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INFLUENCE OF IONIC STRENGTH ON THE REMOVAL OF As^{5+} BY ADSORBING COLLOID FLOTATION

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ABSTRACT

The aim of this work was to study the influence of ionic strength (IS) (with NaCl and Na_2SO_4) on the removal of As^{5+} by adsorbing colloid flotation (ACF), using as collector sodium dodecylsulfate (SDS). The morphology of the precipitate retained in the foam was analyzed by scanning electron microscopy (SEM/EDS).

The effect of an increase in the IS by adding NaCl proved to be insignificant on the As^{5+} removal by ACF. On the other hand, by adding SO_4^{2-} ions, the same increase in IS resulted in a removal decrease of 62.2%. By introducing, however, $80\,mg\,L^{-1}$ of Al^{3+} such deleterious effects from IS were minimized since an increase in As^{5+} floatability (37.7% without Al^{3+} and 76.5% with Al^{3+}) was noticed.

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Through SEM/EDS analyses, it was possible to observe that both morphology and composition of the precipitate produced in the solution and retained in the foam depend on the physicochemical conditions of the system, i.e., on the species present in the solution.

Key Words: Adsorbing colloid flotation; Foam separation; Ionic strength; Arsenic

INTRODUCTION

In the mining industry, effluents from mineral processing plants, particularly from nonferrous metal mines, usually contain arsenic. The discharge of wastewaters containing arsenic to an aquatic system pose a potential threat to the environment, causing a deleterious effect on animals, plants, and human beings.[1,19]

Arsenic compounds in the environment are vulnerable to chemical and biological transformations. Arsenic forms oxyacids, salts known as arsenates (AsO_4^{3-}), and arsenites (AsO_2^{-}). The oxyanions comprise most of the aqueous chemistry of arsenic.[1] The main arsenic species found in the aqueous solution are: H_3AsO_4 ($pH < 2$), $H_2AsO_4^{-}$ ($2.0 < pH < 6.0$), $HAsO_4^{2-}$ ($6.0 < pH < 11.0$) and AsO_4^{3-} ($pH > 11.0$).[2,3,19]

Owing to the arsenic toxicity and the increased amount thereof being processed by metallurgical industry for the last decades, the scientists have discussed and developed appropriate technologies concerning the treatment of effluents and industrial application of this metal. Commercial use of arsenic is very low as far as the present offering is concerned. Accordingly, most of the processed arsenic in metallurgy has to be discarded in an environmentally appropriate way.[4,19]

Numerous techniques exist to remove heavy metal from wastewater, such as chemical precipitation (generally with lime or NaOH), ion exchange, reverse osmosis, adsorption on activated carbon, and solvent extraction.[5,11,19] These methods are relatively expensive and require costly equipment.

Adsorbing colloid flotation (ACF) involves the addition of a coagulant, usually ferric chloride or alum, to form a floc, usually positively charged. The dissolved heavy metal is then adsorbed onto the floc particle and/or coprecipitated with it. A surfactant is then added, it adsorbs onto the floc particle and renders it hydrophobic, and the floc (with adsorbed metal ions) is removed by flotation. The surfactant added is called the collector.[12] With dilute wastes, this process possesses some distinct advantages—low metal concentrations, rapid operation, limited space requirements, production of small volumes of sludge, flexibility of application to various metals at various scales, and moderate costs.[1,7,8] However, this approach, generally presents a drawback such as the efficiency decrease as ionic strength (IS) increases due to the presence of different inorganic and organic species.[1,9,20] Because industrial wastewater is typically a complex mixture, this drawback restricts the applicability of foam separations for wastewater treatment and is a major reason why these techniques are not used much for wastewater treatment despite their advantages.[6] On the other hand, to minimize such deleterious effect, other alternate means have been used such as, for example, the use of a mixture of collectors (sodium dodecylsulfate—SDS/sodium oleate) and the addition of activators (Al(III) and Mn(II)). These alternatives have proved to be effective on solving this problem.[1,6,10]

When some ions are present in a system, the ACF efficiency decreases due to the increase in the IS of the system. This phenomenon happens due to the competition of the colligent and the other ions present in the attached process with the collector.[1,13–15]

Ions with opposite charge to that of the collector have a stronger effect than the ones with the same electrical charge. Moreover, the higher the charge of these ions, the greater the contribution to overall IS of the solution. The order of interference is: trivalent ions > divalent ions > monovalent ions.[1,13,15]

Pinfold[13] suggested three possible reasons for the removal decrease of metal ions by ACF with high IS: (a) ζ-potential of particles decreases upon increasing IS, resulting in a poor interaction between surfactant and particles; (b) surfactant flotation is faster, probably due to the decrease in repulsion among bubbles, and (c) bubbles are more likely to be disrupted and quickly drained, therefore, their redispersion occurs more freely.

Some works concerning the mixing of collectors (SDS/Sodium Oleate) have been carried out to compensate for the deleterious effect from an increase in IS on ACF.[5,10,16] On the other hand, studies on the addition of activators such as, Mn(II) in heavy metal removal (Cd, Pb, Zn, Cr)[6] and Al(III) in As removal[1] have been reported.

The aim of this work was to study the influence of the IS (with NaCl and Na_2SO_4) on the removal of As^{5+} by ACF.

MATERIALS AND REAGENTS

The following reagents were used: sodium arsenate ($Na_2HAsO_4 \cdot H_2O$); sodium dodecylsulfate (SDS: $C_{12}H_{25}NaO_4S$) as a collector; ferric chloride ($FeCl_3 \cdot 6H_2O$) as a coprecipitant agent; sodium chloride (NaCl) and sodium sulfate (Na_2SO_4) for IS research; caustic soda (NaOH) and hydrochloric acid (HCl) to adjust solution pH.

For each test, solutions were prepared from 20 mL of As concentrated stock solution (1.000 mg L^{-1}) in a beaker. A predetermined concentration of Fe^{3+} was added and the solution pH (Ion Analisador—Analion IA 601, Ribeirão Preto-SP, Brazil) was set to the proper range of each test. The solution was stirred by means of a magnetic stirrer for 10 min. A predetermined amount of collector (SDS) was then added and the solution was stirred for an additional length of time of 5 min and its pH was set once more. For each test, the test solution was prepared by combining the required amount of stock solution to make up 1 L of solution under the intended test conditions. All test solutions contained 20 mg L^{-1} As^{5+}. All tests were carried out at a pH range of 5.0–6.0. Coprecipitation tests with Fe^{3+}, with a varying pH from 2 to 12 and a varying Fe^{3+} concentration from 60 to 240 mg L^{-1}, have always yielded a minimum As residual concentration in the pH range between 5 and 6.[18]

The ACF tests were carried out in a 95 cm high acrylic column cell with an internal diameter of 5.7 cm (Fig. 1).[18] Even before the beginning of each flotation, the solutions had already shown floclike precipitates, showing that the coprecipitation step had already occurred. During the first half an hour of flotation, the foam presented a dense aspect, however, as the test progressed the foam began to dry out, through drainage and evaporation, especially at the very top where the solid precipitate was retained.

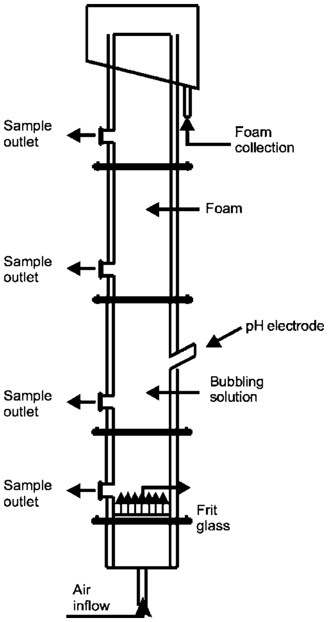

Figure 1. Column flotation.

RESULTS AND DISCUSSION

Effect of Ionic Strength

Figures 2 and 3 show the IS effect on As^{5+} removal in the presence of NaCl and Na_2SO_4, respectively. The effect of Cl^- anion on As removal has proved to be insignificant since upon increasing IS of the system from 3.49×10^{-3} to 3.49×10^{-1} mol dm^{-3} As removal has reduced to 4.2% only. The SO_4^{2-} being present, has significantly reduced As^{5+} removal. It should be observed that the increase in IS by adding these "foreign" ions has reduced As removal by 62.2%. According to results found in literature,[1] significant reduction in percent As removal by sulfate anions may be due to: (a) competitive adsorption of SO_4^{2-} ions and anion surfactant (SDS) on the positively charged ferric hydroxide surfaces or (b) the specific interaction with ferric hydroxide surfaces.

According to Peng and Di,[1] the adsorption of SO_4^{2-} anions on the positively charged floc surfaces reduces the ζ-potentials of the flocs and, thereby reduces their attraction to the negatively charged As(V) species and SDS. Divalent oxyanions coordinate two surface iron cations directly. In the case of divalent oxyanion SO_4^{2-}, the ferric sulfate complex is formed by substitution of hydroxyl group for sulfate anion.[1] For monovalent oxyanion, Cl^- is mainly adsorbed on the surface of ferric hydroxide by electrostatic force.

Peng and Di[1] have shown the effect of the increase in IS by adding NO_3^-, SO_4^{2-}, and PO_4^{3-} anions in As^{5+} removal by ACF. The NO_3^- addition had no effect on As^{5+} removal. On the other hand, by adding SO_4^{2-} and PO_4^{3-} anions, removal decreased from about 99% to amounts below 10% in both cases.

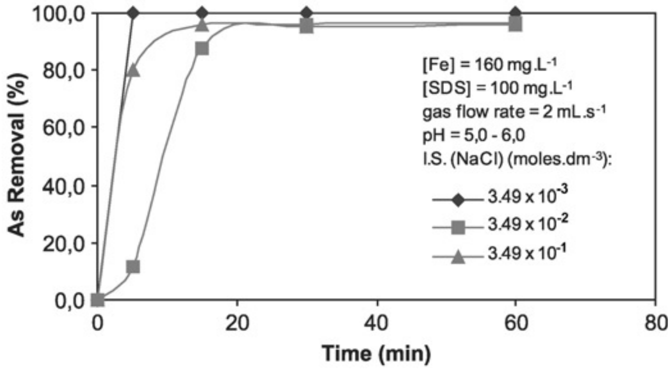

Figure 2. Effect of an increase in IS on the floatability of As^{5+} by adding NaCl. $[Fe] = 160\,mg\,L^{-1}$; $[As^{5+}] = 20\,mg\,L^{-1}$; $[SDS] = 100\,mg\,L^{-1}$; gas flow rate $= 2\,mL\,sec^{-1}$; pH = 5.0–6.0.

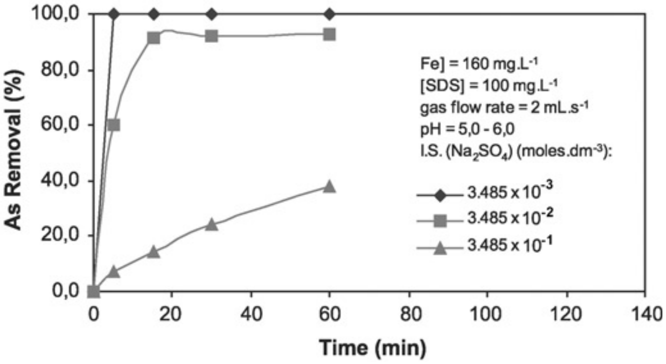

Figure 3. Effect of an increase in IS on the floatability of As^{5+} by adding Na_2SO_4. $[Fe] = 160\,mg\,L^{-1}$; $[As^{5+}] = 20\,mg\,L^{-1}$; $[SDS] = 100\,mg\,L^{-1}$; gas flow rate $= 2\,mL\,sec^{-1}$; $pH = 5.0–6.0$.

Figure 4 shows a photomicrography of the precipitate formed in the As/Fe/SDS system without the addition of NaCl and Na_2SO_4, i.e., without the increase in IS of the system. For this system, As removals of 99.9% were obtained and it can be seen that the precipitate appears as aggregated flocs containing Fe and

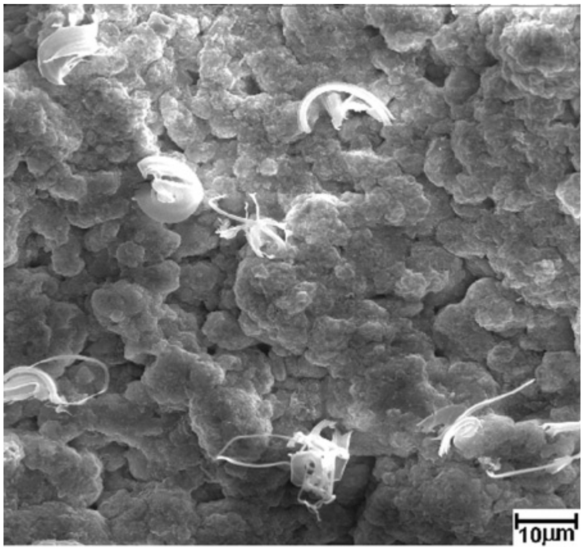

Figure 4. Photomicrograph of the precipitate formed in the As/Fe/SDS system. $[SDS] = 100\,mg\,L^{-1}$; $[Fe^{3+}] = 160\,mg\,L^{-1}$; $IS = 3.49 \times 10^{-3}\,mol\,dm^{-3}$; 1000 × .

As. Through SEM/EDS analyses, it can be found that, at high IS, the precipitate exhibited a thinner and less flocculent appearance in the As/Fe/SDS/NaCl system (Fig. 5). For the As/Fe/SDS/Na_2SO_4 system, the precipitate exhibited a further more compact and thin appearance, without appearing in a flocculent form (Fig. 6). Chemical analyses of precipitates from the systems containing NaCl and Na_2SO_4 have shown that Fe, As, Cl, and S were present, denoting the association of Cl and S with a certain positively charged Fe complex.

Effect of Al^{3+} Adding with High Ionic Strength

Figure 7 shows the inhibition of the deleterious effect on As^{5+} removal due to the increase in IS, by adding trivalent ion, Al^{3+}. It could be observed that at high IS, without adding Al^{3+}, As^{5+} removal was very low (37.7%). However, with the addition of $40\,mg\,L^{-1}$ Al^{3+} a little increase in As^{5+} removal (49.4%) could already be observed and with the addition of $80\,mg\,L^{-1}$ Al^{3+} such removal increased to 76.5%.

This result confirms the data found in a study disclosed by Peng and Di[1] which has shown that the addition of Al^{3+}, in the presence of SO_4^{2-} or PO_4^{3-}

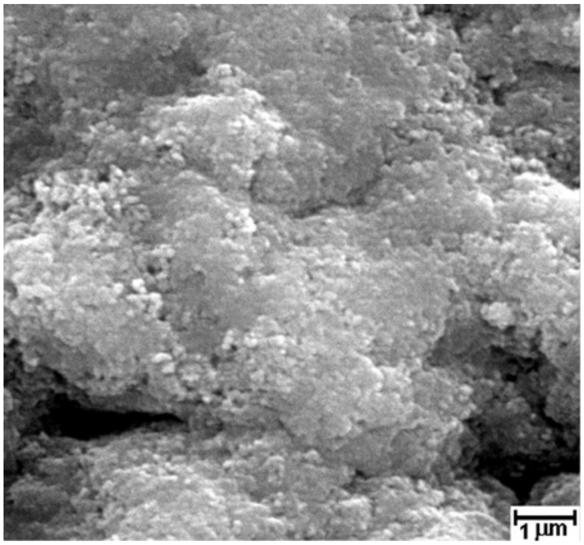

Figure 5. Photomicrograph of the precipitate formed in the As/Fe/SDS/NaCl system ($[SDS] = 100\,mg\,L^{-1}$, $[Fe] = 160\,mg\,L^{-1}$, $[As^{5+}] = 20\,mg\,L^{-1}$, $IS = 3.49 \times 10^{-1}\,mol\,dm^{-3}$). 10,000 × .

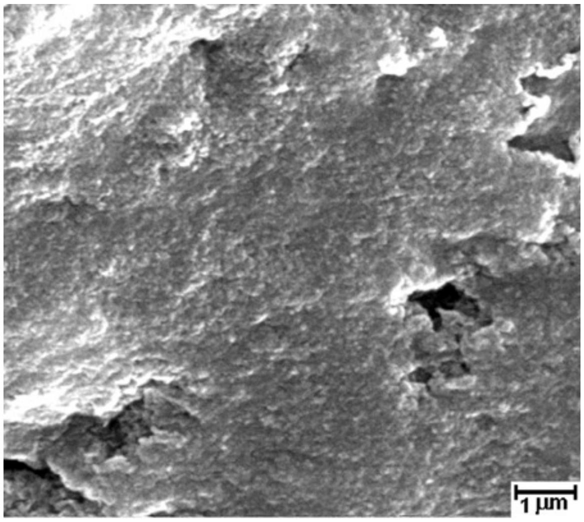

Figure 6. Photomicrograph of the precipitate formed in the As/Fe/SDS/Na_2SO_4 system ([SDS] = $100\,mg\,L^{-1}$, [Fe] = $160\,mg\,L^{-1}$, [As^{5+}] = $20\,mg\,L^{-1}$, IS = $3.49 \times 10^{-1}\,mol\,dm^{-3}$). 10,000 × .

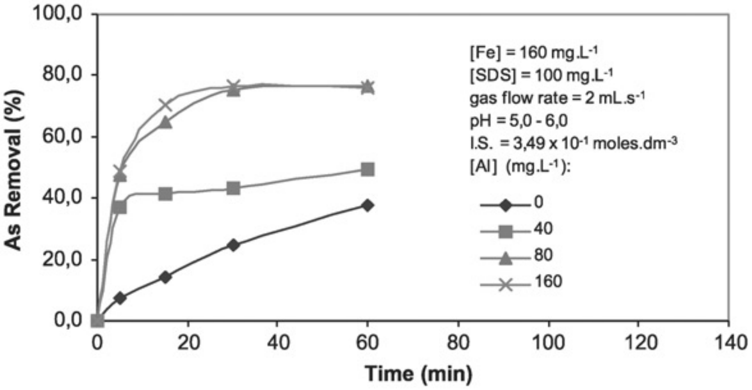

Figure 7. Effect of Al^{3+} addition with high IS (Na_2SO_4) on the As removal. [Fe] = $160\,mg\,L^{-1}$; [As^{5+}] = $20\,mg\,L^{-1}$; [SDS] = $100\,mg\,L^{-1}$; gasflowrate = $2\,mL\,sec^{-1}$; IS = $3.49 \times 10^{-1}\,mol\,dm^{-3}$; pH = 5.0–6.0.

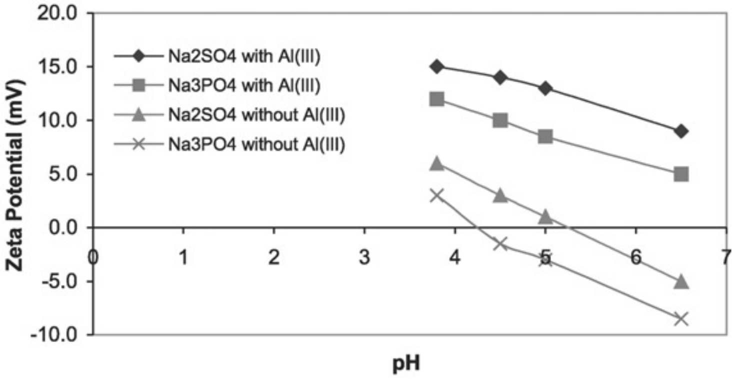

Figure 8. As(V)–$Fe(OH)_3$ flocs ζ-potential as pH function in the presence of SO_4^{2-} or PO_4^{3-} with or without Al(III) addition. $[SDS] = 35\,mg\,L^{-1}$; $[Fe(III)] = 80\,mg\,L^{-1}$; $[As(V)] = 10\,mg\,L^{-1}$.[1]

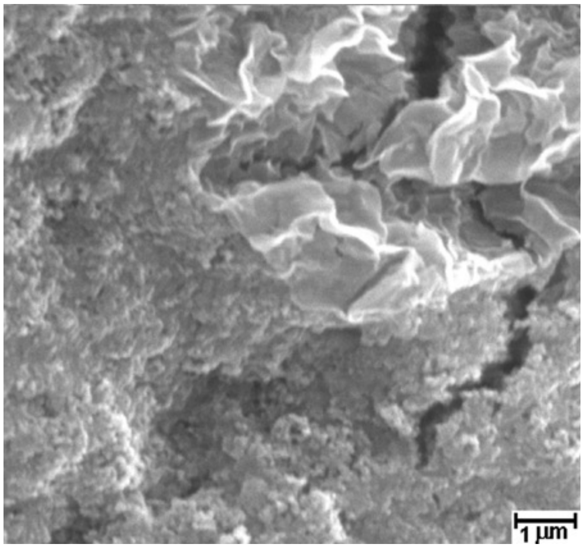

Figure 9. Photomicrograph of the precipitate formed in the As/Fe/Al/SDS/Na_2SO_4 system ($[SDS] = 100\,mg\,L^{-1}$, $[Fe] = 160\,mg\,L^{-1}$, $[As^{5+}] = 20\,mg\,L^{-1}$, $[Al] = 80\,mg\,L^{-1}$, $IS = 3.49 \times 10^{-1}\,mol\,dm^{-3}$). 10,000 ×.

anions, increased As^{5+} removal from amounts below 10% to amounts above 90% in both cases.

This "activating" effect from Al(III) addition probably occurs due to the fact that Al(III) increases ζ-potential of flocs (Fig. 8), thereby increasing the affinity between coprecipitant and anionic collector providing a greater efficiency on As^{5+} removal.[1,17] This precipitate ζ-potential curve shifting, in turn, could be associated to the specific adsorption of the $Al(OH)_2^+$ hydroxy-complex and the positively charged and heterocoagulated aluminum hydroxy on the As containing colloid surface.[21,22]

The addition of Al^{3+} has clearly proved to compensate for the deleterious effect from increasing IS on As^{5+} removal.

Through SEM/EDS analyses it could be observed that by adding Al^{3+} with high IS to the As/Fe/SDS/Na_2SO_4 system, the precipitate exhibited again a flocculent appearance (Fig. 9). Chemical analyses of precipitate have shown that Fe, As, and S were present, denoting the association of S with a certain positively charged Fe complex.

CONCLUSION

The effect of an increase in IS by adding NaCl proved to be insignificant on As^{5+} removal by ACF. The addition of SO_4^{2-}, on the other hand, has dramatically reduced As^{5+} removal. The increase in IS from 3.49×10^{-3} to $3.49 \times 10^{-1}\,\text{mol dm}^{-3}$ was found to reduce As^{5+} removal by 4.2 and 62.2% when NaCl and Na_2SO_4 were, respectively, added. By introducing the latter one, the deleterious effect occurred most likely due to the competitive adsorption of SO_4^{2-} ions and ion collectors on the positively charged ferric hydroxide surfaces or the specific interaction therewith.

The addition of $80\,\text{mg L}^{-1}$ of Al^{3+} in the presence of high IS (with Na_2SO_4) increased As^{5+} removal from 37.7 (without Al^{3+}) to 76.5%, minimizing such deleterious effect occurring in the metal removals.

Through SEM/EDS analyses, it was possible to derive that changes in the physico-chemical conditions of the system affect the precipitate morphology produced in the solution and retained in the foam. It could be observed that by increasing IS of the system, the precipitate appeared be more compact and fine and less flocculent.

ACKNOWLEDGMENTS

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