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ДЕСТРУКЦИЯ ВОДНЫХ РАСТВОРОВ 2,4-ДИХЛОРФЕНОЛА В ПЛАЗМЕННО-КАТАЛИТИЧЕСКОМ РЕАКТОРЕ БАРЬЕРНОГО РАЗРЯДА

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В работе были исследованы процессы деструкции водных растворов 2,4-дихлорфенола в диэлектрическом барьерном разряде атмосферного давления в среде кислорода, с находящимся внутри реактора катализатором Pt/Al_2O_3. Экспериментально показано, что 2,4-дихлорфенол разрушается в плазме достаточно эффективно (степень деструкции достигает не менее 70 %). В работе были оценены кинетические параметры и определены основные промежуточные и конечные продукты процесса разложения 2,4-дихлорфенола под действием активных частиц плазмы в присутствии катализатора. Деструкция исходного соединения описывается кинетическим уравнением первого порядка по концентрации 2,4-дихлорфенола. Эффективная константа скорости слабо зависит от условий эксперимента и составляет 0,43 $с^{-1}$. Состав продуктов деструкции был изучен методом газовой хроматографии, а также флуоресцентным, спектрофотометрическим и потенциометрическим методами. В качестве конечных продуктов деструкции выявлены Cl^- в жидкой фазе, а также CO_2 в газовой фазе, а промежуточными продуктами деструкции являются карбоновые кислоты и альдегиды, но их концентрации невелики относительно диоксида углерода. Молекулярный хлор в газовой фазе не обнаружен. Установлено, что озон не вносит существенного вклада в процесс окислительной деструкции 2,4-дихлорфенола, т.е. в процессе окисления основную роль играют другие активные частицы плазмы, например, гидроксильные радикалы и атомарный кислород.

Ключевые слова: 2,4-дихлорфенол, диэлектрический барьерный разряд, плазма, кислород, водоочистка, катализатор

DESTRUCTION OF AQUEOUS SOLUTIONS OF 2,4-DICHLOROPHENOL IN A PLASMA-CATALYTIC BARRIER DISCHARGE REACTOR

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In this work, the processes of destruction of aqueous solutions of 2,4-dichlorophenol in a dielectric barrier discharge of atmospheric pressure in an oxygen atmosphere with a Pt/Al_2O_3 catalyst located inside the reactor were investigated. It has been shown experimentally that 2,4-dichlorophenol is destroyed in plasma quite efficiently (the degree of destruction reaches at least 70%). In this work, the kinetic parameters the destruction process were estimated and the main intermediate and final products of the decomposition of 2,4-dichlorophenol under the action of active plasma particles in the presence of a catalyst were determined. The destruction of the starting compound is described by a kinetic equation of the first order on the concentration of 2,4-dichlorophenol. The effective rate constant weakly depends on the experimental conditions and it was equal to 0.43 s^{-1}. The composition of the destruction products was studied by gas chromatography, as well as by fluorescence, spectrophotometric, and potentiometric methods. Cl^- in the liquid phase, as well as CO_2 in the gas phase, were identified as the end products of destruction, and the intermediate products of destruction are carboxylic acids and aldehydes, but their concentrations are low relative to carbon dioxide. Molecular chlorine was not detected in the gas phase. It was found that ozone does not make a significant contribution to the oxidative degradation of 2,4-dichlorophenol, while other active plasma particles, for example, hydroxyl radicals and atomic oxygen, play the main role in the oxidation process.

Key words: 2,4-dichlorophenol, dielectric barrier discharge, plasma, oxygen, water treatment, catalyst

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INTRODUCTION

Toxic and oxidation-resistant organic compounds pose a serious threat to the environment and public health [1]. Chlorinated phenols (CP) belong to the group of priority organic pollutants, ubiquitous in the environment [1-3]. They are highly toxic, carcinogenic and resistant to biodegradation [4, 5].

One of the most toxic CP is 2,4-dichlorophenol (2,4-DCP) [6, 7]. Sources of 2,4-DCP in the environment are the production of chlorine-containing herbicides, organic synthesis, landfills, and waste incineration plants [8-10]. Despite the absence of direct commercial use, 2,4-DCP enters industrial wastewater in concentrations from 10 to 1000 mg/L [11]. There are various physicochemical methods for treating CP emissions and wastewater. But most of them have various disadvantages, such as low destruction efficiency, high economic costs and the formation of more toxic end products [10, 12, 13].

In recent years, domestic and foreign researchers have been paying attention to technologies for water purification from organochlorine compounds based on advanced oxidative processes (oxidation using Fenton's reagent [8, 14], photocatalytic oxidation [1, 5, 8] and oxidation in supercritical water [15]), as well as high-energy chemistry methods (for example, plasma processes [14, 16]). There are a number of publications on the study of CP decomposition in a dielectric barrier discharge (DBD) [17-19], which provide not only kinetic data, but also the main decomposition products [1, 2].

A qualitatively new direction in plasma-chemical systems for environmental protection, which makes it possible to significantly intensify the decomposition of organic compounds and reduce energy consumption, is the use of combined plasma-catalytic processes (CPCP) [20]. When the solution enters the reactor, where the catalyst is located in the discharge zone, the active components of the plasma act on both the catalyst and the solution, which can lead to an acceleration of the destruction of organic compounds dissolved in water, as well as to a change in the composition of the resulting destruction products. Therefore, the study of the kinetics of the transformation of organic compounds (for example, 2,4-dichlorophenol dissolved in water) under the action of DBD and in combined plasma-catalytic processes is relevant.

MATERIALS AND EXPERIMENTAL METHODS

A schematic of an experimental setup for processing aqueous solutions of 2,4-DCP in DBD is presented in [20]. The voltage was measured with a high-voltage probe (2000:1), and the discharge current was determined from the voltage drop across the resistor (100 Ohm) connected in series to the ground circuit. Both signals were recorded by a digital two-channel oscilloscope GW Instek GDS-2072 (Instek, Taiwan). The input power, P, was determined by integrating the product of the current and voltage waveforms over a period. The rms voltage in the experiments was 16.5 kV. In this case, the rms discharge current was 13.08 mA. The frequency of the voltage applied to the electrodes was 800 Hz. The volumetric power input into the discharge (W, W/cm^3) was 8.63 W/cm^3 and was calculated by the formula:

$$W = \frac{P}{V_p}, \tag{1}$$

where V_p, cm^3, is the volume of the discharge zone, calculated by the formula:

$$V_p = S_{sech..} \cdot L_{r.s.}, \tag{2}$$

where $S_{sech.}$, cm^2 is the cross-sectional area of the discharge zone, $L_{r.s.}$, cm, is the length of the discharge zone. The volume of the discharge zone of the DBD reactor with the coaxial arrangement of the electrodes was 25 cm^3. Industrial oxygen was used as a plasma-forming gas in all experiments. The oxygen flow rate in all experiments was 500 ml/min (8.33 ml/s).

Pt/Al_2O_3 was used as a catalyst. This catalyst has a large specific surface area (155.4 ± 1.1 m^2/g). The mass of the catalyst placed in the plasma combustion zone was 1 g.

The pollutant used was 2,4-DCP, the concentration (C_{in}) of which in the aqueous solution was 100 mg/L. The solution flow rate was varied from 0.1 to 0.4 ml/s. The residence time of the liquid (τ_k) in the discharge zone was determined by the formula (3), where D is the diameter of the inner electrode, h is the thickness of the solution film, L = 8 cm is the length of the discharge zone, and Q is the solution flow rate.

$$\tau_k = \frac{\pi D \cdot h \cdot L}{Q}, \tag{3}$$

The thickness of the liquid film (h) was calculated using the equation for a smooth laminar flow [20]. The residence time, τ_k, varied in the range 1.2-2.9 s. The concentration of 2,4-DCP in the solution after reaching a steady state was determined at the inlet and outlet of the reactor by gas-liquid chromatography [16,21] using a Chromatek 5000.2 chromatograph (Khromatek, Russia). The relative determination error is 30% at a confidence level of 0.95.

The efficiency of purification (degree of decomposition) of aqueous solutions from 2,4-DCP (α) was estimated according to the equation (2):

$$\alpha(\%) = \frac{C_{in} - C}{C} \cdot 100, \tag{4}$$

where C_{in} and C are the concentration of 2,4-DCP at the reactor inlet and outlet, respectively.

The total concentration of carboxylic acids (CA) was obtained by measuring the optical density of the color reaction of acids with ammonium m-vanadate at a wavelength of λ 400 nm [22]. For these purposes, a Hitachi U-2001 spectrophotometer (Hitachi, Japan) was used. The overall measurement error did not exceed ± 10% [22].

The total concentration of aldehydes was measured by the fluorescence method (spectrofluorimeter Fluorat-02, Russia). The fluorescent substance was formed as a result of the interaction of an aldehyde group and 1,3-cycloxeganedione in the presence of ammonium ions. The relative determination error was 25% at a confidence level of 0.95 [23].

To measure the concentration of chloride ions in water and Cl_2 in the gas phase, we used a potentiometric method using a chlorine-selective electrode with a crystal membrane "ELIS-131 Cl" [24].

The CO_2 content in the gas phase at the reactor outlet was estimated by gas chromatography (Khromatek-5000.2 (Khromatek, Russia)) with a methanator and a flame ionization detector [25]. Measurement of the content of carbon oxides in the system made it possible to assess the fulfillment of the carbon balance (i.e. the completeness of the determination of intermediate and final products), which was determined by the formula:

$$\delta = \frac{Y_{pr}}{Y_{in}}, \tag{5}$$

where Y_{pr} is the carbon content in the system (i.e., in the liquid and gas phases) after the treatment of aqueous solutions of 2,4-DCP (products of its destruction), taking into account the incompleteness of its destruction, Y_{in} is the carbon content in the initial solution 2,4-DCP [26].

The concentration of ozone formed in the plasma-chemical reactor was measured by absorption spectroscopy by the absorption of light at a wavelength of 253.7 nm, at the maximum of the O_3 photoabsorption cross section at $\sigma = 3.52 \cdot 10^{-18}$ cm^2 [27] using a spectrophotometer (UNICO, mod. 2804). The ozone content was calculated using the expression [27]:

$$N_{O_3} = \frac{\ln(I_0 / I)}{\sigma \cdot l}, \tag{6}$$

where I_0, i is the initial light intensity of the Hg resonance line without excitation of the discharge, rel.

units; I – also, but when the discharge is excited, rel. units; σ – cross section of photoabsorption, cm^2, l is the length of the cuvette with quartz glasses (2.5 cm). The error in determining the ozone concentration in the experiments did not exceed 15% at a confidence level of 0.95.

Determination of the degree of mineralization of the initial compound was carried out by changing the concentration of total organic carbon after treatment of aqueous solutions of 2,4-DCP in DBD. For this, the indicator of chemical oxygen demand (COD) was evaluated – the amount of oxygen in water required for the complete oxidation of organic substances contained in the sample to CO_2. The measurement is based on the treatment of a water sample with sulfuric acid and potassium dichromate at a temperature of 150 °C in the presence of an oxidation catalyst – silver sulfate and the addition of mercury (II) sulfate and measurement of the optical density of the solution on a Fluorat-02M fluorometer. The method error is ± 15% [28].

RESULTS AND DISCUSSION

The kinetic curves of 2,4-DCP destruction were processed in accordance with the relationship obtained in [29] and valid for a plug-flow reactor ($R^2 > 0.99$) :

$$C = C_{in} \cdot e^{-K \cdot \tau_K}, \qquad (7)$$

where C_{in} is the 2,4-DCP concentration at the reactor inlet, μmol/L, C is the 2,4-DCP concentration at the reactor outlet, μmol/L, K is the effective decomposition rate constant, s^{-1}.

The kinetic curves (Fig. 1) are satisfactorily described by pseudo-first order equations with effective rate constants (0.36 ± 0.04) and (0.43 ± 0.03) s^{-1} when treating solutions without a catalyst and with Pt/Al_2O_3, respectively.

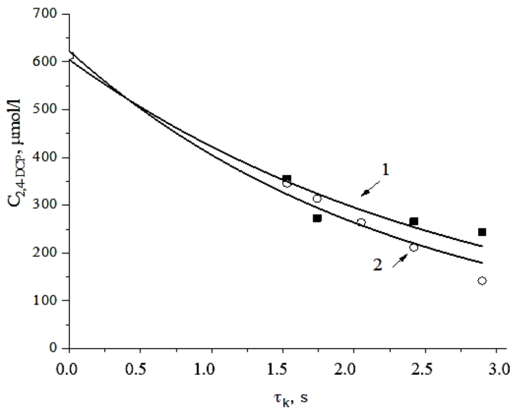

Fig. 1. Destruction kinetic of 2,4-DCP. Initial 2,4-DCP concentration is 100 mg/l, inputted power is 8.63 W/cm^3, O_2 flow rate is 0.5 l/min (1-without catalyst, 2-with Pt/Al_2O_3)

Рис. 1. Кинетика деструкции 2,4-ДХФ. Начальная концентрация -100 мг/л, вложенная мощность – 8,63 Вт/см^3, расход кислорода – 0,5 л/мин (1 – без катализатора, 2 – в присутствии Pt/Al_2O_3)

The rates and energy consumption of the decomposition of 2,4-DCP were estimated for the residence time of the solution with the plasma zone $\tau_k = K^{-1}$. The rates of the decomposition process were $9.82 \cdot 10^{17}$ and $8.16 \cdot 10^{17}$ cm^{-3}·s^{-1}. The energy consumption was 0.0144 and 0.012 molecules/100 eV. Thus, the use of Pt/Al_2O_3 increases both the degree of decomposition (from 60 to 76% for the given processing parameters) and the rate and energy efficiency of the destruction process. However, the obtained values are much lower than those during the decomposition of 2,4-DCP in a reactor by combined plasma-sorption processes (when using diatomite as a sorbent) [29].

It should be noted that during the processing of aqueous solutions in the CPCP, an increase in the degree of mineralization of the initial compound was also observed. It is confirmed both by a decrease in the content of total organic carbon in the system after treatment, and by an increase in the concentration of carbon dioxide and carbon monoxide at the outlet of the reactor in the gas phase. The results obtained show that a synergistic effect is observed in the plasma catalytic system, which makes it possible to significantly increase the environmental parameters of the wastewater treatment process.

The course of the kinetic curves of the formation of aldehydes and chlorine ions in a solution after treatment of the solutions is shown in Fig. 2.

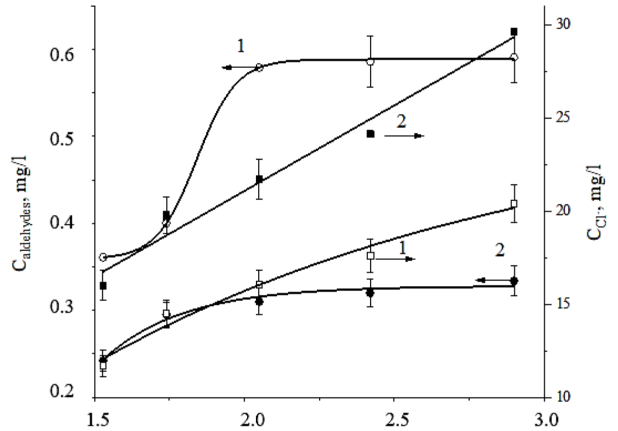

Fig. 2. Change in the concentration of aldehydes and Cl$^-$ ions as a function of the residence time. Initial 2,4-DCP concentration is 100 mg/l, inputted power is 8.63 W/cm^3, O_2 flow rate is 0.5 l/min (1-without catalyst, 2-with Pt/Al_2O_3)

Рис. 2. – Изменение концентрации альдегидов и Cl$^-$ в зависимости от времени контакта. Начальная концентрация -100 мг/л, вложенная мощность – 8,63 Вт/см^3, расход кислорода -0,5 л/мин (с 1- Pt/Al_2O_3, 2 - без катализатора)

Cl_2 was not detected in the gas phase. Both in the presence of Pt/Al_2O_3 and in the DBD reactor without a catalyst, the concentration of aldehydes in the solution increases with a residence time of up to 2 s. With a further increase in the residence time of the solution with the plasma combustion zone, their concentration remains unchanged, which indicates that they are the end products of the 2,4-DCP degradation process. It should also be noted that in CPCP the concentration of aldehydes after treatment of solutions is approximately 2 times lower than when the solution is exposed to only DBD. One of the main decomposition products of 2,4-DCP is chlorine, which is formed in solution in the form of chloride ion. With an increase in the processing time of the solutions, the concentration of chloride ions increases both in the presence of a catalyst in the reactor and in its absence. The chlorine balance in the system, taking into account the decomposition efficiency of 2,4-DCP, is fulfilled by 90%. The decomposition of one 2,4-DCP molecule leads to the formation of two chlorine ions, i.e. it can be assumed that the formation of other chlorine-containing compounds (within the sensitivity of the control methods) does not occur. Indeed, the results of gas chromatography show the absence of any chlorine compounds, with the exception of 2,4-DCP.

The course of the kinetic regularities of the formation of carboxylic acids is similar to that for aldehydes (Fig. 3). At short residence times, their growth is observed with a further reaching a stationary value, which leads to a change in the pH of the solution to values of 3.8-3.5, characteristic of the treated solutions containing organic compounds in DBD plasma [30-31].

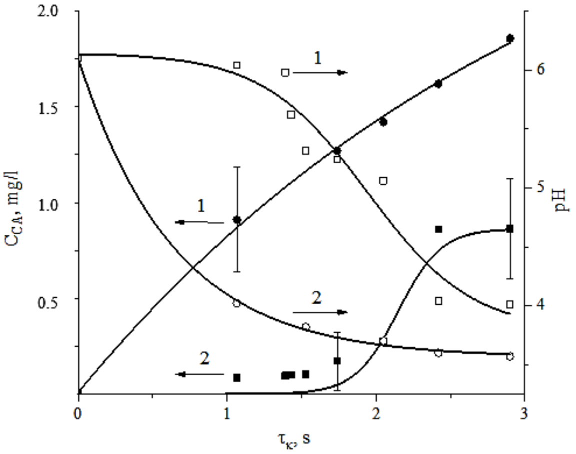

Fig. 3. Change in pH and CA concentration as a function of the residence time. Initial 2,4-DCP concentration is 100 mg/l, inputted power is 8.63 W/cm^3, O_2 flow rate is 0.5 l/min (1-without catalyst, 2-with Pt/Al_2O_3)

Рис. 3. – Изменение pH и концентрации КК в зависимости от времени контакта. (1 - в присутствии Pt/Al_2O_3, 2-без)

Evaluation of the carbon balance showed that the total yield of carbon oxides varies in the range of 60-68% of the initial carbon content in the system. This is confirmed by the value of the degree of mineralization in the system, which also increased during the treatment of aqueous solutions in the CPCP and at a maximum is 68% (which is 1.3 times higher than during the treatment in DBD).

It is known that ozone is one of the main oxidants in DBD [32-35]. The contribution of ozone to the degradation processes of 2,4-DCP can be estimated from the difference in its concentrations during the treatment of aqueous solutions with 2,4-DCP and without it (Table).

Table

Assessment of the contribution of ozone to the degradation process of 2,4-DCP

***Таблица.* Оценка вклада озона в процесс деструкции 2,4-ДХФ**

Experimental conditions. Условия эксперимента	Ozon concentration, cm^{-3}	Ozon concentration, mmol/L
Without catalyst, without solution treatment.	$3.3\cdot10^{16}$	1.221
Without catalyst, solution treatment.	$2.47\cdot10^{16}$	0.914
Pt/Al_2O_3, without solution treatment.	$4.097\cdot10^{16}$	1.513
Pt/Al_2O_3, solution treatment.	$3.85\cdot10^{16}$	1.426

At the exit from the reactor without using a catalyst, the ozone concentration is $3.3\cdot10^{16}$ cm^{-3} at the specified processing parameters. And in the presence of 2,4-DCP - $2.47\cdot10^{16}$ cm^{-3}, that is, $0.83\cdot10^{16}$ cm^{-3} or 0.3 mmol/L ozone can participate in oxidative processes.

The stoichiometric equation of the oxidation reaction of 2,4-DCP has the form

$$C_6H_4OCl_2 + 4O_3 = 2Cl^- + 6CO_2 + 2H^+ + H_2O$$

According to this reaction, the complete oxidation of 1 mol of 2,4-DCP requires 4 mol of ozone, i.e. its concentration is insufficient, therefore, ozone is not the main oxidizing agent. The insignificant contribution of ozone to oxidation processes is also indicated by the fact that, despite an increase in the rate of destructuring of 2,4-DCP in the presence of a catalyst, the ozone concentration, both with Pt/Al_2O_3 in the reactor and without, is practically the same. When using Pt/Al_2O_3, 0.09 mmol/L ozone is consumed for oxidation, which is 3 times less than without it, therefore, other active particles formed in the discharge zone should participate in oxidative processes, and an increase in their concentration in the discharge combustion zone can be initiated by the presence of a catalyst.

The results obtained suggest a probable mechanism for the decomposition of 2,4-DCP (Fig. 4). The interaction of active plasma particles with 2,4-DCP occurs initially with the opening of an aromatic ring and the formation of intermediate organic compounds with a lower molecular weight (such as aldehydes and carboxylic acids), which are subsequently oxidized to CO_2 and H_2O, which is confirmed by a high degree of mineralization (Fig. 4).

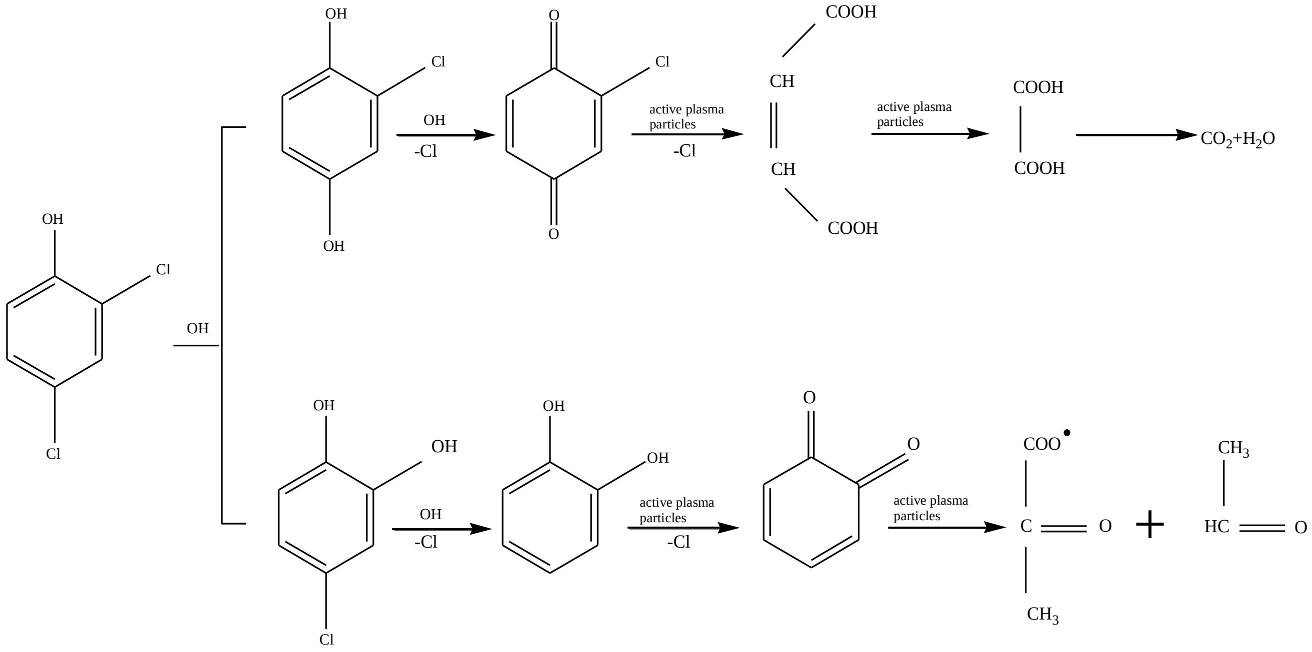

Fig. 4. The probable mechanism of destruction of 2,4-DCP

Рис. 4. Вероятный механизм деструкции 2,4-ДХФ

CONCLUSION

It has been shown experimentally that 2,4-DCP is destroyed in CPCP quite efficiently (the destruction efficiency reaches 75%), which confirms earlier studies on the destruction of organic pollutants of various compositions in DBD plasma. The kinetic parameters were estimated and the main intermediate and final products of 2,4-DCP decomposition under the action of active plasma particles were determined. Cl^- ions, aldehydes, carboxylic acids in the liquid phase, and CO_2 in the gas phase were identified as the main decomposition products. It was found that the contribution of ozone to the oxidative degradation of 2,4-DCP is insignificant. The results obtained show that a synergistic effect is observed in the CPCP, which makes it possible to significantly increase the environmental and economic parameters of the wastewater treatment process. Presumably, the decomposition of 2,4-DCP in both DBD and CPCP proceeds with the opening of the aromatic ring and the formation of organic compounds with a lower molecular weight (such as aldehydes and carboxylic acids with a total contribution to the carbon balance of less than 5%), and their further oxidation to carbon dioxide, water and formation of inorganic chlorine compounds.

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The authors declare the absence a conflict of interest warranting disclosure in this article.

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