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OPTIMIZATION SOLVENT SUBLATION OF DYES

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The object of this study is the process of treatment of wastewater contaminated with dyes by solvent sublation. Synthetic dyes are toxic, carcinogenic, and mutagenic, they cause serious problems with human health and are not subject to biological decomposition.

Thus, there is an urgent need to devise cost-effective and environmentally safe approaches to the treatment of wastewater containing dyes before their discharge into the environment.

A solvent sublation technology is proposed, which combines the advantages of ionic flotation and liquid extraction.

The influence of process parameters on the efficiency of solvent sublation treatment of wastewater containing synthetic dyes has been investigated to ensure maximum efficiency (minimum values of residual pollutant concentrations).

The dependences of purification efficiency for four dyes on the selected parameters such as pH, initial pollutant concentration, gas consumption and surfactant:dye ratio have been experimentally obtained.

Based on the research, a mathematical apparatus of the STAR system was used to construct a 2nd-order mathematical regression model. The approximation error is 0.834; therefore, the proposed model describes the experimental data with a reasonable degree of accuracy.

The stated optimization problem was solved by using the "OPTIMIZ-M" program; the optimal process conditions were determined, under which the maximum removal of dyes (97.20 %) is achieved:

– pH: 6;
– initial pollutant concentration: 20 mg/dm^3;
– surfactant:dye ratio: 1.5:1;
– gas flow rate: 140 cm^3/min.

Optimizing solvent sublation treatment provides high quality wastewater treatment at minimal costs, reducing dye emissions into the environment, which could potentially increase the competitiveness of enterprises in the market

Keywords: solvent sublation, wastewater treatment, correlation analysis, mathematical model of the solvent sublation process

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1. Introduction

Water is the most important resource for the existence of life. However, in the last few decades, a large amount of wastewater has entered freshwater bodies, making them unsuitable for use by living beings. The main cause of water pollution is anthropogenic activity [1]. Municipal waste, industrial waste, agricultural wastewater, and radioactive waste are among the main sources of water pollution. Natural phenomena (volcanoes, earthquakes, etc.) also deteriorate the quality of freshwater. In the last few decades, water pollution has been increasing at an alarming rate and poses a serious threat to the environment. According to the State Agency of Water Resources of Ukraine, about 4 billion m^3 of polluted wastewater is discharged into the country's water bodies annually. In particular, in many rivers, the concentrations of biochemical oxygen demand exceed the maximum permissible concentrations by 2–4 times, and the phosphate content reaches 1.5–2.5 mg/dm^3 with a standard of ≤0.5 mg/dm^3. The main indicators of water quality assessment are biochemical oxygen demand (BOD), chemical oxygen demand (COD), heavy metals (lead, cadmium, mercury), nitrates, phosphates, and microplastics. These indicators are regularly recorded during monitoring of water bodies according to WHO standards and national environmental services. One of the main pollutants of industrial wastewater is dyes. Synthetic dyes are toxic, non-biodegradable, carcinogenic, and mutagenic materials that cause serious health problems in both humans and aquatic systems [2, 3].

The largest amount of colored wastewater is generated at light industry enterprises. Thus, in dyeing and finishing industries, textile, knitted, leather and fur products undergo successive mechanical and chemical preparation for dyeing, dyeing, and final processing.

The high stability of dyes ensures their high resistance to aerobic decomposition, light, heat, and oxidants. Therefore, the separation of dyes from aqueous solutions is a complex problem that has been faced in recent years. Some of the widely used methods for purifying water saturated with dyes are coagulation, precipitation, filtration, reverse osmosis, photodegradation, ion exchange, electrochemical methods, and adsorption [4, 5].

Devising an effective, environmentally friendly, and inexpensive technique for removing dyes from wastewater is an urgent task.

2. Literature review and problem statement

The increasing cost of tap water and the obligation to comply with environmental standards for wastewater disposal have forced manufacturers to rethink wastewater management. The authors of [6] suggest considering wastewater with a high dye content as a resource, especially for consumers with high water consumption. At the same time, the authors note the need for further research to explore the possibilities of scaling up the proposed solutions and integrating different technologies with simultaneous resource recovery from them. Reducing water consumption, wastewater treatment, and the possibility of wastewater reuse should become crucial factors for sustainable production.

In [7], it is shown that the textile industry emits the largest amount of dye wastewater, which accounts for more than half (54 %) of the existing dye wastewater discharged into the environment worldwide. The large amount of textile waste is caused by the rapid population growth and the increasing demand for textile products. The transition to a circular economy is one way to reduce waste, but the textile industry is only taking the first steps on this path. One of the barriers is the high cost of waste processing. An option to overcome this barrier is to find optimal process conditions and devise simple operating procedures to automate the process and increase the cost-effectiveness of implementation in the industry.

In [8], the benefits of wastewater reuse are considered, such as reducing the environmental burden, improving productivity, and increasing the amount of treated water. At the same time, it is shown that existing methods cannot completely remove color from wastewater. A similar conclusion is drawn in [9]: the goal of measures to develop innovative technologies should be not only to reduce pollution but also to preserve water resources, restore and reuse water.

There are many technologies for removing dyes from wastewater, each with its own characteristics and differing in environmental friendliness, efficiency, and cost-effectiveness. However, research is still ongoing, as there is no method that fully meets the needs of consumers. The aim of the research is not only to reduce pollution but also to conserve water resources through innovative technologies that support water recovery and reuse.

In [10], the removal of methyl blue dye from wastewater and its simultaneous recovery in the foam phase were considered. Foam fractionation is an adsorption bubble separation method that is considered suitable for treating low-concentration wastewater. It is widely used for removing dyes from wastewater and is attracting more and more attention due to its simple equipment, low investment, and low energy consumption.

The authors of [11] proposed a foam fractionation method for dyeing wastewater and wastewater containing dyes and surfactants simultaneously. Model solutions contained the dye rhodamine B, which is a common organic dye, used in many industries and difficult to remove by conventional and biochemical methods. The work reports a high degree of purification – 95 %. The optimal pH range for effective removal of the dye is 5.5–10.5. Increasing the temperature reduces the efficiency of dye removal and leads to foam instability, which is a negative factor.

Despite its effectiveness, the foam fractionation method of dyes has several drawbacks. Thus, the effectiveness of the method strongly depends on the pH of the solution, the concentration of electrolytes, temperature, the type and concentration of the surfactant, and the size of the bubbles. That is, careful selection of parameters is required for each specific case. In addition, the resulting foam, which contains concentrated dyes and surfactants, must be further purified or neutralized. This can create certain environmental problems.

The solution to this problem can be the solvent sublation method, which is a variety and improvement of ionic flotation. The method differs in that the concentration of the dye does not occur in the foam but in the organic layer of a liquid that does not mix with water. Therefore, all the problems associated with foam are absent.

In work [12], the authors note that the use of solvent sublation is the most widely used method for the removal and recovery of organic pollutants, such as dyes, toxic organic solvents from the aqueous phase. Many methods have been devised for the removal of dyes that form complexes with various surfactants from the aqueous phase.

For example, in [13], the anionic dye bromophenol blue was effectively removed from an aqueous solution as a complex with hexadecyl-pyridine chloride into the organic layer of isopentanol. The stoichiometric amount of surfactant (surfactant:dye=2:1) was the most effective for removal. More than 95 % of the dye was removed from the aqueous solution in 10 min. The removal rate was slightly increased by increasing the air flow rate, but the purification efficiency decreased at high gas flow rates due to an increase in the average bubble radius. This is explained by the decrease in bubble residence time because larger bubbles moved faster to the extractant layer. Acidic pH increased the removal rate, but pH above 10 reduced the efficiency of dye removal.

In [14], the cationic dye methyl violet was removed from aqueous solution by solvent sublation of a complex of methyl violet with sodium dodecylbenzenesulfonate in 2-pentanol. The stoichiometric amount of surfactant (surfactant:dye=1:1) was the most effective for removal, with more than 97 % of the dye being removed from the aqueous solution in 10 min. Increasing the air flow rate enhances the solvent sublation process provided that the bubble size remains small. The highest efficiency of dye removal was observed without pH adjustment. However, lower pH values reduced the removal efficiency.

Indigo carmine, an anionic dye, was removed from aqueous solution by solvent sublation of a complex of indigo carmine and cetyltrimethylammonium bromide in 2-octanol [15]. The stoichiometric amount of surfactant (surfactant:dye=2:1) was the most effective for removal, with more than 93 % of the dye being removed from the aqueous solution in 5 min. The removal rate increased with higher air flow rates and was almost independent of the volume of organic solvent in the upper part of the flotation column.

The authors of [16] investigated the solvent sublation of a complex of bromocresol green with the cationic surfactant hexadecyl pyridine chloride in 2-octanol. The surfactant to dye ratio (1.25:1) was the most effective for removal, with more than 99 % of the dye being removed in 5 min. The removal rate increased with increased air flow rates and was somewhat dependent on the volume of organic solvent. The dye removal efficiency reached maximum values at pH 3 to 4 and was 99 % in 5 min, but higher pH values reduced the degree of removal.

Solvent sublation is very suitable for removing traces (or ultra traces) of elements from the aqueous phase into the organic phase. However, at high concentrations of solutions, the separation efficiency is unsatisfactory. Therefore, the authors of [17] do not propose a solvent sublation method for real wastewater treatment due to secondary contamination of the organic solvent and lower separation efficiency for concentrated solutions.

One of the options for overcoming this problem is to construct new adequate mathematical models to study the influence of factors on the efficiency of the solvent sublation process and predict the quality indicators of the purified water.

Although much work has been done on solvent sublation, laboratory studies prevail, so scaling up this technology for wastewater treatment can be very difficult and time-consuming.

The introduction of the solvent sublation method into industry is hampered precisely because of the presence of numerous factors that affect the efficiency of the process.

Therefore, it can be argued that it is advisable to conduct a study aimed at highlighting the factors that could ensure maximum efficiency of solvent sublation purification from dyes of various structures. These studies will allow us to propose a mathematical model on the basis of which the optimal conditions for the solvent sublation process will be determined.

3. The aim and objectives of the study

The purpose of our study is to formalize and solve the problem of optimizing the process of solvent sublation of dyes from model solutions. This will provide an opportunity to deepen knowledge about the process and highlight the capabilities of this method for wastewater treatment under industrial conditions.

To achieve the goal, the following tasks were set:

– to perform a correlation analysis of factors affecting the efficiency of the solvent sublation process of dyes, and to conduct a study of the process to determine the conditions of the main experiment;

– to design an experimental plan and conduct experimental studies in accordance with the plan;

– based on the results of experimental studies and correlation analysis of the parameters of the solvent sublation process, to obtain and investigate a mathematical model that describes the degree of wastewater treatment from dyes by the solvent sublation method.

4. The study materials and methods

The object of our study is the process of solvent sublation treatment of wastewater contaminated with dyes.

The subject of the study is the influence of process parameters on the efficiency of solvent sublation treatment of wastewater from synthetic dyes to ensure maximum efficiency (minimum values of residual pollutant concentrations).

The hypothesis of the study assumes that the efficiency of the solvent sublation process for removing dyes from wastewater could be significantly increased by determining the most important process parameters using correlation analysis and experimental studies. The results to be obtained would become the basis for building an adequate mathematical model, the study of which involves determining the optimal conditions for removing dyes of various structures.

Solvent sublation is a combined method that combines flotation (removal of impurities to the surface using gas bubbles) and extraction (transition of impurities to the organic phase using an extractant). When treating wastewater, this method allows for the effective removal of heavy metal ions, organic pollutants, and petroleum products. Gas (usually air) is introduced into the flotation column from the bottom through a disperser, forming microbubbles that capture hydrophobic particles with contaminants and carry them to the surface of the extractant.

Fig. 1 shows the parameters that affect the efficiency of solvent sublation purification of dyes from aqueous solutions.

It was assumed that the correlation between the factors and the quality indicators of the solvent sublation process is linear.

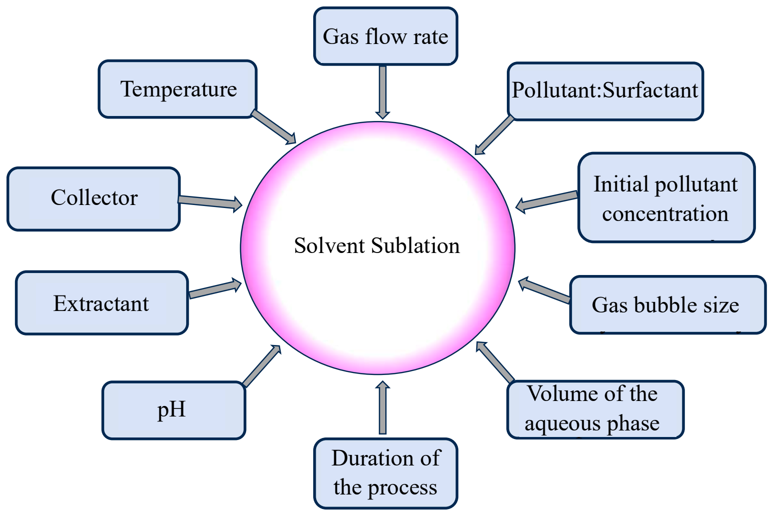

Fig. 1. Factors affecting the efficiency of solvent sublation of dyes

Model dye solutions (active bright red (BR), active bright blue (ABB), bromocresol green (BCG), indigo carmine (IC)) were studied, which imitate wastewater contaminated with dyes. For simplification, solutions containing one dye were used. Solvent sublation removal of dyes occurred in the form of a complex or ionic associate with surfactants. Descriptions of the laboratory setup and experimental research methodology are given in [18, 19]. The degree of purification (removal) of the dye was taken as a measure of the efficiency of the solvent sublation process.

The correlation analysis method was used to establish a correlation between factors that affect the degree of purification of wastewater from synthetic dyes, as well as to assess the strength of the relationship between the parameters under study. The strength of the relationship was estimated using the Pearson correlation coefficient according to the following formula [20]:

$$r_v = \frac{S_{xy}}{\sqrt{S_y S_x}}, \quad (1)$$

where:

$$S_{xy} = \sum_{1}^{n} \left(x_i - \bar{x}_i\right) \cdot \left(y_i - \bar{y}_i\right),$$

$$S_x = \sum_{1}^{n} \left(x_i - \bar{x}_i\right)^2, \; S_y = \sum_{1}^{n} \left(y_i - \bar{y}_i\right)^2.$$

At the stage of the preliminary experiment, the process parameters varied within the limits determined from the literature. This approach allowed us to determine the conditions of the main experiment and the type of model.

The synthesis of the D-optimal experimental plan [21] and the coefficients of the mathematical model of the process involved using the mathematical apparatus of the STAR system [22]. The general form of the mathematical model:

$$y = a_0 + \sum_{1}^{k} a_i x_i + \sum_{\substack{i,j=1 \\ i \neq j}}^{k} b_{ij} x_i x_j + \sum_{1}^{k} c_i x_i^2, \qquad (2)$$

where y is the quality indicator of the solvent sublation process, x_i, x_j (i, j=1, k) are the factors that have the greatest impact on the process and are selected based on the results of correlation analysis; a_i , b_{ij}, c_j are the coefficients of the mathematical model.

The adequacy of the resulting model was assessed using the following model characteristics, which are calculated using the STAR system: F-ratio, correlation ratio, standard deviation, as well as the estimated and critical values of the Student's t-test for the model coefficients. The approximation error was calculated using the following formula:

$$\sigma = \sqrt{\frac{\sum_{1}^{n} \left(y_i - y_{ip}\right)^2}{n-1}}, \qquad (3)$$

where n is the number of experiments; y_i, y_{ip} are the experimental and calculated values of the degree of dye extraction, respectively.

To solve the optimization problem, the program "OPTIMIZ-M" [23] was used, which makes it possible to determine the optimal conditions for the processes described by regression equations.

5. Results of investigating the influence of parameters on the efficiency of solvent sublation removal of dyes

5. 1. Correlation analysis and determination of the conditions of the main experiment

5. 1. 1. Results of correlation analysis

The values of the Pearson correlation coefficient were calculated using formula (1). The generalized results of the correlation analysis are shown in Fig. 2. Parameters that have a significant effect on the degree of dye extraction are marked with green flags, and parameters that have an insignificant effect on the solvent sublation process are marked with red flags; all other factors are marked with yellow flags.

Parameters for which the Pearson correlation coefficient values are close to unity have a significant impact on the process of dye removal from wastewater by solvent sublation. Therefore, the following parameters were selected for further experimental studies: pH, initial pollutant concentration, surfactant:dye ratio, and gas flow rate. The variation intervals of these parameters were selected based on the results of investigating their impact on solvent sublation removal of dyes.

Investigated factors	Initial pollutant concentration	pH	Surfactant:Dye ratio	Gas flow rate	Volume of organic phase	Process duration
Initial pollutant concentration	1	0.86	0.93	0.93	0.97	0.88
pH	0.86	1	0.96	0.99	0.42	0.34
Surfactant:Dye ratio	0.93	0.96	1	0.95		0.59
Gas flow rate	0.93	0.99	0.95	1	0.66	0.26
Volume of organic phase	0.97	0.42		0.66	1	0.01
Process duration	0.88	0.34	0.59	0.26	0.01	1

Fig. 2. Values of the Pearson correlation coefficient for the studied parameters of the solvent sublation process: green flag – a parameter that has a significant effect on the degree of dye extraction; red flag – a parameter that has an insignificant effect on the solvent sublation process; yellow flag – a parameter that has an intermediate value of the correlation coefficient

5. 1. 2. Dependence of the degree of extraction on the initial concentration of the dye

The dependence of the degree of removal of dyes on its initial concentration over time was investigated. The results are given in Tables 1, 2.

The nature of change in the degree of removal of the BR dye depending on the initial concentration over time is shown in Fig. 3.

Fig. 3 shows that at initial dye concentrations of 5...20 mg/dm^3, the degree of removal of active bright red reaches a maximum after 10 min. On the other hand, when the initial concentration is increased to 50 mg/dm^3, the maximum degree of purification is observed after 25 min.

The nature of change in the degree of removal of the ABB dye depending on the initial concentration over time is shown in Fig. 4.

Table 1

Dependence of the degree of extraction of the active dye BR on its initial concentration

Time, min	Starting concentration, mg/dm^3				
	5	10	20	25	50
5	80.34	91.09	85.10	70.57	21.58
10	89.11	96.14	87.87	75.25	30.68
15	89.31	96.04	90.54	88.44	64.58
20	89.11	96.04	93.60	93.58	89.14
25	89.11	96.10	95.80	96.44	97.12

Table 2

Dependence of the degree of extraction of the ABB dye on its initial concentration

Time, min	ABB starting concentration, mg/dm^3				
	5	10	20	25	50
5	82.75	90.34	90.69	66.34	23.70
10	92.40	97.24	92.59	75.17	32.84
15	93.80	97.24	96.2	87.17	64.69
20	93.80	97.59	96.72	93.66	91.45
25	93.10	97.24	96.9	95.17	97.93

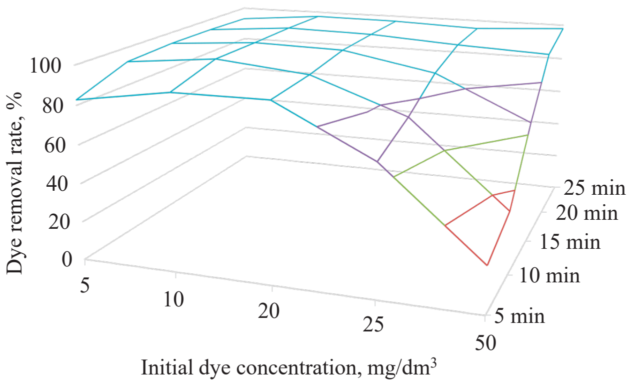

Fig. 3. Dependence of the degree of extraction on the initial concentration of the active bright red dye for different process durations: ■ – degree of purification from 20 to 40 %; ■ – degree of purification from 40 to 60 %; ■ – degree of purification from 60 to 80 %; ■ – degree of purification from 80 to 100 %

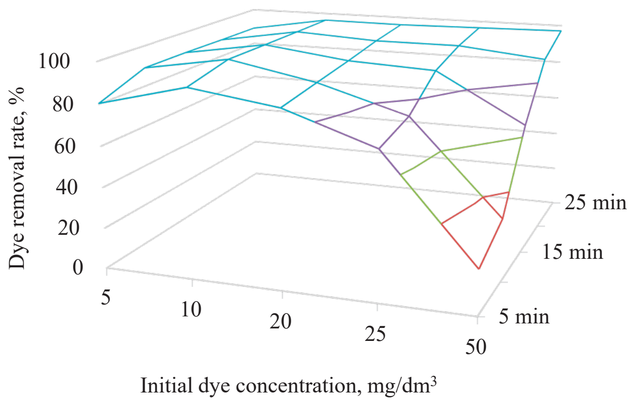

Fig. 4. Dependence of the degree of extraction on the initial concentration of the active bright blue dye for different durations of the process: ■ – degree of purification from 20 to 40 %; ■ – degree of purification from 40 to 60 %; ■ – degree of purification from 60 to 80 %; ■ – degree of purification from 80 to 100 %

Fig. 4 shows that in the case of removal of active bright blue dye with a concentration of 5...25 mg/dm^3 the process reaches a maximum after 10 min. When the dye concentration increases to 50 mg/dm^3 the maximum degree of purification is observed after 20 minutes. In general, in all cases, a degree of purification of 91...97 % is achieved after 20–25 minutes. The maximum degree of extraction – 97.93 % – is observed at a dye concentration of 50 mg/dm^3 after 25 minutes.

5. 1. 3. Dependence of the degree of pollutant extraction on pH

The influence of pH on the process of solvent sublation of active bright red was experimentally investigated. The initial solution has a pH of 6. The results are given in Table 3.

The nature of the influence of pH on the extraction of active bright blue was investigated. The pH range: 2–11. The pH of the initial solution is 5.5. The results are given in Table 4.

Fig. 5 shows the dependence of the degree of purification of the BR dye on pH over time.

Table 3

Dependence of the degree of extraction of the BR dye on pH

Time, min	pH				
	2	4	6	8	10
5	88.80	90.70	91.10	90.30	89.80
10	93.86	95.25	96.13	95.44	94.85
15	94.06	95.55	96.04	95.54	94.95
20	94.06	95.64	96.04	95.74	94.95
25	94.06	95.64	96.14	95.74	95.05

Table 4

Dependence of the degree of extraction of ABB dye on pH

Time, min	pH value				
	2	3	6	9	11
5	76.90	88.97	90.34	86.20	76.20
10	85.86	95.52	97.24	93.45	84.48
15	86.55	96.55	97.24	93.45	85.17
20	86.55	96.55	97.59	93.80	85.52
25	86.90	96.90	97.24	93.80	85.52

Fig. 6 shows the dependence of the degree of purification of the active bright blue dye on pH over time.

The nature of change in this parameter shows that the change in pH affects the efficiency of solvent sublation of active bright blue over the entire time period.

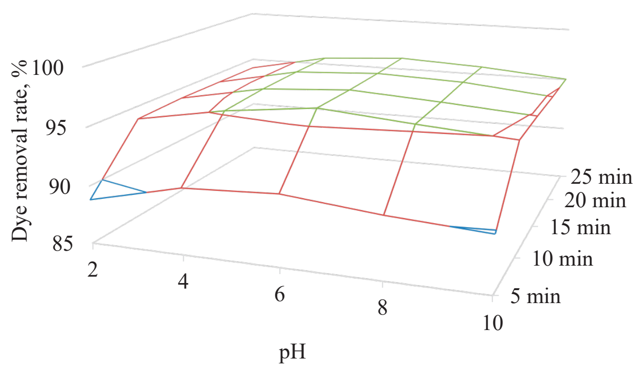

Fig. 5. Dependence of the degree of extraction of the active bright red dye on pH for different process durations: ■ – degree of purification from 20 to 40 %; ■ – degree of purification from 40 to 60 %; ■ – degree of purification from 60 to 80 %

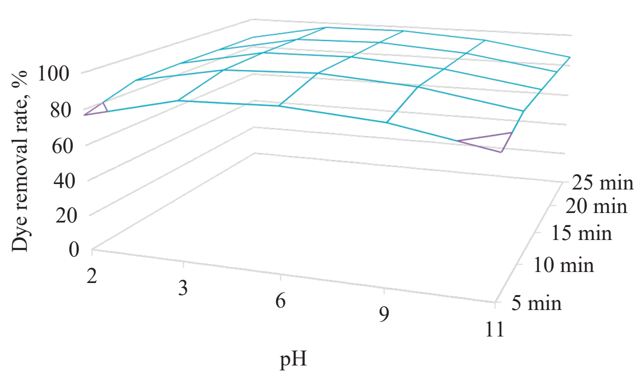

Fig. 6. Dependence of the degree of extraction of the active bright blue dye on pH for different process durations: ■ – degree of purification from 60 to 80 %; ■ – degree of purification from 80 to 100 %

5. 1. 4. Dependence of the degree of removal of pollutants on gas flow rate

A study was conducted on the dependence of the efficiency of extraction of active bright blue on gas flow rate in the range of 65...146 cm^3/min. The results are given in Table 5.

Table 5

Dependence of the degree of extraction of the ABB dye on gas flow rate

Time, min	Gas flow rate, cm^3/min			
	65	96	127	146
5	82.75	85.52	90.34	78.96
10	88.62	91.72	97.24	86.2
15	89.66	94.14	97.24	86.2
20	90.34	94.48	97.59	86.9
25	90.34	94.48	97.24	86.9

Fig. 7 shows the dependence of the degree of purification of the ABB dye on gas flow rate. The most efficient extraction of the dye is at an air flow rate of 140 cm^3/min and is equal to 97.71 % in 10 min.

The maximum extraction of the dye occurs at a gas flow rate of 127 cm^3/min – after 20 minutes of solvent sublation, the degree of purification is 97.59 %.

The results of experiments investigating the dependence of the efficiency of bromocresol green removal on gas flow rate in the range of 75–140 cm^3/min are given in Table 6.

Table 6

Dependence of the degree of extraction of the BCG dye on gas flow rate

Time, min	Gas flow rate, cm^3/min			
	75	90	115	140
5	–	49.89	62.36	90.24
10	24.16	77.24	86.09	97.71
15	34.88	81.80	86.89	91.85
20	47.88	84.34	87.96	92.25
30	60.35	86.35	89.97	92.52

Fig. 8 shows the dependence of the degree of purification of bromocresol green on gas flow rate. The most efficient extraction of the dye is at an air flow rate of 140 cm^3/min and is equal to 97.71 % in 10 min.

The dependence of the efficiency of indigo-carmine dye removal on gas flow rate was investigated. The experimental results are given in Table 7 and Fig. 9.

Table 7

Dependence of the degree of IC dye extraction on gas flow rate

Time, min	Gas flow rate, cm^3/min		
	40	80	120
5	58.34	20.27	18.26
10	77.37	35.68	30.99
15	78.71	77.37	63.83
20	80.19	83.67	85.01
30	80.99	87.96	91.31

The most efficient extraction of indigo carmine is observed at a flow rate of 120 cm^3/min and is 91.31 % in 30 min.

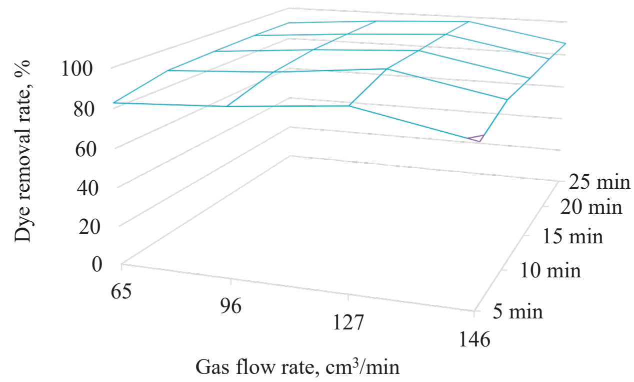

Fig. 7. Dependence of the degree of extraction of the active bright blue dye on gas flow rate for different process durations: – degree of purification from 60 to 80 %; – degree of purification from 80 to 100 %

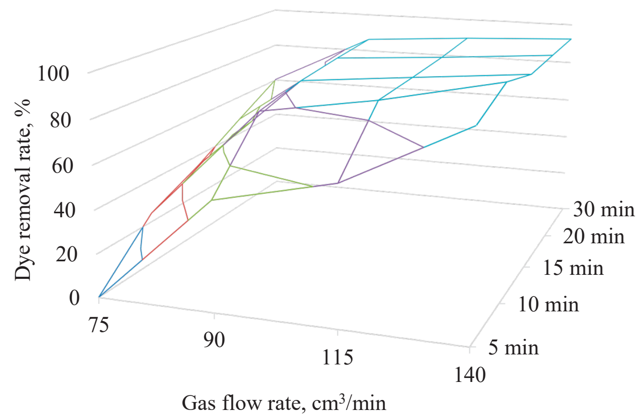

Fig. 8. Effect of gas flow rate on the degree of removal of bromocresol green dye over time: – degree of purification less than 20 %; – degree of purification from 20 to 40 %; – degree of purification from 40 to 60 %; – degree of purification from 60 to 80 %; – degree of purification from 80 to 100 %

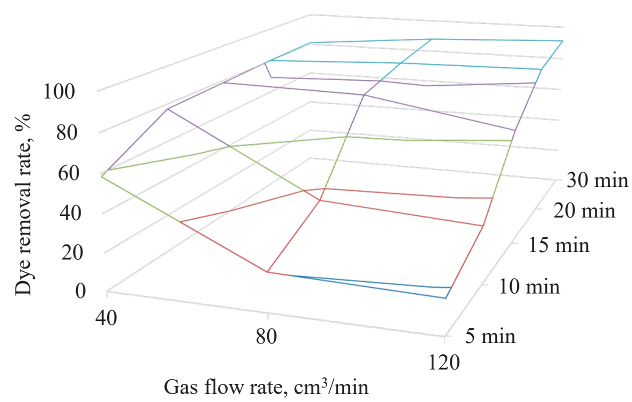

Fig. 9. The effect of gas flow rate on the degree of extraction of indigo-carmine dye: – degree of purification less than 20 %; – degree of purification from 20 to 40 %; – degree of purification from 40 to 60 %; – degree of purification from 60 to 80 %; – degree of purification from 80 to 100 %

5. 1. 5. Dependence of the degree of removal of pollutants on the surfactant:pollutant ratio

A series of experimental studies were conducted and the change in the degree of removal of active bright blue over time was determined for different ratios of dye:surfactant. The studies were conducted for ratios of 1:0.5; 1:1; 1:1.5; 1:2. The results are given in Table 8 and Fig. 10.

The purification efficiency in just 10 minutes is 97.24 %. When using other molar ratios of surfactant:dye, the efficiency of pollutant removal is lower.

A series of experiments were conducted for bromocresol green and the change in the degree of removal of this dye over time for different ratios of dye:surfactant was determined. The results are given in Table 9 and Fig. 11.

To study the efficiency of solvent sublation, a series of experiments were conducted and the change in the degree of purification of the indigo-carmine dye over time was investigated for different dye:surfactant ratios. The results are given in Table 10.

The most effective molar ratio for indigo carmine is the ratio of dye:surfactant=1:1 (Fig. 12). This ratio provides 86.7 % removal of the indigo-carmine dye in just 10 minutes.

Table 8

Dependence of the degree of extraction of ABB on the ratio of surfactant:dye

Time, min	Surfactant:dye ratio			
	0.5:1	1:1	1.5:1	2:1
5	39.66	80.34	90.34	78.28
10	54.50	82.10	97.24	86.55
15	55.17	84.14	97.24	88.97
20	57.24	84.48	97.59	93.10
25	57.58	84.14	97.24	93.45

Table 9

Dependence of the degree of extraction of BCG on the ratio of surfactant:dye

Time, min	Surfactant:dye ratio at pH 5				
	1:0.5	1:1	1:1.5	1:2	1:2.5
5	45.47	58.34	20.27	18.26	24.29
10	46.27	77.37	35.68	30.99	28.04
15	46.68	78.71	77.37	63.83	35.82
20	50.56	80.19	83.67	85.01	41.45
30	54.05	80.99	87.96	91.31	51.77

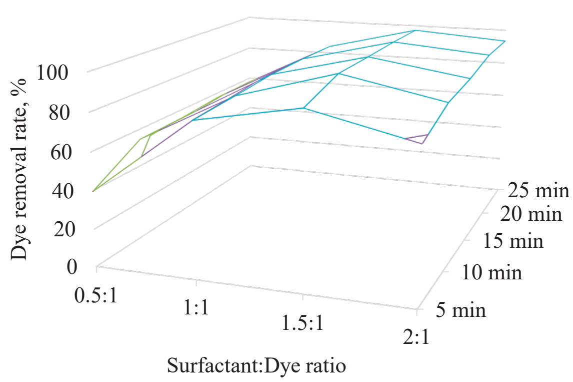

Fig. 10. Dependence of the degree of extraction of the active bright blue dye on the ratio of surfactant:dye for different process durations: ■ – degree of purification from 40 to 60 %; ■ – degree of purification from 60 to 80 %; ■ – degree of purification from 80 to 100 %

Table 10

Dependence of IC extraction degree on the surfactant:dye ratio

Time, min	Surfactant:IC dye ratio			
	1:0.5	1:1	1:1.5	1:2
5	64.50	74.43	57.93	53.21
10	74.90	86.70	65.94	59.98
15	75.38	83.87	68.77	59.34
20	72.08	83.40	71.60	62.64
30	69.25	80.09	74.43	65.00

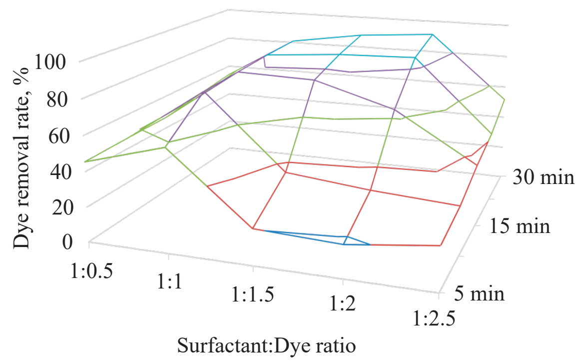

Fig. 11. Change in the degree of purification of bromocresol green over time depending on the ratio of dye:surfactant: ■ – degree of purification less than 20 %; ■ – degree of purification from 20 to 40 %; ■ – degree of purification from 40 to 60 %; ■ – degree of purification from 60 to 80 %; ■ – degree of purification from 80 to 100 %

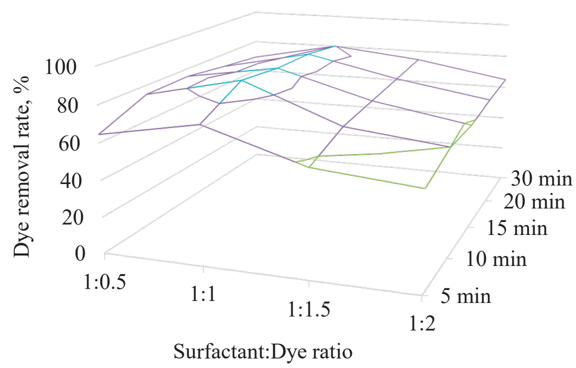

Fig. 12. Dependence of the degree of extraction of indigo carmine on the molar ratio of dye: ■ – degree of purification from 40 to 60 %, ■ – degree of purification from 60 to 80 %, ■ – degree of purification from 80 to 100 %

At other molar ratios, worse purification degrees are observed.

5. 2. Results of the main experiment

According to the results of the previous experiment, the maximum and minimum values of the parameters that have the greatest impact on the solvent sublation process were selected (Table 11), and a D-optimal experimental plan was synthesized using the STAR system.

For each point of the plan, three parallel experiments (y_1, y_2, y_3) were conducted on the extraction of dyes (active bright red (ABR), active bright blue (ABB), bromocresol green (BCG), and indigo carmine (IC)) by solvent sublation. The experimental results, which correspond to the best mathematical model, are given in Table 12.

Table 11

Intervals of variation in parameters for the solvent sublation process

Parameter	Designation	Minimum and maximum parameter value	
		x_{min}	x_{max}
pH	x_1	2	10
Initial dye concentration, mg/dm^3	x_2	5	250
Ratio of surfactant:pollutant	x_3	0.5:1	2:1
Gas flow rate, cm^3/min	x_4	40	146

Table 12

Experimental results from three parallel experiments

Pollutant removal rate, %	y_1	y_2	y_3
1	95.05	91.10	86.89
2	94.06	91.10	84.44
3	95.05	91.10	93.448
4	94.06	93.10	91.10
5	95.05	85.52	84.44
6	94.06	84.44	86.90
7	95.05	85.52	89.11
8	94.06	89.11	57.59
9	95.05	91.10	93.45
10	94.06	91.10	93.45
11	91.10	93.45	95.05
12	93.10	93.46	94.06
13	95.05	85.52	84.44
14	94.06	84.44	80.99
15	95.05	93.10	85.52
16	94.06	93.10	89.11

The results were used to identify the coefficients in the mathematical model of general form (2).

5. 3. Mathematical model of solvent sublation removal of dyes and its analysis

In total, 25 variants of mathematical models were calculated and analyzed. Regression models of 1st and 2nd orders were proposed as models.

When modeling using the STAR program, the best was the 2nd order regression model of the following form:

$$\begin{aligned} y = {} & 79.01 + 7.1\cdot10^{-2}x_1 + 6.6\cdot10^{-3}x_2 + 5.3x_3 + \\ & + 2.9\cdot10^{-3}x_4 - 8.1\cdot10^{-2}x_1x_2 - 5.2\cdot10^{-2}x_1x_3 - \\ & - 4.05\cdot10^{-2}x_1x_4 - 0.25x_2x_3 - 4.8\cdot10^{-2}x_2x_4 - \\ & - 0.18x_3x_4 - 2.3\cdot10^{-2}x_1^2 - 9.9\cdot10^{-2}x_2^2 - \\ & - 1.2\cdot10^{-2}x_3^2 - 0.23x_4^2, \end{aligned} \tag{4}$$

which describes a change in the degree of dye removal depending on pH (x_1), initial pollutant concentration (x_2), surfactant:pollutant ratio (x_3), and gas flow rate (x_4).

Characteristics of the resulting model: *F*-ratio is 68.18; correlation ratio r=0.99 standard square deviation σ=2.09.

The approximation error calculated from formula (3) is 0.834; therefore, the proposed model describes the experimental data with a reasonable degree of accuracy.

In order to study the response surface, the parameters were sequentially changed from the minimum to the maximum value, while fixing the other values. The results of the study on the influence of parameters of the solvent sublation process on the degree of dye extraction are shown in Fig. 13.

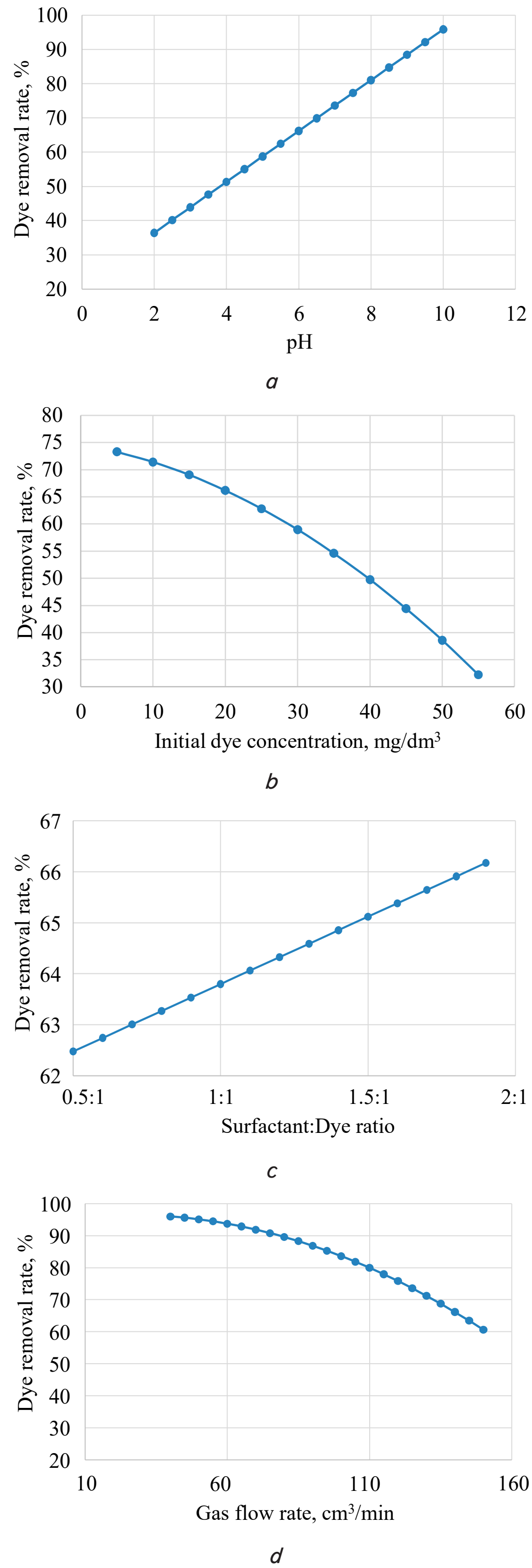

Fig. 13. Dependence of the degree of dye extraction on:
a – x_1 (pH) at x_2, x_3, x_4 – const;
b – x_2 (initial pollutant concentration) at x_1, x_3, x_4 – const;
c – x_3 (surfactant:pollutant ratio) at x_1, x_2, x_4 – const;
d – x_4 (gas flow rate) at x_1, x_2, x_3 – const

The mathematical model (4) was used as an objective function to find the optimal conditions for the solvent sublation process. The degree of pollutant removal from wastewater was chosen as the optimization criterion. Then the optimization problem can be stated as follows: let it be necessary to maximize function (4), where the following constraints are imposed on x_1, x_2, x_3, x_4:

$$2 \le x_1 \le 10,$$

$$5 \le x_2 \le 250,$$

$$0.5:1 \le x_3 \le 2:1,$$

$$40 \le x_4 \le 146.$$

According to the instructions for the program "OPTIMIZ-M", the number of factors and responses, their limits, and coefficients of equation (4) were introduced, as well as the search direction – maximization of the optimization criterion.

As a result of the work of "OPTIMIZ-M", the following optimal parameter values were obtained:

x_1=6, x_2=20 mg/dm^3, x_3=1,5:1, x_4=140 cm^3/min.

These parameters provide the maximum degree of removal of the studied dyes from aqueous solutions – 96.2 %.

6. Discussion of results based on the experiment, modeling, and optimization of the solvent sublation process

From the experimental results shown in Fig. 3, 4, one can see that the degree of purification of 89...97 % is achieved in all cases within 25 min. At the same time, the maximum degree of extraction – 97.12 % – is observed at a concentration of 50 mg/dm^3 after 25 min. The relatively short time of the solvent sublation process can be explained by the easy formation of complexes of dyes with surfactants, which are adsorbed on the surface of gas bubbles, which contributes to rapid mass transfer.

Under known methods for removing dyes from aqueous solutions, such as photocatalytic [24] and adsorption on zeolites [25], a similar value of the degree of purification is achieved in 30 min. and 50–100 min., respectively.

However, the removal of bright blue dye using an adsorbent based on Zizyphus Spina-Christi [26] requires an increase in temperature to 45 °C. Thus, unlike photocatalytic and adsorption methods, solvent sublation dye removal takes less time and does not require temperature adjustment.

Analysis of the results shown in Fig. 5, 6 revealed that pH has a negligible effect on the efficiency of solvent sublation, in contrast to methods using photocatalytic-hybrid materials and sorbents.

In [25] it is shown that the best results were obtained at pH 8 for adsorption on zeolites. The photocatalytic-hybrid composite material considered above, which the authors of [24] used to remove the bright red dye (acid red 1), is most effective at pH 7. In a similar study [27], the highest degree of dye extraction was also observed at pH 7 for photocatalytic water purification.

The results reported in [28] indicate that for biosorbents based on magnetized peanut shells and tea waste, the optimal pH value is 8 at a temperature of 312 K.

Unlike the methods considered, solvent sublation removal of dyes does not require pH adjustment, and the best results were obtained at the initial pH of the aqueous solution of the dye.

Studies on the dependence of the degree of pollutant extraction on gas flow rate (Fig. 7–9) showed that it is rational to carry out the solvent sublation process at a gas flow rate in the range of 110–130 cm^3/min. This makes it possible to achieve high degrees of extraction (over 97 %) without destroying the organic layer.

Further increase in the intensity of gas flow leads to a significant decrease in the purification efficiency since the integrity of the organic solvent and the formed sublate is destroyed. As a result, only partial removal of the pollutant and the reverse transition of the sublate from the organic to the aqueous phase is carried out, which causes re-contamination of the water.

It should be noted that for the removal of bromocresol green at a gas flow rate of 75 cm^3/min, only 60 % removal was observed in 30 min. To achieve higher removal values, it is necessary to increase the process time.

The ratio of surfactant:pollutant significantly affects the purification efficiency, which is illustrated in Fig. 10–12.

In the case of ratios of 0.5:1...1:1, worse purification efficiency is observed. This is explained by the fact that incomplete formation of the ionic associate occurs due to the lack of collector (surfactant). When the excess of surfactant is 2 or 2.5 times greater, the degree of removal also decreases, because there is competition of the excess amount of collector for space on the gas bubble with the hydrophobic dye:surfactant complex. The excess amount of surfactant also causes emulsification of the extractant, due to which the sublate from the organic phase partially returns back to the aqueous phase, and as a result, re-contamination occurs.

Perhaps, for ratios less than stoichiometry, incomplete formation of the dye-surfactant ionic associate occurs, which is why lower degrees of purification are observed. But if the number of moles of surfactant is increased, then there is competition between the sublate and the excess surfactant for a place on the surface of the gas bubble. The study on the influence of ratios of dye and surfactant on the efficiency of purification of aqueous solutions requires further investigation.

At other molar ratios, we observe worse degrees of purification, and therefore a higher residual concentration of the dye in water. For example, in the same 10 min for the ratio of dye:surfactant=1:0.5, only 74.9 % of dye extraction is achieved, for 1:1.5 – 65.94 %, and for 1:2 – 59.98 %.

The mathematical model (4) makes it possible to calculate the degree of purification of wastewater from dyes with high accuracy. This is confirmed by the small approximation error calculated from formula (3), as well as other characteristics of the model obtained by means of the STAR system. Comparison of the calculated values of the Student's t-test with the critical values for two levels of significance (q=0.05 and q=0.01) showed that all coefficients of model (4) are significant.

An important advantage of our model is the possibility of its application not only for finding the optimal conditions for the solvent sublation process but also for predicting the degree of wastewater purification from the dyes studied. The proposed mathematical model can be used as part of the mathematical support in automated control systems for the process of purification of industrial wastewater from synthetic dyes. Model (4) is universal, i.e., the results of the calculation by the model have the same accuracy for all dyes considered in the work. This is its difference from the mathematical models given in [22], which describe the dependence of the residual concentration for each dye separately. Compared with the models reported in [22], the proposed mathematical model takes into account all parameters that have a significant impact on the quality of solvent sublation purification. The presence of a universal mathematical model of the solvent sublation process significantly simplifies the integration of the method with other promising technologies, which would make it possible to more effectively resolve the task related to the growing amount of industrial waste.

The optimization results given in chapter 5. 3 define the optimal conditions for the solvent sublation process: the highest degree of purification is achieved at pH 6 with an initial pollutant concentration of 20 mg/dm^3, the optimal surfactant:pollutant ratio is 1.5:1, and the gas flow rate is 140 cm^3/min. Our results are confirmed by the experimental data shown in Fig. 13.

Solving the task of optimizing the solvent sublation process of dyes accelerates the introduction of the solvent sublation method into industry while applying the “OPTIMIZ-M” program will make it possible to quickly adjust the optimal area when moving from laboratory to industrial conditions.

Carrying out the solvent sublation process under optimal conditions will improve the quality of wastewater treatment and thus reduce the total cost of processing textile industry waste. The ranges of variation of the input variables, determined at the stage of the preliminary experiment, will make it possible to quickly adapt the process to industrial operation conditions.

It should be noted that the mathematical model and optimal conditions for the solvent sublation process were obtained for a data set with a limited number of dyes (active bright red, active bright blue, bromocresol green, and indigo carmine).

In addition, all experimental data were obtained using model solutions, which is a drawback of this study. In the future, it is necessary to investigate the process of solvent sublation removal of dyes on real wastewater.

Further research to build on our study should include verification of mathematical models and determination of optimal solvent sublation conditions for other dyes and their mixtures.

7. Conclusions

1. The relationship between quantitative and qualitative characteristics that affect the degree of solvent sublation wastewater treatment from dyes has been analyzed. The degree of dye purification was 89...97 % in 25 min without pH adjustment, at room temperature, and gas flow rate of 110–130 cm^3/min. The ratio of surfactant:pollutant significantly affects the purification efficiency. The following parameters were selected for experimental studies: pH, initial concentration of the pollutant, gas flow rate, and the ratio of surfactant:pollutant.

2. The experimental part was carried out according to the D-optimal experimental plan. The dependences of purification efficiency for four dyes on the selected parameters were obtained.

3. Based on our studies, by using the mathematical apparatus of the STAR system, mathematical models were constructed, and the best one was selected. This is a 2nd order regression model. The approximation error is 0.834; therefore, the proposed model describes the experimental data with a reasonable degree of accuracy. The stated optimization problem was solved using the “OPTIMIZ-M” program; the optimal process conditions were determined, under which the maximum removal of dyes (97.20 %) is achieved:

– pH: 6;
– initial pollutant concentration: 20 mg/dm^3;
– surfactant:pollutant ratio: 1.5:1;
– gas flow rate: 140 cm^3/min.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study, as well as the results reported in this paper.

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Data availability

The data will be provided upon reasonable request.

Use of artificial intelligence

The authors used artificial intelligence technologies within acceptable limits to provide their own verified data, which is described in the research methodology section.

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