Kinetic Studies of Caffeic Acid - Pb(II)\textsubscript{aq} Reaction and of Their Flotation Process

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The paper presents kinetic aspects for the caffeic acid - Pb(II) reaction and flotation process (ion and precipitate flotation) of the formed compound. The experiments of the precipitation/complexation reaction were performed at two pH values of the solution (pH = 5.5 and 6.0) at various [caffeic acid]:[Pb(II)] molar ratios (1.25:1; 1.5:1; 2:1) and at different stirring rates (245; 215; 180; 150 rot/min). The kinetic studies of the flotation process were performed at pH=6.00, [caffeic acid]:[Pb(II)] molar ratio = 1:1, 245 rot/min stirring rate for ion flotation and at pH=11.00, [caffeic acid]:[Pb(II)] molar ratio = 0.05:1, 245 rot/min stirring rate for precipitate flotation. In both cases (the precipitation/complexation reaction and flotation processes) were studied the variation of $C_{[Pb]} = f (time)$, based on which was calculated the determination coefficient ($R^2$), rate constant (k) and order of the reaction (n) by integral method and by applying some kinetic models with different adjustments. The obtained results suggest that both, the precipitation/complexation reaction and flotation processes (ion and precipitate flotation) follow a 1st global kinetic order (n=1).

Keywords: Pb(II), caffeic acid, reaction, flotation, kinetics

Lead is one of the most abundant heavy metals from the environment which may come from different sources: the chemical industry, mining, electrochemical industry, metallurgical industry, weapons manufacturing, waste incineration etc. [1]. Pb(II) toxicity on environmental organisms is a concern of the specialists [2-7].

In order to select a separation method, it is important to know the lead speciation in the aqueous media, because these species will be involved in the reactions that allow their immobilization and removal from the system. Studies on the speciation of Pb(II) in solution were performed by several researchers. According to the studies made by Matis and Zouboulis the speciation distribution is dependent on the pH and concentration of the solution. At pH < 7 the predominant species is Pb\textsuperscript{2+}, and at pH = 9.00-11.50 the predominant species is Pb(OH)\textsubscript{2}, which reaches a maximum at pH range pH = 10.00 to 11.00 [8-11].

A technique for Pb(II) 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 [12].

The use of the caffeic acid (3-(3,4-Dihydroxyphenyl)-2-propenoic acid) as collector in flotation requires experimental studies, performed in order to establish the optimum parameters for lead immobilization and removal from aqueous solutions.

The main reasons for selecting caffeic acid as collector reagent are presented as follows: caffeic acid can be found in nature in certain plants and therefore, the by-products resulted from pharmaceutical industry (after plant processing) represent an important source; [13-16]; caffeic acid presents complexing capacity for toxic metal ions [17-19]; in the scientific literature, the data regarding caffeic acid complexation with metallic ions [18-21] and, in particular with caffeic acid - Pb(II) complex [17] are limited.

The kinetics of the flotation process is complex and difficult to approach due to the multitude of micro-processes arising simultaneously or successively, that define it on the whole [12]; nevertheless flotation presented interest for many authors in terms of the kinetics study [22-26] and treating of polluted water [27-31].

The separation of Pb(II) with caffeic acid by flotation consist in two stages: a first stage that involves the precipitation/complexation reaction with caffeic acid and a second stage - flotation of the formed insoluble species. Thus, a study concerning the dynamics of the Pb(II) separation process by flotation with caffeic acid involves a stage of precipitation, which was not previously studied according to information from the literature.

For the first stage of the flotation process, that involves the caffeic acid-Pb(II) 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 [12]; 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 [12].

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 1\textsuperscript{st} or 2\textsuperscript{nd} order [12].

The aim of this study was to investigate the kinetics of the precipitation/complexation reaction of the lead(II) with caffeic acid and of the flotation processes, respectively (after the flotation experiments performed for lead(II) removal from aqueous systems) by:
- establishing the probable rate order for the precipitation/complexation reaction and for the flotation process.
- verifying of some kinetic models with different adjustments for the flotation process.

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The rate constant for the $1^{st}$ order reaction, $k_1$, and for $2^{nd}$ order reaction, $k_2$, is determined with the relations (1) and (2) respectively [12,32]:

$$k_1 = \frac{1}{t} \ln \left( \frac{c_0}{c_t} \right) = \frac{2.303}{t} \ln \left( \frac{c_0}{c_t} \right)$$  \hspace{1cm} (1)\\

$$k_2 = \frac{1}{t} \frac{c_t - c_0}{c_t}$$  \hspace{1cm} (2)

where:
- $c_0$ – initial concentration of the coligand, mg L$^{-1}$;
- $c_t$ – coligand concentration (mg L$^{-1}$) in the solution at the $t$ time (s).

For the experimental data obtained in the process of flotation of Pb(II) with caffeic acid as collector, kinetic models available in the literature were verified; these kinetic models initially were established to ores flotation and has been tested to the precipitates flotation. Thus, four models with different adjustments were verified for 1st kinetic order (table 1) that take into account the heterogeneity of the particles and the process stages.

**Experimental part**

**Reagents**
- Pb(NO$_3$)$_2$ stock solution 5000 mg L$^{-1}$ and working solutions with different concentrations;
- caffeic acid (C$_9$H$_8$O$_4$) Sigma Aldrich (working solution was alcoholic solution water: ethanol = 70:30 vol with 0.0125 M concentration);
- NaOH solution 0.1 M and 2M;
- Praestol 610 BC aqueous solution (0.02%), weak cationic flocculant.

**Equipment**
- Heidolph Vibramax 100 stirrer, with variable speed;
- 290A ORION pH-meter;
- dissolved air flotation (DAF) unit [12];
- AAS UNICAM PAY SP9 atomic absorption spectrophotometer, with Pb cathode lamp.

**Methods**

In the first stage, a 200 mg L$^{-1}$ Pb(NO$_3$)$_2$ working solution was mixed with caffeic acid solution. The sample was maintained under stirring until the $pH$ was adjusted using NaOH solutions. After the $pH$ adjustment, the final concentration (C$_{pH=5.5}$) of the sample was determined. The solutions were used immediately after their preparation to avoid transformation and decomposition reactions. The kinetic experiments were performed at $pH=5.5$ and 6.0 values (because at these $pH$ values Pb(II) reacted with caffeic acid forming a compound of high flotability) in the presence of air, at different stirring rates. The obtained results were processed with Excel program for determining the probable order of the reaction.

For the flotation process, were verified the kinetic equations proposed by different researchers [12] for the ores flotation. 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.

The experimental data obtained after Pb(II) separation by precipitation/flotation were processed using Solver analysis tool of Excel program. For each studied model was obtained the dependence of separation efficiency versus time, $R\% = f(t)$, for 0-10 min (after steady state is reached) appreciated as the time to steady state is reached, at constant temperature ($T=20°C$). Comparing the theoretical curves of each model with the experimental data obtained at the separation parameters (table 2), allowed a qualitative evaluation on the kinetics of flotation process.

The obtained results were processed with Solver tool of the Excel program in order to determining the global order, $n$, and to establishing the kinetic model for the flotation processes. The separation parameters are presented in the table 2.

**Results and discussions**

**Kinetic studies for of Pb(II)-caffeic acid precipitation/complexation reaction**

The kinetic study for cafeic acid-lead(II) reaction was performed (fig. 1) at the variable $pH$ values ($pH=5.5$ and 6.0) and [caffeic acid]:[Pb(II)]=1.25:1 molar ratio. From the figure 1 one observes that the linear allure of the graphical representation certifies a $1^{st}$ order kinetics.

Different reaction orders have been tested ($n= 0.5$; 1; 1.5; 2) for each $pH$ value ($pH=5.5$ and 6.0) and the calculated kinetic parameters were collected in table 3.

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Kinetic equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>The $1^{st}$ order classic model</td>
<td>$R = R^* [1 - \exp(-kt)]$</td>
</tr>
<tr>
<td>The $1^{st}$ order in two stages</td>
<td>$R = R^* \times [k(k-k^<em>)\times(1-\exp(-k^<em>t)) - k^</em>(k-k^</em>)\times(1-\exp(-kt))$</td>
</tr>
<tr>
<td>The $1^{st}$ order reversible</td>
<td>$R = R^* \times \left(k_r\times(1-\exp(-k_r t))\right)$</td>
</tr>
<tr>
<td>The $1^{st}$ order with zero time adjustment</td>
<td>$R = R^* \times [1-\exp(-k(t+t^*))$</td>
</tr>
</tbody>
</table>

1$R$ – separation efficiency at the $t$ time, $R^*$ - separation efficiency at the infinite time, $k$ – rate constant
2$k^*$ - the rate constant of the transfer process of the component from the liquid phase in the foam, $k_r$ - rate constant of the transfer process of the component from the foam in the concentrate
3$k^*$ - rate constant of the transfer process component from the liquid phase in the foam, $k_r$ - rate constant of the reverse transfer process of the component from the foam in liquid phase
4$t^*$ - time correction

<table>
<thead>
<tr>
<th>Separation parameters / Type of the process</th>
<th>cafeic acid - Pb(II) reaction</th>
<th>Precipitates flotation</th>
<th>Ion flotation</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.5; 6.0</td>
<td>11.00</td>
<td>6.0</td>
</tr>
<tr>
<td>Molar ratio C$<em>{cafeic\ acid-C</em>{Pb(II)}}$</td>
<td>1.25:1</td>
<td>0.05:1</td>
<td>1:1</td>
</tr>
<tr>
<td>Stirring rate, (rot/min)</td>
<td>245; 215; 180; 150</td>
<td>245</td>
<td></td>
</tr>
<tr>
<td>Initial concentration Pb(II), (mg L$^{-1}$)</td>
<td></td>
<td>240.2</td>
<td></td>
</tr>
<tr>
<td>V$<em>{sample}$/V$</em>{water}$</td>
<td>3:1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure, (N/m$^2$)</td>
<td>4x10$^4$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 1** STUDIED KINETIC MODELS [12]

**Table 2** PARAMETERS OF THE CAFFEIC ACID – Pb(II) REACTION AND OF THE FLOTATION SEPARATION PROCESS
From the table 3 one can observe the high value of the determination coefficient ($R^2 = 0.9888$ at $pH = 5.5$ and $R^2 = 0.9847$ at $pH = 6.0$), obtained from the plot $\ln(C_0/C_t) = f(t)$, which confirms a 1st order kinetics for the caffeic acid-Pb(II) reaction.

The kinetic studies performed in order to determine the influence of the stirring rate on the probable reaction order (table 4, figs. 2,3) showed that the optimum stirring rate is 245 rot/min, because at this stirring rate were obtained maximum values of the determination coefficient, $R^2$, ($R^2 = 0.9888$ for $pH = 5.5$ and $R^2 = 0.9847$ for $pH = 6.0$), that is why all other kinetic studies were performed at this stirring rate. The maximum value of $R^2$ is in agreement with the values of the maximum separation efficiency ($R\%$) obtained for Pb(II) separation by flotation with caffeic acid at the same speed of 245 rot/min. For all studied values of the stirring rate, the probable reaction order obtained by the integral method was $n = 1$ (table 4).

Kinetic study of the Pb(II)-caffeic acid flotation process

Kinetic studies performed for the flotation process were conducted by applying the classical kinetic equations and the kinetic models with certain adjustments.

Kinetic study based on classical kinetic equations

The flotation experiments were performed with Pb(NO$_3$)$_2$ solutions of 250 mg L$^-1$ Pb(II) at different $pH$ values ($pH = 6.0$ in the case of ion flotation and respectively, $pH = 11.00$ in the case of precipitate flotation) and at different [caffeic acid]:[Pb(II)] molar ratios (1:1 in the case of ion flotation and respectively, 0.05:1 in the case of precipitate flotation). For each molar ratio different dependences were studied (fig. 4) in order to establish the flotation process order.

Different orders for the flotation process have been tested ($n = 0.5; 1; 1.5; 2$) for each [caffeic acid]:[Pb(II)] molar ratio at $pH = 6.0$ and 11.0. The calculated kinetic parameters were collected in table 5 from which one can observe that the high value of $R^2$ ($R^2 = 0.9901$ for ion flotation process and $R^2 = 0.9880$ for precipitate flotation process) determined from the $\ln(C_0/C_t) = f(t)$ plot, certifies a 1st order kinetics for the flotation process of the formed compound.

Kinetic study based on verification of some kinetic models with different adjustments

Kinetic models in ion flotation process

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 classical kinetic
Kinetic models for precipitate flotation process

By examining the values of the correlation coefficient, $r$, it can be observed that the experimental data better fitted the theoretical curve for the 1$^{st}$ order classical, 1$^{st}$ order in two stages and 1$^{st}$ order with zero time adjustment kinetic models ($r=0.9997$ for all three kinetic models) compared to the 1$^{st}$ order reversible kinetic model ($r=0.9996$).

The standard error values, $e$, for the three models mentioned are larger than the standard error value for 1$^{st}$ order reversible kinetic model ($e=0.05364$) compared with SRR values for the other three models confirm that the 1$^{st}$ order classical kinetic model, 1$^{st}$ order in two stages and the 1$^{st}$ order with zero time adjustment model is better overlapping on the experimental data compared with 1$^{st}$ order reversible kinetic model.

Given that, for the 1$^{st}$ order kinetic model with zero time adjustment, the obtained value for time, $t^*$, is very small ($t^*=4.55 \times 10^{-6}$) and the value of rate constant, $k$, is identical with the $k$ value for the 1$^{st}$ order classical model ($k=1.475$ s$^{-1}$), the equation of 1$^{st}$ order reversible model reduces to the classical equation of 1$^{st}$ order classical model.

For the 1$^{st}$ order classical model was obtained a SRR value smaller than the SRR value for 1$^{st}$ order model in two stages, which leads to conclude that, from the four kinetic models, the 1$^{st}$ order in two stages, 1$^{st}$ order reversible (\(k=0.9994\) for all three kinetic models). These results are also sustained by the low values of the standard error, $e$, for the three previously mentioned models compared to the 1$^{st}$ order kinetic model with zero time adjustment.

The lowest value of SRR (sum of squares of residues) was obtained for: 1$^{st}$ order classic model (SRR=0.001055) and 1$^{st}$ order reversible (SRR=0.001055) but, given that the value of rate constant, $k$, for the 1$^{st}$ order reversible model is small and can be neglected, and the value of rate constant, $k$, (\(k=1.299\) s$^{-1}$) for the 1$^{st}$ order classical model is almost identical with the value of rate constant, $k$, (\(k=1.258\) s$^{-1}$) for the 1$^{st}$ order reversible model, the equation of 1$^{st}$ order reversible model reduces to the 1$^{st}$ order classical model equation.

By comparing the SRR values obtained for 1$^{st}$ order classic (SRR = 0.001055) and of 1$^{st}$ order in two stages model (SRR = 0.001056), although there is low difference between the SRR values, one can conclude that the 1$^{st}$ order classical model is fitted better on the experimental data.

Based on the data represented in figure 5a and table 6 it can be concluded that from all the four kinetic models studied, the 1$^{st}$ order kinetic classical model describes better and fits on the experimental data of the overall flotation process.

### Table 5

<table>
<thead>
<tr>
<th>$n$</th>
<th>pH</th>
<th>$k$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>6.0</td>
<td>0.162</td>
<td>0.9808</td>
</tr>
<tr>
<td>11.0</td>
<td>0.162</td>
<td>0.9876</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>6.0</td>
<td>0.021</td>
<td>0.9901</td>
</tr>
<tr>
<td>11.0</td>
<td>0.0006</td>
<td>0.9880</td>
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<tr>
<td>1.5</td>
<td>6.0</td>
<td>0.002</td>
<td>0.9857</td>
</tr>
<tr>
<td>11.0</td>
<td>0.002</td>
<td>0.9446</td>
<td></td>
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<tr>
<td>2</td>
<td>6.0</td>
<td>0.0006</td>
<td>0.9683</td>
</tr>
<tr>
<td>11.0</td>
<td>0.0005</td>
<td>0.8675</td>
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### Table 6

<table>
<thead>
<tr>
<th>Model / Determined parameters</th>
<th>$R^*$</th>
<th>$k/k_0$</th>
<th>$k^<em>/k^{</em>/0}$</th>
<th>SRR</th>
<th>$r$</th>
</tr>
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<tbody>
<tr>
<td>The 1$^{st}$ order classic model</td>
<td>0.98684</td>
<td>0.1475</td>
<td>-</td>
<td>0.00052484</td>
<td>0.9997</td>
</tr>
<tr>
<td>The 1$^{st}$ order in two stages</td>
<td>0.98682</td>
<td>0.1508</td>
<td>1.6047</td>
<td>0.00052510</td>
<td>0.9997</td>
</tr>
<tr>
<td>The 1$^{st}$ order reversible</td>
<td>0.9793</td>
<td>1.0235</td>
<td>0.0034</td>
<td>0.0005364</td>
<td>0.9996</td>
</tr>
<tr>
<td>The 1$^{st}$ order with zero time adjustment</td>
<td>0.9897</td>
<td>0.1475</td>
<td>4.55 \times 10^{-6}</td>
<td>0.000525</td>
<td>0.9997</td>
</tr>
</tbody>
</table>

### Table 7

<table>
<thead>
<tr>
<th>Model / Determined parameters</th>
<th>$R^*$</th>
<th>$k/k_0$</th>
<th>$k^<em>/k^{</em>/0}$</th>
<th>SRR</th>
<th>$r$</th>
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</table>

Fig. 4 Kinetic curves for the caffeic acid-Pb(II) ion flotation ([caffeic acid]:[Pb(II)]=1:1 molar ratio, pH=6.0) and for the caffeic acid-Pb(II) precipitate flotation ([caffeic acid]:[Pb(II)]=0.05:1 molar ratio, pH=11.0) at 245 rot/min, for the reaction order, $n=1$.
models studied, the 1st order classical model is better fitted experimental data and describes the kinetic of the overall flotation process (table 7, fig. 5b).

Conclusions

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

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

References