



Research Article

Catalytic/inhibitory effect of the joint presence of two dyes on its destruction by underwater plasma processes: a tool for optimization parameters of treatment

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Abstract

The underwater plasma was used for the destruction of two-dye mixture. The Direct Blue azo dye and xanthene dye of Rhodamine 6G used as the model pollutants. The concentration of one of them is varied for modeling the processes in which one of the classes of the dye exceeded other dyes. The catalytic/inhibitory effect of the joint presence of two dyes is studied. The effect of initial temperature and the role of H₂O₂ in the mechanism of destruction were also investigated. It was established that the processes of decay of organic dyes proceed through the stages of the formation of intermediate products, which are catalysts or inhibitors of further degradation processes. An increase in the temperature of the solution has almost no effect on the degree of decolorization of the solution of the dye mixture. It is established that the destruction of Direct Blue 1 occurs under the action of hydrogen peroxide or HO₂ radicals, while Rhodamine 6G is destroyed by interaction with hydroxide radicals. The comparison of energy yield values with published data showed that underwater plasma is an effective method for removing the organic dyes from wastewater.

Keywords Underwater plasma · Destruction · Dyes mixture · Rhodamine 6G · Direct Blue 1 · Energy yield

1 Introduction

Dyes are complex organic compounds that are used in various industries (textile, chemical, dyeing, electronics, etc.). The disposal of organic compounds from wastewater is one of the main issues of treatment. Recently, there has been significant interest in using advanced oxidative processes to solve this problem [1–5]. Of interest are developments based on the use of nonthermal plasma in contact with a liquid, as reflected in recent papers [6–9].

There are many features of different types of electrical discharges. For example, the gliding arc discharge generates the nonthermal plasma in the gas phase with a high concentration of charged and neutral reactive species. On the other hand, the replacement of the plasma zone in a liquid volume and creating underwater discharge have

some advantages in comparison with electrical discharges above liquids. It is a large size of the contact of plasma zone and liquids, convective flows, and cavitation effect.

There are a lot of data in which the destruction of single dyes by electrical discharges treatment is studied [10–39]. One of the most popular objects of research is methylene blue dye, which is one of the thiazine dyes [10, 12, 16, 18, 21]. A large number of works are devoted to studying the effect of electric discharges on azo dyes due to the widespread use of this class of dyes [14, 15, 17, 19, 25–27, 30, 32, 34]. It should be noted that the growth of studies on the decomposition of anthraquinone dyes because of carcinogenic properties in water [20, 23, 24, 29, 31, 33, 35]. However, the wastewater of industrial factories contains more than one dye. It is the mixture of the organic and inorganic compounds. At present, there are

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some references regarding the application of nonthermal plasmas to a mixture of the organic dyes [39–42]. In [42], it was found that the destruction of two dyes occurs faster in their mixture than in the solutions, which contain only one dye. It was assumed that the dyes in a mixture or its by-products could be a catalyst in the degradation process.

In this work, the object of research was a plasma treatment of a mixture of dyes Rhodamine 6G and Direct Blue 1. The choice of dyes was determined by their belonging to different classes of dyes. Rhodamine 6G is a representative of the class of xanthene dyes, which are used in both the textile and electronics industries. Direct Blue dye 1 is an azo dye. Its choice is explained by the fact that about 70% of the dyes used in the industry account for this class of dyes. The underwater diaphragm discharge was used as the nonthermal plasma. The main goal of this paper is to investigate the effect of a concentration of azo dye on decolorization efficiency and the rate of the destruction of dye's mixture by underwater plasma treatment. Varying the concentration of azo dye concerning Rhodamine 6G models processes in which the content of azo dyes exceeds the concentration of other classes of dyes. Based on the early published data, we suggest that the presence of two or more organic dyes may induce the catalytic effect for fast degradation of both dyes. In the present work, we try to prove this assumption. The effect of the initial temperature of a solution was also studied.

2 Materials and methods

2.1 Materials

Rhodamine 6G (Rh6G) and Direct Blue 1 (DB) (Reachim, Russia) were used without any future purification. The molecular structures are shown in Table 1. HCl, KMnO_4 , KI, NH_4MoO_4 , $\text{Na}_2\text{S}_2\text{O}_8$, and oxalic acid were purchased from Reachim (Russia) and used as received. All chemicals were p.a. grade. All solutions were prepared using deionized water. To make the conductivity of a solution, the HCl is used (adjusted to pH 6.5). Conductivity of solution was $60 \mu\text{S cm}^{-1}$.

Aminoquinone was synthesized in laboratory at Department of Fine Organic Synthesis (Ivanovo State University of Chemistry and Technology).

2.2 Experimental setup

Schematic diagram of the experimental setup is shown in Fig. 1. An AC high-voltage transformer (50 Hz, 220 V/1 kV) was used to generate the underwater diaphragm discharge. The input power was 75 W. Two graphite rods with a diameter of 5 mm are used as metallic electrodes. One of them is placed in quartz ampoule with the diaphragm with a diameter of 2 mm. The plasma zone is created in water vapor bubble at the diaphragm. The solution volume was 500 mL. Dye's mixture solution was pumped to the reactor through a photometric bath using a peristaltic pump. The circulation rate was 80 mL min^{-1} . After treatment, the solution is collected for further analysis. Time of plasma treatment was 25 min.

Table 1 Molecular structure of dyes

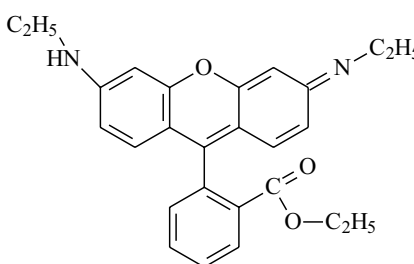
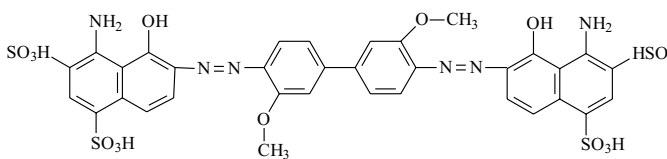
Name	Chemical structure	Chemical nature	λ_{max} (nm)
Rhodamine 6G		Xanten	525 ($\epsilon = 116,000 \text{ cm}^{-1} \text{ M}^{-1}$)
Direct Blue 1		Diazo	600 ($\epsilon = 26,800 \text{ cm}^{-1} \text{ M}^{-1}$)

Fig. 1 Scheme of experimental setup for in situ study of decolorization process 1—a solution of mixture dyes, 2—quartz ampoule, 3—graphite electrodes, 4—spectrophotometric bath, 5—photometric probes, 6—control unit, 7—PC, and 8—plasma zone

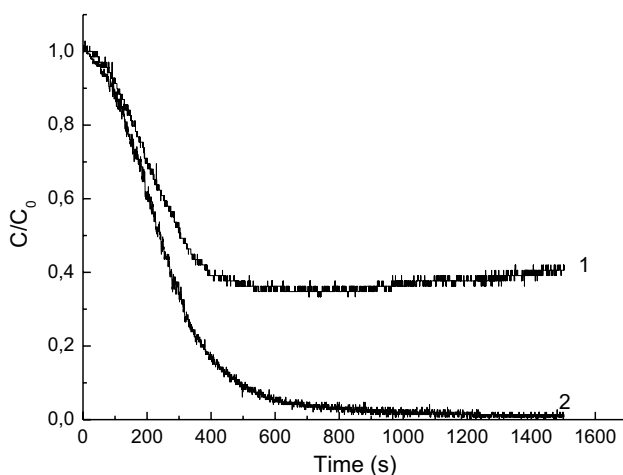
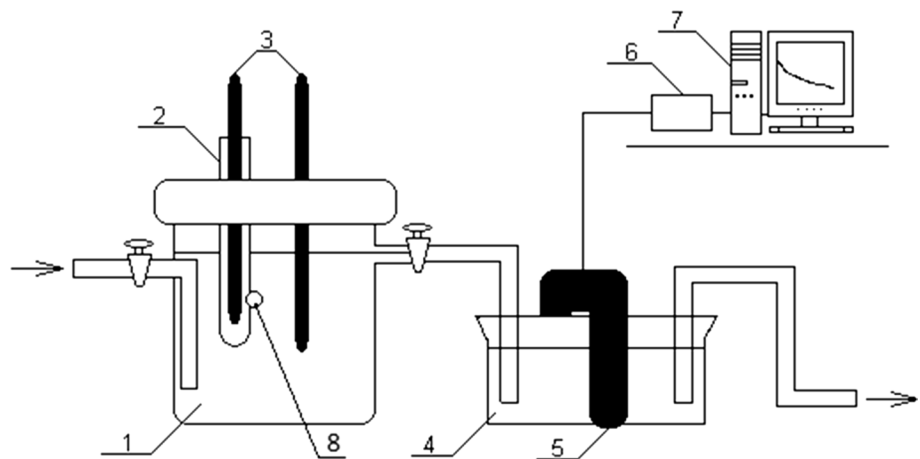


Fig. 2 Kinetic curves absorption intensity during plasma treatment. 1—Direct Blue dye and 2—Rhodamine 6G dye in the experiments with ratio of Rh6G to DB of 1:1.5

2.3 Methods of analysis

The mixtures of dyes were prepared by dissolving two dyes in deionized water. The concentration of Direct Blue 1 dye varied from 4 to 12 mg/L. The concentration of Rhodamine 6G was constant and equaled to 4 mg/L.

The concentration of dyes during plasma treatment was determined according to the Beer–Lambert law using photometric probes with wavelength 530 nm and 595 nm (Laboratory “L-micro”, Russia). The typical curves are depicted in Fig. 2.

The whole absorption spectra in the range of wavelength 190–750 nm were registered by UV–Vis absorption spectroscopy (SF 104, Akvilon, Russia) before and after plasma treatment. The quartz cuvettes with a length of 10 mm were used.

The concentrations of oxidizers were determined using the following methods. The H_2O_2 is detected using the reaction of hydrogen peroxide with KI in the presence of NH_4MoO_4 as the catalyst in an acid medium. The total concentration of oxidizers was determined by using the reaction with potassium permanganate. The products of the degradation process were analyzed by high-performance liquid chromatography (Gilson 302) and gas chromatography mass spectrometry (Shimadzu GCMS QP2010 Ultra).

For investigating an effect of the initial temperature of a solution on dye’s mixture decolorization in the absence of plasma, series experiments were carried out in the range of 10–80 °C. No changes in absorbance spectra are observed for 25 min. It means that dye’s mixture solution is thermally stable.

To determine the role of hydrogen peroxide in the destruction mechanism of dyes, the experiments were carried out without plasma treatment. 2 mL of H_2O_2 (30%) is added to the solutions of dye’s mixture and single dyes every 5 min. The changes of absorbance for both dyes are registered by photometric probes.

The acidity and conductivity of solutions were registered by pH meter I-160 (Akvilon, Russia) and conductivity meter InoLab (WTW, Germany) before and after plasma treatment.

2.4 Calculations

Decolorization efficiency is defined as a percent decrease in absorbance according to Eq. (1):

$$\alpha = \frac{A_0 - A}{A_0} \times 100\%, \quad (1)$$

where A_0 and A are the absorbance intensity of the initial dye's mixture solution and after plasma treatment (25 min).

The Rh6G and DB 1 decolorization rates are estimated according to Eq. (2):

$$r = \frac{dC}{dt} \Big|_{t \rightarrow 0} \tag{2}$$

The effect of temperature on the decolorization rates for Rhodamine 6G and the Direct Blue 1 was studied. The first-order rate constants were estimated for all temperature range (10–80 °C), and the Arrhenius equation in the linear form (Eq. 3) is used to estimate the activation energy of the Rh6G and DB1 destruction reaction in the solution of mixture dyes by plasma treatment.

$$\ln k = \ln A - \frac{E_a}{RT} \tag{3}$$

where E_a is activation energy (J mol^{-1}), A is frequency factor (s^{-1}), R is gas constant ($8.31 \text{ J K}^{-1} \text{ mol}^{-1}$), and T is an absolute temperature (K).

The energy yield is calculated using Eq. (4):

$$G = \frac{(C_0 - C_f) \cdot V}{P \cdot t} \text{ (g/kWh)} \tag{4}$$

where C_0 is an initial concentration of a dye, C_f is a residual concentration of dye after plasma treatment, V is volume of a solution, P is an input power, and t is the time of treatment.

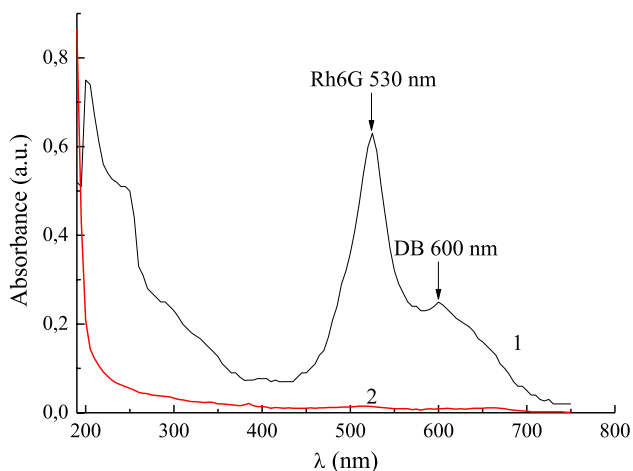


Fig. 3 Absorption spectra of dyes mixture solution before (1) and after (2) plasma treatment. The concentration of both dyes is 4 mg/L

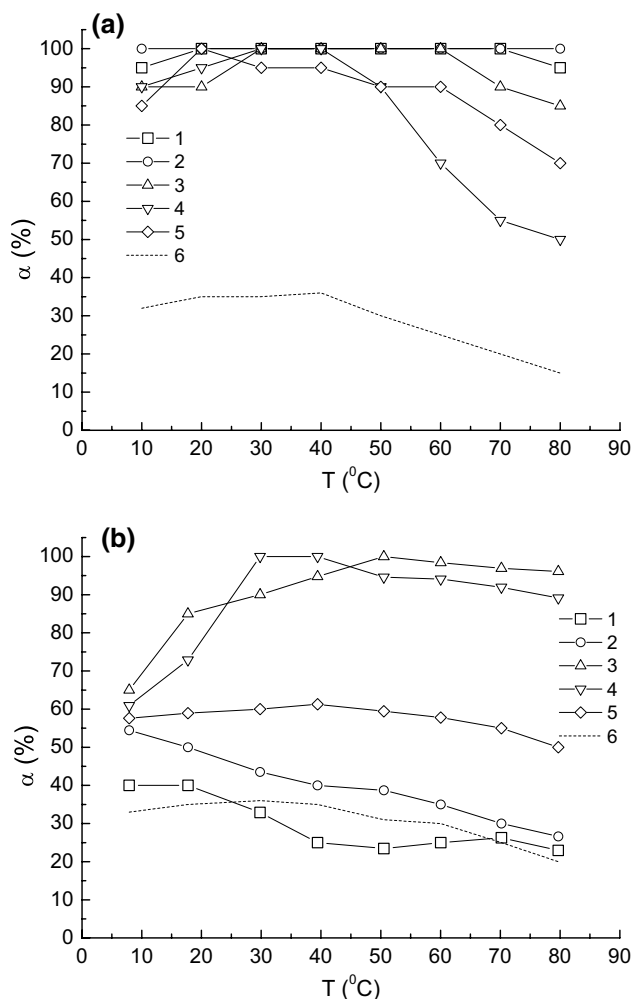


Fig. 4 Effect of initial temperature on the decolorization efficiency for Rhodamine 6G (a) and Direct Blue (b) in their mixture at concentration of DB: 1—4 mg/L, 2—6 mg/L, 3—8 mg/L, 4—10 mg/L, 5—12 mg/L, and 6—single dye. Concentration of Rh6G is 4 mg/L

3 Results and discussion

3.1 Decolorization efficiency (a)

The absorbance spectra of untreated and treated solutions of the dye's mixture are depicted in Fig. 3. The plasma discharge treatment leads to the disappearance of peaks for both dyes in the visible region and peaks in the range of 200–300 nm. However, the peak at $\lambda < 200 \text{ nm}$ has appeared. It can be a peak at 190 nm that corresponded to oxalic acid [43].

The pH of treated solution did not change significantly ($\Delta\text{pH} = -0.5$), whereas the conductivity of these solutions increased (up to $190 \mu\text{S cm}^{-1}$). This can be connected with appearance of anions in solutions. One can assume that an increase in the electrical conductivity of the solution

may prevent the complete decomposition of the Direct Blue dye (Fig. 2).

The effect of the conductivity of the solution on the generation/accumulation of reactive species or the destruction of organic compounds in aqueous solutions under the action of non-equilibrium plasma is a very interesting and still open question. Thorough research is required to answer this question. In the works [25, 30], it was found that an increase in the electrical conductivity of the solution leads to a decrease in the destruction efficiency of the dye. To date, we can only assume that an increase in electrical conductivity leads to an increase in the channels of expenditure of reactive species (competing reactions).

The effect of the initial temperature of a solution and concentration of DB dye on decolorization efficiency of two dyes in their mixture is presented in Fig. 4. The obtained results showed that the temperature range of 30–60 °C is optimal for reaching the maximal value of decolorization efficiency for Rhodamine 6G in all ranges of the dye's ratios. It should note that the maximal values of α for both dyes were reached at $T=50$ °C at concentration of blue dye of 8 mg/L and in the range of 30–40 °C at the concentration of DB of 6 mg/L. For the comparison, data on the efficiency of decolorization of single dye (not in a mixture) at plasma treatment are also given (curve 6 in Fig. 4). The dye concentration was 4 mg/L. One can see the decolorization efficiency for Rhodamine 6G is increased by three times. In the case of an azo dye with the same concentrations, the effect is noticeable only at low temperatures.

3.2 Rate of destruction

The rates of destruction were estimated by numerical differentiation of the kinetic curves of decolorization. Our results showed that the rates changed with the time of treatment. The same behavior was found in our previous studies [39–41]. It means that the serial-parallel reactions pass in the solution and finally we have some effective process of destruction. As known, the ignition of electrical discharge inside or above the aqueous solution initiates the formation of reactive species in a solution. We suggested that the dyes react with reactive species at the initial stage of plasma action. And then, not only reactive species but intermediates take part in the destruction process. In this case, the values of the rate of destruction at the initial time of treatment were chosen for the comparison of the rate of destruction for both dyes at various experimental conditions.

Our experimental results showed that the initial rate of destruction of the Direct Blue 1 dye increases with the concentration in a solution (Fig. 5). It is the following data of

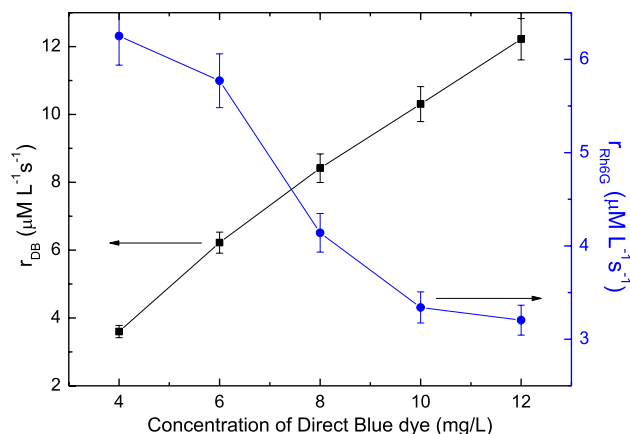


Fig. 5 Effect of DB1 dye concentration on the destruction rates for Rhodamine 6G (r_{Rh6G}) and Direct Blue (r_{DB}) dyes at initial temperature of solution of 20 °C

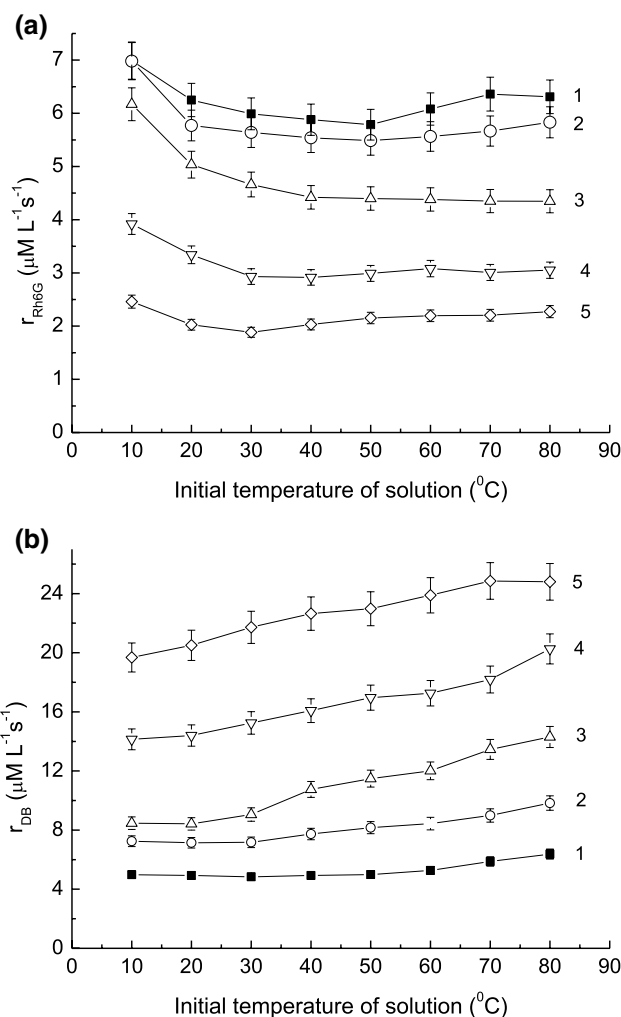


Fig. 6 Destruction rates for Rhodamine 6G (a) and for Direct Blue 1 dye (b) as a function of an initial temperature of dye's mixture solution at different concentrations of DB1: 1—4 mg/L, 2—6 mg/L, 3—8 mg/L, 4—10 mg/L, and 5—12 mg/L. The concentration of Rh6G is 4 mg/L

work [44], where authors found that in the range of small concentration of dye (33–150 mg/L) rate of destruction is linear with an increase in concentration. In the case of Rh6G, the increasing concentration of the DB1 dye in a solution leads to decreasing the rate of destruction. It is obviously due to competing reactions with the participation of the reactive species.

3.3 Effect of initial temperature

For Rhodamine 6G dye, in the temperature range of 10–30 °C, the increasing temperature induces the decrease in the destruction rate values (Fig. 6a). It can be connected with the formation of a dimer form of this dye [45, 46]. In the temperature range of 30–80 °C, increase in the initial temperature of a solution has little effect on the rate of the destruction. It is possible only in the case that the reaction passes into an intradiffuse zone of a solution. As known, the reactive species are formed in the small volume of a solution near to plasma zone [47]. The interaction of the hydroxyl radicals and molecule of Rh6G occurs in this small area, which can relate to an intradiffuse zone.

The formation of hydrogen peroxide can occur as in the small volume of a solution near to plasma zone as well as in the bulk of a solution (diffuse zone). In this case, the temperature of solution effects on the rate of the interaction as reflected for Direct Blue 1, the increase in initial temperature of a solution leads to the growth in the rate of destruction (Fig. 6b).

3.4 A possible mechanism of the destruction

When the plasma is ignited above or inside aqueous solutions, the reactive species, such as hydrogen atoms, hydroxyl radicals, hydrated electrons, and oxygen, are formed in a liquid. The main oxidative agent is OH[•] radical, which leads to the destruction of organic dyes [48–50]. It was assumed that the hydroxyl radicals are responsible for the destruction of both dyes. However, analysis of kinetic curves for Rh6G and DB1 showed that the reactive species that are responsible for destruction might be different. According to data of kinetics of the decolorization, the process for Rhodamine 6G is faster than for Direct Blue 1. This means that the destruction process may occur with primary reactive species, such as OH[•] radicals for Rh6G. It is possible because of the high rate constant reaction of hydroxyl radical with Rh6G ($1.1 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$) [51].

There are a lot of publications related to the study of formation and accumulation of hydrogen peroxide in aqueous solution by plasma treatment which is collected in the review Locke and Shih [52]. Thus, H₂O₂ can be the reactive agent responsible for the destruction process also.

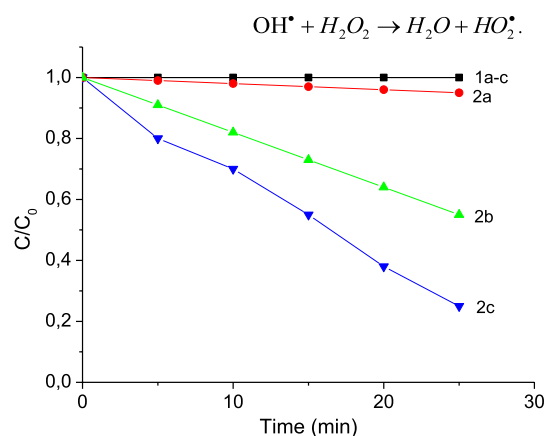
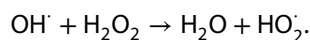


Fig. 7 Kinetic curves of destruction for Rhodamine 6G (1) and Direct Blue 1 (2) dyes at next conditions: (a) adding hydrogen peroxide to solution of single dye without plasma, (b) joint action of plasma and H₂O₂ on the solution of single dye, and (c) addition of H₂O₂ to solution of dyes mixture

A series of experiments were carried out on the effect of the addition of hydrogen peroxide on the decomposition of Rhodamine 6G and Direct Blue 1 dye individually and in a mixture without plasma and with combined action (Fig. 7). The results showed that the Rh6G is very resistant to hydrogen peroxide (curves 1 in Fig. 7). The absence of any effect with the combined action of hydrogen peroxide and plasma on the solution of a single dye is explained by the occurrence of a competing reaction involving the hydroxyl radical and H₂O₂ [51].



In the case of the azo dye, the addition of hydrogen peroxide without the plasma treatment of single-dye solution leads to 5% decomposition (curve 2a in Fig. 7). The combined effect of H₂O₂ and plasma causes 45% of DB1 destruction (curve 2b in Fig. 7). The greatest effect was registered in a mixture of dyes with the addition of hydrogen peroxide (curve 2c in Fig. 7).

We supposed that HO₂[•] or H₂O₂ reactive species are responsible for the destruction of DB dye. The dimerization of hydroxyl radicals is not one of the ways for the production of hydrogen peroxide. Moreover, the results of chemical analysis showed that the concentration of total oxidizers is 0.3 mM/L, whereas the concentration of H₂O₂ is 0.225 mM/L and concentration of ozone did not exceed 0.05 mM/L. This means that about 0.025 mM/L of long-lived (stable) compounds with oxidizing properties is present in the solution.

The results of GC/MS analysis in positive electrospray mode showed a dominant signal at $m/z = 319$ corresponds to 4-amino-5-hydroxynaphthalene-1,3-disulfonic acid

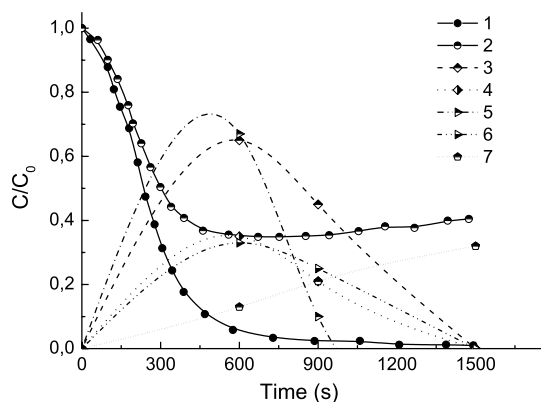


Fig. 8 Rhodamine 6G and Direct Blue 1 by-products evolution during plasma treatment: 1—Rh6G, 2—DB1, 3—3-aminophenol, 4—benzaldehyde, 5—1,1-dimethoxybenzidine, 6—SS acid, and 7—oxalic acid

(SS acid) as the main by-product. Additional peaks were registered at $m/z = 244$ (dimethoxybenzidine), $m/z = 123$ (aminoquinone), $m/z = 109$ (aminophenol), and $m/z = 106$ (benzaldehyde). The mass spectra of solution after 25 min of treatment showed the significant decrease in these peaks. This means that products of partial destruction of the organic dyes are also oxidizers and could take part in the oxidation processes. This is confirmed by the results of

LC (Fig. 8). The results of liquid chromatography analysis of solution after plasma treatment showed the presence of the oxalic acid and inorganic anions, such as nitrate, sulfate, and chloride ions.

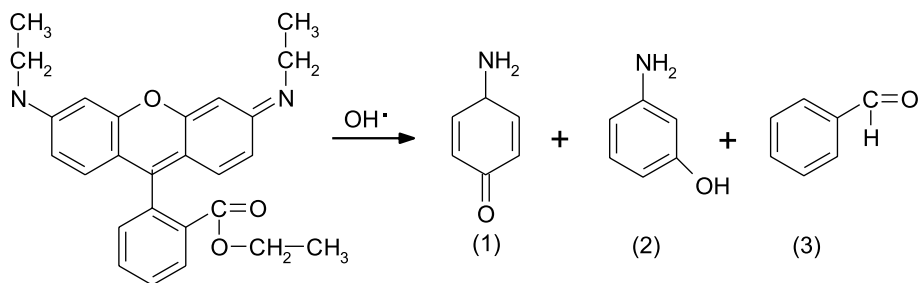
Based on the results of GC/MS analysis, we suggested the possible chemical pathways for destruction processes of dyes. In the case of Rhodamine 6G, the interaction between hydroxyl radicals and the molecule of dye leads to the break of the oxygen bridge that is responsible for the intensity of the color and removal of an ether group. Further destruction process leads to the production of an aminoquinone (1) in Scheme 1), which also has a high oxidizing ability. The formation of aminophenol (2) and benzaldehyde (3) is possible (Scheme 1).

In the case of Direct Blue 1, the reactive species react with the molecule's aminonaphthol part. It leads to the destruction of double nitric bonds, which are responsible for the color of this class of dyes. We suggest the formation of SS acid (4) and dimethoxybenzidine (5) which are transparent where the visible spectrum region occurs (Scheme 2).

3.5 Activation energy

Creating a plant for the treatment, the appropriate physical–chemical parameters are needed. In particular, the

Scheme 1 Possible destruction pathway of Rhodamine 6G and formation of by-products



Scheme 2 Possible degradation pathway of Direct Blue dye

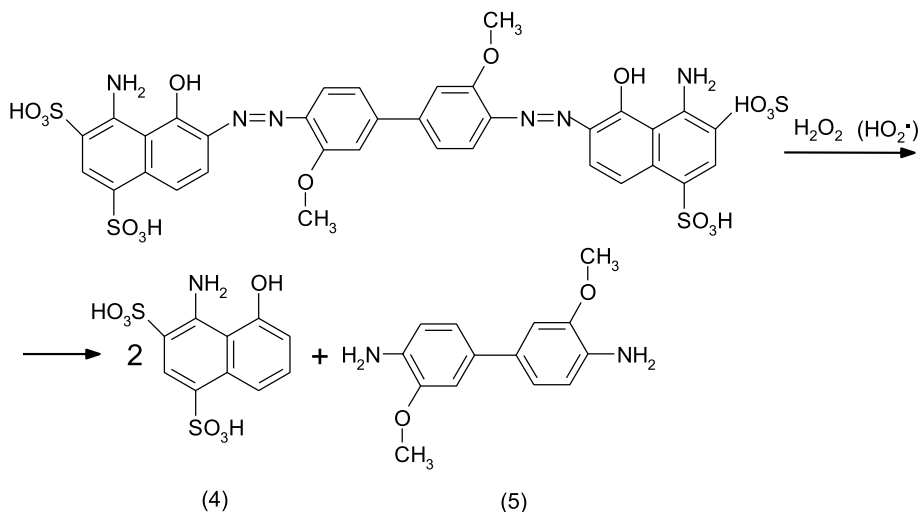


Table 2 Apparent activation energy values

Concentration of DB1 (mg/L)	E_a (kJ mol ⁻¹)	
	Rh6G	DB1
4	6.01	14.99
6	13.72	14.5
8	17.54	13.82
10	31.26	7.75
12	33.29	6.28

activation energy is one of a parameter that can predict the behavior of a reaction. In the case of single-step reactions, the value of E_a is determined easily. In the case of complex reactions, the activation energy value can estimate as an apparent E_a .

We took into account the fact that the efficacy of dye's destruction decreased at $T > 50$ °C. The estimation of energy activation values is carried out in the temperature range of 10–50 °C using Eq. (3). Calculated values are presented in Table 2. The low values of E_a (6–17 kJ mol⁻¹) attribute to reaction with radicals (OH[•] and HO₂[•]) [51]. Obtained values are comparable with published data [53–59].

Decreasing activation energy values for Direct Blue 1 dye means that the substance/catalyst is present in the solution which eases the destruction process. It could be aminoquinone. And reverse, increasing E_a for Rhodamine 6G with growth concentration of blue dye means that the inhibitor appeared in the solution. This can be one of the products of DB1 destruction process, for example oxalic acid. To check these assumptions, the two series of experiments were carried out without plasma treatment. In the first experiment, synthesized aminoquinone is added to dyes mixture at a ratio of dyes of 1:1 at 20 °C. The obtained results showed that the decolorization efficiency of Direct Blue 1 dye is increased to 85% and the initial rate of destruction is increased by 1.4 times. This means that the by-product of Rhodamine 6G is a catalyst for the destruction process of DB1. In the other experiments, the oxalic acid was added to dyes mixture at the same conditions. The initial rate of destruction for Rh6G is decreased by 25%. And it means that oxalic acid is an inhibitor of the destruction process of Rh6G. The obtained results are consistent with previously published data [58, 60], which were found that oxalic acid is an inhibitor of the decomposition reaction of the dye Rhodamine B.

3.6 Energy yield

The energy efficiency (yield) is a basic parameter of suggesting a method for cleaning. This parameter is determined as the amount of destroyed dye divided by the consumed energy (G). The results of calculations using

Eq. (4) are presented in Table 3. Despite the decrease in the efficiency of azo dye bleaching, the values of G become constant at concentrations of 8–12 mg/L. Our results are in qualitative agreement with the data of work 42. The values of the energy yield are higher for dyes taken in excess.

Using the methylene blue dye as an example, we can trace that different values of G are obtained using the same dye concentration and even the same electrode configuration system (the same type of electric discharge). It should be noted that in the work [16], to accelerate the decomposition process, the experiments are carried out in an oxygen atmosphere, whereas the authors of [21] used the addition of iron(II) ions. According to the energy yield values, conducting the experiments in an atmosphere of O₂ is more efficient.

An analysis of the data presented showed that the energy the yields are determined by the concentration of the dye, the degree of its decomposition, and the energy input. The combination of low-temperature plasma with the addition of hydrogen peroxide [12, 30, 31], iron(II) ions [12, 21, 25, 30, 35], bubbling with ozone [10, 14], or conducting experiments in an oxygen atmosphere [12, 16, 17, 33, 38], as well as the use of nanoparticles [14, 24, 32], accelerates the destruction processes and increases G .

The following point should be noted. When calculating the value of G , it is assumed that all the input energy is spent on the destruction processes. According to works [47, 61, 62], most of the input energy of 55–60% is consumed in heating the solution. Around 30% is distributed among radiant energy, generation of acoustic waves, and initiation of the chemical processes (23%) [47]. As was mentioned above, the increase in temperature of a solution does not induce the degradation processes. This means that most part of input energy does not take part in the destruction processes. In [53, 59, 63, 64], it was found that destruction of dyes occurs by acoustic waves and radiant energy (UV and visible radiation) also. Hence, only 1/3 part of input energy is consumed in the destruction processes in a solution. In our case, this means that the G values should be higher and it could be improved by applying at treatment facilities of a textile factory.

4 Conclusions

The application of the underwater AC diaphragm discharge plasma for the destruction of a mixture of two dyes was found to be effective. The efficiency of the destruction process was proved by UV-Vis spectra and HPLC-GC/MS analysis, which indicated that the destruction process occurs via the formation of the by-products. Experimentally proven that the Rhodamine 6G degradation by-product (aminoquinone) is a catalyst for the Direct Blue

Table 3 Energy yields of dyes by electric discharge treatment

Dye	Concentration (mg/L)	Decolorization (%)	G (g/kWh)	References
<i>Solution of mono dye</i>				
Methylene Blue	50	50	1.3	[21]
	4.8	52	0.035	[28]
	10	90	4.6	[12]
	40	93	0.29	[13]
	50	95	57	[16]
Acid Black 52	13.25	100	30	[10]
	4.6	100	0.008	[35]
Acid Blue 25	10	50	0.0012	[29]
	30	50	2.4	[23]
Acid Orange 7 (Orange II)	20	50	5.61	[27]
	1000	41.5	251	[19]
Acid Red 4	20	100	4.36	[20]
Acid Red 27	10	100	5.5	[14]
Acid Red 88	25	100	2.88	[17]
Alizarin red S	80.5	82	0.053	[42]
Aluminon	50	65	0.14	[37]
Amaranth azo dye	50	95	4.17	[15]
Aniline Blue	50	95	0.18	[37]
Azocarmine B	50	100	0.28	[37]
Bismark Brown	50	96	0.245	[37]
Congo Red	50	61.8	1.39	[30]
	1000	56.41	179	[19]
Crystal Violet	4.1	100	4.23	[38]
Direct Blue 1	4	30	0.005	This work
Indigo Carmine	30	40	0.4	[36]
Malachite Green	50	96	0.255	[37]
Methyl Orange	40	82	0.52	[13]
Methyl Red	40	90	0.57	[13]
Methyl Yellow	40	60	0.38	[13]
Naphthol Green B	50	50	0.07	[37]
Naphthol Blue Black	1000	53.25	215	[19]
Orange G	1000	50.81	215	[19]
	100	82	0.066	[42]
Phenol Red	40	93	1.17	[13]
Pyrocatechol Violet	50	70	0.145	[37]
Reactive Blue 4	20	100	4.36	[20]
Reactive Blue 19	20	87	0.027	[31]
	100	100	8	[33]
Rhodamine 6G	4	35	0.009	This work
Sulfanilic acid azochromotrop	50	97	0.18	[37]
Stilbazo	50	70	0.15	[37]
<i>Mixture of dyes</i>				
Alizarin red S + Orange G	322 + 100	80 for both dyes	0.206 (AR)	[42]
			0.064 (OG)	

Table 3 (continued)

Dye	Concentration (mg/L)	Decolorization (%)	G (g/kWh)	References
Rhodamine 6G + Direct Blue 1	4 + 8	25 (Rh6G)	0.032	[41]
		20 (DB1)	0.051	
	0.4 + 0.4	100 (Rh6G)	0.013	[40]
		58 (DB1)	0.007	
	4 + 4	100 (Rh6G)	0.13	This work
		40 (DB1)	0.051	
	4 + 6	100 (R6G)	0.13	
		50 (DB1)	0.096	
	4 + 8	90 (R6G)	0.12	
		85 (DB1)	0.22	
	4 + 10	95 (R6G)	0.12	
		73 (DB1)	0.23	
	4 + 12	100 (R6G)	0.13	
		60 (DB1)	0.23	

1 destruction process and oxalic acid is an inhibitor for the destruction of Rh6G. It is confirmed by the estimated energy activation of the destruction process for both dyes. The final compounds in a solution are oxalic acid and inorganic anions.

The results showed that the maximal decolorization efficiency (100%) is reached in the temperature range of 30–50 °C. This temperature range is an important parameter in the further application of this method to the real textile wastewater. It allows using the underwater diaphragm discharge with real wastewater without preliminary heat, since the real sewage of textile factories has a temperature around 30–40 °C. The presence of a catalyst in the system allows optimizing the conditions for cleaning. The formation of aminoquinone occurs for the first minutes of plasma treatment, and maximal concentration can reach for 10 min. The presence of catalyst and by-products can initiate the destruction process after plasma off (so-called post-effect). This allows reducing processing time and decreases energy costs. Based on these results, the next work is expected to develop the module prototype for cleaning textile wastewater in a sump of the textile factory.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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