Removal Of As(V) from Mine Waters by Sorptive Flotation

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The paper investigates the separation of As(V) from aqueous solutions by sorptive flotation (DAF technique). As(V) removal is achieved by adsorption/coprecipitation on ferric hydroxide introduced in solution as a support – in order to produce a floc. A collector (sodium dodecyl sulfate) is added to aqueous solution and adsorbs physically and chemically onto the floc, rendering it hydrophobic. The arsenic-bearing flocs formed are floated at the surface by ascending bubbles of air. The experiments were conducted to investigate the influencing factors (pH, molar ratio, As(V) concentration, presence of foreign anions (SO_4^{2-}), to determine the optimum parameters for operating the process.

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1 Introduction

Arsenic is present, in different forms and concentrations, in underground water, ground water, soil, air, vegetables, marine flora and fauna, body fluids. The main source of arsenic pollution is industry, including mining activities. The discharge of wastewater containing arsenic such as effluents from the mining industry, especially from non-ferrous metal mines, to an aquatic system could severely alter the human health due to arsenic extremely high level of toxicity. Arsenic speciation exhibit very different toxicological properties, which varies from inorganic to organic species, oxidation states: organic compounds are less toxic than the inorganic forms; As(III) is more toxic than As(V) species. Arsenic is a cumulative toxic, and exposure to inorganic arsenic may increase the risk of cancer and increase DNA damage (ATSDR 1998)

In a clean environment, arsenic concentrations vary from a few $\mu g \cdot L^{-1}$ to hundreds of $\mu g \cdot L^{-1}$, for example in seawater 6–30 $\mu g \cdot L^{-1}$, in surface waters 0–1300 $\mu g \cdot L^{-1}$, in geothermal springs 100–500 $\mu g \cdot L^{-1}$. In urban or industrial areas arsenic concentration is much greater and could reach, in a polluted zone, even tens or hundreds of $mg \cdot L^{-1}$ (over 60 $mg \cdot L^{-1}$ in drinking water, over 20 $mg \cdot L^{-1}$ in ground water; BURGUERA & BURGUERA 1997). All these values of arsenic concentrations show the potential threat of arsenic presence for the human health. The regulation for maximum As(V) level is 50 $\mu g \cdot L^{-1}$ until the year 2006 when it will become more stringent: 10 $\mu g \cdot L^{-1}$ (U.S. Environmental Protection Agency, ATSDR 1998). Taking all these into consideration, it is highlighted the importance of finding technologies and methods to reduce the hazard of contamination, to reduce pollution and to find very efficient separation techniques for wastewater treatment. In the last few years, the methods based on mass transfer as separation procedures by adsorptive bubbles have been continuously developed. Sorptive flotation is an adsorptive bubble separation method that applies surface properties at interfaces with the aim of ion-molecular and colloidal species separation from aqueous systems (STOICA 1997). Sorptive flotation had proved its feasibility in arsenic separation from aqueous solutions and is a flotation method which involves interactions in liquid phase between arsenic species and surfactant (collector) after coprecipitation or adsorption on the surface of a solid support (coagulant) and removal of hydrophobic complexes formed in solution by gas microbubbles using one of the flotation techniques (dispersed air flotation, dissolved air flotation, electroflotation). Sorptive flotation has several distinct advantages including the high efficiency of the separation process, the ability to treat low residual metal concentration, flexibility of application to various metals at various scales, small energy requirements, less need of surfactant, less space requirements, rapid operation, production of small volumes of sludge highly enriched with the contaminant, moderate costs.

2 Materials and Methods

2.1 Reagents

All chemicals used in this study were of analytical reagents grade. The following reagents were used: sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$), ferric chloride ($FeCl_3 \cdot 6H_2O$) as a coagulant agent, sodium dodecyl sulfate (SDS: $C_{12}H_{25}OSO_3Na$) as anionic surfactant and frother, sodium sulfate ($Na_2SO_4 \cdot 10H_2O$) as source of foreign anions, NaOH as precipitant agent and to adjust solution pH. Synthetic minewater (20 mg As per L) was prepared from a concentrated stock solution (1000 mg As per L) using deionized bi-distilled water.

2.2 Equipment

Measurements of pH were made using a digital pH-meter (Orion 290A). Residual concentrations of As(V) were determined with an atomic absorption spectrophotometer (Varian Spectr. AA 880, GTA 100). The removal of As(V) from aqueous solution was studied using a batch dissolved air flotation unit with a glass laboratory flotation cell and auxiliary units: an air compressor and a saturation vessel with manometer, release valve and needle valve.

2.3 Procedure

The feed water for each flotation test was prepared from 300 cm^3 of 20 mg As per L solution in a beaker. Such values of arsenic concentrations are usually met in spent mine waters. A predetermined concentration of $FeCl_3$ was added in order to form in situ the solid support ($Fe_2O_3 \cdot xH_2O$) for As(V) coprecipitation/adsorption. The pH of the solution was adjusted with NaOH to the desired value ± 0.05 pH units. The pH adjustment resulted in the formation of a colloidal precipitate $Fe(OH)_3$. The mixed solution was stirred for 5 min using a magnetic stirrer to allow the reaction to proceed to completion, then a predetermined amount of SDS was added. The solution was stirred for another 3 min and its pH was set one more time to the desired value. The sample was quantitatively transferred to the flotation cell where the colloidal particles were floated with gas microbubbles generated by dissolved air (pressure) flotation technique (DAF). To start the flotation test, the sample was diluted with water pre-saturated with air at 4 bar ($V_{sample}:V_{saturated\ water} = 3:1$). At the top of the flotation cell, a thin layer of foam was form, consisting of floated precipitate. The foam was generally a small amount of the original sample volume. After 10 min of flotation time a small amount of remaining solution was taken from the lower part of the flotation cell to determine the residual arsenic concentration. The temperature of solutions was constant and equal to the ambient temperature (18^0 C). The samples for infrared analysis were measured using an IR Specord spectrophotometer.

3 Results and Discussion

3.1 Influence of Solution pH on As(V) Removal

The removal efficiency of As(V) as a function of pH is shown in figure 1. In order to investigate the influence of solution pH on the separation efficiency of arsenic by sorptive flotation using $Fe(OH)_3$ as support and SDS as collector, 4 sets of experiments were performed with various concentrations of Fe(III) at a pH range between 4.0 and 7.5.

The efficiency of the separation of As(V) is expressed as: $R\ (\%) = \left(1 - \frac{c_{As(V)}}{c_{As(V),0}}\right) \cdot 100$, where $c_{As(V)}$ and $c_{As(V),0}$ are the final (residual) and initial concentrations of As(V) in solution, respectively. Experimental data are fitted with Microsoft Excel and the trendlines for each set of data are plotted. The polynomial equations and error coefficients (R-squared values) for each curve are displayed on charts. The exception is figure 3, where because of the complexity of the curves, the data are fitted with Table Curve 2D.

Dissolved air pressure was set at optimum value of 4 bar as the experimental data showed that lower values do not advantage the flotation process, and higher values may be destructive to the flocs, therefore reducing the separation efficiency.

Experimental data and the curves that best describe the curves are shown in figure 1.

On each of the 4 curves As(V) – removal efficiency there are two distinct segments:

- ***a maximum removal*** of As(V) over 99.5 % in the pH range of 4.0–4.5,

- ***a decrease*** of As(V) separation efficiency at pH above 5.0,

In the pH range 4.0–4.5, ferric hydroxide flocs bear positively charged surfaces, which are favorable for the adsorption of negatively charged ions: As(V) and DS^- ions from the surfactant (SDS). At higher values of pH, Fe(III) flocs tend to have less positive surface charges and the positive charge decreases as the pH increases. At a pH value of 7 or higher, the flocs bear negatively charged surfaces, which are unfavorable for electrostatic adsorption of anions on the surface (PENG & DI 1994). Therefore, As(V) removal efficiency is decreasing.

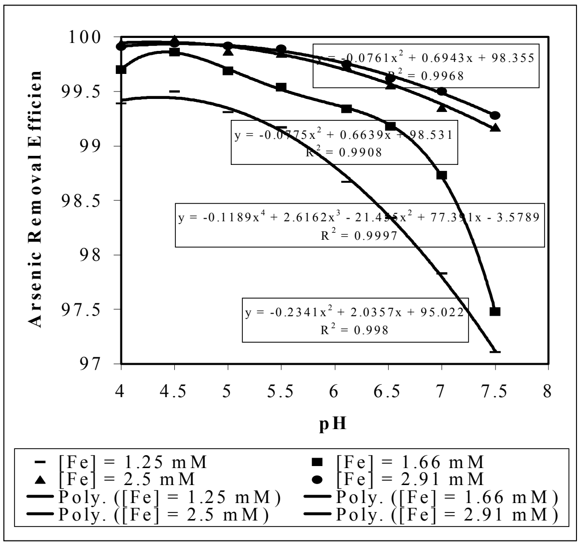

Figure 1: Influence of solution pH on arsenic removal by sorptive flotation. Experimental conditions: [As(V)] = 0.26 mM; [SDS] = 0.07 mM; flotation time = 10 min; dissolved air pressure = 4 bar.

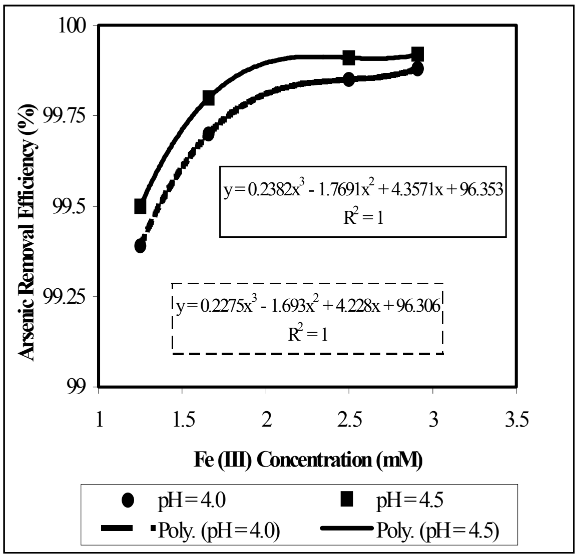

Figure 2: Removal of As(V) as affected by support (Fe(OH)3) concentration. Experimental conditions: [As(V)] = 0.26 mM; [SDS] = 0.02 mM; flotation time = 10 min; dissolved air pressure = 4 bar.

The results show that the optimum pH range for arsenic removal by sorptive flotation with Fe(III) and SDS is the pH range of 4.0–4.5. The arsenic removal efficiency can be, for the optimum operating parameters, more than 99 %.

3.2 Influence of Support (Coprecipitant) Concentration

Figure 2 shows the influence of $Fe_2O_3 \cdot x\ H_2O$, used as colloidal support, on arsenic removal by sorptive flotation.

It can be observed that the efficiency of separation improves significantly as the concentration of Fe(III) increases. Higher concentrations of support provide a larger surface area available for the adsorption of arsenic oxyanions and collector (SDS).

The increase in removal efficiency is followed, over a value of 2.5 mM Fe(III), by a plateau, showing that an increase of Fe(III) concentration is no longer increasing the removal efficiency.

Experimental data are fitted and the equations that best describe the curves are 3-order polynoms as shown inside figure 2.

The only limitations in setting support concentrations are costs associated with the chemicals and the amount of solid wastes generated from the wastewater treatment.

3.3 Influence of Collector Concentration

Figure 3 shows the influence of anionic surfactant (collector), sodium dodecyl sulfate, concentration on arsenic removal efficiency.

Experimental data were fitted using *Table Curve* and the curve-fit is described by the following equations:

for pH = 4.5:

$$y = a + b\ln x + c(\ln x)^2 + d(\ln x)^3 + e(\ln x)^4 + f(\ln x)^5$$

R^2=0.9964

for pH = 4.0:

$$y = \frac{a + c \ln x + e(\ln x)^2}{1 + b \ln x + d(\ln x)^2}$$

$R^2=0.9971$

The highest efficiency of arsenic removal can be obtained for a relatively narrow range of surfactant concentrations. Very low concentrations can't remove completely the colloidal support and the foam layer is thin and unstable. On the other hand, excessive amounts of SDS may form hydrophilic micelles on the floc particle surfaces, thus causing the unfloatability of the flocs.

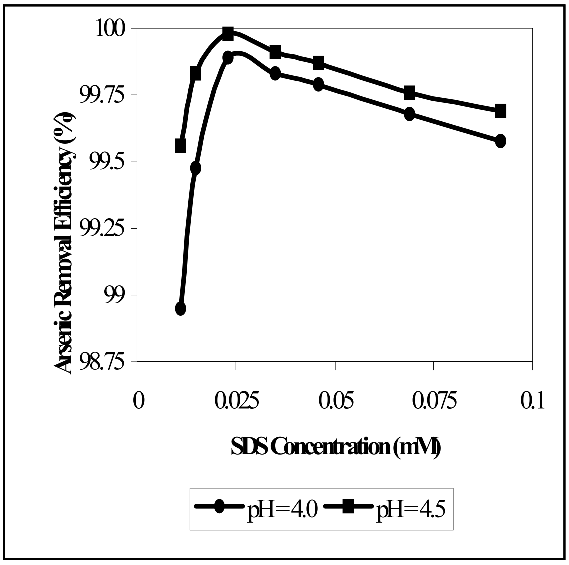

Figure 3: Removal of As(V) as affected by collector (SDS) concentration. Experimental conditions: [As(V)] = 0.26 mM; [Fe(OH)3] = 2.5 mM; flotation time = 10 min; dissolved air pressure = 4 bar.

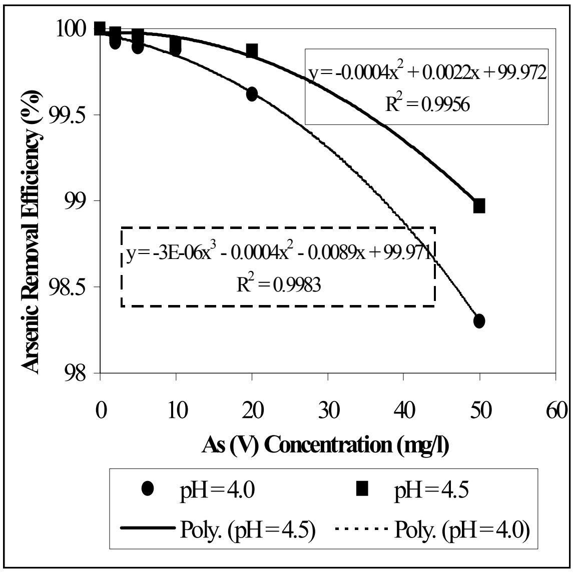

Figure 4: Removal of As(V) as affected by As(V) concentration. Experimental conditions: [Fe(OH)3] = 2.5 mM; [SDS] = 0.02 mM; flotation time = 10 min; dissolved air pressure = 4 bar.

For a concentration of 0.02 mM SDS, the removal efficiency is maximum (99.9 %) and a stable form is formed. The optimum surfactant concentration was determined, for this study, at a value of 0.02 mM.

3.4 Influence of As(V) Concentration

Figure 4 shows the influence of arsenic oxyanions concentration on the separation efficiency by sorptive flotation, at pH = 4.0 and pH = 4.5, respectively.

Experimental data show that for concentrations of arsenic in solutions lower than 50 mg·L^{-1} it can be achieved removal efficiency over 99.5 %. Equations that best fit experimental data are a 3-order, respectively 3-order polynoms.

3.5 Influence of Ionic Strength

In mine waters anions such SO_4^{2-} commonly coexists with arsenic oxyanions. The presence of such "foreign" anions in mine wastewater is increasing the ionic strength of the system. Figure 5 shows the influence of foreign anions (SO_4^{2-}) on the removal efficiency of As(V) by sorptive flotation.

The effect of an increase in the ionic strength by adding Na_2SO_4, as the source of SO_4^{2-} anions, is a significantly decrease of the efficiency of arsenic separation.

Accordingly to results found in literature (PENG & DI 1994; PACHECO & TOREM 2002) significant reduction in As(V) removal by sulfate anions may be due to: competitive adsorption of SO_4^{2-} anions and anionic surfactant (SDS) on the positively charged ferric hydroxide surfaces, or to some specific interactions with the ferric hydroxide surface. The adsorption of SO_4^{2-}anions on the positively charged floc surfaces reduces their attraction to the negatively charged As(V) species and SDS.

The presence of sulfate anions is increasing the ionic strength of the solution and is decreasing the separation efficiency of arsenic. Experimental data were fitted and the equation that best describe the decrease of the removal efficiency as a function of sulfate anions is a 2-order polynom, as written inside the figure 5.

3.6 Interaction Mechanism between SDS and $Fe_2O_3 \cdot x\ H_2O$.

The interaction As(V) – Fe(III) – SDS is a complex issue owed to all possible competitive equilibrium in aqueous solution. Some information regarding interaction mechanism are obtained from interpretation of IR spectra of the chemical species from the system.

The characteristic infrared frequencies and assignments of plain ferric hydroxide, of SDS, of ferric hydroxide conditioned with SDS and ferric hydroxide conditioned with DSD and As(V) are presented in table 1.

By comparing infrared spectrum for Fe_2O_3, SDS and Fe_2O_3 + SDS, there are changes at the adsorption bands which suggest a chemical adsorption between DS- anions from SDS molecules and Fe^{3+} ions from support Fe_2O_3 surfaces to form iron dodecyl sulfate.

The displacements of the characteristic frequencies for SO_4^{2-} species show stronger interactions with As(V) than into SDS single complex. The OH- species suffer displacements that indicate involvement into complex formation.

The model solution used in experimental research has a similar composition with those of aqueous systems of complex sulphur minerals where arsenic is associated.

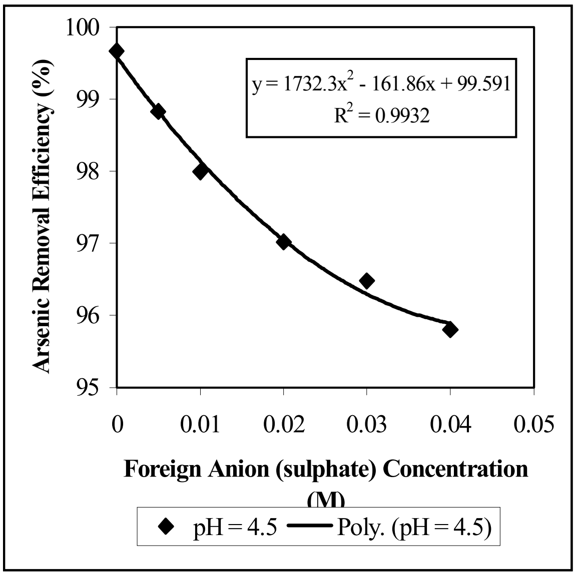

Figure 5: Removal of As(V) as affected by foreign anions (SO42-) concentration. Experimental conditions: [As(V)] = 0.26 mM; [Fe(OH)3] = 2.5 mM; [SDS] = 0.02 mM; pH = 4.5; flotation time = 10 min; dissolved air pressure = 4 bar.

Table 1: Characteristic infrared frequencies and assignments.

	$\nu_{OH(s)}$	$\delta_{HOH(w}$	$\nu_{CH_2(s)}$	$\nu_{SO_2(s)}$ $[RSO_3^-]$	$\nu_{SO_2(as)}$ $[RSO_3^-]$	$\nu_{SO(s)}$. $[RSO_3^-$.	$\nu_{1AsO_4^{3}}$	$\nu_{2ASO_4^3}$	$\nu_{3AsO_4^3}$	ν_{FeO_6}
					IR frequencies (cm^{-1})					
Literature*	3400 - 3600	1640	2850	1220	1080	700	830	830	440	340 – 350
$Fe_2O_3x\ _2O$	3600	1640	-	-			-	-	440	-
SDS	-	-	2855	1050	1180	700	-	-	-	-
Fe_2O_3 +SDS	3550	1640	2850	1250	1170	650	-	-	450	-
Fe_2O_3+SDS+As(V)	3550	1630	2850	1045	1160	650	830	870	445	350

4 Conclusion

Arsenic in diluted or concentrated aqueous solutions (surface waters, industrial or mine waters) can be removed by sorptive flotation with Fe(III) as support and sodium dodecyl sulfate (SDS) as collector and frother, using dissolved air flotation technique (DAF). The high efficiency of the separation process (more than 99.5 %) and the extremely low residual arsenic concentration recommend this method.

The results of atomic absorption spectrophotometry (AAS) analysis for arsenic residual samples show that the concentration of As(V) in the treated aqueous solution can be, for the optimum operating parameters, less than 10 $\mu g \cdot L^{-1}$. This value represents the maximum admissible concentration for drinking water recommended by World Health Organization. The limit imposed by actual regulations for arsenic in drinking water is still 50 $\mu g \cdot L^{-1}$, until February 2006 when it will be reduced at 10 $\mu g \cdot L^{-1}$.

The experimental data show that the most important influencing factor is the pH of the solution. The pH is a critical factor for precipitation/coprecipitation of As(V) in solution as ferric arsenate, for the surface charges of colloidal particles of ferric hydroxide and for the physical or chemical adsorption of arsenic oxyanions and anionic surfactant onto the flocs.

The optimum parameters of the separation process are as follows: pH = 4.0–4.5; support concentration [Fe(III)] = 2.5 mM for a molar ratio Fe(III) : As(V) = 2.5 : 0.26; surfactant concentration [SDS] = 0.02 mM for a molar ration SDS : As(V) = 0.02 : 0.26.

The presence of sulfate anions in solution reduces the efficiency of arsenic removal.

The adsorption of anionic surfactant may be due to electrostatic adsorption at a pH range of 4.0–4.5 or/and may be due to chemical adsorption, as proved by infrared analysis.

5 References

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