SIMULATION OF SOLVENT SUBLATION PROCESS TO FORECAST THE AMOUNT OF REMOVED DYES

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The solvent sublation technique was applied to remove water-soluble dyes from aqueous solutions. The aim of this work is computer simulation of the solvent sublation process in prediction the amount of removed dyes. In this study, mathematical statistic methods were used to define the process variables that have the real impact on the solvent sublation process. The STAR system mathematical tools were used to find a proper model that govern the change of dye residual concentration over time, as well as to carry out parametric identification. The simulation results show that the models have a good performance in the simulation and prediction of the cationic and anionic dyes removal from aqueous solutions. The results can be used to optimize the solvent sublation process as a technique of wastewater treatment.
Keywords: dye, simulation, solvent sublation, waste water.

Introduction

A large amount of wastewater contains a variety of toxic and hazardous dyes. Significant part of the wastewater comes from the factories producing these dyes, as well as from the textile industry. An undertreated wastewater entering the water objects as a result of intensive industry activity has led to the fact that in the last 25-30 years the resource of self-healing properties of water resources of Ukraine has almost been depleted (Ratnaweera et al., 2015).

Dyes form a large part of organic compounds that contains unsaturated bonds (chromophores) such as $-C=C-$, $-N=N-$ and $-C\equiv N-$, as well as functional groups such as $-NH$, $-OH$, $-COOH$ and $-SO_3H$. Chromophores define coloring ability of dyes while functional groups responsible for dyes fixation on tissues.

The textile industry uses active dyes with high color characteristics that have resistant physico-chemical and physical-mechanical parameters. Therefore, getting into the environment, dyes easily color the water and the surrounding area, thereby creating unfavorable aesthetic perception, worsening the organoleptic indicators of water. In addition, dyes can also significantly affect the photosynthesis capability of the water objects inhabitants, reducing the intensity of light penetration and may also be toxic to some aquatic species of flora and fauna due to aromatic rings and chlorine substitutes. This can lead to mass death of fish, violation of self-purification processes, sanitary state of the water objects, severe human poisoning.

According to recent publications (Nesterova and Saribekov, 2010, Forgacs et al., 2004, Leskiv, 2008), hybrid methods application allows to treat waste water more efficiently. One of the advanced wastewater treatment technique that removed dyes is solvent sublation (Lu, 2001, Bi 2007, 2010). This technique combines two methods – ion flotation and solvent extraction - and is based on the ascension of gas bubbles to the surface; thus, the polutant (sublate) is transferred to the organic phase (Lu 2001, 2007). Surfactants are used in the solvent sublation process as collectors. The surfactant molecules directly participate in the formation of the sublate and affect the removal rate. The surfactants reduce the value of free surface energy at the boundary of the organic and water phases, and stabilize the surface of the bubbles. The surfactants are bound to dye ions in insoluble hydrophobic sublattices, which are ascended from the water phase to organic (Lu 2003, Astrelin I. M. et al., 2013).

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Simulation of the solvent sublation processes of dyes removal allows studying the influence of the process variables on the efficiency of the process, to justify the choice of the surfactants and to predict the amount of the removed dye.

The aim of the paper is simulation of the solvent sublation process as a wastewater treatment technique in order to specify the process variables that have a significant impact on the removal of various types of dyes.
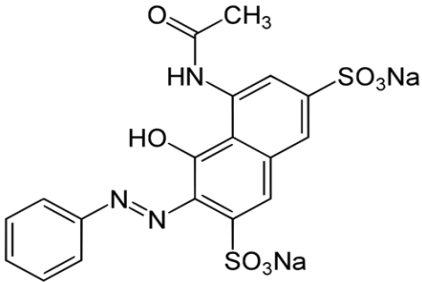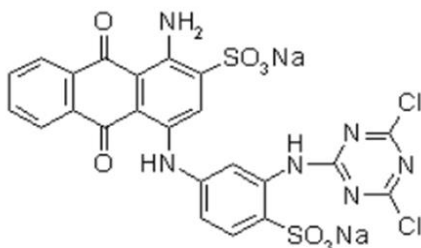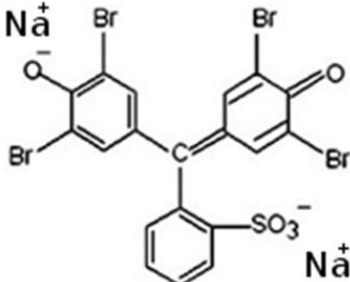
Experimental Part
Equipment and Materials Used
A cylindrical glass column with a diameter of 35 mm, compressor to supply air at the bottom of the column through a porous glass partition were used to simulate the solvent sublation process. The gas flow was controlled by a rotameter. Scanning spectrophotometer Portlab 501 model was used to define a residual dye concentration. PH meter PH-150MI model was used to measure pH of aqueous solutions.

Dyes which are analyzed include water-soluble cationic and anionic dyes: Malachite green, Methyl violet, Crystal violet, Methylene blue, Bromocresol green, Bromophenol blue, Disodium Reactive Blue 4, Indigo carmine and Acid Red 1. A brief description of each type of dyes are presented in Tables 1 and 2. Sodium hydroxide 0.1 mol/dm^3 and Hydrochloric Acid 0.1 mol/dm^3 were used to the pH correction. Anionic surfactant sodium dodecyl sulfate and cationic surfactant hexadecylpyridinium bromide were used to remove cationic and anionic dyes respectively.
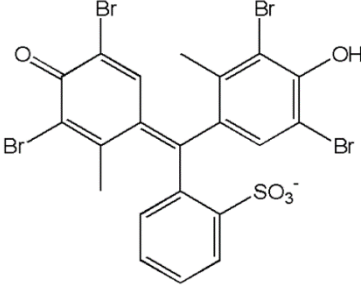
Table 1. Anionic Dyes.

#	Name	Chemical and Skeletal formulas	Brief description
1	Acid Red 1	$C_{18}H_{13}N_3Na_2O_8S_2$	Homogeneous powder of red color is used for dyeing of natural and artificial silk. Coloring is easily washed off with hot soapy water.
2	Disodium Reactive Blue 4	$C_{23}H_{12}Cl_2N_6Na_2O_8S_2$	Dichlorotriazin active dye, giving the material a navy color. Like other triazine active dyes, it is fixed as a result of interaction the dye with the functional groups of the fiber to form a covalent bond.
3	Bromophenol blue	$C_{19}H_{10}Br_4O_5SNa_2$	Natural dye, also used in laboratory practice as a pH-indicator and marker for electrophoresis. It can be applied in the pH range from 3.0 to 4.6. At pH below 3.0, the solution is yellow, above 4.6 is purple.
4	Indigo carmine	$C_{16}H_8N_2Na_2O_8S_2$	It is used at ink manufacture, food coloring (E132, also known as indigotin), as well as in chemistry

| | | | as redox and acid-base indicator and reagent for the O_2 and O_3 photometric determination. It is well known in medicine as a diagnostic material, for example, in histological studies. |

Table 2. Cationic Dyes.

#	Name	Chemical formula	Brief description
1	Malachite green	$C_{23}H_{25}N_2Cl$	It is an acid-base indicator: in aqueous solutions in a strongly acidic medium, it has a yellow color, and at pH above 11.6 it is discolored due to addition of hydroxyl to form triphenylcarbinol. It has a wide use, although it is traditionally used as a dye. It is also used in microscopy, veterinary, photometric studies.
2	Methyl violet	$C_{24}H_{28}N_3Cl$	It belongs to the class of aniline dyes. It is an acid-base indicator, thus it is most often used in analytical chemistry. In addition, it is used in microbiology for the coloring of pathogenic organisms and their detection. The industry uses it as an ingredient in the ink and it is used limited to the fabrics and wool dyeing.
3	Crystal violet	$C_{25}N_3H_{30}Cl$	It is also known as the Gencian Violet and belongs to the class of aniline dyes. It is most often used in analytical chemistry as an indicator, in microbiology as a detecor of pathogenic organisms. In industry it is used as an ink component the or as a dye for fabrics.
4	Methylene blue	$C_{16}H_{18}ClN_3S$	Organic basic thiazine dye used for dyeing cotton, wool and silk in a bright blue color, but the paint is destroyed in the light. In analytical chemistry it is used to determine chlorates, perchlorates, cations of mercury, tin, magnesium, calcium, cobalt, cadmium. In medicine, it is used as an antiseptic and antidote for poisoning with cyanide, carbon monoxide and hydrogen sulfide. Also used in microscopy, aquarium and photography.
5	Bromocresol green	$C_{21}H_{14}Br_4O_5S$	It is actively used in analytical chemistry in acid-base titration. During researches it is possible to observe the transition of coloring of solution from light yellow to blue color at pH interval from 3.8 to 5.4. Due to its excellent chemical properties,

| | | | such a reagent is often used to precisely determine albumin in plasma or serum. |

Static laboratory tests

Laboratory tests are carried out for each analyzed dye at 25°C and to study the effect of process variables such as pH, the dye:surfactant ratio and the process time. In all tests, the initial dye concentration is 10 mg/dm³, the volume of the studied aqueous solution - 200 cm³, the organic part - 10 cm³. The solvent sublation process lasted until the residual dye concentration came to stay at constant level.

Dye removal degree is calculated by equation (1):

$$R(\%) = (\frac{C_0 - C_r}{C_0}) \times 100, \tag{1}$$

in which, C_o and C_r are the initial concentration of dye in the solution (mg/dm³) and the residual concentration of dye (mg/dm³) respectively.

Solvent Sublation Process Simulation

In order to determine the process variables that have a real impact on the solvent sublation process, a correlation analysis is performed. A scatter plot is used to define a matching between process variables and dye residual concentration. Correlation coefficient is calculated for each "process parameter- residual concentration" pair.

Using system the STAR (Sanginova and Kulevskiy, 2018) software, it is proposed to use an ordinary first-order differential equation (2) as a mathematical model that simulate residual concentration behaviour of various dyes:

$$T \cdot y' + y = Q(x_1, x_2, \text{K}, x_n) \tag{2}$$

in which, y is the residual dye concentration mg/dm³, x_i ($i = \overline{(1, n)}$) are the process variables that have the large impact on the process, n – number of process variables.

The coefficients of mathematical models for each dye are computed using the GEM subsystem of the STAR system. The GEM subsystem is also used to calculate such statistical parameters as multiple correlation coefficient r, Fisher ratio F and root-mean-square deviation (RMSD) σ.

Results and discussion

The results of correlation analysis showed that pH, dye:surfactant ratio and process time the most closely related to the dye residual concentration. An example of a scatter plot for Methylene blue is shown in Fig. 1, in which X is the dye:surfactant ratio and Y is the residual concentration. The correlation coefficient in this case is -0.889, thus, the matching between the dye:surfactant ratio and the dye residual concentration is quite strong. Correlation analysis is performed for each type of dye. The summarized results of the correlation analysis are presented in Tables 3 and 4.
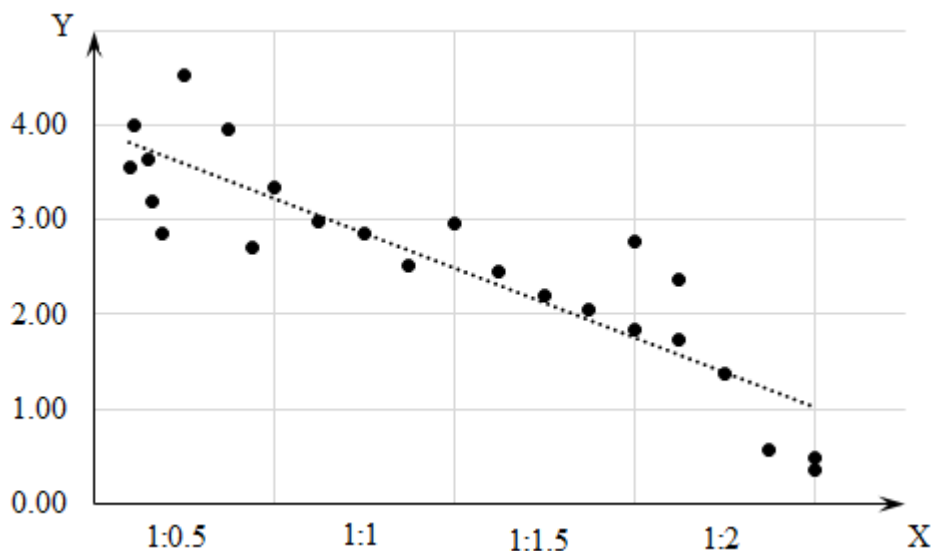
Fig 1. Scatter plot for Methylene blue: X is the dye:surfactant ratio, Y is the dye residual concentration

Table 3. Degree of correlation between process variables and anionic dyes residual concentration.

Process variables	Correlation coefficient of Anionic Dyes			
	Acid Red 1	Disodium Reactive Blue 4	Bromophenol blue	Indigo carmine
pH	0.835	0.883	0.825	0.696
Contact time	-0.877	-0.583	-0.590	-0.771
Dye : surfactant ratio	-0.328	-0.318	-0.758	0.466

Table 4. Degree of correlation between process variables and cationic dyes residual concentration.

Process variables	Correlation coefficient of Cationic Dyes				
	Malachite green	Methyl violet	Crystal violet	Methylene blue	Bromocresol green
pH	0.381	0.291	0.966	0.915	0.234
Contact time	-0.823	-0.916	-0.686	-0.724	-0.669
Dye : surfactant ratio	0.467	-0.325	-0.774	-0.889	0.712

At the next stage of the simulation, the coefficients of the mathematical model (2) are calculated. The example of mathematical model for Bromophenol blue dye is presented below:

$$5{,}18 \cdot y' + y = -0{,}10 \cdot x_1 - 5.09 \cdot 10^{-2} \cdot x_2 + 0.37 \cdot x_3, \tag{3}$$

in which y is the dye residual concentration mg/dm^3; x_1 is pH value, x_2 is the dye : surfactant ratio; x_3 is the process time, min.

Fisher ratio in this case is 9.01, multiple correlation coefficient is 0.94 and RMSD is 0.219. Thus, matching between experimental data and predicted results is quite satisfactory. The graph of the dye residual concentration change over time is shown in Fig. 2. As can be seen, the equation (3) describes the process of changing the Bromophenol blue dye concentration over time with a sufficient degree of accuracy. The equation (3) can be used to predict changes in the Bromophenol blue dye concentration.

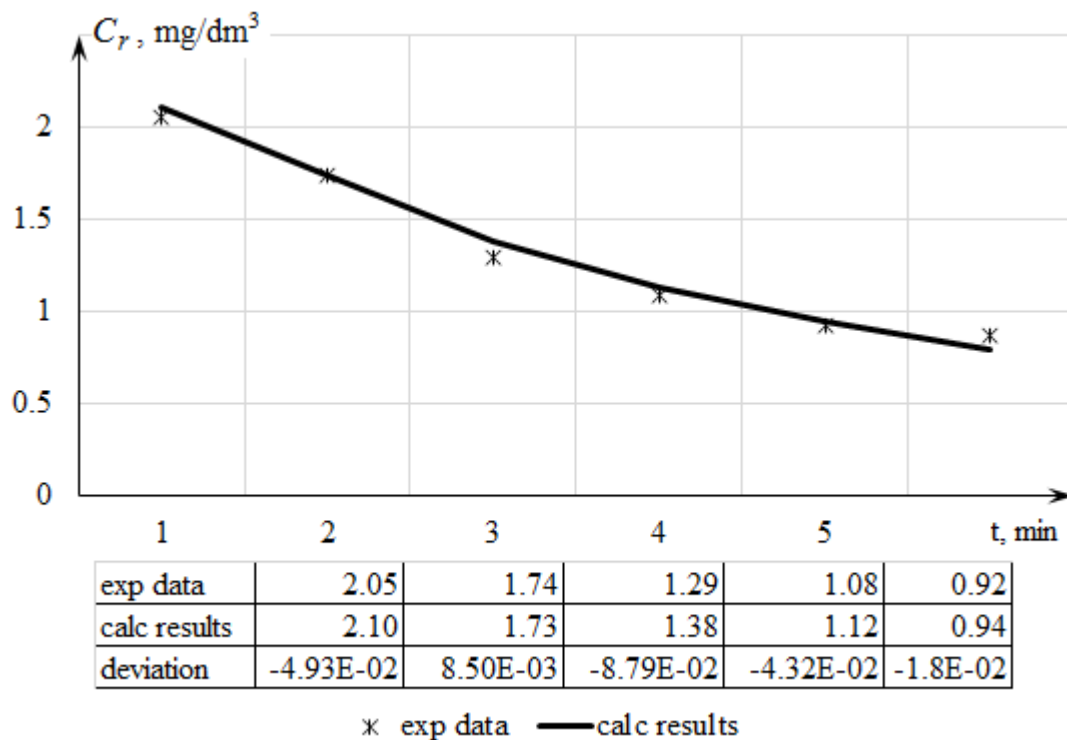|	1	2	3	4	5
exp data	2.05	1.74	1.29	1.08	0.92
calc results	2.10	1.73	1.38	1.12	0.94
deviation	-4.93E-02	8.50E-03	-8.79E-02	-4.32E-02	-1.8E-02

✳ exp data　——calc results

Fig 2. The Bromophenol blue dye residual concentration change over time

Table 5 shows the results of simulation of studied dyes residual concentration as well as statistical parameters of the obtained models. The output graphs of solvent sublation process simulation are shown in Fig. 3 and 4.

Table 5. Comparative table of studied dyes.

| #	Water-soluble dyes	Coefficients of Equation (2)				Statistical Parameters		
		T	k_1	k_2	k_3	F	r	σ
	Anionic Dyes							
1	Acid Red 1	11.08	$1.49·10^{-2}$	-0.07	0.30	2.42	0.77	0.42
		5.98	0.01	-0.06	0.23	3.30	0.84	0.25
2	Disodium Reactive Blue 4	10.80	-0.02	-0.06	0.24	2.33	0.76	0.38
3	Bromophenol Blue	5.18	-0.10	-0.05	0.37	9.01	0.94	0.22
		9.96	-0.06	-0.04	0.22	4.02	0.87	0.27
	Cationic Dyes							
1	Malachite Green	5.88	-0.03	-0.12	0.60	2.64	0.79	0.50
		5.46	0.07	-0.06	0.14	2.27	0.75	0.41
2	Methyl Violet	19.95	0.01	0.00	0.01	1.97	0.70	0.15
3	Crystal Violet	5.52	-0.15	-0.10	0.68	7.87	0.93	0.40
		6.90	-0.18	-0.09	0.62	5.73	0.91	0.51
4	Bromocresol Green	6.40	0.32	-0.08	0.11	3.04	0.82	1.34
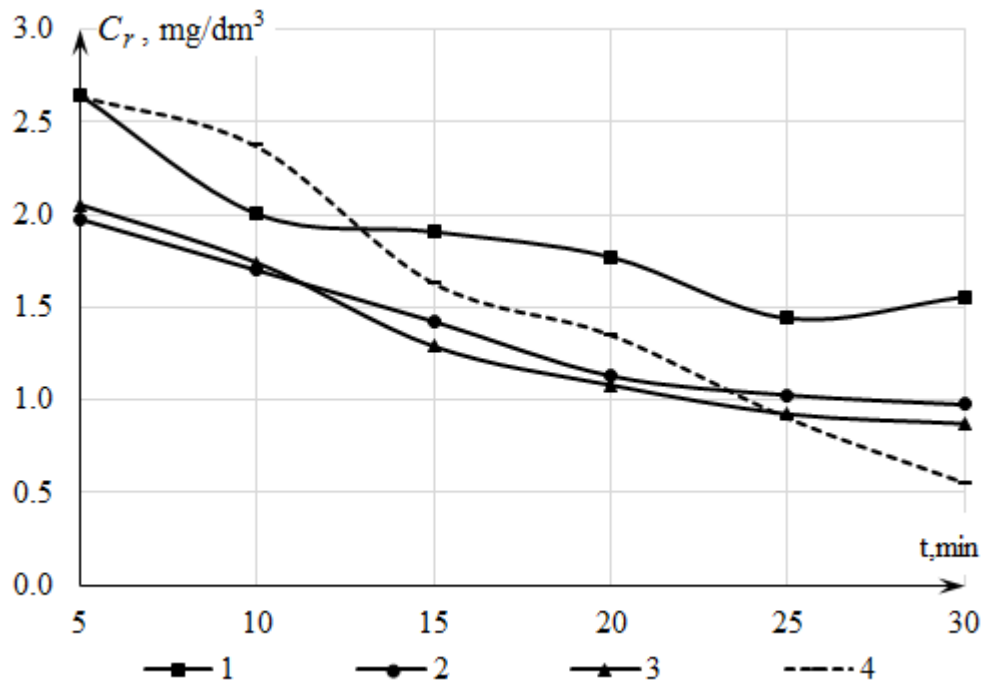
Fig. 3. Anionic dyes concentration change over time: 1 - Acid Red 1, 2 - Disodium Reactive Blue 4, 3 - Bromophenol Blue, 4 - Indigo Carmine.
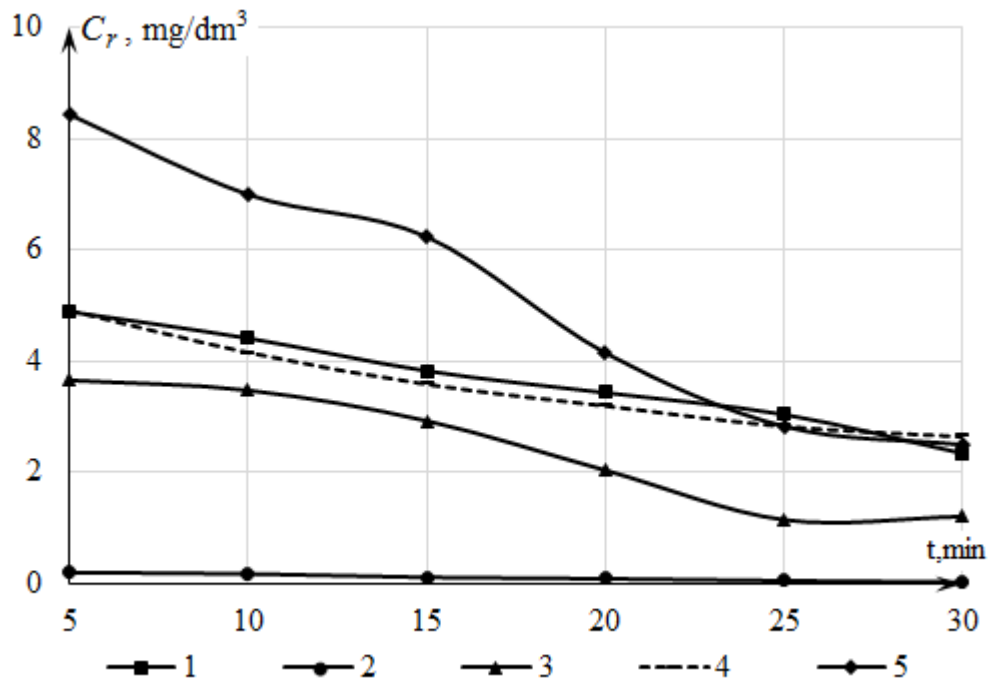

Fig. 4. Cationic dyes concentration change over time: 1 - Malachite Green, 2 - Methyl Violet, 3 - Crystal Violet, 4 - Methylene Blue, 5 - Bromocresol Green.

It should be noticed that for the Indigo carmine and Methylene blue dyes are not possible to obtain a mathematical model with satisfactory statistical parameters. The residual concentration for these dyes is presented at Fig. 3 and 4 in the dotted line. In contrast, the models for dyes presented in the Table 5 can be used to predict the amount of dyes removal and to solve optimization tasks.

Conclusion

In this paper, the correlation analysis has been used to determine the process variables that have a significant impact on the solvent sublation process and the STAR software has been applied to simulation of the different dye removal process. The ordinary first-order differential equation is used as a basic model describing the change in the dye concentration as a function of pH value, dye:surfactant ratio and the process time. The data set taken at various experimental conditions has been used to perform parametric identification. The performance of each model has been evaluated by statistical parameters and the studies have shown that the simulation model of Bromophenol Blue dye has a higher ability in prediction of dye removal in comparison with the other models. The obtained results can be used to improve the efficiency of the existing solvent sublation technique.

МОДЕЛЮВАННЯ ПРОЦЕСУ ФЛОТОЄКСТРАКЦІЇ ДЛЯ ПРОГНОЗУВАННЯ ВИДАЛЕННЯ БАРВНИКІВ З ВОДНИХ РОЗЧИНІВ

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Видалення водорозчинних барвників аніонного та катіонного типів з водних розчинів здійснювали методом флотоекстракції. Метою досліджень є комп'ютерне моделювання процесу флотоекстракції як методу очищення стічних вод від барвників катіонного і аніонного типів.

У даному дослідженні методи математичної статистики були використані для визначення факторів, які мають найбільший вплив на процес флотоекстракції. Встановлено, що такими чинниками є pH, співвідношення барвник : поверхнево-активна речовина і тривалість процесу. Математичний апарат системи STAR використовувався для пошуку математичних моделей, які з достатнім ступенем адекватності описують зміну залишкової концентрації барвника в часі. У якості базової моделі запропоновано використовувати звичайне диференціальне рівняння першого порядку, яке описує зміну концентрації барвника у часі. Параметричну ідентифікацію моделей для кожного барвника виконано засобами підсистеми GEM системи STAR. За результатами порівняльного аналізу статистичних характеристик математичних моделей визначено модель, яка найкращим чином описує процес видалення барвника з водного розчину.

Математичні моделі отримані для наступних барвників: легкозмиваємий червоний, активний яскраво-блакитний, бромфеноловий синій, малахітовий зелений, метиловий фіолетовий, кристалічний фіолетовий і бромкрезоловий зелений. Адекватність отриманих моделей оцінювалася з використанням таких статистичних характеристик, як відношення Фішера, коефіцієнт множинної кореляції і середньоквадратичне відхилення. Результати моделювання показали, що отримані моделі мають прийнятні характеристики і можуть бути використані для прогнозування ступеня видалення барвників катіонного і аніонного типів з водних розчинів а також для оптимізації процесу флотоекстракції.

Ключові слова*: барвник, математичне моделювання, стічні води, флотоекстракція.*

МОДЕЛИРОВАНИЕ ПРОЦЕССА ФЛОТОЭКСТРАКЦИИ ДЛЯ ПРОГНОЗИРОВАНИЯ УДАЛЕНИЯ КРАСИТЕЛЕЙ ИЗ ВОДНЫХ РАСТВОРОВ

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Удаление водорастворимых красителей анионного и катионного типов из водных растворов осуществляли методом флотоэкстракции. Целью исследования является компьютерное моделирование процесса флотоэкстракционного удаления красителей катионного и анионного типов. В данном исследовании методы математической статистики использовались для определения факторов, оказывающих наибольшее влияние на процесс флотоэкстракции. Математический аппарат системы STAR использовался для поиска математической модели, с достаточной степенью адекватности описывающую изменение остаточной концентрации красителя во времени. Результаты моделирования показывают, что полученные модели обладают удовлетворительными характеристиками и могут быть использованы для прогнозирования степени удаления красителей катионного и анионного типов из водных раствора, а также для оптимизации процесса флотоэкстракции.

Ключевые слова*: краситель, математическое моделирование, сточные воды, флотоэкстракция.*

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