denver laboratory flotation machine, with a 1 L capacity cell. 2 L of a 1.5×10^{-3} M gallium and aluminum stock solution were prepared separately from gallium nitrate and aluminum chloride dissolved in hydrochloric acid. From these solutions, other diluted solutions were prepared. Therefore, 1 L of an equimolar solution Ga(III) and Al(III) $(1.5 \times 10^{-4}$ M) in addition to a measured amount of cupferron with different molar ratio, was stirred at 1000 rpm for 3 min, thereafter, a measured amount of SDS was added to the solution. Subsequently, flotation was started by introducing air; the froth was collected for 5 min. After flotation, the ions concentrations in the cell were measured by ICP-OES analysis. To avoid ion precipitation, samples were acidified with 1–3 M HCl prior to analysis. The separated precipitate was washed twice with distilled water and left to dry in air before FTIR and SEM-EDX analysis. Visual Minteq ver. 3.0 was used for modeling the gallium and aluminum speciation diagram (Gustafsson, 2010). The physicochemical parameters influencing the process, such as the ligand conditioning time, the flotation time and the impeller speed were also evaluated. The percentage removal of ions (R) was calculated according to the following equation (Ehrampoush et al., 2011):

$$R(\%) = [1 - (C/C_0)] \times 100 \tag{1}$$

where C is the residual concentration of the metal ion in the treated solution, and C_0 is the initial concentration of the ion in the feed solution.

The selectivity coefficient corresponding to the charge exchange equilibrium at the interface was also calculated, using the following equation (Micheau et al., 2015):

$$K_X^{Y \text{ reco}} = \frac{R_1}{R_2} \tag{2}$$

where $K_X^{Y \text{ reco}}$ is the apparent charge selectivity coefficient, and R_1 and R_2 are total mole fraction of ions transferred into the foam due to the ions adsorbed at the water/air interface (Micheau

et al., 2015). Consequently, the mole fraction of the extracted ions at the interface during the flotation process can be determined by measuring ion concentration in the initial and final (called residual) solution, and was calculated according to Eq. (1). Each flotation experiment represents the average of two replicate points. The mean and standard deviation (Std) was evaluated for the percentage removal of gallium and aluminum, and also the selective separation of gallium.

2.2. Spectrophotometry

The interaction of gallium with cupferron was investigated spectrophotometrically at different pH values. Several samples, containing 1.5×10^{-4} M Ga(III), were prepared in the pH range of 1–4. After the addition of 1.5×10^{-4} M cupferron to each solution, the electronic absorption spectra of the formed complex was recorded on a LAMBDA 45UV/Vis spectrophotometer (Perkin Elmer Life and Analytical Science, Boston, USA) with 1.0 cm quartz cells. In addition, the variations of maximum absorption of gallium $(1.5 \times 10^{-4}$ M) in the presence of different concentrations of cupferron $(0–3 \times 10^{-4}$ M) at the optimal pH were studied to elucidate the effect of cupferron concentration on the separation of gallium. In addition, the mean and standard deviation (Std) of this result was reported.

2.3. FTIR spectroscopy

The Fourier transform infrared (FTIR) spectra of cupferron were recorded in the presence and absence of gallium in order to elucidate the complexation of cupferron with gallium. The FTIR spectra of the metal complexes obtained during the optimal removal process were also studied to elucidate the nature of the interaction between SDS and the complex formed (cupferron-gallium). The FTIR spectra of samples were obtained on a Bruker FTIR spectrometer, using KBr discs in the spectral range of 4000–400 cm⁻¹, and at a spectral resolution of +4 cm⁻¹. Samples and KBr powder were mixed at a suitable blending ratio (by weight). The powder, prepared using a mortar and pestle, was soft and homogeneous, and was then pressed with a sheeter, and transferred for FTIR measurements.

2.4. Scanning electron microscopy

To investigate the complexation of cupferron with gallium, and the effects of SDS on the characterization of the Ga(III)-cupferron complex, the morphology of the Ga(III)-cupferron complexes in the presence and absence of SDS was investigated. Samples were