

Kinetic Studies of Caffeic Acid - Cr(III)_{aq} Reaction and of the Flotation Process

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Abstract — The paper presents kinetic aspects for the caffeic acid - Cr(III) reaction and for the flotation process of the formed compound, using caffeic acid as collector. The experimental studies were performed at two pH values (6.00 and 7.00) each for two [caffeic acid]:[Cr(III)] molar ratios (1.25:1 and 0.01:1). In both cases (the precipitation / complexing reaction and global flotation processes) the variation of $C_t = f(\text{time})$ were studied by integral method and was calculated the determination coefficient (R^2), rate constant (k) and order of the reaction (n). The obtained results suggest that both, the precipitation / complexing reaction and flotation processes follow a 1st global kinetic order. By applying some kinetic models with different adjustments used in ore flotation and by interpretation of statistical fitting parameters was established the validity of the semi-empirical models for experimental data of the flotation process for caffeic acid-Cr(III) system.

Keywords — Complexing, kinetics, modeling, removal

I. INTRODUCTION

Chromium is an important bioelement and its role in metabolic processes is still a controversial subject, some laboratory studies showing that Cr(III) can cause allergies, and certain compounds of Cr(III) are toxic, even genotoxic to human body [1]. Cr(III) toxicity on environmental organisms is a concern of the specialists ([2]-[5]).

A technique for Cr(III) removal from aqueous media is flotation, in which hydrophobization can be achieved by different ways, one of them being the use of a collector reagent. The flotation process involves two stages: (1) precipitation / complexation followed by (2) the flotation of the formed compound [6].

The Cr(III) immobilization and its removal from aqueous solutions by flotation using the caffeic acid (3-(3,4-dihydroxyphenyl)-2-propenoic acid) as collector require experimental studies regarding kinetics of the precipitation / complexing reaction and of the flotation process.

Caffeic acid can be found in nature in certain plants ([7]-[10]) and presents complexing capacity for toxic metal ions ([11]-[15]). The literature data regarding caffeic acid complexation with Cr(III) are limited [16].

The kinetics of the flotation process is complex and difficult to approach due to the complexity of the overall flotation process determined by multitude of micro-processes which arising simultaneously or successively [6]. Also, this explains limiting of the interpretation of the experimental data only to determining of the reaction order in each case studied, by generally verifying the 1st or 2nd order, in generally [6]. Nevertheless flotation presents interest for many authors in terms of the kinetics study and treating of polluted water [17]-[21].

The separation of Cr(III) by flotation with caffeic acid as collector reagent consist in two stages: a first stage that involves the precipitation / complexation reaction of Cr(III) with caffeic acid; and a second stage - the flotation of insoluble species formed between caffeic acid and Cr(III), aspect which was not previously studied according to information from the studied literature.

For the first stage of the flotation process, that involves the caffeic acid -Cr(III) reaction, we may apply the classical kinetics models. For the entire separation process by flotation, which includes the precipitation, a kinetic study is more difficult to achieve; in this sense, the data available in the literature regarding the kinetics of ions or precipitates flotation indicate the use of chemical kinetics models with different adjustments [6].

The aim of this study was to investigate the kinetics of the precipitation / complexing reaction of the Cr(III) with caffeic acid and of the flotation processes of the caffeic acid - Cr(III) formed compound, respectively by:

- establishing the probable rate order for the precipitation / complexing reaction and for the global flotation process.
- verifying of some kinetic models with different adjustments for the flotation process.

Four kinetic models of 1st order with different adjustments (Table I), which were initially established to ores flotation, have been verified for the experimental data obtained in the flotation process of Cr(III) with caffeic acid as collector. These models take into account the heterogeneity of the particles and the process stages [6].

II. EXPERIMENTAL

Precipitation / complexing reaction experiments: was prepared Cr₂(SO₄)₃ working solution 250 mg L⁻¹ from Cr₂(SO₄)₃ stock solution 5000 mg L⁻¹, which was mixed with caffeic acid, (C₉H₈O₄), solution from Sigma Aldrich (working solution was an alcoholic solution water: ethanol = 70:30 with 0.0125 M concentration mixed with NaOH 2M) in pre-determined [caffeic acid]:[Cr(III)] molar ratios. Working solutions was mixed under stirring (at 245 rot min⁻¹ stirring rate) using a Heidolph Vibramax 100 stirrer.

The solutions were used immediately after their preparation to avoid the transformation and decomposition reactions. The pH was adjusted using NaOH solutions (with 0.1M and 0.2M concentrations) in the presence of air and was measured using a 290A ORION pH-meter. Praestol 610 BC flocculant (weak cationic) 0.02% aqueous solution was used for flocs agglomeration. After the pH adjustment, the samples were collected at certain periods for determination the residual Cr(III) concentration, (C_t) using an AAS UNICAM PAY SP9 atomic absorption spectrophotometer. The obtained results were processed with Excel program for determining the probable order of the reaction.

Flotation process: one proceeded as in the case of the precipitation / complexing reaction and after the pH adjustment, the sample was quantitatively transferred to the flotation column where the colloidal hydrophobic particles were floated to the surface with air micro bubbles (3:1 $V_{\text{sample}}:V_{\text{water}}$ dilution ratio and $4 \times 10^5 \text{ N m}^{-2}$ dissolved air pressure, p) by DAF technique. At certain periods of the flotation time, small amounts of floated solution were collected from the lower part of the cell to measure the residual Cr(III) concentration using an AAS UNICAM PAY SP9 atomic absorption spectrophotometer. The obtained experimental data were processed by applying the kinetic models based on chemical analogy (integral method) and the kinetic models with certain adjustments (Table I) proposed by different researchers for the ores flotation, using Solver analysis tool of Excel program.

TABLE I -- THE STUDIED KINETIC MODELS [6]

Kinetic model	Kinetic equation
The 1st order classical	$R = R^* \times [1 - \exp(-k \times t)]$
The 1st order in two stages	$R = R^* \times [k' / (k' - k^*) \times (1 - \exp(-k^* \times t)) - k^* / (k' - k^*) \times (1 - \exp(-k' \times t))]$
The 1st order reversible	$R = R^* \times [k + (k + k^-) \times (1 - \exp(-(k + k^-) \times t))]$
The 1st order with zero time adjustment	$R = R^* \times [1 - \exp(-k(t + t^*))]$

These equations were deduced by analogy with chemical kinetics, without taking into account the peculiarities of the process and the specific interactions of hydrophobic particles and gas bubbles of the flotation column [6]. For each studied model was obtained the dependence of separation efficiency versus time, $R (\%) = f(t)$, for 0-10 minutes appreciated as the time to steady state is reached, at constant temperature ($t = 20^\circ\text{C}$). Comparing the theoretical curves of each model with the experimental data obtained at the separation parameters (previously established in preliminary flotation experiments) (Table II) was possible a quantitative evaluation on the kinetics of flotation process.

TABLE II -- PARAMETERS OF THE CAFFEIC ACID – Cr(III) REACTION AND OF THE FLOTATION SEPARATION PROCESS

Separation parameters / Type of the process	Caffeic acid –Cr(III) reaction	Flotation process (Variant 1)	Flotation process (Variant 2)
pH	6.0	6.00	7.0
[caffeic acid]:[Cr(III)] molar ratio	1.25:1	1.25:1	0.01:1
Stirring rate / rot min ⁻¹		245	
$C_0 / \text{mg L}^{-1}$		250	
$V_{\text{sample}}:V_{\text{waeter}}$	-		3:1
$p / \text{N m}^{-2}$	-		4×10^5

III. RESULTS AND DISCUSSION

A. Kinetic Studies for the Cr(III)-Cafeic Acid Precipitation / Complexing Reaction

The caffeic acid - Cr(III) reaction order was determined by the integral method using kinetic models based on chemical analogy. The kinetics calculations for caffeic acid-Cr(III) reaction were performed based on concentration and time obtained data at the parameters presented in Table II (pH 6.0 and 1.25:1 [caffeic acid]:[Cr(III)] molar ratio), for which were previously obtained the best results for the flotation experiments.

Different reaction orders have been tested ($n = 0.5; 1; 1.5; 2$) and the calculated kinetic parameters were collected in Table III.

TABLE III-- THE RESULTS OF THE KINETIC CALCULATIONS FOR THE DIFFERENT REACTION ORDERS, n , FOR THE CAFFEIC ACID – Cr(III) REACTION

Experimental conditions	n	k / s^{-1}	R^2
Variant 1 [caffeic acid]:[Cr(III)] 1.25:1 Stirring rate 245 / rot min ⁻¹ pH 6.00	0.5	0.0396	0.9831
	1	0.0043	0.9875
	1.5	0.0004	0.9867
	2	0.00005	0.9812

The better linear adjustment, $\ln(C_0/C_t) = f(t)$, (Figure 1) and the high value of the determination coefficient ($R^2 = 0.9875$) (Table III) for the calculation considering 1st order were obtained. These results suggest that the precipitation / complexing reaction between caffeic acid-Cr(III) follows a 1st order kinetics being represented by the Eq. (1) [6]:

$$\ln\left(\frac{C_t}{C_0}\right) = -k_1 \cdot t$$

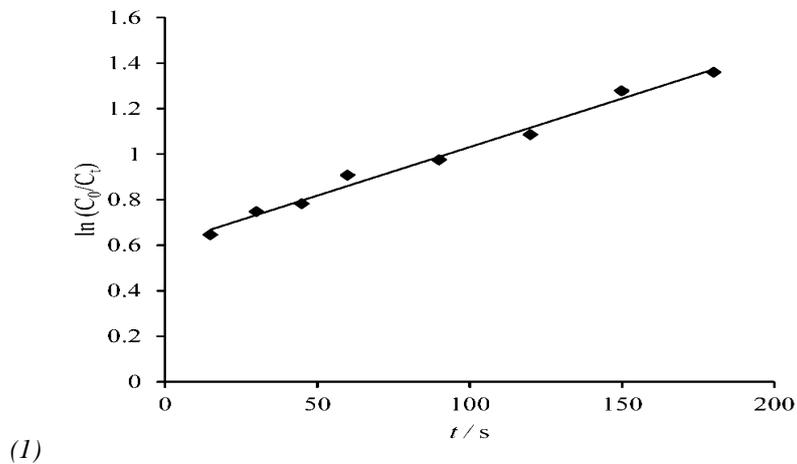


Fig. 1 Kinetic curves for the caffeic acid-Cr(III) reaction (1.25:1 [caffeic acid]:[Cr(III)], molar ratio, pH 6.00), for the 1st reaction order

B. Kinetic Study of the Caffeic Acid - Cr(III) Flotation Process Based on Integral Method

Different orders for the flotation process have been tested ($n = 0.5; 1; 1.5; 2$) for each [caffeic acid]:[Cr(III)] molar ratio and for both pH values studied (Table II).

The better linear adjustment, $\ln(C_0/C_t) = f(t)$, for both flotation processes – variant 1 and 2 (Figure 2 and 3 respectively) and the high value of the determination coefficient ($R^2 = 0.9642$ for variant 1 and $R^2 = 0.9731$ for variant 2) (Table IV) for the calculation considering 1st order were obtained. These results suggest that the flotation process for Cr(III) removal using caffeic acid follows kinetics of 1st order.

TABLE IV -- THE RESULTS OF THE KINETIC CALCULATIONS FOR DIFFERENT REACTION ORDERS, n , IN BOTH VARIANTS (1 AND 2) OF THE FLOTATION PROCESSES

Experimental conditions	n	k	R^2
Variant 1 [caffeic acid]:[Cr(III)] 1.25:1 pH 6.0 Stirring rate 245 / rot min ⁻¹ V _{sample} :V _{water} 3:1 $p / 4 \times 10^5 \text{ N m}^{-2}$	0	0.0367	0.6912
	0.5	0.0122	0.8306
	1	0.0045	0.9642
	1.5	0.0018	0.9422
	2	0.0009	0.8903
Variant 2 [caffeic acid]:[Cr(III)] 0.01:1 pH 7.0 Stirring rate 245 / rot min ⁻¹ V _{sample} :V _{water} 3:1 $p / 4 \times 10^5 \text{ N m}^{-2}$	0	0.0001	0.9557
	0.5	0.0006	0.9691
	1	0.0019	0.9731
	1.5	0.0072	0.9671
	2	0.0277	0.9516

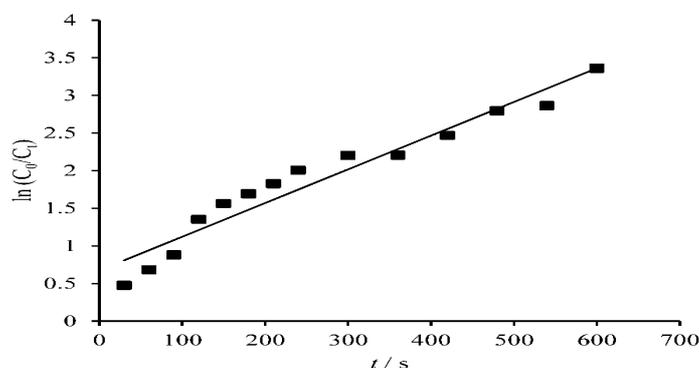


Fig. 2 Kinetic curves for the caffeic acid-Cr(III) flotation – variant 1 (1.25:1 [caffeic acid]:[Cr(III)] molar ratio, pH 6.0), for the 1st order of the global process

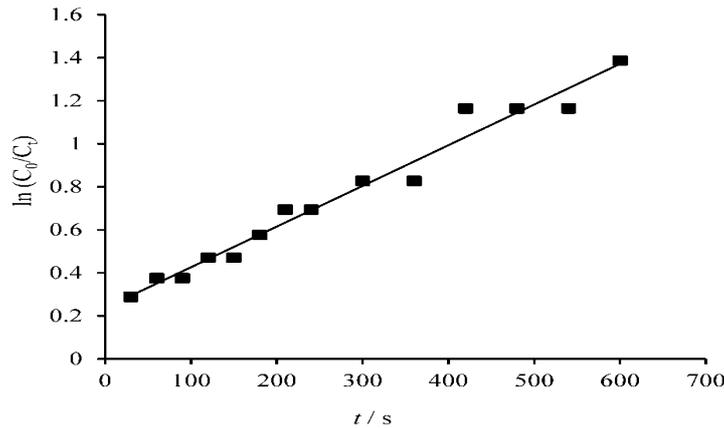


Fig. 3 Kinetic curves for the caffeic acid-Cr(III) flotation – variant 2 (0.01:1 [caffeic acid]:[Cr(III)] molar ratio, pH 7.0), for the 1st order of the global process

C. Kinetic Modeling. Verification of Some Kinetic Models with Different Adjustments for the Caffeic Acid - Cr(III) Flotation Processes

For the experimental data obtained from the flotation processes were verified kinetic models presented in the literature, which were initially established for ore flotation and whose application has been tested to variant 1 of the flotation (Table II) [6]. Thus, were tested four models of 1st kinetic order with adjustments that take into account the heterogeneity of the particles and the deployment stages. The interpretation of statistical fitting parameters was performed in order to establish the validity of each model for the studied system.

The fitting parameters for the flotation process – variant 1 (Table V) shows that only two models describe, in good agreement with experimental data: 1st order in two stages and 1st order reversible kinetic models.

TABLE V -- RATE CONSTANT AND STATISTICAL FITTING PARAMETERS FOR THE STUDIED KINETIC MODELS IN THE FLOTATION PROCESS – VARIANT 1

Model / Determined parameters	R*	k/k+	k*/k/t*	SRR	r	e
The 1st order classic model	0.9603	0.1		0.009318	0.9948	0.00056
The 1st order in two stages	0.9688	1.9937	0.1322	0.001056	0.9993	9.52×10 ⁻⁵
The 1st order reversible	0.9999	0.1258	0.0040	0.001055	0.9993	9.56×10 ⁻⁵
The 1st order with zero time adjustment	0.96808	0.0635	0	0.967886	0.9914	0.00512

By examining the values of the correlation coefficient, r, it can be observed that the experimental data are better fitted by the theoretical curve for: 1st order in two stages and 1st order reversible kinetic models (r = 0.9993 for both kinetic models).

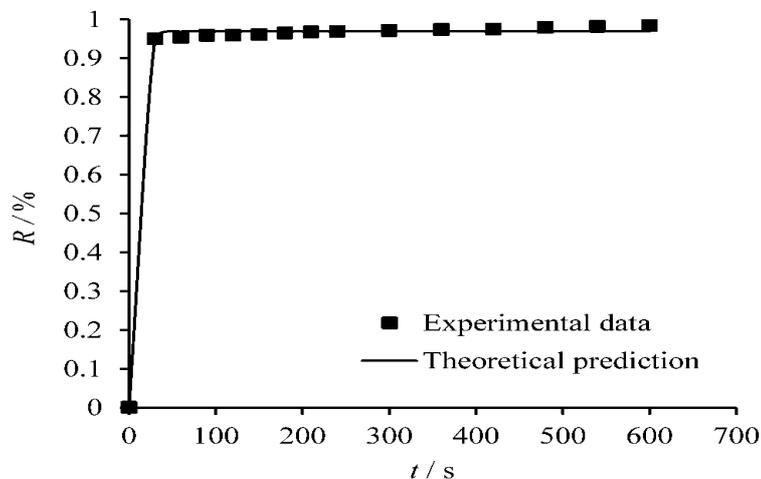


Fig. 4 Fitting of experimental data on theoretical curve for the 1st order in two stages kinetic model for the flotation process – variant 1

These results are also sustained by the low values for the standard error, e, and for the sum of squares of residues, SRR, for the two previously mentioned models compared to the other two models studied (SRR = 0.001056 for 1st order in two stages kinetic model and SRR = 0.001055 for 1st order reversible kinetic model).

Given that the value of rate constant, k , for the 1st order reversible kinetic model is small and can be neglected; thus the equation of 1st order reversible kinetic model reduces to the 1st order classical model equation.

Based on the experimental data (Figure 4) it can be concluded that from all the four kinetic models studied, the 1st order in two stages kinetic model describes better and fits on the experimental data of the overall flotation process.

The fitting parameters for the flotation process – variant 2 (Table VI) shows that only two models describe, in good agreement with experimental data: classical 1st order and 1st order in two stages kinetic models.

By examining the SRR values it can be observed that the experimental data better fitted the theoretical curve for the 1st order in two stages kinetic model ($SRR = 1.49 \times 10^{-7}$) compared to the other three kinetic models studied.

TABLE VI-- RATE CONSTANT AND STATISTICAL FITTING PARAMETERS FOR THE STUDIED KINETIC MODELS IN THE FLOTATION PROCESS – VARIANT 2

Model / Determined parameters	R^*	k/k_+	$k^*/k_-/t^*$	SRR	r	e
The 1st order classic model	0.9996	0.3629	-	1.47×10^{-7}	0.9999	8.64×10^{-11}
The 1st order in two stages	0.9996	0.2715	1.6348	1.49×10^{-7}	0.9999	2.99×10^{-8}
The 1st order reversible	0.9793	1.0234	0.0033	0.0053	0.9999	4.14×10^{-28}
The 1st order with zero time adjustment	0.9997	0.2146	0	1.99×10^{-6}	0.9999	6.34×10^{-7}

Although the difference between the SRR values obtained for the classical 1st order kinetic model ($SRR = 1.47 \times 10^{-7}$) and 1st order in two stages ($SRR = 1.49 \times 10^{-7}$) is small, we can conclude that, from the four kinetic models studied, the 1st order in two stages kinetic model is better fitted experimental data and describes the kinetic of the overall flotation process (Figure 5).

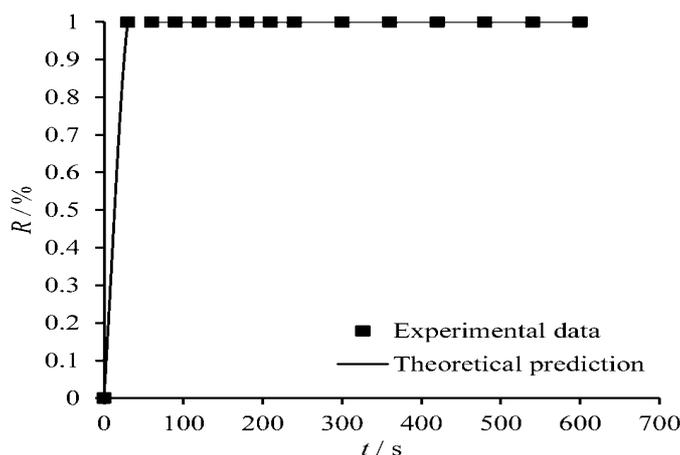


Fig. 5 Fitting of experimental data on theoretical curve for the 1st order in two stages kinetic model for the flotation process – variant 2

IV. CONCLUSIONS

Within this research the kinetic aspects of the flotation process were studied, that include caffeic acid-Cr(III) reaction and flotation process of the formed compound. The obtained results suggest that the caffeic acid - Cr(III) reaction (as first stage of the flotation process) and the global flotation process of the formed compound follow for a formal kinetics of 1st order.

Based on the results obtained after verifying of the kinetic models with different adjustments, one can conclude that the kinetics of the overall flotation process (variant 1 and 2) is described by 1st order in two stages kinetic model, as this model is better fitted by the experimental data.

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