

Plasma-Catalytic Decomposition of 2,4-Dichlorophenol in a Dielectric Barrier Discharge with a Vermiculite ZiO_2 Composite

Grigoriy I. Gusev¹, Andrey A. Gushchin¹, Vladimir I. Grinevich¹, Ekaterina M. Baburina¹, Ekaterina S. Severgina², Natalya E. Gordina²

¹Department of Industrial Ecology, Ivanovo State University of Chemical Technology, Ivanovo, Russia

²Department of Technology of Inorganic Substances, Ivanovo State University of Chemistry and Technology, Ivanovo, Russia
Email: gordinane@mail.ru

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Abstract

The paper presents comparative kinetic characteristics of the decomposition of 2,4-dichlorophenol in a dielectric barrier discharge and a combined plasma-catalytic process. Vermiculite containing 5% zirconium was used as a catalyst. The destruction processes of 2,4-DCP proceed efficiently, the degree of decomposition increases in the combined plasma-catalytic process by a factor of 1.33 and reaches 80%. The experimental results were processed according to the first-order kinetic law ($R^2 > 0.97$), according to which the effective constants (0.36 ± 0.04) and (0.51 ± 0.03) s^{-1} and the decomposition rates of 2,4-DCP (106 and 123 $\mu\text{mol/l}\cdot\text{s}$) when treating model solutions without a catalyst and with vermiculite + Zr 5%, respectively, and the energy costs are 0.012 and 0.017 molecules/100eV. The main decomposition products present in the solution have been determined to be carboxylic acids, aldehydes, the contribution of which does not exceed 2%, as well as chloride ions, and in the gas phase they are carbon dioxide and molecular chlorine (the share of which does not exceed 1.5% of total chlorine content in the system).

Keywords

2,4-Dichlorophenol, Dielectric Barrier Discharge, Plasma, Oxygen, Treatment, Water Treatment, Catalyst, Zirconium, Vermiculite

1. Introduction

Toxic and oxidation-resistant organic compounds, in particular, chlorinated phenols (CP), are a serious threat to the environment and public health [1] [2] [3]. In recent years, Russian and foreign researchers have paid special attention to

the technology of water purification from CP, based on advanced oxidation processes (oxidation using the Fenton agent [4] [5] [6], photocatalytic oxidation [1] [5] [6] and oxidation in supercritical water [7]. Methods of high-energy chemistry, for example, plasma processes, are being developed [6] [8] [9]. The authors of [7] [10] present the results of studies of the CP decomposition process in a dielectric barrier discharge (DBD), which show not only the kinetic regularities of the initial compounds destruction, but also the formation of the main decomposition products.

Among the common group of CPs, 2,4-dichlorophenol (2,4-DCP) is one of the most toxic, having an adverse effect on living organisms [11] [12] [13]. In industry it is used as an intermediate in the synthesis of fungicides and herbicides, for example, 2,4-dichlorophenoxyacetic acid (2,4-D) [12].

A whole new direction in plasma-chemical systems for protecting the environment, which makes it possible to significantly intensify the processes of organic compounds decomposition and reduce energy costs, is the use of combined plasma-catalytic processes (CPCP) [14] [15] [16] [17]. The main catalysts are TiO_2 , MnO_2 , NiO_2 , and a number of other metal-containing materials, the use of which contributed to the development of a synergetic effect of complex organic compounds decomposition in the CPCP [15]. Nevertheless, the search for new catalytic materials to increase the efficiency of CPCC is an urgent task.

Therefore, the study of the kinetics of organic compounds transformation (for example of 2,4-dichlorophenol dissolved in water) under the influence of DBD and in CPCP is relevant. The catalysts that can be used in these processes are composite systems “vermiculite- ZrO_2 ” [18].

2. Materials and Methods

The following materials were used to obtain a catalyst by mechanochemical activation:

a) vermiculite of the Kovdor vermiculite deposit, with a grain size of up to 0.6 mm. The elemental composition of vermiculite corresponds to SiO_2 (37.2%), Al_2O_3 (6.2%), CaO (15.3%), Fe_2O_3 (19%), MgO (13.1%); b) zirconium oxychloride pentahydrate ($\text{ZrOCl}_2 \cdot 5\text{H}_2\text{O}$) [18].

Mechanical activation of sorbent samples was carried out in a vibratory roller-ring mill VM-4 (Czech Republic). Activation conditions: oscillation frequency is 930 min^{-1} , vibration amplitude in the radial direction is 10 mm, in the axial direction is 1 mm, mass of grinding bodies is 1194 g, mass of the loaded material is 40.0 g. The energy intensity of the mill with these parameters is 0.878 kW/kg. The grinding time varied from 5 to 30 min, which corresponds to the amount of energy supplied to the ground substance from 263.3 J/g to 1579.8 J/g, respectively. The synthesis of catalysts was carried out with combined mechanochemical activation of the initial components: vermiculite and zirconium oxychloride pentahydrate ($\text{ZrOCl}_2 \cdot 5\text{H}_2\text{O}$), taken in a ratio that ensures the content of Zr^{4+} in the mixture of 5 wt.% [18] [19]. From mechanochemically modified vermiculite, the molding mass was closed with a moisture content of up to 25 wt.%, then the

resulting paste was extruded by means of a piston-type extruder into granules with a diameter of 3 mm. The granules were dried in an oven at a temperature of 110°C - 120°C to constant weight, then they were subjected to heat treatment in the temperature range of 400°C - 900°C for 2 - 4 hours [20]. In the case of an adsorption-catalytic system, including zirconium oxychloride, the obtained granules were additionally processed by plasma-chemical processing (PCP) in the DBD reactor (plasma-forming gas flow rate—8.3 ml/s, rms voltage value—16.5 kV, voltage frequency—800 Hz).

The surface area, adsorption-desorption isotherms, and pore size distribution data were obtained on a Sorbi-MS apparatus (OOO Meta, Russia). The specific surface area was determined by the BET method (meets the international ASTM and ISO standards) from low-temperature adsorption-desorption of nitrogen. Specific surface area measurement is in the range of 0.1 m²/g - 2000 m²/g. Before the investigation, the samples were treated in a stream of nitrogen at a given temperature for 60 min [21].

Scanning electron microscopy (SEM) of the obtained samples was performed using a Vega 3SBH microscope (TESCAN, Czech Republic) [22].

The scheme of the experimental setup for the treatment of 2,4-dichlorophenol aqueous solutions, as well as for PCP in the dielectric barrier discharge plasma, is given in [22], the main element of which was the dielectric barrier discharge reactor.

Industrial oxygen was used as the plasma-forming gas; the gas flow rate in all experiments was 8.3 ml/s. The carrier gas flow rate was controlled by a gas flowmeter. The barrier discharge was excited by a high-voltage transformer. The rms voltage in the experiments was 16.5 kV. In this case, the discharge current was 13 mA. The frequency of the voltage applied to the electrodes was 800 Hz.

The primary voltage values were controlled by a D 5015 voltmeter. Typical current and voltage waveforms are shown in **Figure 1**. Both signals were recorded by a digital two-channel oscilloscope GW Instek GDS-2072 (Instek, Taiwan). The input power was determined by integrating the product of both forms over the pulse duration. The volumetric power input into the discharge was 8.63 W/cm³, and was defined as the power applied to 1 cm³ of the discharge zone.

The residence time with the reactor discharge zone τ_k varied in the range of approximately 1.2 - 2.9 s. The values of τ_k were calculated by formula (1) [22], where h , cm² is the thickness of the liquid layer during laminar flow in the gravity field; $L = 8$ cm is the length of the discharge zone, Q , cm³/s is the solution flow rate:

$$\tau_k = \frac{\pi D h L}{Q}. \quad (1)$$

The mass of the catalyst placed in the plasma combustion zone was 1 g in all experiments.

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 ranged from 0.1 to 0.5 ml/s. The concentration of the toxicant in aqueous solutions was selected on

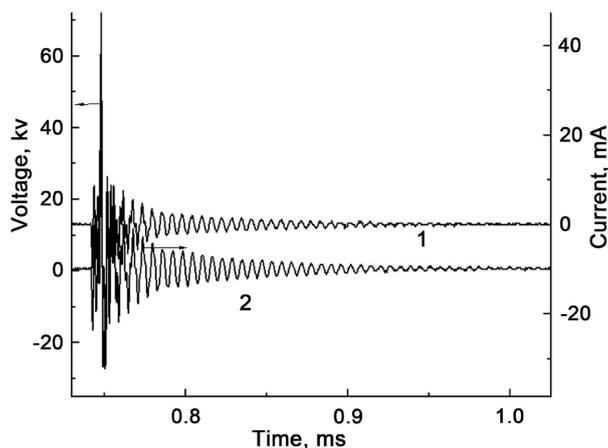


Figure 1. Typical forms of voltage (1) and current (2) pulses.

the basis of typical concentrations of the substance in industrial effluents from which this pollutant most often enters water bodies. Aqueous solutions of 2,4-dichlorophenol were prepared by mixing a sample of 2,4-DCP with a known volume of water.

The concentration of 2,4-DCP in the solution after reaching the steady state was determined at the inlet and outlet of the reactor by gas-liquid chromatography [23] using a Chromatek-Crystal 5000.2 chromatograph (ZAO SKB Chromatek, Russia). The relative determination error is 30% at a confidence level of 0.95.

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

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

where C_{in} and C are the initial concentration and the concentration after treatment of a solution containing 2,4-DCP (mg/l) in DBD.

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 400 nm. For these purposes, a Hitachi U-2001 spectrophotometer (Hitachi, Japan) was used. The overall measurement error did not exceed $\pm 10\%$ [24].

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

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" (OOO "Izmeritelnaya Tekhnika", Russia) [26].

The CO_2 content in the gas phase at the reactor outlet was estimated by gas chromatography (Chromatek-Crystal 5000.2 (ZAO SKB Chromatek, Russia) with

a methanator and a flame ionization detector [27]. 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:

$$\delta = \frac{Y_{pr}}{Y_{in}}, \quad (3)$$

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 2,4-DCP initial solution [28].

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 $\sigma = 3.52 \times 10^{-18} \text{ cm}^2$ [29] using a spectrophotometer (UNICO, mod. 2804, USA). The ozone content was calculated using the equation [30]:

$$N_{O_3} = \frac{\ln(I_0/I)}{\sigma \cdot l}, \quad (4)$$

where I_0 , is the initial light intensity of the Hg resonance line without excitation of the discharge, relative units; I —also, but when the discharge is excited, relative 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.

Estimation of the mineralization degree 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 purpose, 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 (GC Lumex, Russia). The method error is $\pm 15\%$ [31].

3. Results and Discussion

To select a catalyst for its use in CPCP, the structural properties of vermiculite subjected to various treatments (activation) were studied. Mechanochemically and thermally activated vermiculite was used as the starting material for catalytic systems.

The results of the assessment of the specific surface area, pore volume and average pore size by the BET method are given in **Table 1**. The formed porous structure of the original and modified samples has a specific surface ranging from 7 - 21.3 m^2/g , with the minimum being typical for the initial vermiculite

Table 1. The result of the study of the specific surface area and pore volume.

Sample name	Specific surface area S_{sp} , m ² /g	Pore volume, (cm ³ /g)
Initial vermiculite	7	0.017
MCA + 650°C	21.3	0.043
MCA + Zr 5% + PCP(O ₂)	14.9	0.021

and the maximum for the sample obtained during mechanochemical activation (MCA) and subsequent calcination at 650°C.

During MCA and heat treatment of samples, a significant increase in the macroporous structure up to 0.043 cm³/g is observed, which is 150% more than that of the initial material.

A significant change in the properties of the samples was observed during the PCP of the catalyst: the specific surface area is about 14.9 m²/g, the value of the total pore volume is 0.021 cm³/g; the area of the hysteresis loop broadens. The diameter of the globules varies in the range of ~40 - 200 nm; the pores formed between the globules have a width from 4 - 6 nm to 13 - 15 nm (mesopores), and the diameter of the pores formed due to the mineral structure imperfection ranges from 30 to 100 nm (mesopores).

The adsorption isotherm for all the catalyst samples under study (vermiculite, MCA + 650°C, and MCA + Zr 5% + PCP(O₂)) corresponds to a type V isotherm (according to the classification of Brunauer, Deming, and Teller [32] [33]) (Figure 2).

The initial vermiculite has most of the pores related to mesopores. However, larger mica packets have very fine macropores. Under MCA and heat treatment, the number of macropores significantly decreases, and the content of micropores and mesopores increases. It should be noted that the PCP sample has the highest range of micro- and mesopores. Mesoporous materials are of great practical interest as sorbents and carriers for catalysts [33], therefore, in further studies aimed at studying the processes of oxidation of organochlorine compounds dissolved in water, MCA + Zr 5% + PCP materials placed on a special substrate in the plasma combustion zone were used.

When processing the kinetic curves of 2,4-DCP destruction in aqueous solutions in DBD, the equation of continuity of the flux density in cylindrical coordinates was used [7]:

$$C_k = C_n \cdot \exp(-K \cdot \tau_k), \quad (5)$$

where C_n is the concentration of 2,4-DCP at the reactor inlet, μmol/l, C_k is the concentration of 2,4-DCP at the reactor outlet, μmol/l, τ_k is the effective decomposition rate constant, s⁻¹.

The energy efficiency of 2,4-DCP decomposition was determined using the rate formulas (6) and the energy yield for the decomposition of one 2,4-DCP molecule per 100 eV of the input energy (7), respectively:

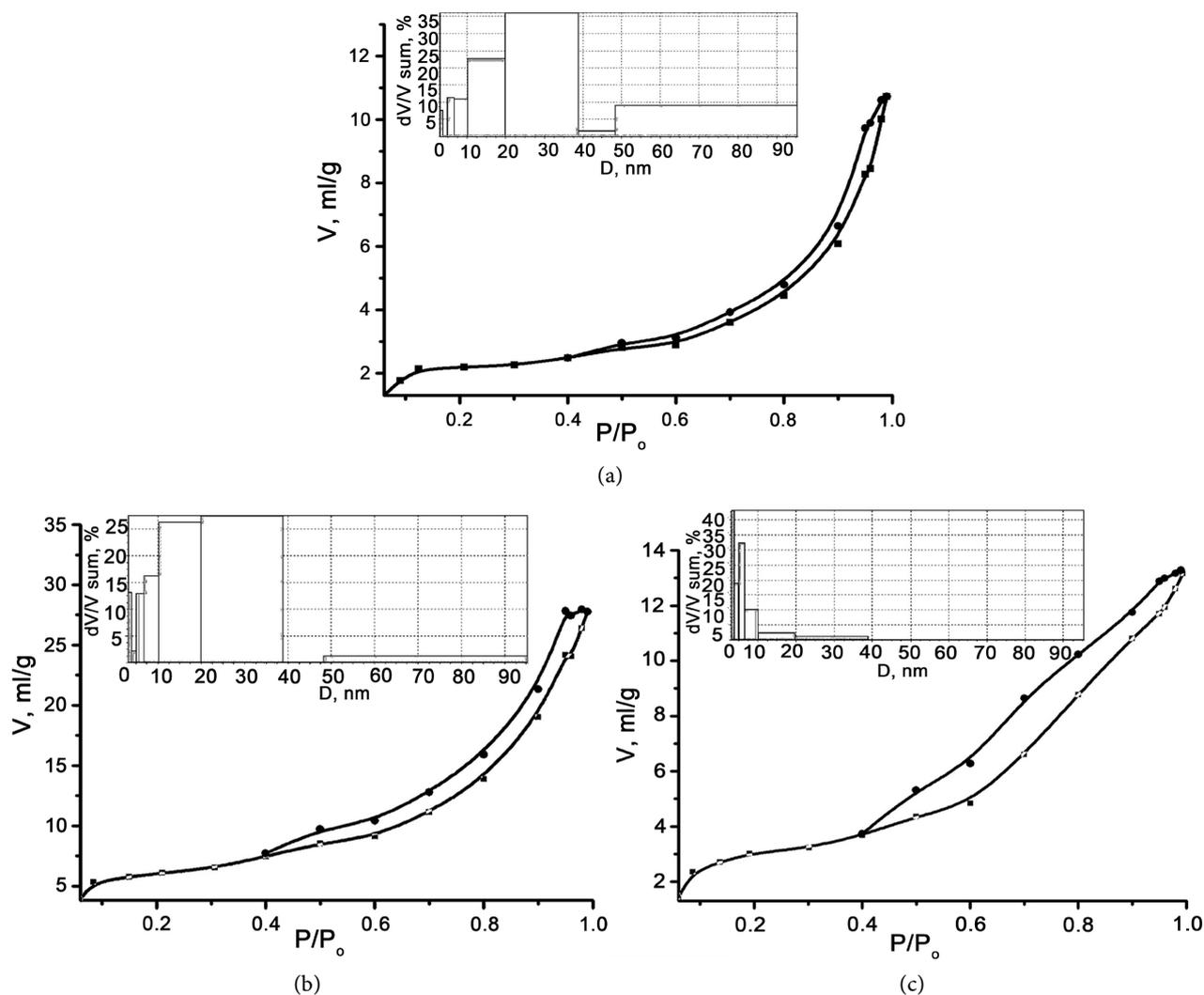


Figure 2. Nitrogen adsorption-desorption isotherms and pore size results. (a) initial vermiculite, (b) MCA + 650°C, (c) MCA + Zr 5% + PCP(2x O₂).

$$W_D = k \cdot C_n \cdot \exp(-1) \quad (6)$$

$$\theta = \frac{Q \cdot C_n \cdot 0.63 \cdot N_{Av} \cdot 1.6 \cdot 10^{-19} \cdot 100}{P} \quad (7)$$

where Q is the flow rate of the model solution supplied for purification, (l/s), required for the demanded degree of pollutant removal; N_{Av} is the Avogadro number, $1.6 \cdot 10^{-19}$ is the electron charge (C), P is the power put into the discharge (W), C_n is the initial concentration of the substance supplied with the solution ($\mu\text{mol/l}$).

The experimental results were processed according to the first-order kinetic law ($R^2 > 0.97$), according to which the effective constants (0.36 ± 0.04) and (0.51 ± 0.03) s^{-1} and the decomposition rates of 2,4-DCP (106 and 123 $\mu\text{mol/l}\cdot\text{s}$) when processing model solutions without a catalyst and with vermiculite + Zr 5%, respectively, and the energy consumption is 0.012 and 0.017 molecules/100 eV.

Thus, the use of vermiculite + Zr 5% increases both the degree of decomposition (from 60% to 80% with the same processing parameters (**Figure 3**) and the speed and energy contribution to the degradation process, despite the fact that the catalyst takes no more than 15% of the volume of the discharge zone of the reactor. This can be explained by the fact that the catalyst, due to the active developed surface, preliminarily sorbs pollutant molecules (the molecular size of which is 6 Å [34] and correlates well with the pore sizes of activated vermiculite), which leads to an increase in the residence time of 2,4-DCP with active plasma particles, increasing the efficiency of oxidative processes.

Comparison of the main characteristics of the destruction process of various kinds of organic compounds in systems implementing DBD is given in **Table 2**.

Analysis of the data in **Table 1** shows that aromatic compounds are more stable than aliphatic chlorine-containing hydrocarbons, which leads to a significant increase (more than 100 times) in energy consumption required for their effective destruction.

According to [12], 2,4-DCP destruction proceeds through the formation of quinones, due to the substitution of the chlorine atom by the OH group, while the replacement of Cl by the phenolic OH group occurs simultaneously with the formation of chlorocatechols. In our case, the results of chromato-mass spectrometry showed the absence of such compounds.

The decomposition of one 2,4-DCP molecule leads to the formation of two chlorine ions, and it can be assumed that the formation of other chlorine-containing organic compounds (within the sensitivity of control methods) does not occur. Indeed, the results of gas chromatography show the absence of any chlorine compounds, except for 2,4-DCP, and the main chlorine-containing degradation product is chloride ions, with the maximum concentration in the solution—40 mg/l (**Figure 4**). It should be noted that the chlorine balance in the system, taking into account the efficiency of 2,4-DCP decomposition, is 90% complete, together with the error of control methods, it indicates the completeness of the determination of chlorine-containing products in the system. The ratio of the content of gaseous chlorine at the reactor outlet to the chlorine present in the system at the initial moment is less than 1%, and we can conclude that chlorine, which is part of 2,4-DCP, completely transforms into Cl⁻ when the model solutions are processed in DBD.

The course of the kinetic curves for the aldehydes formation in a solution after treatment of model solutions is shown in **Figure 5**.

Both with vermiculite + Zr 5% and in the DBD reactor without a catalyst, at the starting moment of the process, 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 is important 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.

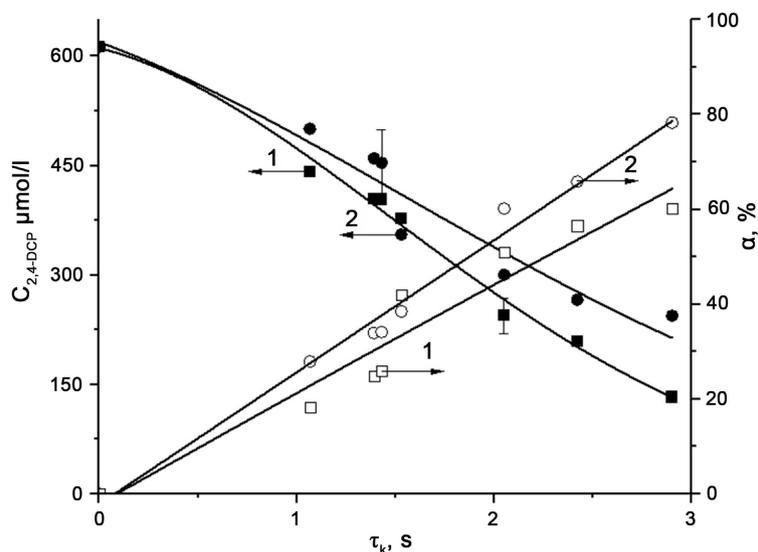


Figure 3. Change in the concentration of 2,4-DCP depending on the processing time in DBD (1—without a catalyst, 2—with vermiculite + Zr 5%).

Table 2. Rates, effective rate constants and energy efficiency of the process of decomposition of aqueous solutions of chlorinated organic compounds.

Pollutant	C_{in} , mol/l	α_{max} , %	V_d , mmol/(l·s)	k , s ⁻¹	θ , mol/ (100 eV)
2,4-DCP	614	80	135	0.56	0.023
2,4-DCP [13]	307	100	227	2.00	0.173
Phenol [30]	53	100	18	0.72	0.028
Sodium lauryl sulfate [30]	17	90	0.9	0.09	0.001
Sulfonol [30]	15	85	2.8	0.31	0.003
Oil products [31] planar system	300	95	0.59	0.002	0.162

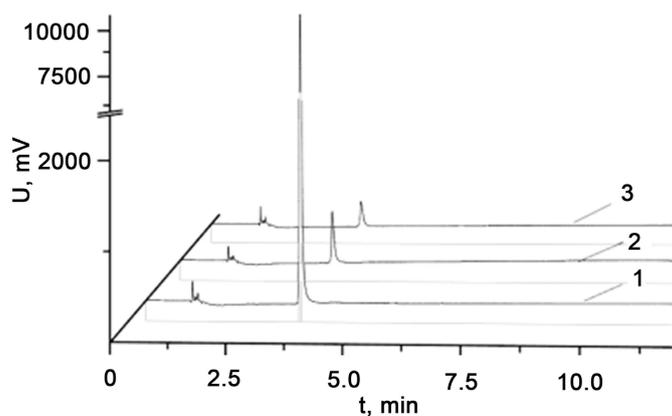


Figure 4. Chromatograms before (1) and after treatment of 2,4-DCP solution in DBD at optimal parameters without a catalyst (2) and with vermiculite + Zr 5% (3).

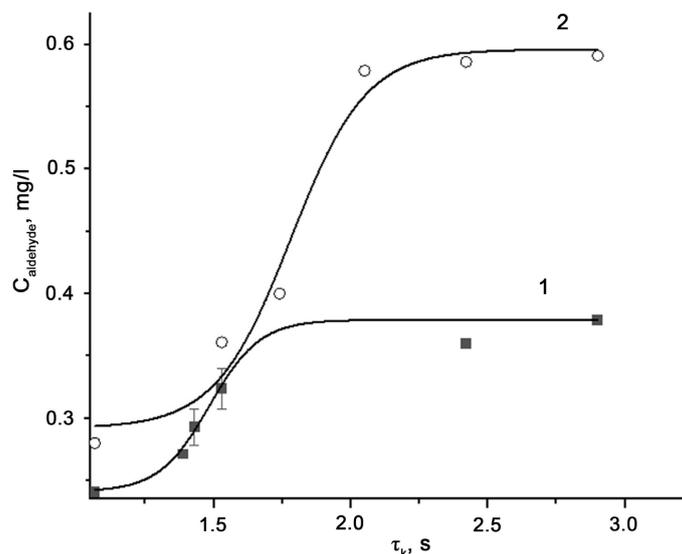


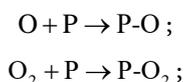
Figure 5. Change in the concentration of aldehydes depending on the time of 2,4-DCP processing in DBD (1—with vermiculite + Zr 5%, 2—without a catalyst).

The course of the kinetic regularities of carboxylic acids (CA) formation (**Figure 6**, **Figure 7**) is similar to that for aldehydes, at the starting moment of processing, an increase in the content in the solution is observed, which leads to a decrease in the pH value with the concentration further reaching a stationary value. The range of CA concentrations, both with a catalyst and without it, is the same within the error and amounts to 0.1 - 5.5 mg/l.

It should be noted that during the aqueous solutions treatment in CPCP, an increase in the degree of mineralization of the initial compound was observed, the maximum being 80% (that is 1.3 times higher than during treatment in DBD). This is confirmed by both a decrease in the content of total organic carbon in the system after treatment and an increase in the concentration of carbon dioxide and carbon monoxide in the gas phase at the reactor outlet.

It is known that ozone is one of the main oxidants in DBD [35] [36] [37] [38]. 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 3**).

At the reactor outlet without using a catalyst, the ozone concentration is $3.3 \times 10^{16} \text{ cm}^{-3}$, and with 2,4-DCP it is $6.0 \times 10^{16} \text{ cm}^{-3}$, so a catalyst in the system leads to an ozone concentration increase by about 1.8 times with the same parameters of the process. This fact is in good agreement with [39] [40] [41] [42], where it is shown that reactions on the surfaces of catalysts and sorbents are one of the channels for the ozone formation. This mechanism can be presented by [43]:



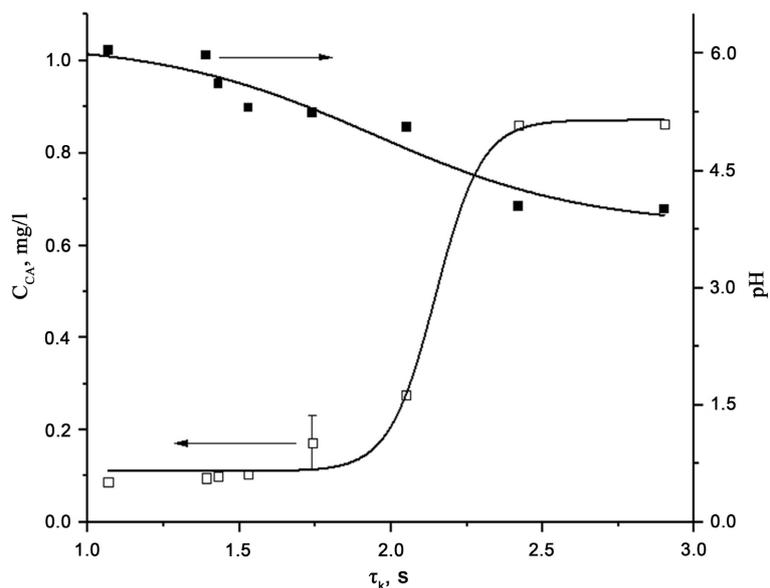


Figure 6. Changes in pH and CA concentration depending on the processing time in DBD without a catalyst.

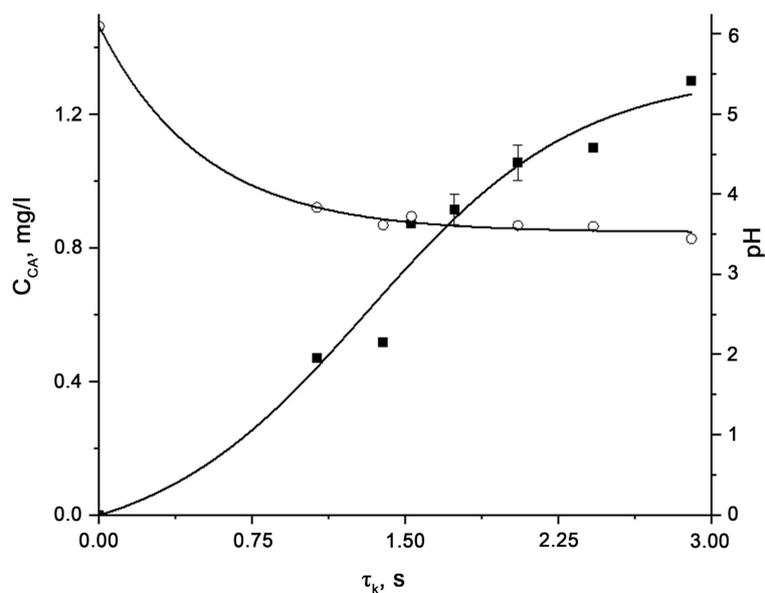
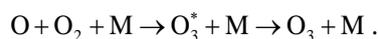
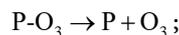
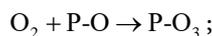
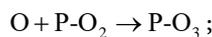


Figure 7. Changes in pH and CA concentration depending on the processing time in DBD with vermiculite + Zr 5%.

Table 3. Ozone influence on the process of 2,4-DCP destruction.

Experimental conditions	C (O ₃), cm ⁻³	C (O ₃), mmol/L
Without catalyst, without solution treatment	3.3×10^{16}	1.2
Without catalyst, solution treatment	2.5×10^{16}	0.91
Vermiculite + Zr 5% + PCP, without solution treatment	6.0×10^{16}	2.2
Vermiculite + Zr 5% + PCP, solution treatment	2.9×10^{16}	1.1



where P is active sites on the catalyst surface.

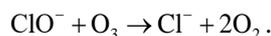
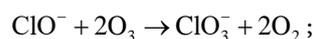
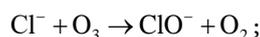
In the traditional scheme of ozone formation in the system, the dielectric acts as the third body (M), which takes away the excess dissociation energy [43]. The catalyst gives a significant increase in ozone concentration, as the main active particle involved in the oxidation of organic compounds.

The stoichiometric equation for the 2,4-DCP oxidation reaction is:

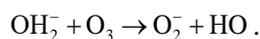
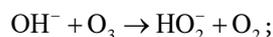


that is, 4 moles of ozone are required for the complete oxidation of 1 mole of 2,4-DCP. The initial concentration of 2,4-DCP in the system being equal to 100 mg/l (0.61 mmol/l), 2.44 mmol/l of ozone is required. According to the experimental data (Table 2), the difference between the ozone concentrations in water at the reactor inlet and outlet is 1.1 mmol/l, *i.e.* with such O₃ content, no more than 45% of 2,4-DCP can be oxidized.

It should be noted that ozone will be consumed not only for the 2,4-DCP oxidation, but also for the destruction of organic compounds that are intermediate products of its decomposition (for example, carboxylic acids, aldehydes). There are also other channels of ozone destruction, for example, interaction with chloride ions present in the solution promotes the formation of active chlorine (sum of free chlorine Cl₂, hypochlorous acid HClO, hypochlorite ions ClO) [44] [45]:



It is also known that ozone dissolved in water decomposes with the formation of OH radicals [46], the oxidation potential of which is significantly higher than that of ozone:



At present, the rate constants of the reaction of 2,4-DCP with OH radicals, O and O₃ atoms in the liquid phase are not known. If we take into account similar processes occurring in the gas phase, then for chlorophenols the rate constants of interaction with O atoms and OH radicals are $2.9 \times 10^{-13} \text{ s}^{-1}$ and $1.65 \times 10^{-12} \text{ s}^{-1}$, respectively [47] [48]. For chlorobenzene, the rate constants of the reaction with O atom and the OH radical are comparable and equal $(5 - 6) \times 10^{-13} \text{ s}^{-1}$ [49] [50], for chlorotoluene, the rate constant for the reaction with ozone is $6 \times 10^{-20} \text{ s}^{-1}$ [51]. The ratio of the rate constants confirms the conclusion that ozone contribution to the 2,4-DCP decomposition of is not dominant, even taking into account that

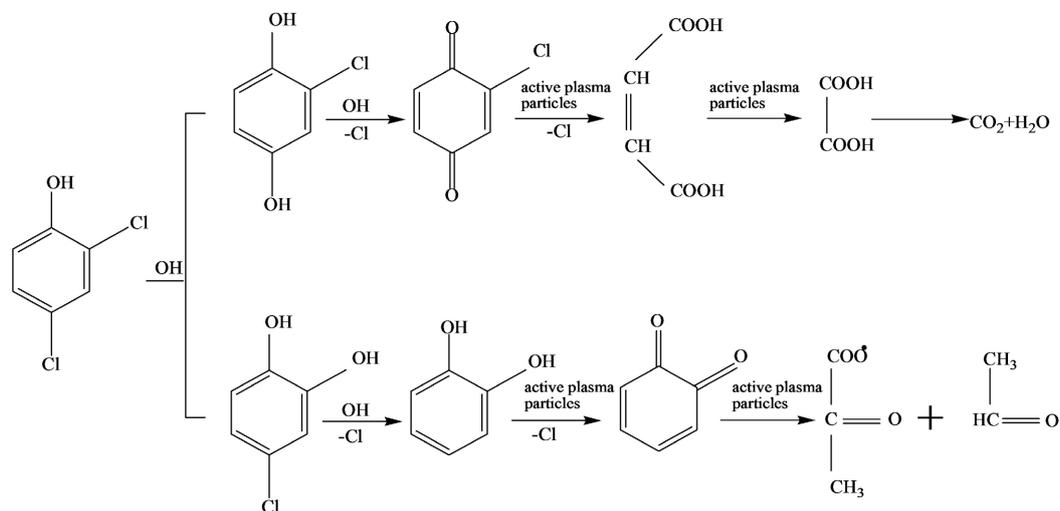
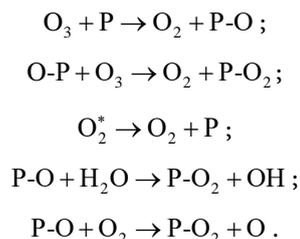


Figure 8. The probable mechanism of 2,4-DCP destruction.

its concentration in DBD is significantly higher than that of O atoms and OH radicals (by 6 orders of magnitude) [52]. The main contribution to 2,4-DCP destruction is made by other active species, and the presence of a catalyst in the discharge zone can significantly affect their concentration. For example, not only the processes of ozone generation but also its destruction can occur on the catalyst surface, accompanied by the formation of hydroxyl radicals, atomic oxygen [53]:



The results obtained suggest a probable mechanism for the decomposition of 2,4-DCP (**Figure 8**).

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 CO₂ and H₂O, that is confirmed by a high degree of mineralization

4. Conclusion

It has been experimentally shown that 2,4-DCP is destroyed in CPCP quite efficiently (the destruction efficiency reaches 80%), 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

CO₂ in the gas phase were identified as the main decomposition products. It was found that ozone contribution to the oxidative 2,4-DCP destruction is not dominant (maximum 45%). The results obtained show that a synergetic effect is observed in the CPCP, which makes it possible to increase the environmental and economic parameters of wastewater treatment process significantly. Presumably, the 2,4-DCP decomposition 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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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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