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MODELING OF SOLVENT SUBLATION PROCESS AND IDENTIFICATION OF PARAMETERS AFFECTING THE REMOVAL OF Ni(II), Cu(II) AND Fe(III) IONS

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The solvent sublation method was used to remove Ni(II), Cu(II) and Fe(III) ions from wastewater. The purpose of this work was to develop a mathematical model of the solvent sublation process and identify the parameters that affect the degree of pollutant removal. The correlation analysis was used to evaluate parameters that influence on the process, and multiple correlation coefficient, Fisher's test and root-mean-square deviation were calculated to assess the adequacy of the suggested model. It was shown that such parameters as pollutant initial concentration, organic extractant type, the Me:surfactant ratio, temperature, and the process time have a significant impact on the solvent sublation process efficiency. The removal degree of the studied ions above 90% was achieved with the following parameters: pH of 9, 5 and 7 for solutions with Ni(II) ions, Cu(II) ions and Fe(III) ions, respectively; and Me:surfactant ratio of 2:1, 1.5:1 and 2:1 for solutions with Ni(II), Cu(II) and Fe(III) ions, respectively. The process time for all type of pollutants should be 15–20 minutes, and the initial concentration should be more than 100 mg/dm^3. The results showed that the models successfully allows simulating the process efficiency and predicting Ni(II), Cu(II) and Fe(III) ions removal. The obtained results can be used to optimize the solvent sublation process as a technique for post-treatment of wastewater produced in electroplating industry.

Keywords: solvent sublation, heavy metal, wastewater, mathematical modeling, correlation analysis.

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Introduction

Notwithstanding the ever water quality requirements tightening, the overall water pollution is steadily increasing. Among the most dangerous pollutants are heavy metals. As reported by the Ministry of Energy and Environment Protection of Ukraine[1], heavy metals make a significant contribution to the water pollution in Ukraine. According to studies, they enter water bodies together with insufficiently treated wastewater from electroplating industry, tanning and other processing industries [1]. Most often, wastewater treatment technology in such enterprises includes only pre-clarification and mechanical impurities and suspended solids removal in the settling tanks, and heavy metal ions treatment is almost not carried out [2]. Thus, the existing wastewater treatment methods require revision and extension.

The solvent sublation technique is one of the available methods, which combines the advantages of flotation and extraction [3–5]. The model approach makes it possible to study the influence of process parameters on the removal of heavy metal ions from contaminated water, as well as to predict the residual concentration of pollutants over time [6].

[1] National report on drinking water quality and the state of drinking water supply in Ukraine in 2019. Official website of the Ministry for Communities and Territories Development of Ukraine. URL: https://www.minregion.gov.ua/wp-content/uploads/2020/11/proekt-nacz.-dop.-za-2019.pdf.

In this paper, the modeling of solvent sublation process is used to assess the impact of technological parameters on the Ni^{2+}, Cu^{2+} and Fe^{3+} removal from the model waters, which simulate real wastewater.

Experimental

Equipment and materials

The solvent sublation process was carried out in a cylindrical glass column where a model solution, a surfactant and organic extractants were added [7–9]. The compressor supplied gas to the bottom of the column through a porous glass baffle. The gas flow rate was flattened out by a rotameter. Determination of the residual pollutant concentration was carried out by means of a scanning spectrophotometer Portlab 501 and pH of aqueous solutions was defined with a ionometer pH-150MI.

Ni^{2+}, Cu^{2+} and Fe^{3+}-containing model solutions were prepared from $NiSO_4 \cdot 7H_2O$, $CuSO_4 \cdot 5H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$, respectively. The stock solution concentration was 1 g/dm^3 for Ni^{2+} and Cu^{2+} model solutions, and 0.5 g/dm^3 for Fe^{3+} ions. Working concentrations of each type of pollutant are presented in Table 1.

Table 1

Working concentrations of the studied pollutants

Pollutant	Stock solution, g/dm^3	Working concentrations, mg/dm^3
Ni^{2+}	1	5, 10, 20, 50, 100, 150, 200, 250 and 300
Cu^{2+}	1	20, 50, 100, 150, 200 and 250
Fe^{3+}	0.5	10, 20, 50 and 100
Cu^{2+} and Ni^{2+}	0.5	50, 100 and 150
Fe^{3+} and Ni^{2+}	0.5	5, 10, 20, 50 and 100

Potassium palmitate, potassium laurate and sodium caprylate surfactants (0.05 mol/dm^3) were used to remove pollutants. Hexane, heptane, octane, 2,2,4-trimethylpentane, butan-1-ol, 2-methylpropan-1-ol, hexan-1-ol, decan-1-ol, 3-methylbutan-1-ol and propan-1-ol were used as organic extractants. Sodium hydroxide (0.1 mol/dm^3) was used to adjust the pH value. All studies were conducted in the temperature range 15–30^{0}C.

Laboratory tests

Laboratory tests were performed in order to determine the effect of variables of solvent sublation process, such as pH, pollutant initial concentration, organic extractant type, the Me:surfactant ratio, temperature, and the process time, on the removal degree of Ni^{2+}, Cu^{2+} and Fe^{3+} heavy metal ions. In all experiments, the volume of the studied aqueous solution was 200 cm^3 and the volume of organic extractant was 10 cm^3. The solvent sublation process lasted until the residual heavy metal ions concentration stays at a constant level [10].

Pollutant removal degree X (%) was calculated by the following equation (1):

$$X = \frac{C_0 - C_r}{C_0} \cdot 100\%, \qquad (1)$$

where C_0 and C_r are the initial concentration of pollutant in the solution (mg/dm^3) and the residual concentration of pollutant (mg/dm^3), respectively.

Correlation analysis and modeling of solvent sublation process

Correlation analysis was fulfilled to define process variables, which have a significant impact on the solvent sublation process. A matching between process parameters and heavy metal ions Ni^{2+}, Cu^{2+}, Fe^{3+} removal degree was assessed using a scatter chart. The sample correlation coefficient r was calculated by the following equation:

$$r = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(u_i - \bar{u})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2 (u_i - \bar{u})^2}}, \qquad (2)$$

where x_i and u_i $\left(i = (\overline{1, n})\right)$ are the pollutant removal degree and the studied process variables, respectively; $\bar{x}$ and $\bar{u}$ are the means of X and U, respectively; n is the number of measurements.

As a mathematical model, it was proposed to choose an ordinary differential first-order equation:

$$T \cdot C_r' + C_r = f(u), \qquad (3)$$

where C_r is the residual concentration of pollutant (mg/dm^3); and u is the process variables that significantly influence on the process.

Using system the STAR [11] software, the mathematical model coefficients and such statistical parameters as multiple correlation coefficient R, Fisher's test F and root-mean-square deviation (RMSD) σ for each pollutant were calculated.

Results and discussion

The scatter charts and calculated correlation coefficients showed that the following process variables have a significant impact on the heavy metal ions removal degree: pH, pollutant initial concentration, organic extractant type, the Me:surfactant ratio, and the process time, whereas temperature has a minor effect on the process

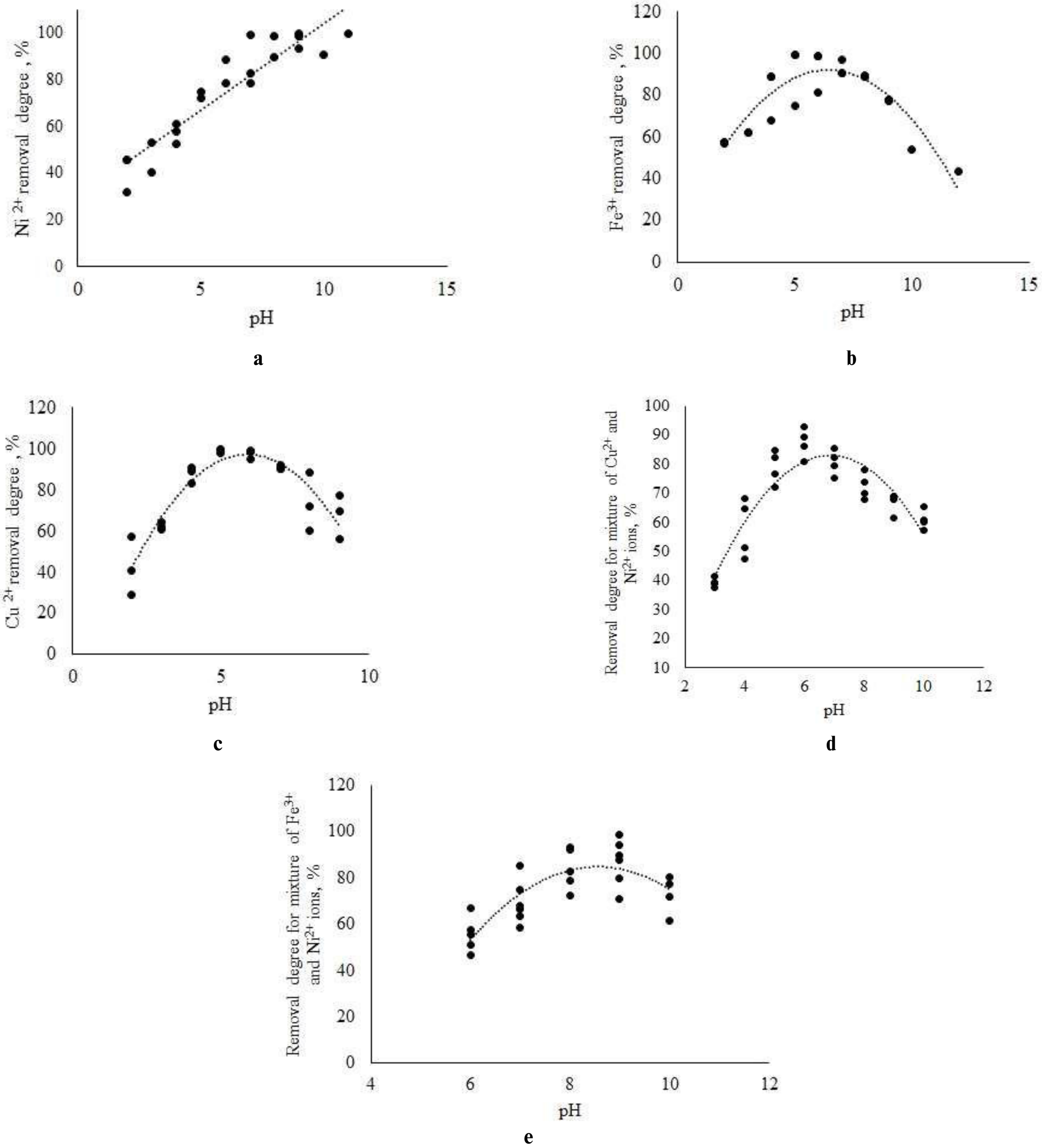

Fig. 1. Scatter chart for the studied pollutants and their mixtures: a – Ni^{2+} removal degree and pH; b – Fe^{3+} removal degree and pH; c – Cu^{2+} removal degree and pH; d – mixture of Cu^{2+} and Ni^{2+} ions removal degree and pH, mixture of Fe^{3+} and Ni^{2+} ions removal degree and pH

efficiency. An example of a scatter charts for studied pollutants is shown in Fig. 1, which depicts dependence of the Ni^{2+}, Cu^{2+}, Fe^{3+}, mixture of Cu^{2+} and Ni^{2+} ions and mixture of Fe^{3+} and Ni^{2+} ions removal degree on pH. The sample correlation coefficient varies from 0.795 to 0.928 (Table 1); the maximum value was obtained for Ni^{2+} ions, while the minimum value was obtained for the mixture of (Fe^{3+}+Ni^{2+}) ions. Thus, the matching between the pH and the removal degree is quite strong. It should be noted that cases (b)–(e) in Fig. 1 have a nonlinear dependence.

Similar results were obtained for other process parameters: pollutant initial concentration, the Me:surfactant ratio, temperature, and the process time. The generalized results are presented in Table 2.

Figure 2 shows that the 3-methylbutan-1-ol is most versatile of the studied organic extractants. From the laboratory tests, it can be observed that the highest removal degrees are achieved at the following parameters: pH is 9, 5, and 7 for solutions containing Ni^{2+} ions, Cu^{2+} ions, and Fe^{3+} ions, respectively;

Table 2

Degree of correlation between process variables and heavy metal ions removal degree

Process variables	Correlation coefficient of studied pollutants				
	Ni^{2+}	Cu^{2+}	Fe^{3+}	mixture of Cu^{2+} and Ni^{2+} ions	mixture of $Fe^{3+}$and Ni^{2+} ions
pH	0.928	0.913	0.887	0.919	0.795
Pollutant initial concentration	0.999	0.883	0.459	0.858	0.679
Me:surfactant ratio	0.643	0.998	0.826	0.642	0.775
Temperature	–0.779	–0.188	0.264	–	–
Process time	0.971	0.255	0.945	0.858	0.661

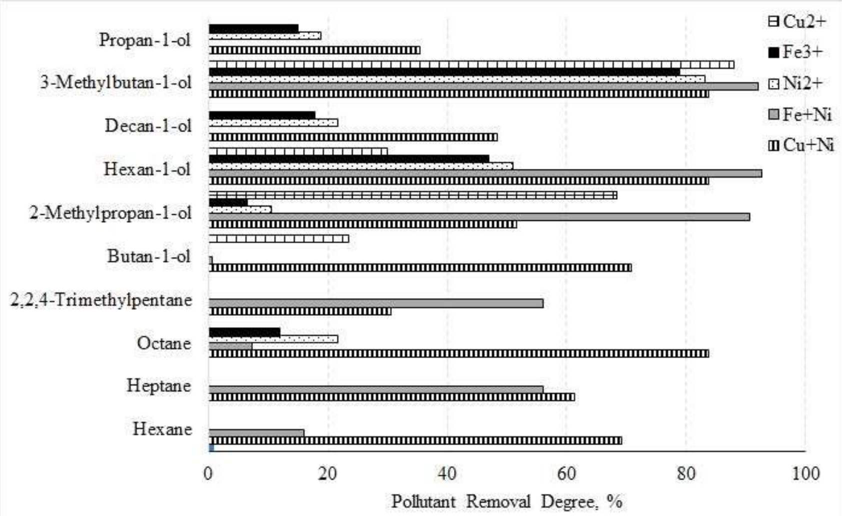

Fig. 2. Bar chart for organic extractants and the removal degree of Ni^{2+}, Cu^{2+} and Fe^{3+} ions and their mixtures

Table 3

Comparative table of constructed mathematical models

Case description	Coefficients of Eq. (4)		Statistical parameters		
	T	k	F	r	root-mean-sc deviatioı
Model water with initial concentration of Ni^{2+} ions is 20 mg/dm^3, pH 9, Me:surfactant ratio=2:1, organic extractant is 3-methylbutan-1-ol	11.77	0.0017	5.53	0.9	0.0520
Model water with initial concentration of Ni^{2+} ions is 100 mg/dm^3, pH 9, Me:surfactant ratio=1:2, organic extractant is 3-methylbutan-1-ol	17.13	0.0586	5.59	0.91	0.4700
Model water with initial concentration of Fe^{3+} ions is 10 mg/dm^3, pH 7, Me:surfactant ratio= 2:1, organic extractant is 3-methylbutan-1-ol	14.45	0.0642	7.04	0.93	0.0393
Model water with initial concentration of Fe^{3+} ions is 10 mg/dm^3, pH 7, Me:surfactant ratio=2:1, organic extractant is 3-methylbutan-1-ol	21.34	0.0626	10.44	0.95	0.0668
Model water with initial concentration of Cu^{2+} ions is 20 mg/dm^3, pH 5.5, Me:surfactant ratio=1.5:1, organic extractant is 3-methylbutan-1-ol	9.48	0.0102	6.65	0.92	0.0580
Model water with initial concentration of Cu^{2+} ions is 100 mg/dm^3, pH 5.5, Me:surfactant ratio=1:1, organic extractant is 3-methylbutan-1-ol	15.23	0.0403	5.81	0.91	0.4600
Model water with initial concentration of Cu^{2+} ions is 10 mg/dm^3, pH 9, Me:surfactant ratio=2:1, organic extractant is 3-methylbutan-1-ol	14.06	0.0210	7.49	0.93	0.4000
Mean value	14.78	0.037			

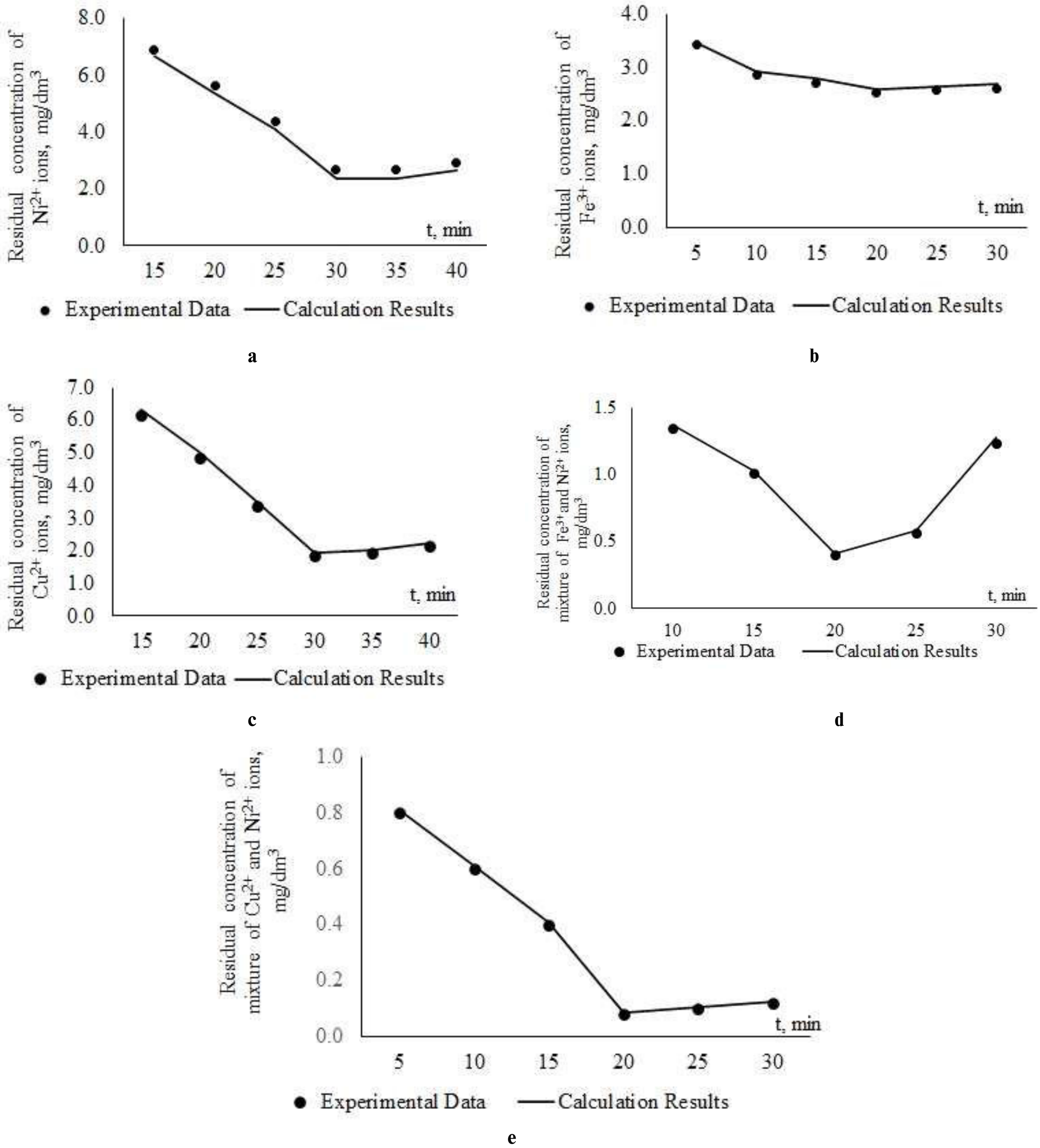

Fig. 3. Comparative chart of experimental data (Exp_data) and calculated results (Calc_res): a – change in Ni^{2+} residual concentration over time; b – change in Fe^{3+} residual concentration over time; c – change in Cu^{2+} residual concentration over time; d – change in mixture of Fe^{3+} and Ni^{2+} ions residual concentration over time; and e – change in mixture of Cu^{2+} and Ni^{2+} ions residual concentration over time

Me:surfactant ratio is 2:1, 1.5:1, and 2:1 for solutions containing Ni^{2+}, Cu^{2+}, and Fe^{3+} ions, respectively; the optimal process time for all studied solutions is 15–20 minutes. The highest removal level is achieved at the initial concentration of more than 100 mg/dm^3.

With regard to the solvent sublation process simulation, the mathematical model (3) parameters were calculated. In total, 7 models were constructed with satisfactory statistical parameters: multiple correlation coefficient is higher than 0.9 and RMSD is less than 0.5. The coefficients and statistical parameters of the obtained models are shown in Table 3. Since the obtained coefficients are similar, it was proposed to use a generalized model with averaged coefficients as presented below:

$$14.78 \cdot C_r' + C_r = 0.037u, \qquad (4)$$

where C_r is the residual concentration of studied pollutant (mg/dm^3); and u is the process variable.

Matching between experimental data and results calculated by Eq. (4) is quite satisfactory, as can be seen from Fig. 3.

Thus, Eq. (4) can be used to forecast how residual concentration of different type of pollutants changes over time. It can also be used to study the solvent sublation process kinetics and to predict residual concentration of the pollutant in operating conditions.

Conclusions

The removal patterns of Ni^{2+}, Cu^{2+}, Fe^{3+} ions from aqueous solutions by solvent sublation were studied. Statistical relation between solvent sublation process parameters and the removal degree of studied ions and their mixtures was analyzed. It was shown that such parameters as pollutant initial concentration, organic extractant type, the Me:surfactant ratio, temperature, and the process time have a significant impact on the solvent sublation process efficiency.

The removal degree of the studied ions above 90% is achieved with the following parameters: pH is 9, 5 and 7 for solutions with Ni^{2+} ions, Cu^{2+} ions and Fe^{3+} ions, respectively; Me:surfactant ratio is 2:1, 1.5:1 and 2:1 for solutions with Ni^{2+}, Cu^{2+} and Fe^{3+} ions, respectively. The process time for all type of pollutants should be 15–20 minutes, and the initial concentration should be more than 100 mg/dm^3.

The data set obtained under various experimental conditions and STAR software was used to construct mathematic model. The ordinary first-order differential equation was used as a primal model. The performance of each model was assessed by such statistical parameters as multiple correlation coefficient, Fisher's test and root-mean-square deviation. Among the 27 obtained models, 7 were selected that have the best statistical parameters, and a generalized model was constructed by averaging coefficients. The proposed generalized model has a high ability to predict a pollutant residual concentration. The results obtained can be used both for studying solvent sublation process kinetics and for predicting the water quality after treatment.

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МОДЕЛЮВАННЯ ПРОЦЕСУ ФЛОТОЕКСТРАКЦІЇ І ВСТАНОВЛЕННЯ ПАРАМЕТРІВ, ЯКІ ВПЛИВАЮТЬ НА ВИДАЛЕННЯ ІОНІВ Ni(II), Cu(II) І Fe(III)

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Для видалення іонів Ni(II), Cu(II) і Fe(III) із стічних вод використано метод флотоекстракції. Метою даної роботи було математичне моделювання процесу флотоекстракції для оцінювання параметрів, що впливають на ступінь видалення забруднюючих речовин. Кореляційний аналіз було виконано для оцінювання параметрів, що впливають на процес, а для оцінювання адекватності запропонованої моделі розраховано коефіцієнт множинної кореляції, коефіцієнт Фішера та середньоквадратичне відхилення. Показано, що такі параметри як початкова концентрація забруднювача, тип органічного екстрагенту, відношення метал:поверхнево-активна речовина, температура і тривалість процесу мають найбільший ефект на ефективність процесу флотоекстракції. Ступінь вилучення досліджених іонів вище 90% була досягнута за наступних значень параметрів: pH 9, 5 і 7 для розчинів, що містять іони Ni(II), Cu(II) і Fe(III), відповідно; відношення метал:поверхнево-активна речовина 2:1, 1,5:1 і 2:1 для розчинів, що містять іони Ni(II), Cu(II) і Fe(III), відповідно. Для всіх типів іонів тривалість процесу має становити 15–20 хв, а початкова концентрація повинна бути вищою, ніж 100 мг/дм^3. Результати показали, що отримані моделі мають прийнятні характеристики і можуть бути використані для прогнозування видалення іонів Ni(II), Cu(II) і Fe(III). Результати можуть бути використані для оптимізації процесу флотоекстракції як методу доочищення стічних вод гальванічної промисловості.

Ключові слова: флотоекстракція, важкі метали, стічні води, математичне моделювання, кореляційний аналіз.

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