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As(V) Recovering-Separation from Aqueous Systems by DAF Technique

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Abstract: As(V) oxyanions removal from aqueous systems by dissolved air flotation (DAF) using $Fe_2O_3 \cdot xH_2O$ as solid support and sodium laurate as anionic surfactant was investigated. The influencing factors of the process: pH, support, surfactant, and As(V) concentrations, the presence of flocculant and foreign ions, conditioning time and dissolved air pressure were discussed, as they may affect in a great extent the separation efficiency. The systematic study aims to establish the optimum operating parameters of the process, to investigate the equilibrium and mechanism of separation.

Keywords: Arsenic separation, adsorption, coprecipitation, DAF technique, separation mechanism

INTRODUCTION

Arsenic may be present in aqueous systems due to natural sources (minerals, sediments, geothermal springs) and anthropogenic sources, by discharge from industrial facilities like mining activities, non-ferrous metal production, microelectronics, or by leaching from landfills or soils treated with arsenical pesticides (1, 2, 3). In residual waters, the values of arsenic concentration may reach an order of 10^2 mg/L, while in surface waters are usually between 10^{-2} and 10^{-1} mg/L (3).

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As environmental standards for the arsenic level in waters have been re-evaluated in the last years (i.e. for drinking waters, the maximum allowable total arsenic concentration is 0.01 mgAs/L (4), more efficient and economical techniques to remedy arsenic-contaminated aqueous systems are required.

The types of processes used to treat arsenic-bearing solutions include: flotation (5–13)—ionic, precipitate, sorption-flotation—with removal efficiencies %R > 98, chemical precipitation (14, 15) with lime or ferric salts %R > 90, adsorption (14, 16–20) on different materials as activated carbon, activated alumina, clay minerals, fly ash, industrial wastes, oxides, sand %R > 95, ion exchange (14) %R > 95, oxidation-reduction (21) membrane filtration (14) %R > 85, reverse osmosis (14) %R > 95, and biotechnologies with living or non-living biomass (10). Arsenic removal from aqueous systems is achieved by transferring arsenic compounds into a solid phase (filters, resins, sorbents, precipitates impregnated with arsenic ions) that is considered a hazardous waste and must be further treated before safe storage and disposal.

The group of the separation methods by adsorptive bubbles, which include flotation, represents an effective alternative to classical ones, like settling or filtration, sustained by the fast rate of separation, minutes compared with days in case of precipitation, moderate costs associated with equipment and reagents, small volumes of wastes that allow the recovery of valuable species, and/or the support regeneration.

Flotation is an adsorptive bubble separation method that applies surface properties at interfaces of contacted phases (the differences between natural or artificial surface activities of the system's components). During the flotation process, the separation procedure of a certain component from the liquid phase is based on mass transfer by adsorptive gas bubbles produced by one of bubbles generation techniques: dispersion through porous diaphragms (dispersed air flotation), pressure reduction of water pre-saturated with air (dissolved air flotation), or electrolysis (electroflotation or electrocoagulation flotation). The separation efficiency by flotation techniques depends on chemical factors (pH, support and collector concentrations, ionic strength, composition of aqueous solution, activators) and hydrodynamic and mass transfer factors (bubble size, gas flow rate, foam stability) (7, 22).

Sorption–flotation, part of the adsorptive bubbles separation methods, is a wastewater treatment technology used especially for the separation of heavy metal cations and anions from aqueous diluted solutions by adsorption and/or coprecipitation with colloidal particles (iron (III) and aluminum (III) hydroxides are commonly used as solid support) which are then floated. As collector reagents are usually used ionic surfactants, depending on the ion that has to be removed (7, 23–27) or even a mixture of collectors (sodium lauryl sulfate and sodium oleate) (12). Applications of this type of separation methods for different metallic ions, in mono- and multi-component systems, are mentioned in detail by Caballero, 1990 (28).

Related to arsenic removal from aqueous systems, there are a large number of papers in literature that investigated As(III) and/or As(V) separation by DAF, using different supports (Fe(II) (8) and Fe(III) (9, 12, 24, 23, 29) oxy-hydroxides) and collectors (sodium lauryl sulfate (9, 12, 8, 24, 25), sodium oleate (26, 25), lauryl ammonium chloride, sodium laurylbenzene sulphonate (30), cetyl-trimethyl-ammonium bromide (31).

The present paper investigates arsenate separation from dilute model systems by sorption–flotation using $Fe_2O_3 \cdot xH_2O$ as solid support, sodium laurate (NaL) as anionic surfactant (collector), and dissolved air technique for the generation of bubbles. Related to arsenic removal from aqueous media, the present research is studying As(V) separation with an unstudied collector, sodium laurate, that was selected on considerations of solubility, forms of existence in aqueous solution and acid-base character of the couple lauric acid/laurate ions.

The systematic approach of experimental research for As(V)–Fe(III)–NaL system includes as objectives: the study of influencing factors: pH, support and collector concentrations, As(V) concentration, the presence of foreign ions, conditioning time, dissolved air pressure, generally mentioned in literature, the influence of a synthetic nonionic polyacryl amide based flocculant (Superfloc N 300), selected on the basis of preliminary data. The paper investigates the recovery of the solid support from the foam for reuse and of As(V) compounds for enrichment. The separation equilibrium and several aspects of process dynamics were studied by the dependence $C_{\mathrm{final\ As(V)}}$, respectively $\%R = f$ (flotation time). Some considerations on separation mechanism were discussed with respect to the correlation structure–properties and possible interactions As(V)–Fe(III)–NaL.

EXPERIMENTAL

Reagents

All chemicals used in this study were of analytical reagents grade.

- As_2O_5 in H_2O p.a. (Merck) stock solution 1 g/L used to prepare working solutions with As(V) concentrations similar to real systems (1–100 mg As(V)/L);
- $FeCl_3 \cdot 6H_2O$ p.a. (U.C.B.) solution 0.5 M used to prepare the solid support *in situ*;
- $CH_3(CH_2)_{10}COONa$ (NaL) solution 0.2% (Fluka)—anionic surfactant (collector);
- Superfloc N 300 (Cyanamid) solution 0.1%—nonionic polymeric flocculant;
- $NaNO_3$, Na_2SO_4, Na_2HPO_4 (Chimopar) solutions 0.1–0.5 M—sources of foreign ions;
- NaOH (Lach-Ner) and HCl (Merck) solutions 0.1–2 M—precipitating agent and to adjust the pH values.

Equipment

- Batch dissolved air flotation (DAF) unit, with glass laboratory column ($D_{int} = 5.5$ cm), cylindrical nozzle ($D_{int} = 1.5$ mm) and auxiliary units (5)—for flotation experiments;
- AAS 880 Varian Spectrometer (with deuterium lamp for background correction, 8 cathode lamps, double fascicle, monocromator Czerny-Turner) coupled with graphite furnace GTA 100 (313–3273 K, with automatic control of two gases), programmable sample dispenser (PSD) (50 positions, injected volume 1–70 μL), refrigerated recirculator Neslab CFT 33, N_2 generator Domnick Hunter Nitrox (3 L/min, 99.999% purity), Ar tank (4.0 purity)—for total arsenic absorbance measurements;
- FT-IR Spectrometer Jasco 620 (4000–400 cm^{-1}, resolution 4 cm^{-1}, scanning speed 2 mm/s, dry samples in KBr pellets −3 mg sample in 300 mg of spectral grade (Merck) KBr)—for spectral investigations of isolated species at optimum flotation parameters;
- Derivatograph Q 1500 D, MOM (sample weight 100 mg, temperature range 291–1273 K, heating rate 10 K/min, inert material Al_2O_3)—for thermal decomposition of samples;
- Water system de-ionizator USF Elga Maxima (18.2 MΩ, 2L/min);
- Centrifuge 5416 Eppendorf;
- Digital Orion 290 A pH-meter;
- Magnetic stirrer.

Method

The general parameters of the analytical method for arsenic detection were: sampling mode: automix, calibration mode: concentration, measurement mode: peak height, smoothing: 9 points, wavelength: 193.7 nm, slit width: 1.0 nm, EHT: 338 V, lamp current: 10.0 mA, recalibration rate: 10, calibration lower limit: 20.0%, calibration upper limit: 150.0%, calibration algorithm: new rational ($A/C = a + b \cdot A + c \cdot A^2$ where A – absorbance, C – concentration, a, b, c calibration coefficients), volume reduction factor: 2, RSD limit: 5.0%, correlation coef. limit: 0.99, sample volume 10^{-2} mL, total volume $1.5 \cdot 10^{-2}$ mL.

The method uses two standard replicates and two sample replicates, with automatic quality control (relative standard deviation RSD $< 2.8\%$), a temperature program in 16 steps (Table 1) with an atomization temperature of 2600°C, nitric acid solutions: 0.1% for make-up and 1% for rinse water, with no matrix modifiers, and allows a detection limit of 10^{-3} mgAs/L.

Flotation experiments: 0.3 L samples of aqueous As(V) solutions, with initial concentrations 1–100 mgAs(V)/L, were treated with predetermined volumes of $FeCl_3$ solution 0.5 M to form *in situ* the solid support ($Fe_2O_3 \cdot xH_2O$) by precipitation with NaOH. The pH was adjusted to different values and the solution was magnetically stirred for 5 min, then

Table 1. Temperature program used for total arsenic detection by AAS-GTA

Step	Temperature (K)	Time (s)	Flow (L/s)	Gas type	Read	Signal storage
1	313	1.0	0.05	Nitrogen	No	No
2	358	5.0	0.05	Nitrogen	No	No
3	358	5.0	0.05	Nitrogen	No	No
4	368	40.0	0.05	Argon	No	No
5	393	10.0	0.05	Argon	No	No
6	393	1.0	0.05	Argon	No	No
7	523	10.0	0.05	Argon	No	No
8	523	1.0	0.05	Argon	No	No
9	1473	6.0	0.05	Argon	No	No
10	1473	1.0	0.05	Argon	No	Yes
11	1473	2.0	0.00	Argon	No	Yes
12	2873	0.7	0.00	Argon	Yes	Yes
13	2873	2.0	0.00	Argon	No	Yes
14	2873	1.0	0.05	Argon	No	Yes
15	313	21.5	0.00	Argon	No	No
16	313	10.0	0.00	Nitrogen	No	No

NaL was added and stirred another 3 min. The sample was quantitatively transferred to the flotation column where the colloidal hydrophobic particles were floated to the surface with air microbubbles by the DAF technique. At the top of the flotation cell, a thin layer of foam was formed, consisting of floated arsenic-bearing precipitate. Small amounts of the floated solution were collected, at certain flotation time, from the lower part of the cell to measure the residual arsenic concentration by AAS. The foam obtained at optimum parameters was isolated, washed, and dried at 378 K for physical-chemical analysis. The recovery of solid support and the recovery of As(V) aqueous species as sodium arsenate were obtained by washing the foam with dilute solution of NaOH (2 N). During the experiments, the temperature of the solutions was constant and equal to the ambient temperature (295K).

The separation efficiency of As(V) is calculated as: $\%\mathrm{R} = (1 - C_{f\mathrm{As(V)}}/C_{i\mathrm{As(V)}}) \cdot 100$, where $C_{\mathrm{f\ As(V)}}$ is the final (residual) As(V) concentration, and $C_{\mathrm{i\ As(V)}}$ is the initial concentration of As(V) in solution, respectively.

Experimental data (represented in graphics as points) were fitted, and the curves plotted (as continuous lines) indicate the correlation coefficient r, mentioned as a measure of fitting quality.

$$r = \sqrt{r^2} = \sqrt{1 - \frac{\sum_{i=1}^{n}[y_i - f(x_i, a_1 \ldots a_k)]^2 \cdot w_i}{\sum_{i=1}^{n}(y_i - \bar{y})^2}} \tag{1}$$

where $y_i = f(x_i, a_i \ldots a_k)$, a = parameters.

RESULTS AND DISCUSSION

Influencing Process Factors

pH

Solution pH determines the structure and charge of aqueous species, the degree of collector ionization and the foam stability. Arsenic removal by sorption–flotation with Fe(III) as solid support depends both on the surface charge of colloidal $Fe_2O_3 \cdot xH_2O$ and the ionic form of As(V) species in solution.

The aquatic chemistry of Fe (III) is important in controlling the separation process since hydrolysis species determine the formation and dissolution of hydrated insoluble ferric hydroxide or even of hydroxocomplexes. Furthermore, the polymerization of complex hydroxospecies in aqueous solution generates, over a characteristic pH range, polynuclear compounds and colloidal hydroxopolymers and finally insoluble colloidal precipitates ($Fe_2O_3 \cdot xH_2O$) (32). The cationic type of polymeric hydroxospecies predominates in the range of $pH < pH_{iep}$ ($pH_{iep} = 8.0$ (8)–8.5 (33) corresponds to the isoelectric point of colloidal precipitate of $Fe(OH)_{3(s)}$), and the anionic species predominates in the range of $pH > pH_{iel}$.

Literature data show that the presence of As(V) modifies, by specific adsorption of $H_xAsO_4^{x-3}$ ions, the surface charge of ferric hydroxide flocs, shifting the isoelectric point to the acidic pH range ($pH_{iep} = 4.0$) (8).

As(V) aqueous solution may contain, as a function of pH, different oxyanions: H_3AsO_4 ($pH < 2$), $H_2AsO_4^-$ ($2 < pH < 6$), $HAsO_4^{2-}$ ($6 < pH < 11$) and AsO_4^{3-} ($pH > 11$), in their hydrated forms (34).

In solution, pH changes generate modifications in the structure of the collector. Sodium laurate, as a salt formed from a weak acid and a strong base, is involved in a hydrolysis equilibrium (hydrolysis constant $K_h \cong 8.3 \cdot 10^{-10}$ and hydrolysis grade $h \cong 2.7 \cdot 10^{-4}$) and the lauric acid formed participates to a ionization equilibrium:

$$CH_3(CH_2)_{10}COONa + H_2O \Longleftrightarrow CH_3(CH_2)_{10}COOH + Na^+ + HO^-$$
$$CH_3(CH_2)_{10}COOH \Longleftrightarrow CH_3(CH_2)_{10}COO^- + H^+$$

The molecular or ionized form of lauric acid is influenced by pH, carboxylic acids ionization becoming important at $pH > 7$.

Experimental data for the As(V) + Fe(III) + NaL system (Fig. 1) show pH effects on As(V) separation efficiency by flotation. The optimum flotation pH was determined by the dependence $\%R = f(pH)$ for different initial As(V) concentrations (10, 20, and 50 mg/L) and was established to 4–5.

The preliminary tests for pH values lower than 4 showed a poor removal of As(V) from solution that might be attributed primarily to the absence of

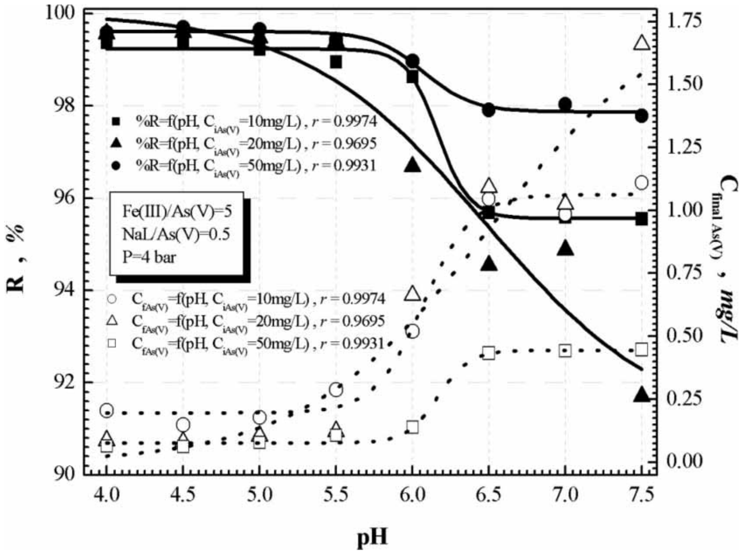

Figure 1. The dependences %R = f (pH) and $C_{\text{final As(V)}}$=f (pH).

sufficient colloidal $Fe_2O_3 \cdot xH_2O$ to collect the anions. In the pH range 4–5, $Fe_2O_3 \cdot xH_2O$ (pK = 38.8) flocs bear positive surface charge: $Fe(OH)^{2+}$ (pK = 11.8) and $Fe(OH)_2^+$ (pK = 22.3), (9) which is favorable for the adsorption of negatively charged ions: $H_2AsO_4^-$ ($pK_a = 2.2$) (9) and $CH_3(CH_2)_{10}COO^-$ and explains the maximum removal efficiencies obtained. In this pH range the concentration of laurate ions (L^-) decreases due to the formation of lauric acid ($pK_a \cong 4.9$ and $pK_{b\ conj} \cong 9.1$). Considering the pK_a/pK_b value of lauric acid and molar ratios Fe(III)/As(V)/NaL in the studied system and also the pK_a value of predominant species of As(V), respectively $H_2AsO_4^-$, the sorption of laurate ions on the support surface is not competing with As(V) speciations sorption. Laurate ions and lauric acid, the predominant species in this pH range, improve the floatability of arsenic-loaded support.

As the pH increases, the surface charge of the flocs modifies, thus reducing the number of available sorption sites. At pH values higher than 7, the support negatively charged surface is completely unfavorable for the electrostatic adsorption of anions.

Support Concentration

Experimental data (Fig. 2) show the effects of support (Fe(III)) concentration, expressed as a function %R = f(molar ratio Fe(III)/As(V)) at optimum pH range = 4–5, for solutions with initial concentrations of 20 mg As(V)/L. The optimum molar ratio Fe(III)/As(V) was established to 5 as the

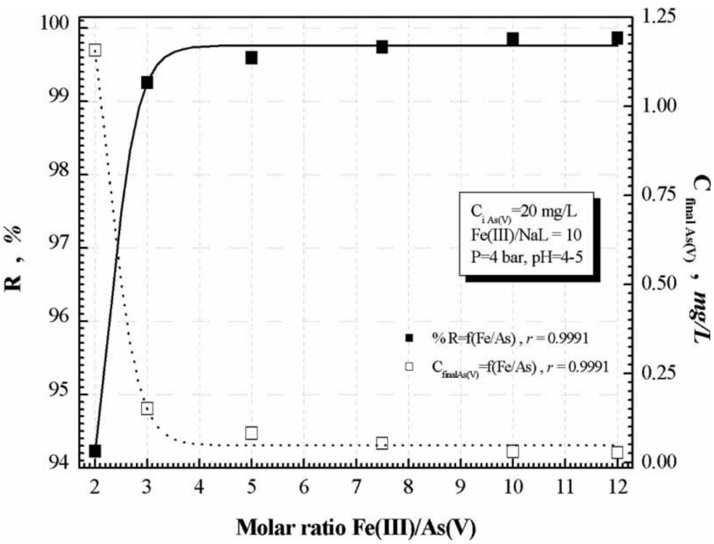

Figure 2. The dependences %R = f (Fe(III)/As(V) molar ratio) and $C_{\text{final As(V)}}$ = f (Fe(III)/As(V) molar ratio).

maximum separation efficiency is %R = 99.6. Although higher ratios allow the achievement of maximum separation efficiencies (%R = 100 for Fe(III)/As(V) > 8), providing a larger surface area available for anions co-precipitation/adsorption, are not justified because it implies the use of higher quantities of chemical reagents and generates a higher amount of hazardous solid wastes, so increasing the total costs (operating, handling and disposal).

Collector (Surfactant) Concentration

Collector concentration is a factor that determines the foam stability, so also the removal efficiency by flotation. For solutions with initial concentrations of 20 mg As(V)/L, at optimum pH range = 4–5, the optimum collector concentration was established in correlation with maximum As(V) separation efficiency from the experimental data (Fig. 3), as a function %R = f(molar ratio NaL/As(V)).

The optimum molar ratio NaL/As(V) was established to 0.5 (corresponding to a molar ratio Fe(III)/NaL = 10) as the maximum separation efficiency is %R = 99.6. The under-stoechiometric consumption of collector may be explained admitting that every macroscopic particle contains a large number of As(V) ions but needs only a mono-layer of collector on its surface in order to concentrate into the foam. An excess of collector reduces the removal efficiency as may result in a strong foaming, may form

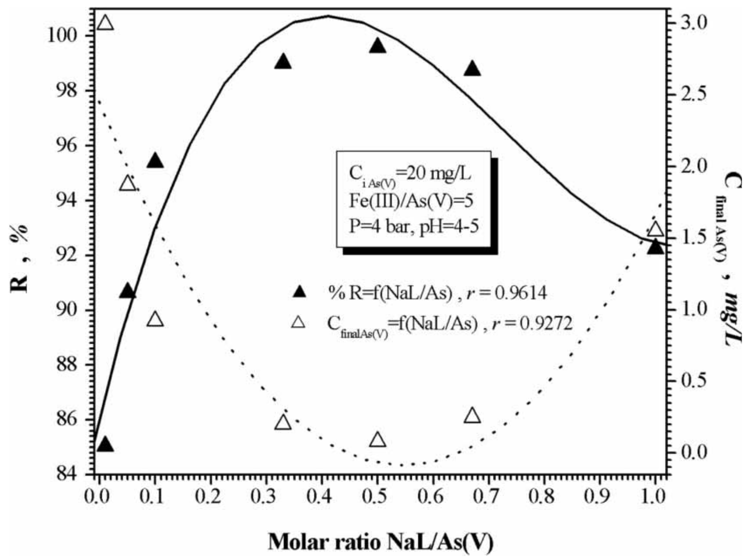

Figure 3. The dependences %R = f (NaL/As(V) molar ratio) and $C_{\text{final As(V)}}$ = f (NaL/As(V) molar ratio).

unfloatable hydrophilic micelles on the flocs surface (critical micelle concentration $CMC_{NaL} = 2.6 \cdot 10^{-2}$ M), or may compete with As(V)-bearing flocs for attachment on the rising bubbles, thus floating only the collector. Very low amounts of collector cannot completely remove the colloidal support loaded with As(V) and may form a foam layer that is thin and unstable, thus also reducing the flotation efficiency.

As(V) Concentration

The effects of As(V) initial concentration on As(V) separation efficiency by flotation at optimum parameters (pre-established for solutions with initial concentrations of 20 mg As(V)/L) is presented in Fig. 4.

The data show that for initial concentrations 10–100 mg As(V)/L, separation efficiencies %R = 99.4 can be achieved. It was not yet determined as to the lower limit of As(V) initial concentration for which the separation is effective, as for values smaller than 5 mg As(V)/L removal efficiencies over 95.2% are still obtained.

For removing arsenic from very dilute aqueous solutions (<5 mg As(V)/L), the optimum molar ratios Fe(III)/As(V) and NaL/As(V) should be reevaluated because the separation efficiency differs sensitively with initial arsenic levels. A molar ratio Fe(III)/As(V) established as optimum for a certain initial As(V) concentration might need to be increased for much lower As(V) initial values.

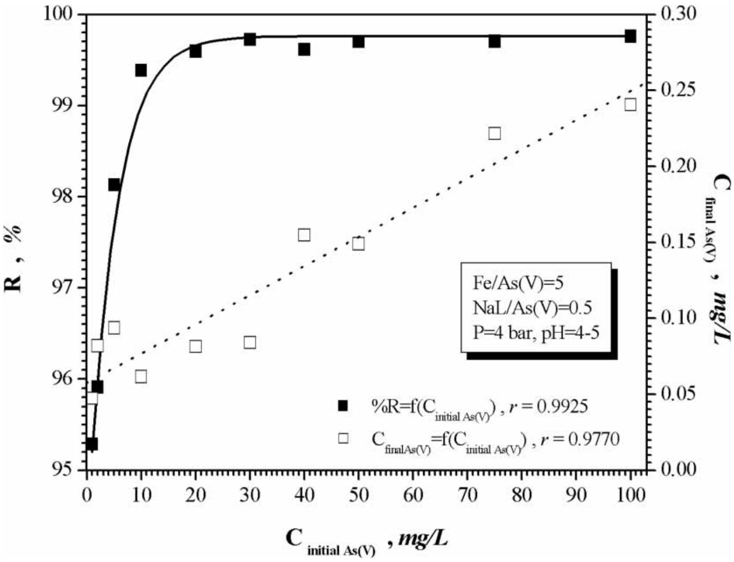

Figure 4. The dependences %R = f ($C_{\text{initial As(V)}}$) and $C_{\text{final As(V)}}$ = f ($C_{\text{initial As(V)}}$).

As a partial conclusion, sorptive flotation of As(V) oxyanions with $Fe_2O_3 \cdot xH_2O$ is recommended for dilute aqueous systems but impose the establishing of optimum operating parameters for distinct ranges of As(V) concentrations in influent.

Flocculant Addition

The addition to the aqueous solution of a nonionic synthetic polyacrylamide-based flocculant (Superfloc N 300), selected on preliminary investigations on different anionic, cationic, and nonionic flocculants, was also studied (Table 2). The flocculant concentration in aqueous systems is limited by legislation, to a maximum admissible value of 4 mg/L. The dosage weight ratio Flocculant/As(V) was established to 1/13 (corresponding to a weight ratio Flocculant/Fe(III) = 1/50). Experimental data show that flocculant addition considerably reduces the volume of the foam, with more than 37.5%, because it enhances the floc growth into large agglomerates that are less gelatinous, more compact than the float themselves, and reduces considerably the residual As(V) concentration with more than 3 times, thus increasing sensitively the separation efficiency to %R = 99.9.

The Influence of Foreign Ions (NO_3^-, SO_4^{2-}, PO_4^{3-})

The presence of neutral salts influences the efficiency of flotation due to the competition for the collector or for the positively charged sites of the solid

Table 2. Experimental values of foam height (H_{foam}), residual As(V) concentration ($C_{f\ As(V)}$) and separation efficiencies (%R) for As(V) removal from aqueous systems by flotation[a]

	Without flocculant			With flocculant		
pH	H_{foam} (mm)	$C_{f\ As(V)} \cdot 10^3$ (mg/L)	R (%)	H_{foam} (mm)	$C_{f\ As(V)} \cdot 10^3$ (mg/L)	R (%)
4.0	7.5	86.26	99.57	5.0	34.93	99.83
4.2	7.5	82.30	99.59	5.0	36.30	99.82
4.5	8.0	81.27	99.59	5.0	22.98	99.89
4.7	7.5	106.70	99.47	5.5	23.80	99.88
5.0	8.0	104.07	99.48	5.5	34.30	99.83
5.2	8.0	123.10	99.38	5.5	41.10	99.79
5.5	8.0	122.80	99.39	5.5	43.13	99.78

[a] Initial conditions: $C_{i\ As(V)} = 20$ mg/L, molar ratios Fe(III)/As(V) = 5, NaL/As(V) = 0.5, weight ratio flocculant/As(V) = 1/13, P = 4 bar.

support between As(V) oxyanions and anions from the added electrolytes. Foreign ions like nitrates, sulfates, or phosphates are frequently found in arsenic contaminated waters, especially wastewaters from mining activities. Their inhibiting effect on arsenic separation efficiency is amplified with the ionic strength and ionic charge and is increased from monovalent to trivalent ions ($PO_4^{3-} > SO_4^{2-} > NO_3^-$) (Fig. 5). The stronger influence of phosphate ions may be explained as the reduction in the number of the adsorption sites available due to structural similarities with arsenate ions, thus being adsorbed on the solid support the phosphate and not the arsenate ions, and due to the precipitation of $FePO_4 \cdot 2H_2O$ (solubility product $K_{sp298K} = 1.3 \cdot 10^{-22}$ as Fe(III) concentration decreases during precipitation of $Fe(OH)_3$ ($K_{sp298K} = 4 \cdot 10^{-38}$).

Conditioning Time

The conditioning (agitation) time of the sample before flotation influences the separation efficiency. The dependence of As(V) removal efficiency on conditioning time, for an initial As(V) concentration of 20 mg/L and for optimum operating parameters, is presented in Fig. 6 as the adsorption density $\Gamma = f\ (\tau_{cond})$, where $\Gamma = n/w$ is the ratio between the number of adsorbed moles of As (V) oxyanions (n), and the unit weight of support $Fe_2O_3 \cdot xH_2O$ (w). The experimental data show that the separation of As(V) oxyanions was virtually complete in 3 min of conditioning. Thus, a period of 5 min of magnetic stirring for co-precipitation/adsorption is more than sufficient for the flotation experiments. The dramatic increase of Γ within a narrow range of conditioning time may be explained by a gradual coverage

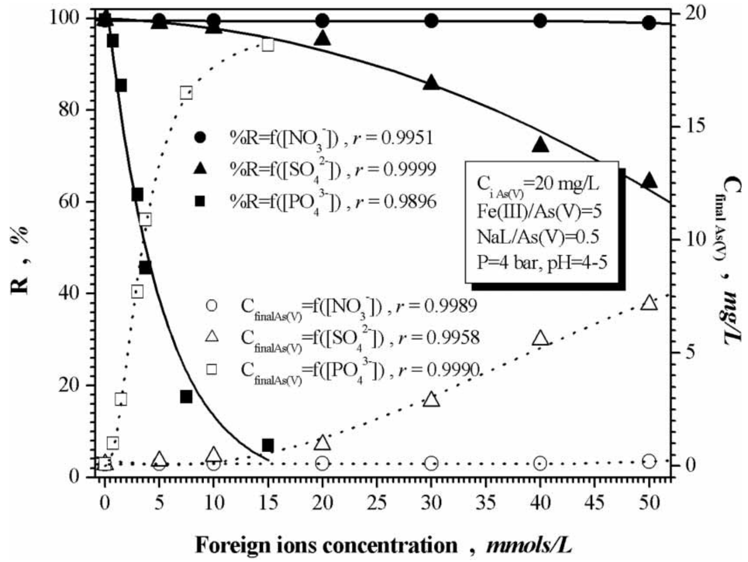

Figure 5. The dependences %R = f ([foreign ions]) and $C_{\text{final As(V)}}$ = f ([foreign ions]).

of the sites for adsorption, until all the sites are completely covered. This suggests that after this virtually complete adsorption, there is progressively less of a chance that an As(V) oxyanion would find a suitable site on which it could be adsorbed, no matter how long the conditioning time is.

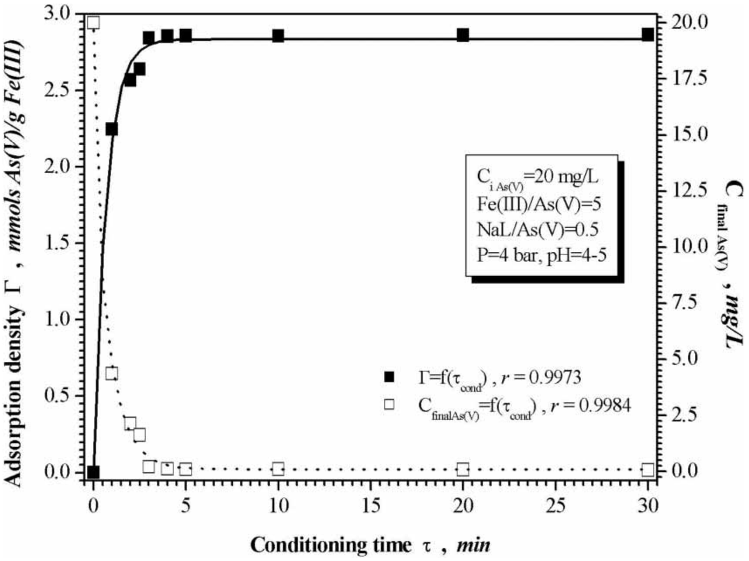

Figure 6. The dependences %R = f (τ_{cond}) and $C_{\text{final As(V)}}$ = f (τ_{cond}).

Dissolved Air Pressure

Preliminary experimental research on the necessary volume of air, expressed as the dilution ratio V_{sample}:$V_{pressurized\ water}$, had been established in correlation with dimensional particularities of the flotation column, with the operating mode of the system (batch), and with the physical-chemical aspects of the process, an optimum dilution ratio 3 : 1.

Experimental results (Fig. 7) presented as a function %R = f (dissolved air pressure) for the Fe(III)+ As(V) + NaL system show that the optimum pressure is 4 bar. An increase over this value may be destructive to the flocs, causes the foam to be too wet, reduces the bubbles' stability and may even alter the bubble–particle collision, thereby reducing the separation efficiency. A decrease under this value does not offer advantages to the flotation process as it reduces the foam density, and thus also the separation efficiency.

Separation Reproducibility

Statistical analysis by the distribution law of W. S. Gosset (*t* distribution) on a lot of 7 repeated tests shows a good reproducibility of the separation process at optimum operating parameters, existing a probability of 99% that the removal efficiency is 99.44 ± 0.09% and the residual As(V) concentration in treated water is (111.75 ± 4.83) $\cdot 10^{-3}$ mgAs(V)/L).

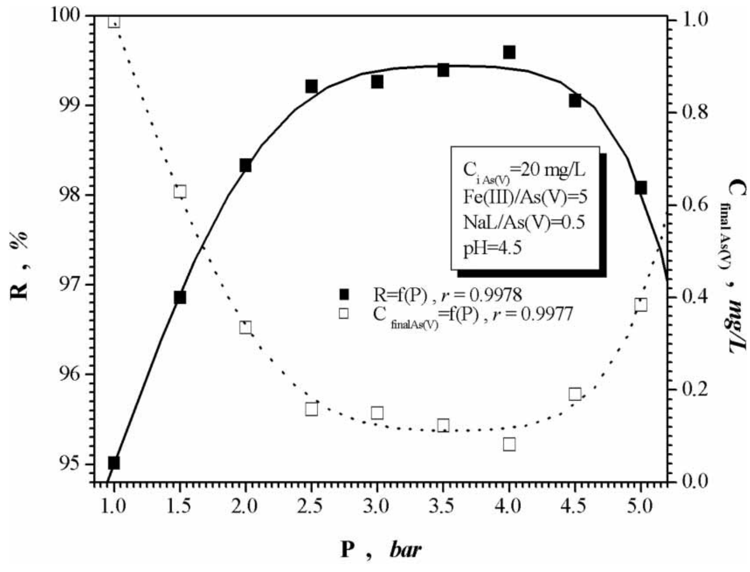

Figure 7. The dependences %R = f (P) and $C_{final\ As(V)}$ = f (P).

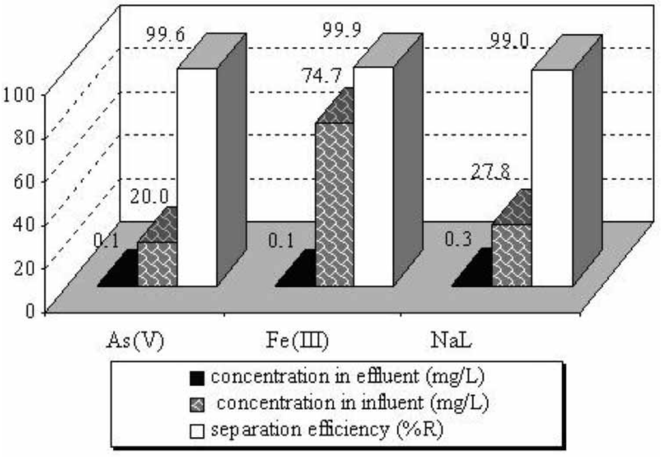

Figure 8. As(V), Fe(III), and NaL concentrations in influents and effluents.

Effluent Analysis at Optimum Parameters

The initial and the mean residual concentrations of As(V), Fe(III), and anionic synthetic detergent in initial samples (influents) and in treated samples (effluents) at optimum operating parameters, are presented in Fig. 8.

The residual concentrations of Fe(III), anionic surfactant, and chlorides (not shown in Fig. 8) meet the regulations for Drinking Water Quality Standards (<0.2, 0.2 and 250 mg/L, respectively).

The residual concentrations of NO_3^-, SO_4^{2-}, and PO_4^{3-} (Fig. 9) are also below the maximum admissible values imposed for drinking water. Only

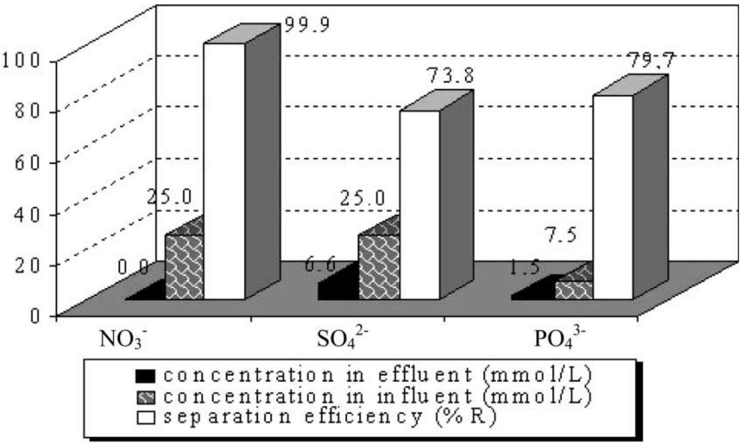

Figure 9. NO_3^-, SO_4^{2-}, and PO_4^{3-} concentrations in influents and effluents.

As(V) concentration in effluent is, even for the optimum operating parameters of the process, more than 0.01 mg/L (the limit for drinking water) although it meets the Treatment Standards for Waste Waters (1.4 mgAs/L) and ambient water quality criteria for aquatic life (0.44 mgAs/L).

As(V) Desorption

Arsenic desorption and recovery from the foam and solid support regeneration may enhance the flotation process by considerably reducing the operation costs.

In order to establish the necessary volume of the desorption agent, the foam collected at the optimum operating parameters ($V_{foam} = 15 \pm 0.2$ mL) was contacted with NaOH solutions 2M in 6 consecutive steps, using for each elution a volume of 3 mL NaOH. After centrifugation, the supernatant solution was analyzed for residual arsenic content.

Experimental results (Fig. 10) show that the equilibrium state is reached after the 4th desorption step and 94.62% of As(V) from the collected foam (foam collecting efficiency 78.93 ± 3.71%) could be desorbed and enriched with more than 13 times as aqueous solution of sodium arsenate (258.47 mg As(V)/L). The percent of 5.38% of As(V) that could not be recovered by desorption shows a partial reversibility of the adsorption reaction, and might be explained by a co-precipitation reaction, when the incorporation of As(V) ions present in the aqueous system into the precipitate matrix is facilitated.

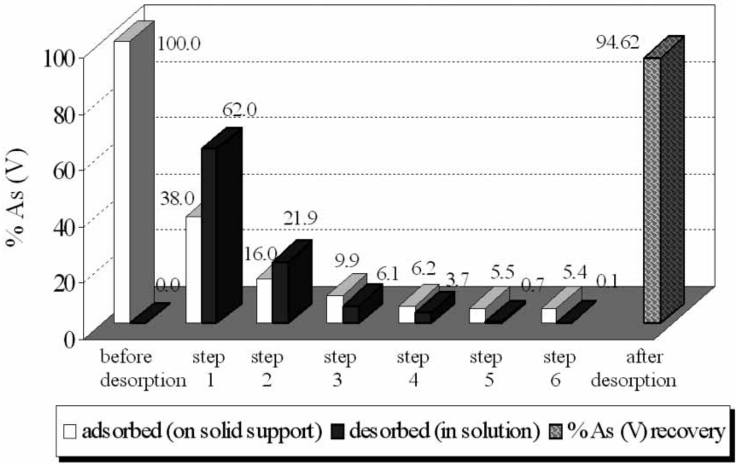

Figure 10. Desorption steps of As(V) from isolated species at optimum operating parameters.

As(V) desorption is favored by NaOH treatment of solid support, confirming the weak nature of its interaction with ferric hydroxide, thus the poor stability of this surface complex in a neutral or an alkaline pH region.

Aspects of Separation Equilibrium and Dynamics of the Process

The theoretical approach and optimization of flotation implies the study of separation equilibrium and the dynamics of the process. The separation equilibrium at optimum parameters, both for the system without flocculant and with flocculant, is shown in Fig. 11 as dependence %R = f (flotation time). Experimental data show that the equilibrium is reached faster in the system with Superfloc N 300, the addition of flocculant increasing sensitively the rate of separation ($k = 0.068 \pm 0.005\ \text{s}^{-1}$, $\%R^* = 98.38 \pm 0.97$) with respect to the system without the flocculant ($k = 0.037 \pm 0.003\ \text{s}^{-1}$, $\%R^* = 94.51 \pm 1.28$).

It can be noticed that the reaching of the equilibrium state is attained in almost 80 s in the system with flocculant and, respectively, in 170 s in the system without the flocculant.

Kinetic studies are difficult to perform due to the overall flotation complexity, determined by the number of simultaneous and succesive microprocesses developed in space and time (collision and attachment of particles-bubbles complexes, rising of agglomerates, detachment), chemical factors (pH, components nature and structure), and hydrodynamic and mass transfer factors (bubble size, gas flow rate, foam stability) (35–37).

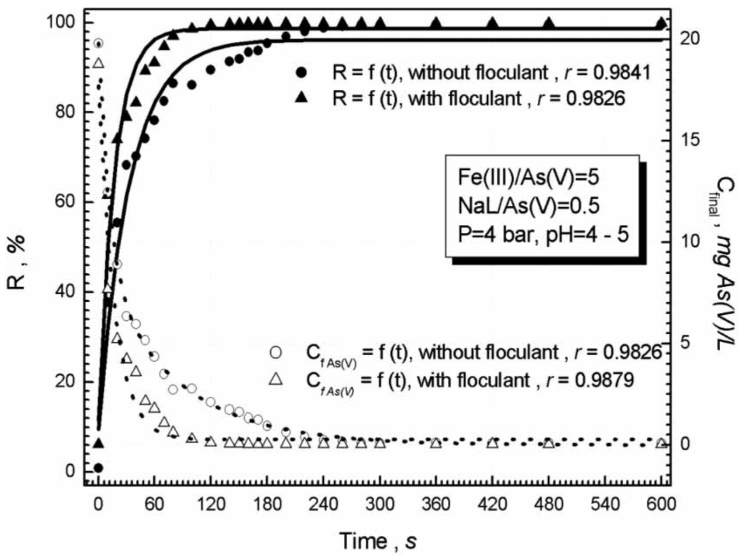

Figure 11. The dependences $\%R = f(\tau_{\text{flotation}})$ and $C_{\text{final As(V)}} = f(\tau_{\text{flotation}})$.

Literature data show that flotation kinetics is tackled by analogy with chemical kinetics, taking into account the particularities of the process.

The kinetic study estimates the overall order of the separation process and the flotation overall rate constant. Kinetic parameters of As(V) separation were determined by differential (initial rates) method, plotting the dependence $\ln v_{\text{initial}} = n \cdot \ln c_{\text{initial}} + \ln k$ (where v_{initial} is initial rate, c_{initial} is initial concentration of As(V), n is the overall flotation order, and k is the overall flotation rate constant): $n = 0.952 \pm 0.073$ and $k = 0.035 \pm 0.007\text{s}^{-1}$.

The separation of As(V) oxyanions by DAF with the anionic collector (NaL) follows an overall first-order kinetics.

Kinetic modeling on different semi-empirical ore flotation models and interpretation of statistical fitting parameters showed that the simulation results with the classical first-order kinetic model (5) are in good agreement with the experimental data.

This model describes macroscopically the flotation of hydrophobic particles, considering the particles monodisperse and with constant floatability:

$$R = R^*[1 - \exp(-kt)]$$

where R = separation efficiency at time t, R^* = separation efficiency at ∞ time; k = rate constant and t = time.

As(V)–Support–Collector Interactions

FT-IR Spectra

The FT-IR spectra of samples: solid support (Fe(III) oxyhydroxide), support conditioned with collector (Fe(III) + NaL), support loaded with arsenate species (Fe(III) + As(V)), and support conditioned with both arsenic and collector (Fe(III) + As(V) + NaL) (Fig. 12), are investigated and further discussed in order to establish the As(V) separation mechanism on $Fe_2O_3 \cdot xH_2O$, taking into account all the possible interactions between As(V) oxyanions, the collector ions and the solid support surface. The band positions and possible assignments are summarized in Table 3.

The spectrum of Fe(III) + NaL (Fig. 12 d) shows that the two bands at 1518 and 1425 cm^{-1} assigned to C=O anti-symmetric and respectively symmetric stretching vibrations are reduced in intensity and shifted from 1569 and 1462 cm^{-1} in respect with the spectrum of NaL. This may be attributed to laurate anions (L^-) linking to Fe^{3+} on $Fe_2O_3 \cdot xH_2O$ surfaces, which causes the absorption bands to shift to lower values, indicating that a chemical adsorption might take place between L^- and Fe(III). The lauric acid monomer is probably adsorbed by hydrogen bonding, as well as by hydrocarbon chain association.

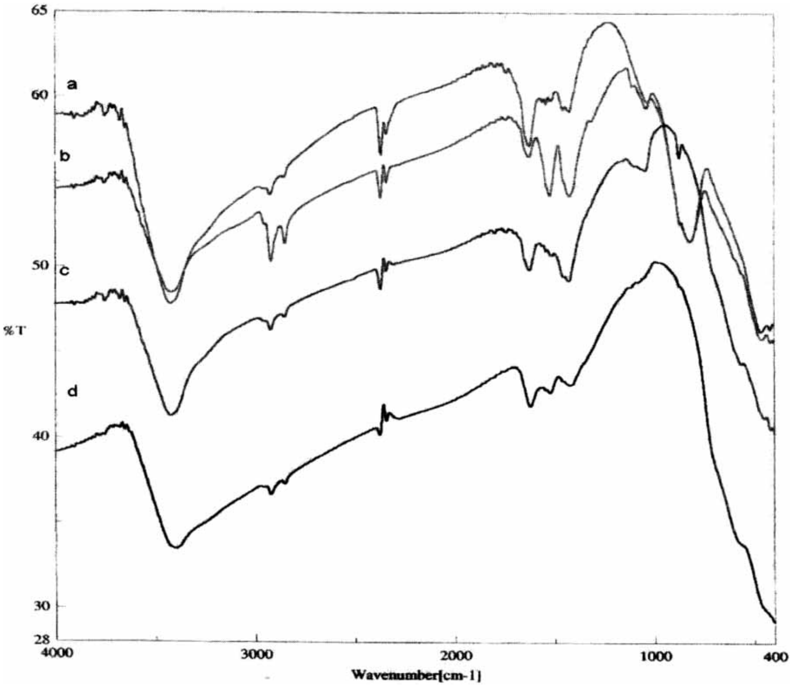

Figure 12. FT-IR spectra of KBr pellets of isolated species for the systems: (a) Fe(III) + As(V), (b) Fe(III) + As(V) + NaL, (c) Fe(III), (d) Fe(III) + NaL.

The spectrum of Fe(III) + As(V) (Fig. 12 a) exhibit IR typical arsenate strong bands at 820, 468 and 425 cm^{-1}. The band at 820 cm^{-1} may be attributed to ν_{As-O} stretching vibrations as the symmetric mode of two equivalent As–O bonds (2). The sharp doublet bands observed at 486 and 425 cm^{-1} may be attributed to O–As–O bending vibrations (38, 39). The spectrum of Fe(III) + As(V) system indicates that As(V) is chemically or electrostatically adsorbed (as a surface complex) on the surface of $Fe_2O_3 \cdot xH_2O$.

In the spectrum of Fe(III) + As(V) + NaL system (Fig. 12 b), when As(V) is adsorbed/co-precipitated with Fe(III) at pH = 4–5 and later on conditioned with NaL, it could be observed that the bands produced by the methyl and methylene groups occur in fixed positions, with very small shifts following adsorption on arsenic-bearing ferric flocs. The bands generated by COO^- groups, corresponding to anti-symmetric and symmetric stretching vibrations $\nu_{C=O}$, were shifted to lower wave numbers at 1523 and 1423 cm^{-1} in respect with 1518 and 1425 cm^{-1} in Fe(III) + NaL spectrum. This indicates an interaction of COO^- group from laurate anion with As(V) bearing $Fe_2O_3 \cdot xH_2O$ surface. FT-IR absorption bands produced by methyl and methylene groups can be used unambiguously to characterize the presence of L^- onto colloidal ferric oxyhydroxide.

Table 3. FT-IR characteristic frequencies and possible assignments of isolated species at optimum operating parameters of the flotation process

Group	Mode of vibration	Characteristic frequencies of isolated species (cm^{-1})				
		Lit (37–40)	Fe(III)	Fe(III) + NaL	Fe(III) + As(V)	Fe(III) + As(V) + NaL
H–OH	Stretching antisym.	3550–3445	3424.41	3400.33	3424.48	3425.48
H–OH	Bending	1650–1600	1626.50	1622.42	1627.57	1627.57
$C-CH_3$	Stretching antisym.	2962–2926	—	2916.37	—	2920.50
$C-CH_3$	Stretching sym.	2872–2853	—	—	—	2850.51
C═O	Stretching antisym.	1610–1550	—	1518.43	—	1523.54
C═O	Stretching sym.	1420–1300	—	1425.43	—	1423.59
						1315.59
As–O	Stretching sym.	837	—	—	820.52	820.52
O–As–O	Bending	463	—	—	468.46	468.46
					425.47	417.46
Fe–OH	Bending	1200–1100	1052.56	—	1036.60	1043.59

The existence of arsenate is also clearly shown by multiples sharp bands situated at almost the same frequencies as in the case of Fe(III) + As(V) system, respectively at 820, 468 and 417 cm^{-1}. These bands may be attributed to $\nu_{As\text{-}O}$ bending and $\nu_{O\text{-}As\text{-}O}$ stretching of As–O–Fe groups and may indicate that As(V) is coordinated by surface sites as a surface complex.

The assignments of the various bands and peaks in this study are in reasonable agreement with those reported in the literature for similar functional groups (2, 38, 39, 40).

Thermal Analysis

The curves of weight loss (TG), rate of weight loss (DTG) and heat absorbed or generated (DTA) were recorded simultaneously and offer additional information about chemical reactions or physical transformations that took place with or without weight change. The thermal analysis curves of insoluble isolated species for different systems show energetic effects associated with weight losses assigned to consecutive processes of loss of water, thermal decomposition of organic and inorganic substances. and the recovery of the final product. Assignments and interpretation of TG and DTA curves are shown in Table 4.

Thermal decomposition of Fe(III) results in the formation of solid stable Fe_2O_3 and gaseous H_2O, following several steps: loss of absorbed water (13.75 wt. % at 343–498 K), loss of molecular water (3.75 wt.% at 498–653 K), formation of oxohydroxide, polymorph transformations, and formation of Fe_2O_3 at 993–1143 K.

The derivatograph of collector shows a continuous total loss of weight (97.50 wt.% in the temperature range 483–583 K and respectively 2.50 wt.% between 583 and 723 K), attributed to successive steps of dehydration, decarboxylation, and thermal decomposition of organic substance into final gaseous products CO_2 and H_2O.

The thermal analysis curve for Fe(III) + NaL system shows a total weight loss of 20.00 wt.% bellow 673 K, corresponding to 4 exothermic peaks on DTA curve, assigned to loss of water and to thermal decomposition of organic substance, and the DTG curve is characterized by a large maximum at 983–1133 K, without mass loss, attributed to Fe_2O_3 re-crystallization.

In the case of Fe(III) + As(V) system the curves have similar shapes with those for Fe(III) at temperatures below 923 K, although the weight change is less pronounced (14.38 wt.%). That fact might be explained by a previous loss of hydroxyl groups and water molecules during the formation of As(V) surface complexes on the hydrous oxide surface. The first process that occurs with heating of the sample is the loss of surface water, and as the temperature increases, the arsenate sorbed on the surface of ferric hydroxide is dehydrated to As_2O_5 (40–43).

Table 4. Thermal analysis of isolated species at optimum operating parameters of the separation process

	TG				DTA	
System	Temperature range (K)	Weight loss (%)	Total weight loss (%)	Assignment	Temperature at DTA maximum (K)	Reaction type
Fe(III)	350–496	13.75	17.50	H_2O	496	Exo
	496–663	3.75		H_2O	663	Exo
NaL	483–583	97.50	100.00	H_2O, CO_2	483; 568; 583	Exo
	583–723	2.50		CO_2	683; 723	Exo
Fe(III) + NaL	341–467	11.25	20.00	H_2O	448	Exo
	467–589	6.25		H_2O; CO_2	518; 558	Exo
	589–673	2.50		H_2O; CO_2	663	Exo
Fe(III) + As(V)	353–513	12.50	14.38	H_2O	—	—
	513–663	1.88		H_2O; O_2; As_4O_6	583	Exo
	663–1163	—		$FeAsO_4$ formation	1003	Exo
Fe(III) + As(V) + NaL	360–520	11.88	15.63	H_2O	520	Exo
	520–633	3.75		H_2O; CO_2; O_2; As_4O_6	—	—
	633–1113	—		$FeAsO_4$ formation	973	Exo

A critical exothermic point on DTA curve, with a maximum at 1003 K and without a corresponding change of weight, is characteristic for the Fe(III) + As(V) system. It can be explained by assuming that only a part of As_2O_5 volatilizes as As_4O_6 (34) and the remainder reacts with ferric oxide to form, by exothermic re-crystallization, ferric arsenates ($FeAsO_4$) (41) or a mixed oxide Fe–O–As that could be thermally stable in the applied temperature program (<1273 K).

Thermal analysis curves for the system with collector (Fe(III) + As(V) + NaL) compared to those without collector (Fe(III) + As(V)) shows that the characteristic decomposition temperatures (DTG peaks) are shifted to lower values when organic matter is present.

CONCLUSIONS

Sorption–flotation (DAF technique) with $Fe_2O_3 \cdot xH_2O$ as solid support and sodium laurate (NaL) as anionic surfactant had proved to be very effective in As(V) removal from contaminated aqueous solutions. For solutions with initial concentrations of 20 mg As(V)/L, the optimum parameters of the separation process were established: $pH_{opt} = 4-5$, optimum molar ratios Fe(III)/As(V) = 5 and Fe(III)/NaL = 10, conditioning time = 5 min, dissolved air pressure $P_{opt} = 4$ bar, dilution ratio $V_{sample}:V_{pressurized\ water} = 3:1$. The influences of different compounds present in aqueous system (flocculants, inhibitors) were also investigated.

The average residual arsenic concentration in effluents treated at optimum operating parameters is $(111.75 \pm 4.83) \cdot 10^{-3}$ mg/L and corresponds to an efficiency %R = 99.44 ± 0.09. The adsorption capacity of solid support was estimated at 284.11 ± 0.26 mgAs(V)/gFe(III). Addition of a non-ionic flocculant (Superfloc N 300) decreases the volume of generated foam with more than 37.5% and reduces the final arsenic concentration more than 3 times, to a value of $(32.84 \pm 2.05) \cdot 10^{-3}$ mg As(V)/L, thereby increasing the efficiency to %R = 99.9.

The investigated flotation process, although used as a wastewater treatment technology, proved to be not only a simple separation–depollution method, but also a recovering-depollution method, allowing the recovery (94.62%) of arsenate species for enrichment, and of ferric hydroxides for re-use in other applications.

Effluent analysis at optimum parameters shows that the treated aqueous solution meets the quality standards for iron and surfactants in drinking water, but arsenic concentration is higher than the maximum admissible level, even with flocculant addition.

Investigations on the separation equilibrium and the dynamics of the process showed that the time needed to reach the equilibrium state is shortened, when the flocculant is added, with more than 3 times (has an order of 80 s). DAF removal of As(V) oxyanions with anionic collector

(NaL) follows a first-order kinetics, the estimated overall rate constant is $k = 0.03\ \mathrm{s}^{-1}$, and the model that simulates the process with best results is the classical first order kinetic model.

FT-IR Spectroscopy and simultaneous thermal analysis indicate that the main separation mechanism of the process is chemical adsorption, As(V) being coordinated as surface complex. The spectra show that chemical adsorption exists between $Fe_2O_3 \cdot xH_2O$ and arsenate ($H_2AsO_4^-$) ions and between $Fe_2O_3 \cdot xH_2O$ and laurate (L^-) ions. Typical arsenate bands are exhibited at 820 and 468 cm^{-1}, being assigned to $\nu_{\mathrm{As\text{-}O}}$ stretching vibrations, and $\delta_{\mathrm{O-As-O}}$ bending vibrations, respectively.

A characteristic exothermic point on the DTA curves of every system that contains As(V), with no corresponding loss of weight and with a maximum at around 973 K, may suggest the possible formation of ferric arsenate ($FeAsO_4$) or of a mixed oxide Fe–O–As that could be thermally stable in the applied temperature program (<1273 K), whose determination of chemical structure requires further investigation.

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