Examination of flotation behavior of metal ions for process water remediation

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ABSTRACT

Solutions containing low concentrations of heavy metal could be produced from any industrial processes and it is important to remove these ions from aqueous solution due to environmental regulations. In this paper, ion flotation method is employed to remove metal ions such as copper, lead, zinc, cadmium and nickel from aqueous solution. Firstly, several parameters such as pH, concentration and type of surfactants were investigated along with copper. After, ion flotation was tested on multiple ions individually and collectively, in different type of flotation machines. The best conditions were found as pH 9, with 1:1 ratio of sodium dodecyl sulfate and metal concentration, 20 mg/L each metal concentration, 3 min flotation time. After flotation the remaining solution contained 0.5 mg/L Cu, 2.5 mg/L Pb, 2.6 mg/L Ni, 3.4 mg/L Cd, 1.5 mg/L Zn. Ion flotation method can be used to clean process waters produced in flotation plants containing low metal concentrations. The overall method is suggested to remediate process waters generated flotation plants.

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1. Introduction

Most of the industrial waste water streams (the metal working, semiconductor, and metal industries, mine water, etc.) contain heavy metals which have several adverse effects on human health and biota, cause environmental–disposal problems due to their non-degradable and persistence nature [1]. Besides mining industry, mineral processing plants and extractive-metallurgical operations produce polluted waters [1,2]. A mineral processing plant if does not recycle or re-use water will need 1.9–3.0 m^3 water for processing 1 tone ore. These waters should be enhanced with an adequate method before discharging or storage because heavy metals in aqueous solution is unstable and increase the metal pollution by transportation, or have some negation on flotation process [3].

There are several methods to remove heavy metals from aqueous solutions such as, precipitation, oxidation or reduction, filtration, ion-exchange, reverse osmosis, membrane technology, evaporation and electroflotation [5]. However some of these methods are ineffective or noneconomic when the metal concentrations are in the range of 1–100 mg/L [1]. In addition they produce secondary wastes which need also purification or removal process [4]. On the other hand ion flotation may be an alternative method which has high recovery and selective separation, is a fast and relatively economical method that can be used to recover or remove most of the metals in the periodic table at low concentrations [6].

Ion flotation is a separation technology for recovering and removing metal ions from large volumes of dilute aqueous solutions [7]. Ion flotation is a surface inactive separation method that involves the collection of ions or molecules (colligend) from aqueous solution by adding surfactant that is adsorbed onto the surface of rising bubbles. The surfactant-colligend product (sublat) may be formed in bulk solution or only at the higher concentrations produced by preferential adsorption on the bubble surface. A hydrophobic product (scum) that is containing concentrated ionic species in a small volume of collapsed foam is formed. Therefore this process is also called as foam flotation [8].

Ion flotation was introduced to literature by Sebba in 1959 [9]. In very first studies it is mostly used for pre-concentration of precious metals from dilute solutions. By this time, ion flotation method has been applied for precious metal recovery [10], selective separation of multiple ions [11], pre-concentrating of rare earth elements [12,13], wastewater and water treatment [4,14].

There are several studies on ion flotation in the literature which are mostly applied on remediation of synthetic waste water samples. Polat and Erdoğan applied ion flotation to selective separation of copper, silver, zinc [4]. Hoseinian et al. used ion flotation method for removal of 10 mg/L nickel and zinc ions from wastewaters at pH 3 using sodium dodecyl sulfate (SDS) 300 mg/L as collector and Dowfroth-250 90 mg/L as a frother [14]. Yuan et al. used tea derived saponin as a surfactant for removal of copper lead and cadmium [15]. However in the literature, it is still not clear the relationship between pH, surfactant and different metals in flotation. The scope of this work is to investigate ion flotation method for removing metal ions from waste water, individually or collectively. Differential surfactants were investigated with

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single ion, and applied for other ions. Various parameters such as pH, type and concentrations of surfactants, flotation cells were tested to determine the optimum flotation conditions.

2. Material and method

Anionic sodium dodecyl sulfate (SDS) from Fluka, cationic hexadecyltrimethyl ammonium bromide (HTAB) from Merck, anionic potassium ethyl xanthate (KEX) from As Chemistry, nonionic bio surfactant Saponin from Aldrich were used as surfactants, methyisobutyl carbinol (MIBC) from Merck was employed as a frother. Some of metal solutions were prepared from their salts such as copper from $(Cu(NO_3)_2 \cdot 3H_2O$ (Merck), lead from $Pb(NO_3)_2$ (Merck), nickel from $NiCl_2 \cdot 6H_2O$ (Carlo Erba), while zinc and cadmium were prepared from 1000 mg/L standard solution of Merck. The synthetic waste water sample was prepared from metal salts dissolving in distilled water as 20 mg/L concentrations, otherwise stated. The pH of the solution was adjusted using NaOH and HCl when necessary. The pH of the solution monitored with Hanna 8314 type pH meter. Double distilled water was used in the experiments.

The experiments were conducted using synthetic waste water. Firstly, the parameters were optimized with 20 mg/L single metal ion (copper), after the parameters were tested with all metal ions (cadmium, zinc, nickel, lead, copper) individually and all together. These experiments were tested first in Hallimond flotation cell, and then Denver flotation machine to examine hydrodynamic effect of mixing system.

In order to determine type of surfactant and pH 20 mg/L copper ion and 20 mg/L surfactants concentrations were used. All the surfactants have both collection and frothing character except KEX, thus 20 mg/L MIBC was added as frothing agent while using this surfactant.

Furthermore, copper precipitation test was applied to make comparison with ion flotation method. In precipitation test 20 mg/L initial copper ion was precipitated using 1 M NaOH, after reaching predetermined pH, the solution was left for 2 h then solid-liquid separation as done by filtering, the remaining solution analyzed for residual copper concentration.

A Hallimond tube was used in ion flotation experiments with synthetic solution. The air flow rate was 200 mL/min in all experiments. The flotation solution was agitated for 3 min after addition of the required surfactant and adjusting the pH of the solution. The froth was collected for 1 min and the products of froth and remaining part were taken two different beakers. The residual metals in the remaining solution were analyzed by atomic absorption spectrometry (AAS).

Laboratory type Denver machine with 1 L of flotation cell was used in to test agitation speed for real application of ion flotation method. Different agitation speeds were tested such as 700, 900 and 1200 rpm. Conditioning time and flotation time were kept same as before 3 min and 1 min, respectively. The froth product and remaining solution were taken into two different beakers, analyzed for metal content and water amount. Metal ion concentrations in the aqueous phase were analyzed by Atomic Absorption Spectrophotometer (AAS).

The results were evaluated by residual metal concentration which is the result of directly from chemical analysis of remaining solution of the test; metal removal and separation efficiency. The metal removal and the separation efficiency were calculated as the formulas below [16]:

$$Metal\ Removal, \% = 100^* (Ci - Ct)/Ct \tag{1}$$

$$Separation\ Efficiency = 100^* ((Ci - Ct)^* Vt)/(Ci^* Vi) \tag{2}$$

$$Water\ Loss = 100 * (Vi - Vt)/Vi \tag{3}$$

where Ci is the initial metal concentration (mg/L), Ct is the residual metal concentration (mg/L), Vi is the initial volume of the solution (mL) and Vt is the remaining solution volume in the cell (mL).

The metal speciation diagrams were drawn using free Medusa-Hydra chemical equilibrium software program to draw fractional metal species diagrams.

The experiments were conducted on firstly copper ion, then other metal ions individually and collectively in Hallimond test tube and optimized conditions were tested with Denver flotation cell. Surfactant amount, surfactant type and pH were investigated to determine the optimum parameters.

3. Results and discussion

3.1. Effect of surfactant type

Different type of surfactants such as anionic SDS and KEX, nonionic Saponin, and cationic HTAB were used to investigate effect of surfactant type on copper ion flotation. The better understand the ion flotation performance, precipitation of copper ion was also investigated and the results are shown in Fig. 1. According to results, between pH 3 to 6 flotation was much more effective than precipitation with all surfactants. Between pH 6 and 9, precipitation was became effective to remove copper ions and in this range only SDS surfactant was able to remove copper ion. Over pH 9, all surfactants were inefficient to remove copper contrary to precipitation. The lowest residual copper concentration was found as 2.2 mg/L at pH 8 using 20 mg/L SDS reagent while the initial copper concentration was 20 mg/L.

When SDS exists in the solution, the dissolved dodecyl sulfate anion (DS^-) adsorbs on positively charged copper species by electrostatic or ion exchange mechanism. Cuming and Schulman [17] explained the reaction occurs between SDS and Cu according to pH and they divided pH scale into three ranges such as low corrosion region pH < 6, strong adsorption region as pH 6–8.5 and weak adsorption region as pH > 8.5. Below pH 6, the copper precipitate is formed as two way such as Cu-(DS) and $Cu(OH)^+$. The insoluble hydrophobic dodecyl sulfate compound is formed only at the pH where $Cu(OH)^+$ concentration is comparatively high. Between pH 6–8.5 the adsorption mechanism can be explained with exchange of DS^- ions for OH^-. As the pH increases over 8.5 the OH^- competes more strongly than DS^- ion and results low adsorption.

SDS and KEX show similar pH trend for removal of copper ion due to being anionic reagents, however the flotation performance of KEX was lower than SDS.

Saponin is a bio-surfactant which was previously used by Yuan et al., [15] for ion flotation and they obtained 81% copper removal. However in this study the lowest residual copper concentration was found as
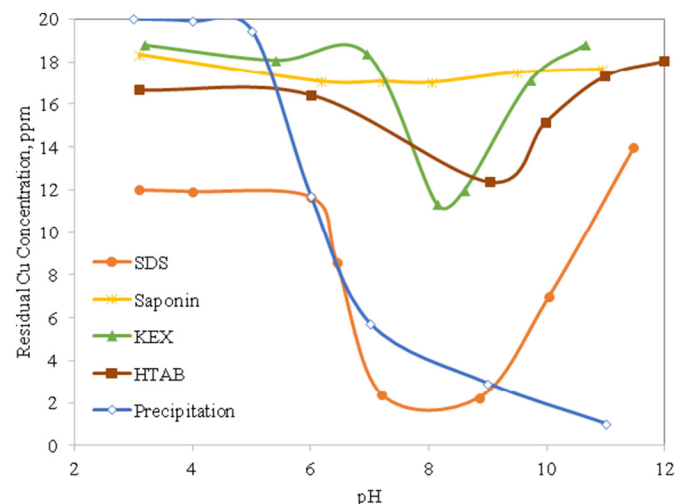

Fig. 1. Effect of surfactant type on copper ion flotation at different pHs.