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РАЗЛОЖЕНИЕ ОРГАНИЧЕСКИХ КРАСИТЕЛЕЙ В ИХ ВОДНЫХ РАСТВОРАХ ПОД ДЕЙСТВИЕМ ЭЛЕКТРИЧЕСКИХ РАЗРЯДОВ АТМОСФЕРНОГО ДАВЛЕНИЯ

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В обзорной работе рассматриваются процессы деградации органических красителей в их водных растворах под действием различных типов разрядов атмосферного давления. Эти процессы имеют важное значения для решения экологической задачи, связанной с очисткой воды от органических загрязнений. Дается краткое описание типов разрядов, используемых для этих целей - диэлектрического барьерного разряда, импульсного коронного разряда, разряда скользящей дуги, тлеющего разряда постоянного тока, диафрагменного разряда, электролиза контактным тлеющим разрядом. Приводятся электрические параметры разрядов – напряжения, токи, вкладываемые мощности. Анализируются результаты по степени деградации более 30 типов красителей в разных типах разрядов. Обсуждаются особенности сравнения разных типов разрядов по их энергетической эффективности процесса деградации – энергии, затрачиваемой на разложение одного грамма красителя. Показывается, что для корректного сравнения результатов по эффективности разложения в разных типах разрядов требует задания, по крайней мере, одинаковой удельной мощности разряда, одинаковой начальной концентрации красителя и одного объема обрабатываемого раствора. Рассматриваются кинетические закономерности процесса разложения и влияние на них различных факторов – начальной концентрации красителя, мощности разряда, pH раствора, строения молекул красителя. Показано, что в большинстве случаев кинетика разложения описывается уравнением первого кинетического порядка по концентрации красителя. Обсуждаются возможности ускорения деградации с использованием гомогенных и гетерогенных катализаторов. Анализируются возможные механизмы протекающих процессов и участие в них активных частиц, образующихся в растворе под действием разряда (радикалов OH, HO_2, озона и других).

Ключевые слова: газовый разряд, краситель, деградация, кинетика

DECOMPOSITION OF ORGANIC DYES IN THEIR AQUEOUS SOLUTIONS UNDER ACTION OF ELECTRIC DISCHARGES OF ATMOSPHERIC PRESSURE

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This review examines the processes of degradation of organic dyes in their aqueous solutions under the action of atmospheric pressure discharges. These processes are important for solving the environmental problem associated with the purification of water from organic pollution. A brief description of the types of discharges used for these purposes is given - dielectric barrier discharge, pulsed corona discharge, gliding arc discharge, direct current glow discharge, diaphragm discharge, and contact glow discharge electrolysis. The results are given on the degree of degradation of more than 30 types of dyes in different types of discharges. The features of comparing different types of discharges in terms of their energy efficiency of the degradation process - the energy spent on the decomposition of one gram of dye - are discussed. The kinetic regularities of the decomposition process and the influence on them of various factors - the initial concentration of the dye, the discharge power, and the pH of the solution are considered. Possibilities of accelerating degradation using homogeneous and heterogeneous catalysts are discussed. Possible mechanisms of the ongoing processes and the participation in them of active particles formed in solution under the action of a discharge (OH, HO_2 and ozone radicals) are analyzed.

Key words: gas discharge, die, degradation, kinetics

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INTRODUCTION

Organic synthetic dyes are widely used in the textile, light and food industries. For these purposes, more than one million tons of these substances are produced annually. As a result of the work of these enterprises, a large amount of wastewater is formed, contaminated with both dyes and other organic substances that are used in the technological process. Removal of synthetic dyes is a major challenge because they are relatively stable compounds and degrade slowly and poorly during physical, chemical or biological cleaning. Many of the dyes are toxic and have low maximum permissible concentration values (MPC). Thus, fluorescein ($C_{20}H_{12}O_5$) has an MPC of 0.0025 mg/L. For comparison, such a well-known toxicant as Cr^{6+} has MPC of 0.05 mg/l. To accelerate the decomposition, various methods of oxidative destruction are used, based on the use of systems containing strong oxidants: ozone (O_3) at pH > 8.5; O_3 and hydrogen peroxide ($O_3 + H_2O_2$); Fenton's system ($H_2O_2 + Fe^{2+}$); O_3 and UV radiation; H_2O_2 and UV; O_3, H_2O_2 and UV; Fenton's photo-system and photocatalytic oxidation (TiO_2 (anatase) + UV). These methods, although effective, are relatively expensive, since they require the use of not only additional equipment (ozonizers, UV lamps), but also additional reagents ($H_2O_2 + Fe^{2+}$, catalysts).

For this reason, in the last twenty years, the increased interest of researchers has been caused by the use of electrical discharges of atmospheric pressure for the oxidative destruction of various organic pollutants in their aqueous solutions. Apparently, for the first time, the possibility of using a discharge for effective destruction of an anthraquinone dye was shown in [1]. The attractiveness of plasma systems lies in the fact that when they act on water, a wide range of chemically active particles appears in it and above it, which have both oxidizing and reducing properties. Oxidants are represented by OH radicals (standard oxidation potential $E^0 = 2.85$ V), HO_2 ($E^0 = 1.70$ V), O atoms ($E^0 = 2.42$ V), hydrogen peroxide ($E^0 = 1.68$ V), ozone ($E^0 = 1.51$ V), and reducing agents – H atoms ($E^0 = -2.3$ V), hydrogen molecules and solvated electrons ($E^0 = -2.68$ V). These particles are formed without the use of any chemical reagents, and the surrounding air can be the plasma-forming gas [2, 3]. In addition, the discharge burning is always accompanied by UV radiation. That is, the action of the discharge leads to the formation of the same reagents that are used in the already mentioned methods.

TYPES OF DISCHARGES

For the treatment of aqueous solutions, various reactors have been proposed that use different types of discharges. Reactor designs are considered in more detail in [4]. The most commonly used are dielectric barrier discharge (DBD) [5], pulsed corona discharge [6], gliding arc discharge (GAD) [7], direct current glow discharge (DCGD) [8], diaphragm discharge [9], contact glow electrolysis discharge (CGED) [10].

The DBD is excited by applying a high AC voltage between metal electrodes. The gas gap between them includes one or more dielectrics located in the path of the discharge current. The solution to be treated is between the electrodes. The frequencies of the alternating voltage are 40 Hz – 500 kHz, and the gas gaps range from tenths of a millimeter to several centimeters. At atmospheric pressure and millimeter gaps, typical values of breakdown voltages are ~ 10 kV. Average discharge currents range from several milliamperes to tens of milliamperes.

The impulse corona belongs to the streamer type of discharge. A streamer (micro-discharge) is a thin current cord. A large number of streamers appear in the positive corona near the anode, which begin to multiply and spread to the cathode, gradually filling the interelectrode gap. The amplitude of current pulses, as a rule, is tens, but can reach hundreds of amperes. Amplitude voltage values reach tens of kilovolts. The pulse repetition rate is usually tens of hertz, and their duration is from tens of nanoseconds to tens of microseconds. Both discharge electrodes can be either in solution (underwater discharge), or one of them is located in the gas phase.

A gliding arc discharge is initiated by applying a high DC or AC (~ 50 Hz) voltage to two electrodes, at least one of which has a diverging curvilinear shape. The discharge is ignited at the narrowest point between the electrodes, the plasma column begins to move along the gas flow in the direction of increasing the interelectrode gap, and at some point the discharge disappears. Then the ignition-extinction cycle is repeated. At atmospheric pressure in air and a minimum gap (1-2) mm, the breakdown voltage is ~ 3 kV. The arc discharge current can vary over a wide range (from several mA to tens of A) and depends on the voltage of the power source (up to several kV), its power and the resistance of the external circuit. The discharge burns either over the solution being treated, or the solution in the form of drops is blown into the discharge zone by the gas flow.

In a DC discharge, one of the electrodes (usually the cathode) is in solution, and the other (anode) is in the gas phase. The discharge burns when a constant voltage is applied between the anode and the surface of the solution. The applied voltages are tens of kilovolts, and the discharge currents are up to 100 mA.

In a diaphragm discharge (DD), both electrodes are in solution, which is divided into two parts by a dielectric diaphragm. The discharge current is concentrated in the diaphragm, causing a strong heating of the electrolyte in it, and, ultimately, to the formation of a vapor bubble, the breakdown of which leads to the discharge burning in it. Since in this case the plasma is not in contact with the electrodes, such a discharge is often called electrodeless. The voltages used are up to 1 kV, and the discharge currents are usually less than 1 A.

In the CGED, both electrodes are in solution. One of them (cathode) is much smaller than the other. Due to the high current density at the cathode at a certain discharge current due to the large heat release around the cathode, a vapor-gas bubble is formed, the breakdown of which leads to the ignition of the discharge in it. Typical voltages usually do not exceed 1 kV, and discharge currents reach several hundred milliamperes.

DECOMPOSITION CHARACTERISTICS OF VARIOUS TYPES OF DYES

Synthetic dyes are relatively large molecules with a molecular weight, usually in excess of 300 g/mol, and contain a characteristic chromophore group (usually a system of conjugated double bonds) responsible for the color of the dye. They differ greatly in their chemical composition, although the most studied are azo dyes (contain the -N = N- group), anthraquinone dyes (anthraquinone derivatives), indole, sulfur, indigo, and triphenylmethyl. Due to the high absorption coefficients, the concentration of dyes is easily determined by spectrophotometric methods. Therefore, dyes are one of the most commonly used model compounds for investigating the efficiency of electric discharge reactors. For this reason, there are quite a few publications on the degradation of various types of dyes, and the main results are shown in Table.

For an CGED, table gives only one example (item 34). Data for solutions of other dyes (cationic blue, methyl orange, acridine orange, acid orange, weak brilliant red B, weak acid flavin G, polar brilliant, crystal violet, methyl violet, alizarin red C, reactive yellow 176, reactive red 239, reactive black 5, cationic red, eosin) can be found in reviews [10, 22].

The presented results show that the use of any type of discharge leads to efficient degradation of dyes in a relatively short time. Unfortunately, the available data do not allow a conclusion about which type of discharge is the most effective. Unlike low pressure discharges [23], for atmospheric pressure discharges there is no similarity theory, which determines the parameters, the fixation of which allows an adequate comparison. An attempt to compare different types of discharges in terms of their efficiency with respect to the decomposition of dyes was undertaken in [24]. The author proposes to use for comparison the energy criterion $G_{50} = m_{50}/(P \cdot t)$, where P is the power supplied to the discharge, t is the duration of the discharge, during which the mass of the initial dye (concentration) decreases by 50% (m_{50}). Energy indicators are of course the most general. But in this case, such an indicator is not too adequate for the following reasons, which are known from the experiment. At the same initial concentration, the decomposition rates nonlinearly depend on the input power. At a given power, the rates increase with increasing concentration, but also nonlinearly. At the same concentration and power, the rates depend on the volume of the treated solution - the smaller the volume, the higher the rate [25]. For this reason, the G_{50} values calculated in [24] even for the same dye and the same type of discharge differ by orders of magnitude. Therefore, the energy criteria can be used to compare the resistance of different dyes to the action of the discharge, if the corresponding results were obtained in the same reactor at the same initial concentration and discharge power. This, for example, was done in [5] (see Table), where the energy required for the decomposition of 1 g of the dye at a decomposition degree of 90% was used as a criterion of persistence. The most persistent was Acid Orange 67 (866 kJ/g), and the least persistent was Basic Red 14 (18.7 kJ/g). Correlations were found between the structure of the dye molecule and its resistance to the action of the discharge. Thus, the most stable dyes CAS 72479-28-8 (392 kJ/g) and Acid Orange 67 (866 kJ/g) have an azo chromophore with a bond cleavage energy of ~ 4.2 eV. The chromophore group of anthraquinone dyes has a bond cleavage energy of ~ 3.6 eV. Degradation of these dyes requires less energy. So, Acid Blue 225 requires costs of 43.3 kJ/g, and Reactive Blue 114 -51.6 kJ/g. It was also reported in [26] that azo dyes containing –OH, $–NH_2$ groups are easier to decompose than those that have $–CH_3$, $–NO_2$, $–SO_3H$, and $–OCH_3$ groups.

Table

Indicators of discoloration of various dyes in their aqueous solutions under the action of various types of discharge

***Таблица*. Показатели обесцвечивания различных красителей в их водных растворах под действием различных типов разряда**

N	Dye	Discharge and solution parameters	Discoloration degree	Reference
1	2	3	4	5
1	Rhodamine B, $C_{28}H_{31}ClN_2O_3$	Positive corona, U = 20 кV, f = 25 Hz, C = 0.01 g/l		[11]
		pH = 3.5	0.78 in 1 h	
		pH = 7.5	0.43 in 1 h	
		pH = 10.3	0.37 in 1 h	
2	Methyl Orange, $C_{14}H_{14}N_3O_3SNa$	Positive corona. U = 20 кV, f = 25 Hz, C = 0.01 g/l		[11]
		pH = 3.5	0.73 in 1 h	
		pH = 7.5	0.38 in 1 h	
		pH = 10.3	0.35 in 1 h	
3	Chicago Sky Blue, $C_{34}H_{24}N_6Na_4O_{16}S_4$	Positive corona, U = 20 кV, f = 25 Hz, C = 0.01 g/l		[11]
		pH = 3.5	0.9 in 1 h	
		pH = 7.5	0.5 in 1 h	
		pH = 10.3	0.37 in 1 h	
4	Rhodamine B, $C_{28}H_{31}ClN_2O_3$	Positive corona, U = 20 кV, f = 25 Hz,		[12]
		C = 0.01 g/	0.95 in 2 h	
		C = 0.05 g/l	0.8 in 2 h	
5	Methyl Orange, $C_{14}H_{14}N_3O_3SNa$	Positive corona, U = 20 кV, f = 25 Hz, C = 0.01 g/l	0.95 in 2 h	[12]
6	Chicago Sky Blue, $C_{34}H_{24}N_6Na_4O_{16}S_4$	Positive corona, U = 20 кV, f = 25 Hz,		[12]
		pH = 3.5 C = 0.01 g/l	0.5 in 0.5 h	
		pH = 7.5 C = 0.01 g/l	0.2 in 0.5 h	
		pH = 10.3 C = 0.01 g/l	0.1 in 0.5 h	

1	2	3	4	5
7	Straight Orange 39, $C_{12}H_{10}N_3SO_3Na$	Positive corona, U = 45 кV, f = 60 Hz, C = 20 mg/l, pH = 4 pH = 6	0.64 in 1 h 0.26 in 1 h	[13]
8	Methyl Yellow, $C_{14}H_{15}N_3$	Positive corona, U = 17 кV, f = 100 Hz, C = 40 mg/l	0.60 in 10 min	[14]
9	Methyl Red, $C_{15}H_{15}N_3O_2$	Positive corona, U = 17 кV, f = 100 Hz, C = 40 mg/l	0.90 in 10 min	[14]
10	Methyl Orange, $C_{14}H_{14}N_3O_3SNa$	Positive corona, U = 17 кV, f = 100 Hz, C = 40 mg/l	0.82 in 10 min	[14]
11	Phenol Red, $C_{19}H_{14}N_3O_5S$	Positive corona, U = 17 кV, f = 100 Hz, C = 40 mg/l	0.93 in 5 min	[14]
12	Methylene Blue, $C_{16}H_{18}ClN_3S$	Positive corona, U=17 кV, f=100 Hz, C=40 mg/l	0.83 in 5 min	[14]
13	Indigocarmine, $C_{16}H_{10}N_2O_8S_2$	Positive corona, U = 8 кV, f = 12-15 кHz, C = 42 mg/l, pH = 3.5 pH = 7.4	0.8 in 10 min 0.5 in 10 min	[15]
14	Methylene Blue, $C_{16}H_{18}ClN_3S$	Positive corona, U = 17 кV, f = 27 Hz, C = 50 mg/l	0.9 in 5 min	[16]
15	Methylene Orange, $C_{14}H_{14}N_3O_3SNa$	Positive corona, U = 2 кV, f = 250 Hz, C = 10 mg/l, pH = 2	1 in 10 min	[17]
16	Methylene Red, $C_{15}H_{15}N_3O_2$	DC, U = 1.5 кV, Current 35-40 мА, C = 30 mg/l, pH = 1	0.98 at solution flow rate of 1 ml/min.	[18]
17	Blue 25, $C_{20}H_{13}N_2O_5NaS$	DC, U = 2 кV, Current 55 мА, C = 10 mg/l, pH = 6.7	0.82 in 1 h	[8]
18	Methyl Orange, $C_{14}H_{14}N_3O_3SNa$	DBD, U = 3.9 кV, f = 60 Hz, C = 10 mg/l	0.93 in 15 min	[19]
19	Acid Red 27, $C_{20}H_{11}N_2Na_3O_{10}S_3$	ДБР, W = 5 W, f = 100 Hz, C = 50 mg/l, pH = 3.	1 in 0.5 h	[20]
20	Basic Red 46, $C_{18}H_{23}BrN_6$,	DBD, W = 10 W, f = 8 kHz, C = 20 mg/l	0.9 in 393 s	[5]
21	PReactive Red 158, $C_{32}H_{18}ClF_2LiN_6Na_2O_{11}S_3$	DBD, W = 10 W, f = 8 кHz, C = 20 mg/l	0.9 in 230 s	[5]
22	Reactive Yellow 125, $C_{22}H_{13}ClF_2N_6Na_2O_7S_2$,	DBD, W = 10 W, f = 8 кHz, C = 20 mg/l	0.9 in 399 s	[5]
23	Acid Blue 117, $C_{24}H_{21}N_5O_8S_2Na$,	DBD, W = 10 W, f = 8 кHz, C = 20 mg/l	0.9 in 44 s	[5]
24	Acid Orange 67, $C_{26}H_{21}N_4O_8S_2Na$,	DBD, W = 10 W, f = 8 кHz, C = 20 mgr/l	0.9 in >600 s	[5]
25	Mixture of CAS 72479-28-8, $C_{22}H_{14}Cl_3N_4NaO_5S$, and CAS 70247-70-0, $C_{19}H_{12}BrCl_2N_5Na_2O_8S_2$	DBD, W = 10 W, f = 8 кHz, C = 20 mg/l	0.9 in >600 s	[5]

1	2	3	4	5
26	Reactive Blue 114, $C_{25}H_{16}ClF_2N_5O_8S_2Na_2$	DBD, W = 10 W, f = 8 кHz, C = 20 mg/l	0.9 in 95 s	[5]
27	Acid Blue 225, $C_{26}H_{20}N_3O_6SBr_2Na$	DBD, W = 10 W, f = 8 кHz, C = 20 mg/l	0.9 in 73 s	[5]
28	Basic Yellow 51, $C_{20}H_{25}N_3O_4S$	DBD, W = 10 W, f = 8 кHz, C = 20 mg/l	0.9 in 91 s	[5]
29	Basic Red 14, $C_{23}H_{26}N_3Cl$,	DBD, W = 10 W, f = 8 кHz, C = 20 mg/l	0.9 in 31 s	[5]
30	Mixture of Basic Blue 159 and Basic Blue 3. $C_{17}H_{25}N_6ZnCl_3$ and $C_{20}H_{26}N_3OCl$	DBD, W = 10 W, f = 8 кHz, C = 20 mg/l	0.9 in 44 s	[5]
31	Optilan Red MF-GRLN, formula unknown	DBD, W = 10 W, f = 8 кHz, C = 20 mg/l	0.9 in >600 s	[5]
32	Lanaset Red 2R, formula unknown	DBD, W = 10 W, f = 8 кHz, C = 20 мg/l	0.9 in 206 s	[5]
33	Alizarin Red S, $C_{14}H_7NaO_7S$	DCGD, U = 600 B, Current 0.16 A, C = 2.5 mg/l	0.9 in 535 s	[7]
34	Brilliant Green, $C_{27}H_{34}N_2O_4S$	CGED, U = 600 V, Current 135 мА, C = 30 mg/l pH = 6.7	0.95 in 600 min	[21]

Примечание: С-начальная концентрация раствора, f-частота, U-напряжение, W-мощность
Note: C-initial concentration of solution, f-frequency, U-voltage, W-power

No one has seriously investigated the reasons for such strong differences in energy indicators. There are only some more or less reasonable hypotheses. Thus, the dependence on the volume of the solution is explained as follows [25]. The initiation of chemical reactions occurs as a result of the bombardment of the solution surface with positive ions accelerated in the cathodic potential drop. The values of cathode drops are ~ (400-700) V [2,3]. The penetration depth of ions into the solution at such energies is several nanometers [27]. The characteristic diffusion length for the formed active particles is ~ 10 μm [28]. Consequently, the size of the reaction zone is significantly less than the characteristic size of the solution as a whole (usually 1 cm or more). At the same time, the chemical analysis of the composition of the solution gives the average concentration over the entire volume of the solution. Therefore, with the same discharge parameters, the apparent decrease in concentration is the smaller, the larger the volume of the solution, that is, the smaller the ratio of the reaction region size to the reactor size. The authors of [29] explain the possible reason for the nonlinear dependence of the decomposition rate on the initial concentration (rate limiting with increasing concentration) by the fact that the reaction of formation of active particles leading to degradation under the action of the discharge becomes the limiting stage of decomposition.

FEATURES OF KINETICS AND MECHANISM OF DYE DEGRADATION

All the data in Table 1. were obtained based on changes in the absorption bands of the chromophore group of the dye. In the only work known to us [21], not only the absorption of the chromophore, but also of other functional groups of the dye molecule was investigated. It turned out that they also undergo degradation, but with rates different from the rates of destruction of the chromophore. Therefore, the overall degradation process includes several parallel channels.

For all types of discharge, in the works where the kinetic dependences of concentration - time were processed, it was noted that the kinetics of degradation obeys the equation of pseudo-first kinetic order in the concentration of the dye. Typical values of these constants depend on the type of dye, conditions and lie in the range $(7\cdot10^{-4}\text{-}7\cdot10^{-2})\ s^{-1}$. Note that this order of magnitude of the constants is common for the degradation processes of all investigated organic compounds, for example, phenols and their derivatives [25, 30]. This indicates the commonality of the initiation stages and the low selectivity of the active particles formed in solution to various functional groups of organic compounds. The constants obtained are, of course, effective and include the concentration of particles leading to degradation. Their independence on time suggests that the concentrations of active particles on the time scale of the process are quasi-stationary. The effectiveness of constants is that they depend on conditions. Thus, with an increase in the initial concentration of the dye, at unchanged discharge parameters, the effective rate constant decreases. But this decrease is less than the increase in concentration. Therefore, the rate of degradation is increasing. As a consequence, the energy efficiency of the process increases, but the degree of decomposition achieved over the same processing time decreases. At the same concentration, the rate constant increases with an increase in the power input into the discharge, as is the rate and degree of decomposition.

Decomposition rates also depend on the pH of the solution. In acidic solutions, decomposition proceeds at a higher rate [8, 12, 28]. One of the reasons for this phenomenon may be related to the fact that the form of the dye in solution depends on its pH. For example, Alizarin S presents three ionic forms in accordance with changes in pH, which correspond to the deprotonation of two phenolic groups, while the molecular form arises from the fixation of H^+ on the sulfonate group (SO^{3-}), and can only be expected in strongly acidic environments. The main form of this colored indicator, In^{3-}, (purple absorption band at about 560 nm); HIn^{2-} (red band, 525 nm); H_2In^- (yellow band, $\lambda = 422$ nm). The equilibrium acidity constants are pKa (H_2I^-/HIn^{2-}) = 5.5 and pKa (HIn^{2-}/In^{3-}) = 10.8. It is clear that different forms can have different reactivity.

The degradation process is accelerated by approximately two times with the additional use of catalysts, both homogeneous and heterogeneous. Solutions of iron salts Fe^{2+} (Fenton's reagent) [12] are used as homogeneous catalysts, and either titanium dioxide suspensions in the anatase modification [8] or fine mesh coated with TiO_2 [20] are used as heterogeneous catalysts. Typical values for Fe^{2+} concentration are a few tenths of mmol/l, and the TiO_2 loading is a few tenths of a gram per liter.

The mechanism of dye degradation processes is poorly understood. To elucidate it, information is needed on the composition of the reaction products and the kinetics of their formation and decay. And such data is extremely limited. So, in work [5], the time course of IR absorption spectra in the range of wavenumbers (500-4000 cm^{-1}) was studied during processing of the dyes presented in the Table (positions 20-32). The disadvantage of IR spectroscopy is that it does not allow to determine a specific chemical compound, but only determines the presence of a functional group. As a result, the authors of [5] concluded that the degradation products of most dyes are similar and include carboxylic acids, nitrates, amides, and amines. In [21], the decomposition products of Brilliant Green in CGED (position 34 of the Table) were investigated by gas chromatography-mass spectrometry. It was found that after 5 minutes of exposure, the decomposition products were benzoic acid, 1,2,3,4,5,6-cyclohexanexaol and carboxylic acids (oxalic acid, succinic acid and hydroxyacetic acid). Data on kinetics and product concentrations are not provided. Apparently, the Brilliant Green molecule (includes 3 benzene rings) first cleaves into benzoic acid and 1,2,3,4,5,6-cyclohexanexaol, and then, after ring opening, many smaller organic acid molecules are formed. Unlike [5], the authors do not indicate the presence of nitrogen-containing compounds, although nitrogen is part of the dye molecule. These data allow us to say only that there is oxidative destruction of the dye molecule. It is difficult to determine which particles are responsible for this process. The available data allow us to express only some general considerations. Thus, the acceleration of decomposition processes when using catalysts indicates that OH radicals are the particles initiating oxidative destruction. Indeed, the generally accepted opinion is that the addition of Fe^{2+} leads to an increase in the concentration of OH radicals as a result of the reactions

$Fe^{2+} + H_2O_2 \rightarrow OH + OH^- + Fe^{3+}$,
$Fe^{2+} + OH \rightarrow OH^- + Fe^{3+}$,
$Fe^{3+} + H_2O_2 \rightarrow H^+ + HO_2 + Fe^{2+}$,
$HO_2 + H_2O_2 \rightarrow H_2O + O_2 + OH$

Hydrogen peroxide is always formed in water under the action of any type of discharges [31].

Titanium dioxide also catalyzes the formation of OH radicals by reactions

$TiO_2 + h\nu \rightarrow e^- + h^+$,
$e^- + H_2O_2 \rightarrow OH^- + OH$,
$h^+ + H_2O_2 \rightarrow H^+ + HO_2$,
$h^+ + H_2O \rightarrow H^+ + OH$

TiO_2 is a semiconductor that, when excited by discharge radiation $h\nu$, generates an electron (e^-) – hole (h^+) pair. The reactions of electrons and holes with water and hydrogen peroxide molecules lead to the formation of OH radicals. The possible participation of OH radicals in oxidative destruction is indicated by the observed decrease in the rate with increasing pH. It is known that in an alkaline solution, OH is rapidly converted into an O- ion, which has a lower oxidizing capacity compared to OH [28]

$OH + OH^- \leftrightarrow O^- + H_2O$ pK= 11.9

Possible oxidants can also be HO_2 radicals and ozone. Typical rate constants for the interaction of OH, HO_2, and O_3 with aromatic compounds are ~10^{10}, 10^3, and 10^2 l/(mol·s), respectively. Typical concentrations of OH and HO_2 in solution are ~10^{-8} and 10^{-5} mol/l [32].

The maximum concentration of ozone in the gas phase (DBD in oxygen) is ~$2 \cdot 10^{-3}$ mol/l. Consequently, the rates of reactions with the participation of O_3 and HO_2 are significantly lower than those with OH radicals.

CONCLUSION

Thus, the effect of any kind of atmospheric pressure discharges on aqueous solutions of dyes is an effective tool leading to effective degradation of dyes.

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