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# ОБРАБОТКА СТОЧНЫХ ВОД, СОДЕРЖАЩИХ 2,4-ДИХЛОРОФЕНОЛ, В ПЛАЗМЕ ДИЭЛЕКТРИЧЕСКОГО 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. Экспериментально показано, что 2,4-дихлорфенол разрушается в плазме достаточно эффективно (степень деструкции достигает 80 %), что подтверждает раннее проведенные исследования по разложению в плазме диэлектрического барьерного разряда различных органических поллютантов. В работе были оценены кинетические параметры и определены основные промежуточные и конечные продукты процесса разложения 2,4-дихлорфенола под действием активных частиц плазмы. Деструкции исходного соединения описываются кинетическим уравнением первого порядка. Эффективная константа скорости слабо зависит от условий эксперимента и составляет 0,56 $с^{-1}$. Состав продуктов деструкции был изучен методом газовой хроматографии, а также флуоресцентным, спектрофотометрическим и потенциометрическим методом. В качестве конечных продуктов деструкции выявлены $Cl^-$ в жидкой фазе, а также CO и $CO_2$ в газовой фазе, а промежуточными продуктами деструкции являются карбоновые кислоты и альдегиды, но их концентрации не велики относительно CO и $CO_2$. 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. Увеличение частоты тока разряда с 50 до 800 Гц, а также отсутствие гидрофобного покрытия внутреннего электрода приводит к уменьшению скорости разложения в 1,7 раза (с 227 до 135 мкмоль/(л.с)).***

**Ключевые слова:** 2,4-дихлорфенол, диэлектрический барьерный разряд, плазма, кислород, обработка

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# TREATMENT OF WASTEWATER CONTAINING 2,4-DICHLOROPHENOL IN DIELECTRIC BARRIER DISCHARGE PLASMA

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***In the work, the processes of destruction of aqueous solutions of 2,4-dichlorophenol in a dielectric barrier discharge of atmospheric pressure in oxygen were studied. It has been experimentally shown that 2,4-dichlorophenol is destroyed in plasma quite efficiently (the degree of destruction reaches 80 %), which confirms the earlier studies on the decomposition of various organic pollutants in a dielectric barrier discharge plasma. The kinetic parameters were estimated and the main intermediate and final products of the decomposition of 2,4-dichlorophenol under the action of active plasma particles were determined. The destruction of the starting compound is described by a first order kinetic equation. The effective rate constant depends weakly on the experimental conditions and it equals to 0.56 $s^{-1}$. The composition of the degradation products was studied by gas chromatography, as well as by fluorescence, spectrophotometric and potentiometric methods. $Cl^-$ in the liquid phase, as well as CO and $CO_2$ in the gas phase, were identified as the final degradation products. And carboxylic acids and aldehydes were intermediate degradation products. But their concentrations are not high relative to CO and $CO_2$. No molecular chlorine was detected in the gas phase. It was found that ozone does not make a significant contribution to the oxidative destruction of 2,4-dichlorophenol. The hydroxyl radicals and atomic oxygen are main active particles involved in oxidative processes. An increase in the frequency of the discharge current from 50 to 800 Hz, as well as the absence of a hydrophobic coating of the internal electrode, leads to a decrease in the decomposition rate by a factor of 1.7 (from 227 to 135 μmol/(l·s)).***

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

## INTRODUCTION

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

One of the most toxic CPhs 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, waste incinerators [8-10]. Despite the lack of direct commercial use, 2,4-DCP is delivered to industrial wastewater in concentrations from 10 to 1000 mg/l [11]. There are various physicochemical methods for purifying CPhs emissions and effluents, 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 organic-chlorine compounds based on advanced oxidative processes (oxidation using the Fenton reagent [8, 14], photocatalytic oxidation [1, 5, 8] and oxidation in supercritical water [15]), as well as methods of high-energy chemistry (for example, plasma processes [14, 16]). There are a number of publications on the study of CPhs decomposition in a dielectric barrier discharge (DBD) [17-19], which provide not only kinetic data, but also the main degradation products, as well as energy costs. In these

studies, when exciting DBD, an alternating current of industrial frequency (50 Hz) was used, as well as a hydrophobic material on the internal electrode, along which the CPhs solution flowed.

This work continues a series of studies devoted to the destruction of highly toxic organic compounds presenting in model aqueous solutions, aimed at the formation of a scientific database on the kinetics and mechanisms of CPhs decomposition occurring in DBD [16, 20-24], but the frequency of the discharge current was 800 Hz, and there was no hydrophilic material on the electrode surface.

## MATERIALS AND METHODS

The experimental installation is shown in Fig. 1. The reactor was a coaxial system consisting of an external Pyrex tube with an internal diameter of 22 mm, which is the dielectric barrier of the discharge, an internal electrode of aluminum alloy with a diameter of 8 mm. The barrier discharge was excited from a high voltage transformer. The voltage applied to the electrodes was 6.5 kV. The volumetric power inputted in the discharge was 1.8 W/cm$^3$. The frequency of voltage applied to the electrodes is 800 Hz. Oxygen was used as the plasma-forming gas. The gas flow rate in all experiments was 8.3 ml/s.

Previously, studies were conducted on the destruction of 2,4-DCP in a plasma-chemical reactor, a detailed description of which is given in [16]. The main differences in the experimental setups were in the power supply – in the second case, a high-voltage transformer with a frequency of voltage applied to the electrodes of 50 Hz was used, as well as in the use of a hydrophilic fiberglass fabric 1 mm thick on the internal electrode, with the help of which the film mode of flow of the solution in the system was ensured.

As a pollutant, 2,4-DCP was used, the concentration ($C_{in}$) of which in an aqueous solution was 100 mg/L. The flow rate of the solution ranged from 0.1 to 0.4 ml/s. The liquid residence time ($t_r$) with the discharge zone was determined by formula (1), where $D$ is the diameter of the internal 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.

$$t_r = \frac{\pi \cdot D \cdot h \cdot L}{Q}, \qquad (1)$$

The liquid film thickness ($h$) was calculated by the equation for a smooth laminar flow [25]. The residence time $t_r$ varied in the range 1.2-2.4 s.

The concentration of 2,4-DCP in the solution after reaching the steady state was determined at the inlet and outlet of the reactor using gas-liquid chromatography [26] using a Chromatec 5000.2 chromatograph (Russian production). The relative error of determination is 30% with a confidence level of 0.95.

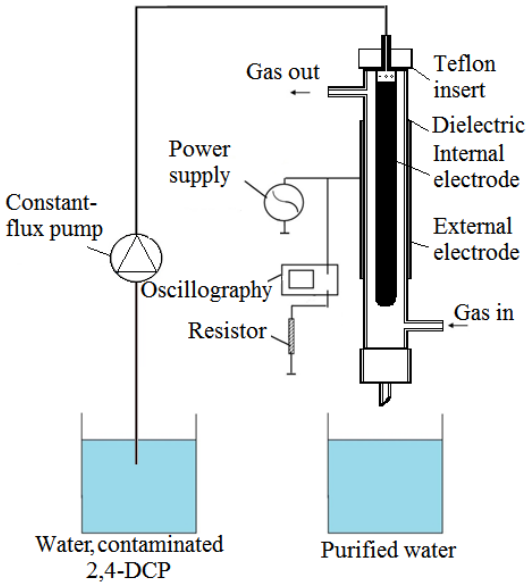


Fig. 1. The experimental installation
Рис. 1. Схема экспериментальной установки

The effectiveness of the purification of aqueous solutions from 2,4-DCP (α) was estimated by equation (2):

$$\alpha(\%) = \frac{C_{in} - C}{C} \times 100, \qquad (2)$$

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

The total concentration of carboxylic acids (CA) was obtained by measuring the optical density of a colour reaction of acids with m-ammonium vanadate at the wavelength, λ, of 400 nm [27]. A Hitachi U-2001 spectrophotometer (Hitachi, Japan) was used for this purposes. The total measurement error did not exceed ±10% [27].

The total concentration of aldehydes was measured by fluorescent method (spectro-fluorimeter Fluorat-02, Russia). The fluorescent substance was formed as the interaction product of aldehyde group and 1,3-cycloxehanedione in the presence of the ammonium ions. The relative error of determination was 25% with a confidence level of 0.95 [28].

To measure the concentration of chloride ions in water and $Cl_2$ in the gas phase, a potentiometric method was used using a chlorine-selective electrode with a crystalline membrane «ELIS-131 Cl» [15].

The content of CO and $CO_2$ in the gas phase at the outlet of the reactor was estimated by gas chromatography (Chromatech-5000 (Chromatek, Russia)) with a methanator and a flame ionization detector [29].

RESULTS AND DISCUSSION

The kinetics and effectiveness of the destruction of 2,4-DCP during processing in DBD is shown in Fig. 2.

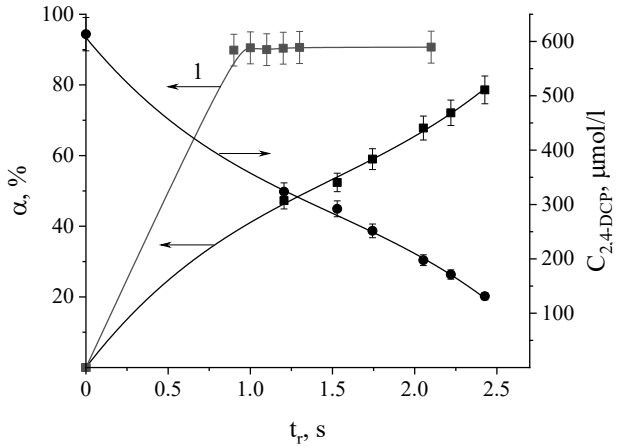


Fig. 2. Kinetics and destruction efficiency of 2,4-DCP. Initial 2,4-DCP concentration is 100 mg/l, inputted power is 1.8 W/cm$^3$, $O_2$ flow rate is = 0.5 l/min; 1 - data from [16])

Рис. 2. Кинетика и эффективность деструкции 2,4-ДХФ. Начальная концентрация -100 мг/л, вложенная мощность – 1,8 Вт/см$^3$, расход кислорода -0,5 л/мин; 1 - данные из [16])

The kinetic curve is satisfactorily described ($R^2 > 0.99$) by a pseudo-first order equation:

$$C = C_{in} \cdot exp(-k \cdot t_r), \quad (3)$$

where $k$ is the effective rate constant, s$^{-1}$. The value of the effective rate constant of the process of destruction of 2,4-DCP was (0.562-0.02) s$^{-1}$.

The rate of destruction of the pollutant ($V_d$) was estimated at a residence time of $t_r = k^{-1}$ [30]. The rate was 134.9 μmol/(l·s). When studying the kinetics of the decomposition of 2,4-DCP in DBD with a low-frequency power supply (50 Hz) and the presence of a coating on the internal electrode, it was shown that the decomposition rate is 1.7 times higher and amounted to 227 μmol/(l·s) [16] at the same conditions.

Since the electrophysical parameters of the discharges (current, power, reduced electric field strength) are close, these differences are most likely associated with the presence of a coating on the internal electrode. It is possible that the coating exhibits catalytic properties.

It should be noted that the specific discharge power does not significantly affect the decomposition efficiency of 2,4-DCP. A change in the range from 1.2 to 1.8 W/cm$^3$ led to an increase in the destruction efficiency by only 10%, and a further increase to 3.3 W/cm$^3$ within the error did not result in a change in the concentration of 2,4-DCP at the reactor outlet. The maximum efficiency under experimental conditions did not exceed 80%. Thus, we can assume that the residence time with the discharge zone is the main parameter that affects the destructive processes occurring in DBD.

Using kinetic data, we can estimate the energy efficiency of the decomposition of 2,4-DCP according to equation (4):

$$\theta(mol/(100eV)) = \frac{Q \cdot C_{in} \cdot 0.63 \cdot N_{Av} \cdot 1.6 \cdot 10^{-19} \cdot 100}{P}, \quad (4)$$

where $Q$ is the flow rate of the solution supplied for purification (l/s) necessary for the degree of contaminant removal equal to 0.63; $N_{Av}$ is the Avogadro number, $1.6 \cdot 10^{-19}$ is the electron charge (C), $P$ is the power inputted to the discharge, (W).

The calculation results are presented in Table.

***Table***

**Energy efficiency of the purification process of various organic compounds in DBD**

***Таблица.*** **Энергетическая эффективность процесса очистки различных органических соединений в ДБР**

| Pollutant | $C_{in}$, μmol/l | $\alpha_{max}$, % | $V_d$, μmol/(l·s) | k, s$^{-1}$ | θ, mol/(100 eV) |
|---|---|---|---|---|---|
| 2,4-DCP | 614 | 80 | 135 | 0.56 | 0.023 |
| 2,4-DCP [16] | 307 | 100 | 227 | 2.00 | 0.173 |
| Phenol [31] | 53 | 100 | 18 | 0.72 | 0.028 |
| Sodium lauryl sulfate [31] | 17 | 90 | 0.9 | 0.09 | 0.001 |
| Sulfonol [31] | 15 | 85 | 2.8 | 0.31 | 0.003 |
| Oil products [32] – planar system | 300 | 95 | 0.59 | 0.002 | 0.162 |

Comparison of the results presented in table. 1, it makes it possible to arrange the studied substances in a series in increasing resistance in DBD: 2,4-DCP < phenol < sulfonol < sodium lauryl sulfate < < oil products.

Important from the point of view of the environmental effectiveness of cleaning methods is not only the efficiency of the destruction of the pollutant, but also the absence of secondary environmental pollutants, which may be more toxic than the starting compound. The experimental results showed that under the action of active particles in the plasma zone, 2,4-DCP decomposes with the formation of carboxylic acids, aldehydes and chloride ions in the liquid phase (Fig. 3), carbon oxide and carbon dioxide in the gas phase (Fig. 4).

Fig. 3 shows the dependence of changes in the concentration of chloride ions in the water that has been treated. As expected, with an increase in the residence

time of the solution with the plasma zone, the yield of chloride ions increases and reaches a maximum of 24 mg/l, which is 73% of the initial chlorine content in the system. The $Cl_2$ was not detected in the gas phase.

During the processing of an aqueous solution of 2,4-DCP in DBD, a decrease in pH occurred, which is possibly associated with the formation of acids. This phenomenon is always observed during the decomposition of organic compounds in atmospheric pressure discharges [16, 21, 32]. So, when processing in DBD, the pH of the initial solution was about 6.5, and at a residence time of 1.5 s, it decreased to a value of 5.1, and at 2.4 s to a value of 4.4. However, the content of carboxylic acids in the solution (Fig. 3) cannot lead to such a significant change in the hydrogen index (up to values of 4.5), i.e. it is likely that the formation of hypochlorous acid and hydrochloric acid occurs in the solution, however, their concentration in the solution was not monitored.

The measurement results showed that carbon oxides are detected only in the gas phase. The concentrations of CO and $CO_2$ at the maximum residence time were 0.14 μmol/cm$^3$ and 0.15 μmol/cm$^3$, which, with a carrier gas flow rate of 0.5 l/min ($8.3\cdot10^{-3}$ cm$^3$/s), gives a rate of 0.13 μmol/s and 1.16 μmol/s, respectively.

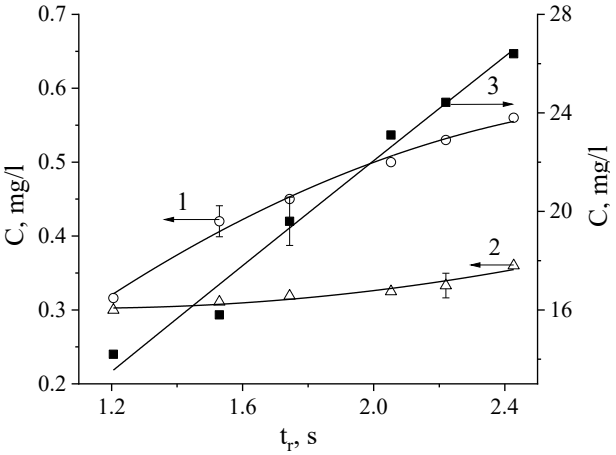


Fig. 3. The formation of the main products of the 2,4-DCP destruction in DBD vs the residence time in the liquid phase (1 - carboxylic acids; 2 - aldehydes; 3 - $Cl^-$)

Рис. 3. Образование основных продуктов деструкции 2,4-ДХФ в ДБР от времени контакта в жидкой фазе (1 - карбоновые кислоты; 2 - альдегиды; 3 - $Cl^-$)

The measurement of the content of carbon oxides in the system made it possible to evaluate the carbon balance (i.e., the completeness of the determination of intermediate and final products), which was determined by the formula:

$$\delta = \frac{Y_{pr}}{Y_{in}}, \qquad (5)$$

where $Y_{pr}$ is the total carbon content in the system in the liquid and gas phases after processing (2,4-DCP and its degradation products), $Y_{in}$ is the carbon content in the initial 2,4-DCP solution.

Assessment of the carbon balance showed that the total yield of carbon oxides varies in the range 89-98% of the initial carbon content in the system. This is confirmed by the results of monitoring the total organic carbon (TOC) in the system – the concentration of TOC before and after purification was 352 mg/l and 43 mg/l, respectively, i.e. the mineralization efficiency of 2,4-DCP reached 88%.

It is known that in DBD, one of the main oxidizing agents is ozone [33]. The change in ozone concentration in the gas phase at the outlet of the reactor at a discharge power of 1.8 W/cm$^3$ is shown in Fig. 5. About $8.6\cdot10^{16}$ cm$^{-3}$ ozone is expended on the oxidation of 2,4-DCP. According to the stoichiometric equation for the reaction of interaction of 2,4-DCP with ozone:

$$3C_6H_4Cl_2O+10O_3=6Cl^-+9CO+9CO_2+6H_2O,$$

the complete oxidation of 1 mol of 2,4-DCP requires 3.3 mol of ozone. Based on the data in Fig. 5 and the volumetric rate of the gas phase in the reactor, the rate of ozone consumption in oxidative reactions was $1.2–10^{-6}$ mol/s. Thus, the ozone in the system is clearly insufficient for the oxidation of 2,4-DCP.

The results obtained suggest the probable mechanism of decomposition of 2,4-DCP (Fig. 6). The interaction of active plasma particles with 2,4-DCP occurs initially with the opening of the 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, $CO_2$ and $H_2O$, which confirms high degree of mineralization (Fig. 6).

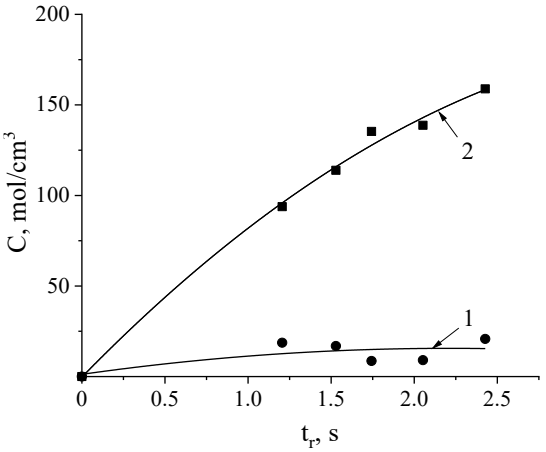


Fig. 4. The concentration of CO (1) and $CO_2$ (2) in the gas phase at the outlet of the reactor vs the residence time of the solution with the discharge zone

Рис. 4. Концентрация CO (1) и $CO_2$ (2) в газовой фазе на выходе из реактора от времени контакта раствора с разрядной зоной

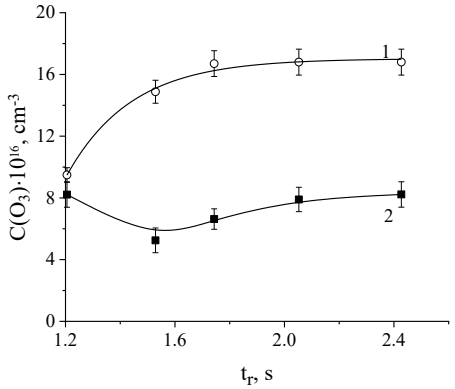


Fig. 5. Dependence of ozone concentration at the outlet of the reactor on the residence time of the solution with the discharge zone (1 - without 2,4 - DCP; 2 - with 2,4 - DCP)
Рис. 5. Зависимость концентрации озона на выходе из реактора от времени контакта раствора с зоной разряда (1 - без 2,4 - ДХФ; 2 - с 2,4 - ДХФ)

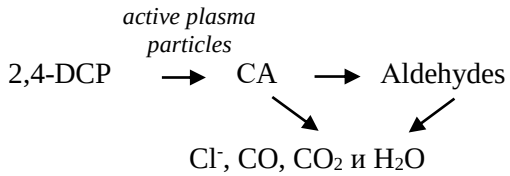


Fig. 6. The probable mechanism of destruction of 2,4-DCP
Рис. 6. Вероятный механизм деструкции 2,4-ДХФ

## CONCLUSION

It has been experimentally shown that 2,4-DCP is destroyed in plasma quite efficiently (destruction efficiency reaches 80 %), which confirms the earlier studies on the destruction of organic pollutants of various compositions in DBD plasma. Kinetic parameters were estimated and the main intermediate and final products of the decomposition of 2,4-DCP under the action of active plasma particles were determined. $Cl^-$, aldehydes, carboxylic acids in the liquid phase, as well as CO and $CO_2$ in the gas phase were identified as the main degradation products. It was found that the contribution of ozone to the process of oxidative destruction of 2,4-DCP is insignificant. An increase in the frequency of the discharge current from 50 to 800 Hz, as well as the absence of a hydrophobic coating of the internal electrode, leads to a decrease in the decomposition rate by a factor of 1.7.

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