Kinetic Modelling of As (V) Separation by Dissolved Air Flotation

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The optimization of arsenic separation by dissolved air flotation requires thoughtful consideration of the kinetics of the process. The overall flotation complexity, determined by several primary simultaneous and succesive micro-processes developed in space and time, chemical factors, hydrodynamic and mass transfer factors, is limiting the kinetic approach to estimate the overall order of the process and the overall rate constant, by analogy with chemical reaction kinetics. Kinetic modelling on different ore flotation models and interpretation of statistical fitting parameters were performed in order to establish the validity of the semi-empirical models for experimental data of the studied system.

Keywords: arsenic separation, flotation, kinetic parameters, kinetic flotation models

Sorption – flotation, part of 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), with the aim of an ascending gaseous flow of micro-bubbles that remove low density hydrophobic particles as a 3-phase foam layer [1].

Flotation applies surface properties at interfaces of contacted phases (the differences between natural or artificial surface activities of the system components). The hydrophoby is increased or assured by adding small pre-determined quantities of collector. As collector reagents are usually used ionic surfactants, depending on the ion that has to be removed, or even a mixture of collectors [1].

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 electro-coagulation flotation). The separation efficiency by flotation techniques depends on chemical factors (*p*H, support and collector concentrations, ionic strength, composition of aqueous solution, activators) and hydrodynamic and mass transfer factors (bubble size, gas flow rate, foam stability).

The group of separation methods by adsorptive bubbles, which include flotation, represents an effective alternative to classical ones, like settling or filtration, sustained by simplicity, flexibility, applicability to different scales and different inorganic or organic species, high efficiency for low initial contaminant concentrations (10^{-6} – 10^{-2} M), fast rate of separation, minutes comparative 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.

Theoretical approach and optimization of flotation for treating large volumes of process effluents or dilute aqueous waste solutions implies the study of the separation equilibrium and the dynamics of the process.

Kinetic studies are difficult to perform due to overall flotation complexity, determined by the number of simultaneous and succesive micro-processes developed in space and time (adhesion, collision and attachment of particles-bubbles complexes, rising of agglomerates, detachment), chemical factors, hydrodynamic and mass transfer factors. The overall flotation complexity is thus limiting the kinetic approach to estimate the overall order of the process and the overall rate constant.

Literature data show that flotation kinetics is generally tackled by analogy with chemical kinetics, taking into account the particularities of the flotation process [2-5].

The present paper represents a part of research objectives of a complex study that investigates As(V) oxyanions separation by sorption/coprecipitation on $Fe_2O_3 \cdot xH_2O$ solid support using sodium laurate (NaL) as anionic surfactant (collector) and dissolved air technique.

In this study, the kinetic parameters of As(V) separation were determined by analogy with chemical reaction kinetics and verified by comparing experimental data with simulations on different semi-empirical ore flotation kinetic models. These models correspond to first- or second-order kinetics with different adjustments, according to the specific interactions between hydrophobic particles and gas bubbles, thus the floatability of the particles to be separated [6-9].

Experimental part

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 *in situ* the solid support;
- $CH_3(CH_2)_{10}COONa$ (NaL) solution 0.2% (Fluka) - anionic surfactant (collector);
- superfloc N 300 (Cyanamid) solution 0.1% - nonionic polymeric flocculant;
- NaOH (Lach-Ner) and HCl (Merck) solutions 0.1 - 2 M - precipitating agent and to adjust the *p*H values.

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Table 1

EXPERIMENTAL CONDITIONS OF As (V) SEPARATION BY DISSOLVED AIR FLOTATION

Studied system		**Fe(III)-As(V)-NaL**
$C_{initial\ As(V)}$ (mg/L)		1 ÷ 100
Optimum operating parameters	pH	4 ÷ 5
	Fe(III)/As(V) molar ratio	5
	NaL/As(V) molar ratio	0.5
	dissolved air pressure (bar)	4
	dilution ratio (V_{sample}:V_{water})	3:1
Temperature (K)		295

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;

- centrifuge 5416 Eppendorf;

- digital Orion 290 A pH-meter;

- magnetic stirrer.

Method

Flotation kinetic experiments: 0.3 L samples of aqueous As(V) solutions, with initial concentrations 1 - 100 mgAs(V)/L, were treated with pre-determined 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 *p*H was adjusted to certain values and the solution was magnetically stirred for 5 min, then NaL was added in pre-determined molar ratios 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 DAF technique. At the top of the flotation cell, a thin layer of foam was formed, consisting of floated arsenic-bearing precipitate. Very small amounts of floated solution were collected with a seringe, at certain periods of flotation time, from the lower part of the cell to measure the residual arsenic concentration by AAS. During the experiments, the temperature of solutions was constant and equal to ambient temperature (295K).

The separation efficiency of As(V) is calculated as:

$$\%\mathbf{R} = \left(1 - \frac{C_{As(V)}}{C_{iAs(V)}}\right) \cdot 100$$

where $C_{As(V)}$ is the As(V) concentration at time *t*, and $C_{i\,As(V)}$ is the initial concentration of As(V) in solution, respectively.

Experimental data (represented in graphics as points) were fitted and the curves were plotted (as continuous lines), using Table Curve and Origin, indicating the correlation coefficient *r* as a measure of fitting quality.

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

where: $y_i = f(x_i, a_1 \ldots . a_k)$, a = parameters

Results and Discussion

Preliminary experimental data required for kinetic study

The kinetic experiments were performed at optimum operating parameters of the separation process, previously established in preliminary flotation experiments table 1.

Table 2

CONFIDENCE LIMITS FOR FINAL CONCENTRATIONS AND REMOVAL EFFICIENCIES Of As (V), AT OPTIMUM OPERATING PARAMETERS OF THE PROCESS, FOR DIFFERENT INITIAL As (V) CONCENTRATIONS (PROBABILITY 95%)

$C_{initial\ As(V)}$ mg/L	$C_{final\ As(V)}$ mg/L	R %
1	0.0472 ± 0.0031	95.28 ± 1.24
2	0.0818 ± 0.0046	95.91 ± 0.92
5	0.0936 ± 0.0048	98.13 ± 0.38
10	0.0616 ± 0.0043	99.39 ± 0.17
20	0.0813 ± 0.0048	99.59 ± 0.09
30	0.0839 ± 0.0034	99.72 ± 0.05
40	0.1548 ± 0.0082	99.61 ± 0.08
50	0.1490 ± 0.0077	99.70 ± 0.06
75	0.2214 ± 0.0112	99.70 ± 0.06
100	0.2405 ± 0.0158	99.76 ± 0.06

The effects of As (V) initial concentration on arsenic removal efficiency (% R) by disolved air flotation are presented in table 2.

Confidence limits were established by statistical analysis using the distribution law of W. S. Gosset (*t* distribution) on a lot of 7 repeated tests and show a good reproducibility of the separation process at optimum operating parameters.

The data show that for initial concentrations 10 - 100 mg As(V)/L, separation efficiencies %R = 99.4 are obtained.

Investigations on the separation equilibrium and kinetic studies were based on selected time-dependent experimental data for systems with initial arsenic concentrations of 20 mg As(V)/L, at optimum operating parameters of flotation process.

Separation equilibrium

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. 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).

The separation equilibrium at optimum parameters, both for the system without flocculant and with flocculant, is shown in figure 1 as dependence % R = f (flotation time).

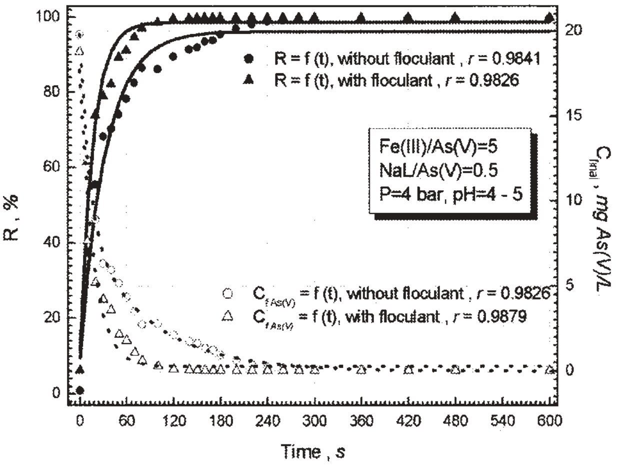

Fig. 1. The dependences %R = f ($\tau_{flotation}$) and $C_{final\ As(V)}$ = f ($\tau_{flotation}$) for the system with and without flocculant

Figure 1 shows that the equilibrium is reached faster (t = 80 s) in the system with Superfloc N 300, the addition of flocculant increasing sensitively the rate of separation (k = 0.068 ± 0.005 s^{-1}, % R_{max} = 98.38 ± 0.97) with respect to the system without flocculant (t = 170 s, k = 0.037 ± 0.003 s^{-1}, % R_{max} = 94.51 ± 1.28).

Estimation of overall kinetic parameters

The overall flotation rate may be written:

$$v_{flotation} = -\left[\frac{dc}{dt}\right] = kc^{n} \qquad (1)$$

where c is the concentration of As (V), t is the time, n is the overall order of the process and k is the overall flotation rate constant. This approach to flotation rate modeling is analogous to that of used in chemical-reaction kinetics. In kinetic modeling, due to the complexity of the studied system, to undeterminable multitude of relationships between simultaneous and succesive micro-processes, it can be often assumed a reaction order and subsequently determined the accuracy of that assumption based upon experimental data. [2, 10-17] Kinetic modeling assuming a first-order process has been found to adequately model most flotation systems, allowing to compare different systems [18-26].

The pseudo-first-order assumption, with n = 1 in equation (1) yields the integrated rate expression:

$$c - c_{initial} = e^{-kt} \qquad (2)$$

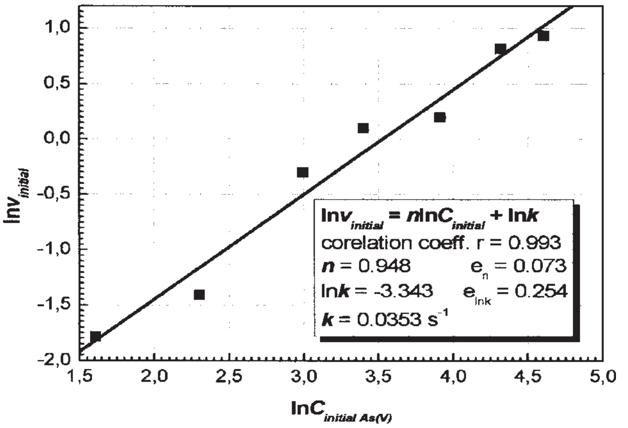

Fig. 2. Dependence $\ln v_{initial}$ = f($\ln c_{initial\ As(V)}$)

or:

$$\ln\left[\frac{c}{c_{initial}}\right] = -kt \qquad (3)$$

The kinetic study estimates the overall order of the separation process and the flotation overall rate constant that were determined by two different methods: differential and integral method [2, 9, 10].

Differential (Initial Rates) Method

The overall flotation constant, k, is determined by plotting (fig. 2) the dependence $\ln v_{initial} = n \times \ln c_{initial} + \ln k$ (where $v_{iinitial}$ is initial rate).

Experimental data presented in figure 2 establish the values of kinetic overall parameters: n = 0.952 ± 0.073 and k = 0.035 ± 0.007 s^{-1}.

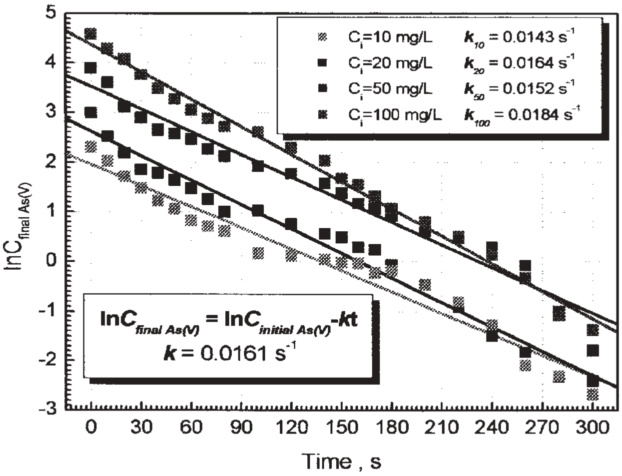

Fig.3. Dependence $\ln c_{final\ As(V)}$ = f(t)

Integral Method

Integral method determines the values of kinetic overall parameters by plotting the dependence $\ln c_{final\ As(V)}$ = f($\ln c_{initial\ As(V)}$ $-kt$) for 4 different initial concentrations of As(V) in solution.

Experimental data (fig. 3) shows the that all the 4 plots are linear, so the assumtion of an overall first-order separation kinetics is valid and the mean value of overall rate constant is k = 0.0161 s^{-1}.

Kinetic modelling. Verification of experimental data on semi-empirical ore flotation kinetic models

Theoretical equations of flotation kinetics presented in literature are generally deduced for ore flotation, by analogy with chemical kinetics, taking into the account the specific interactions between hydrophobic particles and gas bubbles, usually comprising a single solid-particle size and hydrophobic strength. [2, 5, 12, 13, 18, 27] The structural and dimensional characteristics (the distribution of flocs sizes) of the studied system, the special properties of interfaces and physical-chemical specific factors causes difficulties in establishing the kinetic equations that describe macroscopically the flotation process [28-35].

Kinetic modelling on 9 different semi-empirical ore flotation models presented in literature and the interpretation of statistical fitting parameters were performed in order to establish the validity of each model for the studied system (table 3).

Simulated kinetic models correspond to first- and second-order kinetics with different adjustments for a better fit with the experimental data. Most of the models assume that the separation efficiency (%R) is an exponential function of time.

Table 3

STATISTICAL FITTING PARAMETERS FOR KINETIC MODELS

Model	Kinetic equation	R^*	e_{R^*}	k	e_k	r	e_{fit}	Agreement
Classical first-order with constant floatability	$R=R^*[1-\exp(-kt)]$	94.510	1.284	0.037	0.003	0.983	4.567	good
Classical first-order with rectangular floatability	$R=R^*[1-\exp(-kt)/kt]$	83.502	4.878	0.382	0.037	0.417	22.285	bad
First-order with zero-time adjustment	$R=R^*[1-\exp(-k(t+t^*)]$	95.078	1.262	k=0.033 t*=2.525	0.003 1.426	0.985	4.301	good
Reversible first-order	$R=R^*k_1\{1-\exp[-(k_1+k_2)t]\}/(k_1+k_2)$	149.400	6.28e+08	$k_1=0.023$ $k_2=0.014$	98286.04 98286.10	0.983	4.685	bad
Fully-mixed reactor	$R=R^*[1-1/(1+t/k)]$	104.834	0.700	18.517	0.705	0.998	1.549	bad
Gas-solid adsorption	$R=R^*kt/(1+kt)^m$	88.400	4.577	k=0.074 m=0.946	0.008 0.015	0.999	1.243	sufficient
Improved gas-solid adsorption	$R=R^*kt/(1+kt)$	104.834	0.700	0.054	0.002	0.998	1.549	sufficient
Huber-Panu	$R=R^*\{1-[\exp(-k_1t)-\exp(-k_2t)]/(k_2-k_1)\}$	88.240	5.872	$k_1=0.038$ $k_2=1.261$	0.028 0.676	0.544	21.11	bad
Gamma distribution	$R=R^*\{1-[a/(a+t)]^p\}$	122.100	94.367	a=0.300 p=0.122	- 0.070	0.875	12.164	bad

R* - separation efficiency at ∞ time, e - standard error, efit - fit standard error

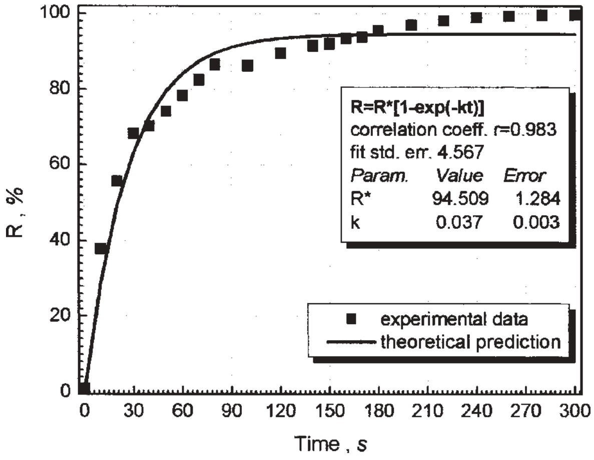

Fig.4. Kinetic modelling on the Classical First-Order Kinetic Model

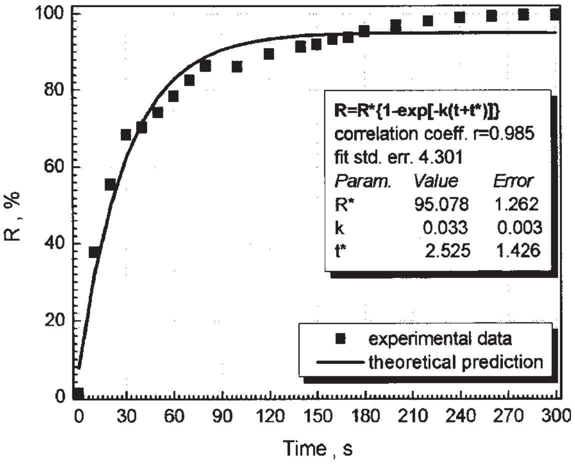

Fig.5. Kinetic modelling on the First-Order Model with Zero-Time Adjustment

The fitting parameters presented in table 3 shows that only 2 models describe, in good agreement with experimental data, the studied separation process: the Classical First-Order Kinetic model and the First-Order Model with Zero-Time Adjustment.

The Classical First-Order Kinetic model describes macroscopically the flotation of hydrophobic particles, considering the particles monodisperse and with constant floatability (fig. 4) and the First-Order Model with Zero-Time Adjustment (fig. 5) modifies the first-order kinetic equation by introducing a *zero-time parameter* (correction factor *t**). The time correction is imposed by the difficulties of establishing time zero ($t^* < 0$ - for stable foams; $t^* > 0$ - for particles with accentuated hydrophoby - float faster).

Conclusions

As (V) oxyanions separation by DAF with anionic collector (NaL) follows an *overall first-order kinetics*: the overall flotation order: $n = 0.952 \approx 1$ and the overall rate constant is $k = 0.03\ s^{-1}$.

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

Simulation results on the first-order kinetic models (with constant floatability and with zero-time adjustment) showed *good agreement with experimental data* ($r = 0.98$, $k = 0.03 \pm 0.003$). The verified ore-flotation models are subjected to further investigations in order to explain the obtained results.

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