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Photochemical oxidation of γ -hexachlorocyclohexane and 4,4'-dichlorodiphenyldichloroethylene

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Authors' contributions

This work was carried out in collaboration between all authors. Authors IZ, TZ and MR designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript.

Authors NM, ID and NK managed the analyses of the study. Authors OL, EO and ID managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Objectives: Utilization of the forbidden organochlorine pesticides demands searching of new ways of their neutralization. In such way there can be a photochemical oxidation of pesticides. As a research objects we chose γ -hexachlorocyclohexane (lindane) and 4,4'-dichlorodiphenyldichloroethylene (DDE). Radiation treatment of solution is carried out by the UF-lamp with a wavelength of 254 nanometers.

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Methods: Residual concentrations of pesticides were determined by "Lyumakhrom" liquid chromatograph. The infrared spectrum of initial lindane, DDE solutions in the process of photochemical oxidation of pesticides by hydrogen peroxide is observed in ZnSe precision cell by Infrared Fourier Transform Spectroscopy "Infralyum of FT-02". The kinetics of photochemical oxidation process of γ -hexachlorocyclohexane (lindane) and 4,4'-dichlorodiphenyldichloroethylene (DDE) is studied.

Findings: The analysis of obtained results shows that use of the homogeneous catalysts, initiating the process of H_2O_2 and H_2O photolysis, reduces the concentration of lindane and DDE in the first hour of treatment. Without catalyst the residual concentration of lindane is $0,289 \cdot 10^{-6}$ mol/dm³, DDE – $0,235 \cdot 10^{-6}$ mol/dm³, while addition of iron (III) to H_2O_2 leads lindane concentration dilution up to $0,029 \cdot 10^{-6}$ mol/dm³, DDE – to $0,046 \cdot 10^{-6}$ mol/dm³. Addition as the Zn (II) catalyst to hydrogen peroxide decreases the concentration of lindane to $0,129 \cdot 10^{-6}$ mol/dm³, DDE – to $0,163 \cdot 10^{-6}$ mol/dm³ in 2 hours. In the presence of iron ions (III) as the homogeneous catalyst initiating the photolysis of hydrogen peroxide and water, the constant rates are increased by six times. The analysis of pesticides photochemical oxidation products by IR spectrums allowed assuming mechanisms of photochemical oxidation of pesticides by hydrogen peroxide. As may be supposed, there is a cycle rupturing in lindane leading to formation of the aliphatic ketones which are restored to secondary alcohols; and DDE have a rupture of C (1) atom benzene ring with formation of chlorophenols and alkenes. From then on chlorophenols are oxidized by hydroxyl radical to the carbon dioxide and water, and alkenes are hydrated to primary alcohols.

Conclusion: The conducted research showed high efficiency of photochemical oxidation process of pesticides in the presence of homogeneous catalyst – iron ions (III).

Keywords: γ -hexachlorocyclohexane (lindane); 4,4'-dichlorodiphenyldichloroethylene (DDE); photochemical oxidation; hydrogen peroxide; process mechanism.

1. INTRODUCTION

The necessity of application of the pesticides in the agriculture leads to the problem of waste generation. In Europe and North America pesticide waste generation problem is essentially due to the wastewater, recycling and utilization of pesticide packaging bag, and also remediation of contaminated soils [1]. For developing countries and, in particular, for Russia, the main problem is the utilization of forbidden or unconditional high toxic pesticides [2]. Nowadays, the high-temperature treatments, such as combustion, pyrolysis, plasma method, or a liquid-phase oxidation are widely used for pesticides degrading process [3-10]. However application of high-temperature methods can lead to formation of toxic after products [11,12]. The chemical substances, such Cl_2 , HCl, CO, C_xH_y , $C_xH_yCl_z$ and dioxin-like compounds are a part of gas phase of chlorine-containing pesticides and contaminate the environment during the thermal decomposition. The slag and ash residues of pesticides contain CuO, ZnO, PbO, KCl, Na_2CO_3 , $CaCO_3$ и SiO_2 [13,14]. Therefore, it is required to search new environmentally friendly methods of neutralization of forbidden and

unconditional organic pesticide preparations [13-18]. One of such methods can be a photochemical oxidation of pesticides.

2. MATERIALS AND METHODS

For conducting of the research the γ -hexachlorocyclohexane (lindane) and 4,4'-dichlorodiphenyldichloroethylene (DDE) were chosen.

Studying of photolysis and photochemical oxidation of lindane and DDE by $1 \cdot 10^{-2}$ mol/dm³ hydrogen peroxide carried out on the model solutions of lindane ($C=1,7 \cdot 10^{-6}$ mol/dm³) and DDE ($C=1,3 \cdot 10^{-6}$ mol/dm³) with addition of hydrogen peroxide in concentration of $1 \cdot 10^{-2}$ mol/dm³ both without, and in the presence of the homogeneous catalysts initiating processes of photolysis of hydrogen peroxide and water. Zinc Zn (II) ($C= 1 \cdot 10^{-5}$ mol/dm³) and Fe (III) ($C= 1 \cdot 10^{-5}$ mol/dm³) were used as the homogenous catalysts which initiate the processes of H_2O_2 and H_2O photolysis. Radiation of 2 cm depth solution was carried out by the UF-lamp with a wavelength of 254 nanometers with constant stirring (Fig. 1).

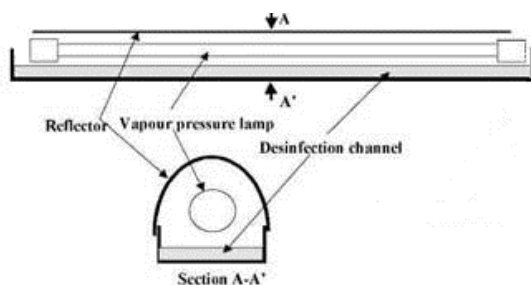


Fig. 1. Flow diagram of photochemical reactor (l=300 mm; b=150 mm; h=120 mm)

Residual concentrations of pesticides determined by the liquid chromatograph "Lyumakhrom".

Infrared spectrum of lindane and DDE initial solutions and solutions obtained after the photochemical oxidation of pesticides by hydrogen peroxide both without, and in the presence of homogeneous catalysts were observed on the IK-Fourier spectrometer "Infralyum FT-02" filled to the basins from ZnSe.

3. RESULTS AND DISCUSSION

Studying the photolysis of lindane and DDE without the hydrogen peroxide revealed that the

efficiency of pesticide oxidation in 240 min was less than 10%. Follow-up study related to the photochemical oxidation of pesticides by hydrogen peroxide with and without of homogenous catalysts.

Kinetic curves of photochemical oxidation of pesticides by hydrogen peroxide are presented in Figs. 2, 3.

The analysis of obtained results shows that use of the homogeneous catalysts, initiating the process of H_2O_2 and H_2O photolysis, reduces the concentration of lindane and DDE in the first hour of treatment. So, for example, without catalyst the residual concentration of lindane is $0,289 \cdot 10^{-6}$ mol/dm³, DDE – $0,235 \cdot 10^{-6}$ mol/dm³, while addition of iron (III) to H_2O_2 leads lindane concentration dilution up to $0,029 \cdot 10^{-6}$ mol/dm³, DDE – to $0,046 \cdot 10^{-6}$ mol/dm³. Addition as the Zn (II) catalyst to hydrogen peroxide decreases the concentration of lindane to $0,129 \cdot 10^{-6}$ mol/dm³, DDE – to $0,163 \cdot 10^{-6}$ mol/dm³ in 2 hours.

The experimental data of photochemical oxidation of lindane and DDE by hydrogen peroxide are presented in Tables 1, 2.

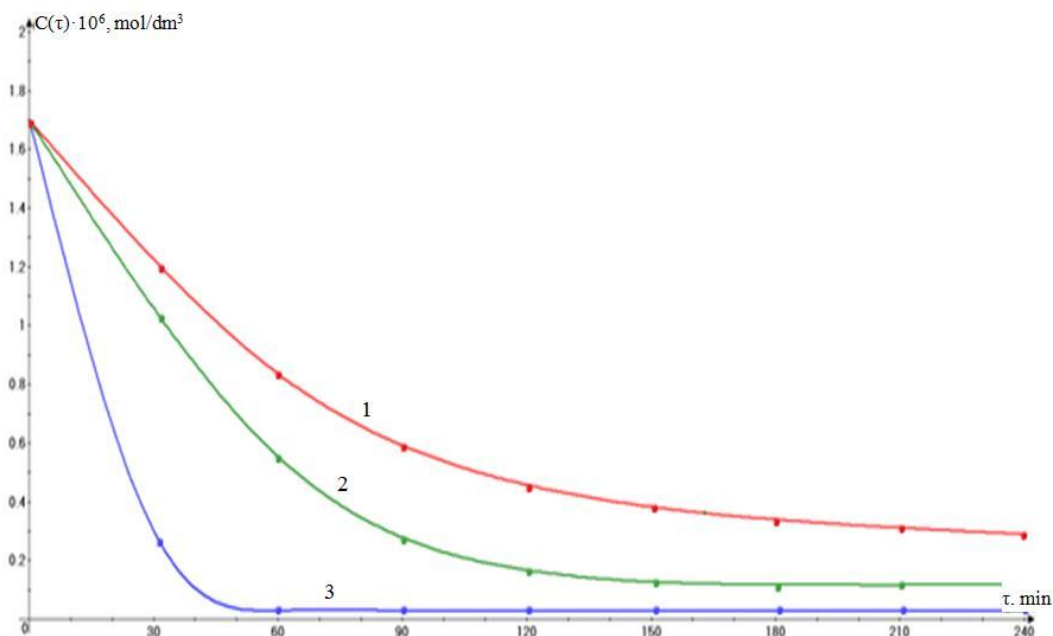


Fig. 2. Kinetic curves of lindane photochemical oxidation by hydrogen peroxide
 1 - kinetic curve of lindane photochemical oxidation by hydrogen peroxide; 2 - Kinetic curves of lindane photochemical oxidation by hydrogen peroxide in presence of Zn (II); 3 - Kinetic curves of lindane photochemical oxidation by hydrogen peroxide in presence of Fe (III)

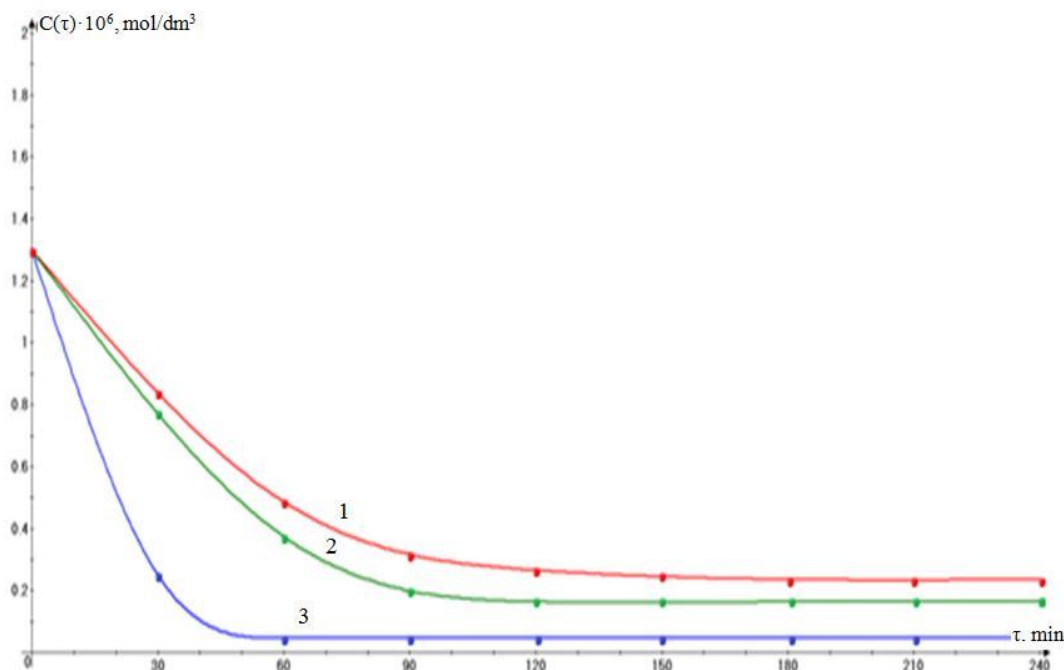


Fig. 3. Kinetic curves of DDE photochemical oxidation by hydrogen peroxide
 1 - Kinetic curve of DDE photochemical oxidation by hydrogen peroxide; 2 - Kinetic curves of DDE photochemical oxidation by hydrogen peroxide in presence of Zn (II); 3 - Kinetic curves of DDE photochemical oxidation by hydrogen peroxide in presence of Fe (III)

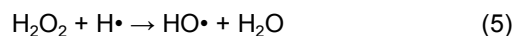
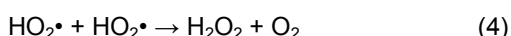
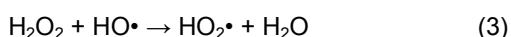
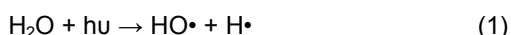
Table 1. Time to reach required rate of lindane photochemical oxidation by hydrogen peroxide

Oxidizer	C ₀ , mole/dm ³	Time to reach oxidation degree, min		
		50%	70%	90%
H ₂ O ₂	1,7 · 10 ⁻⁶	60	110	–
H ₂ O ₂ + Zn (II)	1,7 · 10 ⁻⁶	45	65	120
H ₂ O ₂ + Fe (III)	1,7 · 10 ⁻⁶	15	25	35

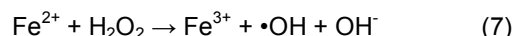
Table 2. Time to reach required rate of DDE photochemical oxidation by hydrogen peroxide

Oxidizer	C ₀ , mole/dm ³	Time to reach oxidation degree, min		
		50%	70%	90%
H ₂ O ₂	1,3 · 10 ⁻⁶	40	60	–
H ₂ O ₂ + Zn (II)	1,3 · 10 ⁻⁶	30	50	120
H ₂ O ₂ + Fe (III)	1,3 · 10 ⁻⁶	15	25	40

As the result of water and hydrogen peroxide photolysis the high oxidizing hydroxyl radical is formed [19-20]:



D-elements ions intensify the hydrogen peroxide decomposition process. The high speed of photochemical decomposition of pesticides is due to further contribution of Fe (III) ions during the process of hydroxyl radicals creation [21]:



For the kinetic characteristic of photochemical oxidation of pesticides by hydrogen peroxide in the presence of homogeneous catalysts the constants of oxidation rates of lindane and DDE were calculated. As the concentration of hydrogen peroxide is 10000 times more than the concentration of pesticides, it can be considered as constant and also the photochemical oxidation of lindane and DDE by hydrogen peroxide is the first order reaction. The homogeneous catalysts initiate the photolysis processes of hydrogen peroxide and water, and, therefore, do not change the order of the photochemical oxidation reaction of pesticides by hydrogen peroxide.

The constants of oxidation rate are shown in Table 3.

To establish the mechanisms of photochemical oxidation of pesticides by hydrogen peroxide the infrared spectrum of lindane and DDE initial solutions, solutions of photochemical oxidation of pesticides by hydrogen peroxide, both without, and in the presence of homogeneous catalysts are collected. Infrared spectrum is presented in Figs. 4-9.

By analyzing the infrared spectrum of lindane initial solution, it is possible to emphasize the following characteristic frequencies [22]:

- $\nu = 2950 \text{ cm}^{-1}$ – stretch vibration H–C–Cl;
- $\nu = 1350 \text{ cm}^{-1}$ – out of plane deformation vibrations H–C–R;
- $\nu = 780 \text{ cm}^{-1}$ – plane deformation vibrations H–C–Cl;
- $\nu = 570 \text{ cm}^{-1}$ – stretch vibration C–Cl.

After 30 minutes of lindane photochemical oxidation by hydrogen peroxide the infrared spectrum of solutions both without catalysts, and in the presence of the catalysts initiating processes of H_2O_2 and H_2O photolysis shows that the stretching band of stretch vibration H–C–Cl are disappeared. The H–C stretch vibration in the methylene group and C=O stretch vibrations in aliphatic ketones are emerged.

Table 3. Oxidation rate constants of pesticides photochemical oxidation by hydrogen peroxide in the presence of homogeneous catalysts

Oxidizer	K 10 ² , min ⁻¹	
	DDE	Lindane
H ₂ O ₂	1,532±0,075	1,087±0,052
H ₂ O ₂ + Zn (II)	1,903±0,091	1,901±0,090
H ₂ O ₂ + Fe (III)	5,532±0,265	6,785±0,335

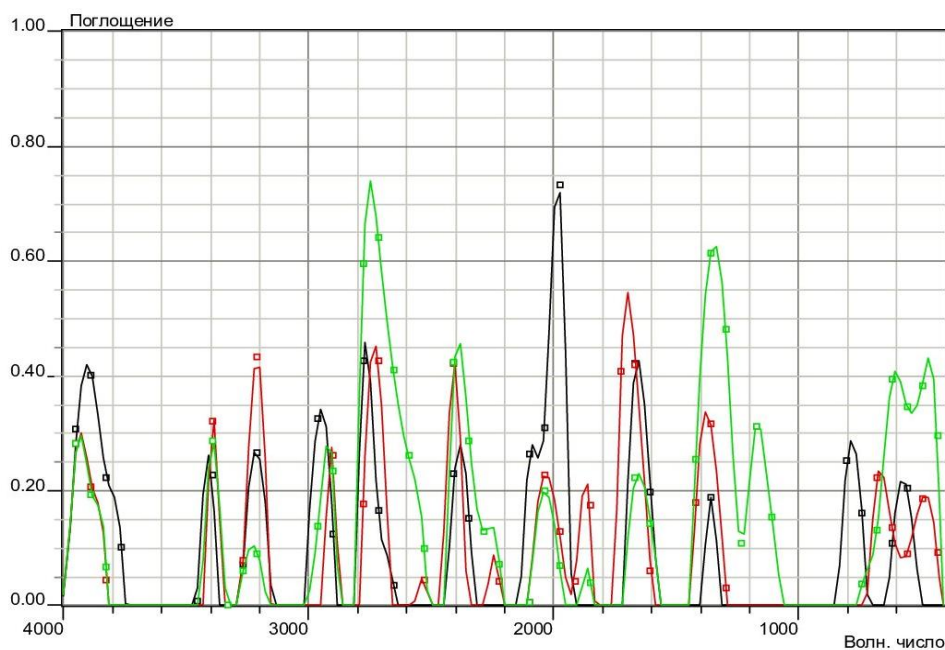


Fig. 4. Infrared spectrum of lindane solutions

— - Lindane initial solution; — - Solution after 30 minute of photochemical oxidation of pesticides by hydrogen peroxide; — - Solution after 120 minute of photochemical oxidation of pesticides by hydrogen peroxide

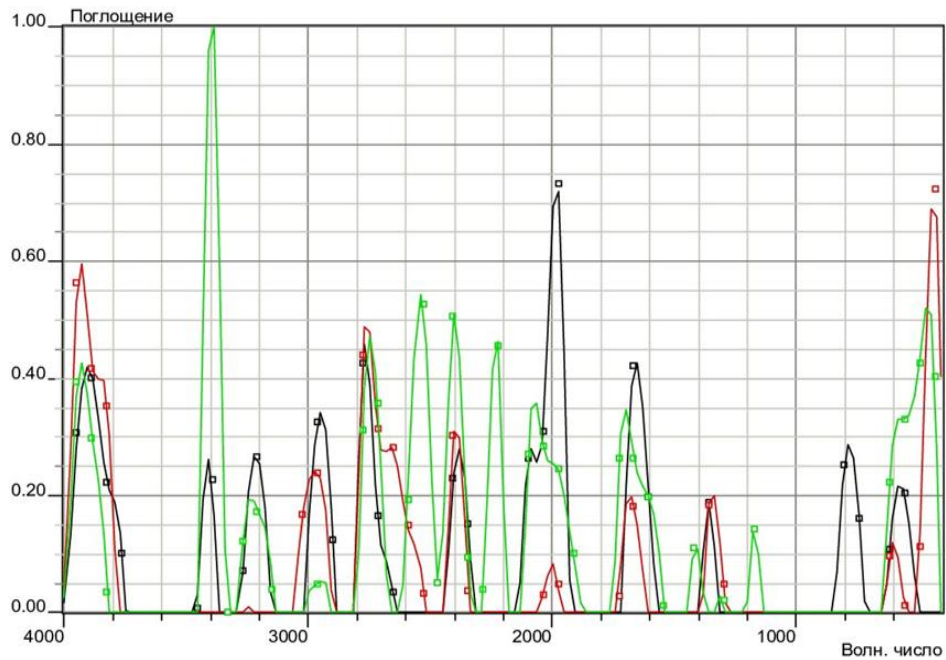


Fig. 5. Infrared spectrum of Lindane solutions in the presence of Zn (II)
— - Lindane initial solution; — Solution after 30 minute of photochemical oxidation of pesticides by hydrogen peroxide in the presence of Zn (II); — Solution after 120 minute of photochemical oxidation of pesticides by hydrogen peroxide in the presence of Zn (II)

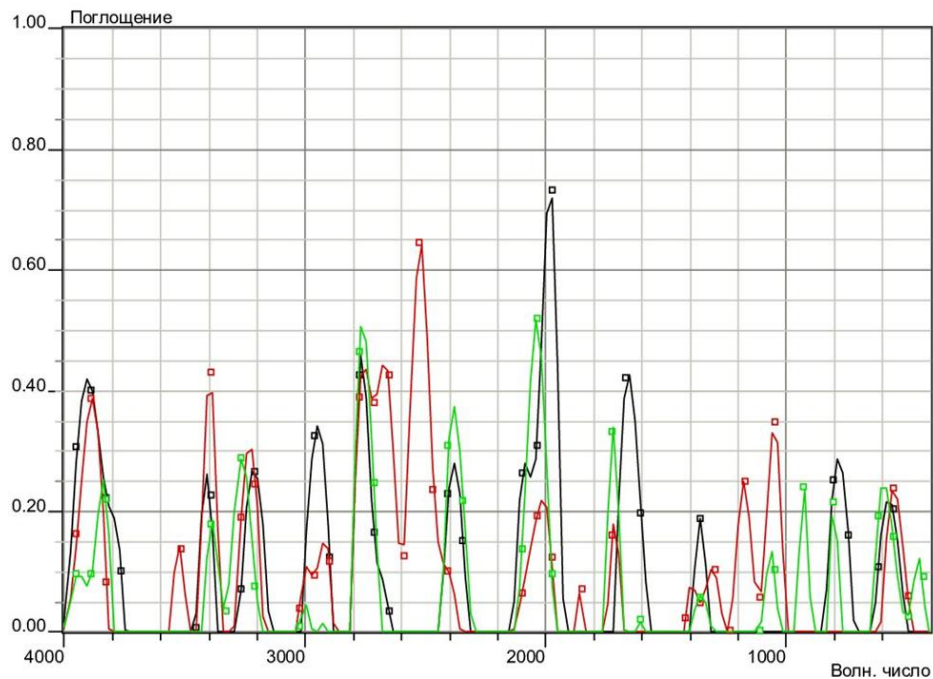


Fig. 6. Infrared spectrum of Lindane solutions in the presence of Fe (III)
— - Lindane initial solution; — Solution after 30 minute of photochemical oxidation of pesticides by hydrogen peroxide in the presence of Fe (III); — Solution after 60 minute of photochemical oxidation of pesticides by hydrogen peroxide in the presence of Fe (III)

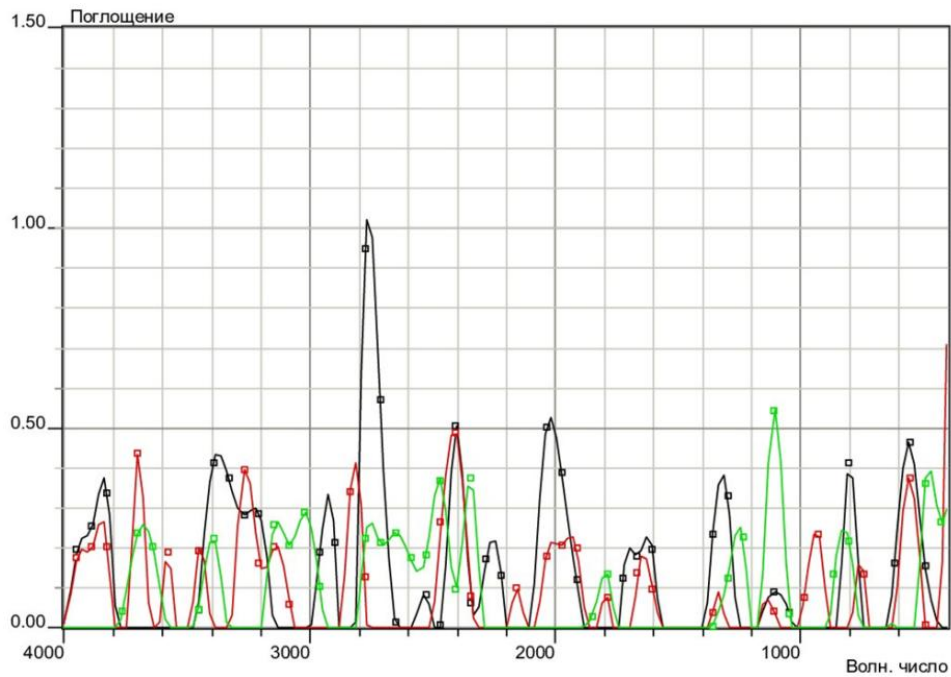


Fig. 7. Infrared spectrum of DDE solutions

— - DDE initial solution; — - Solution after 30 minute of DDE photochemical oxidation by hydrogen peroxide;
— - Solution after 120 minute of DDE photochemical oxidation by hydrogen peroxide

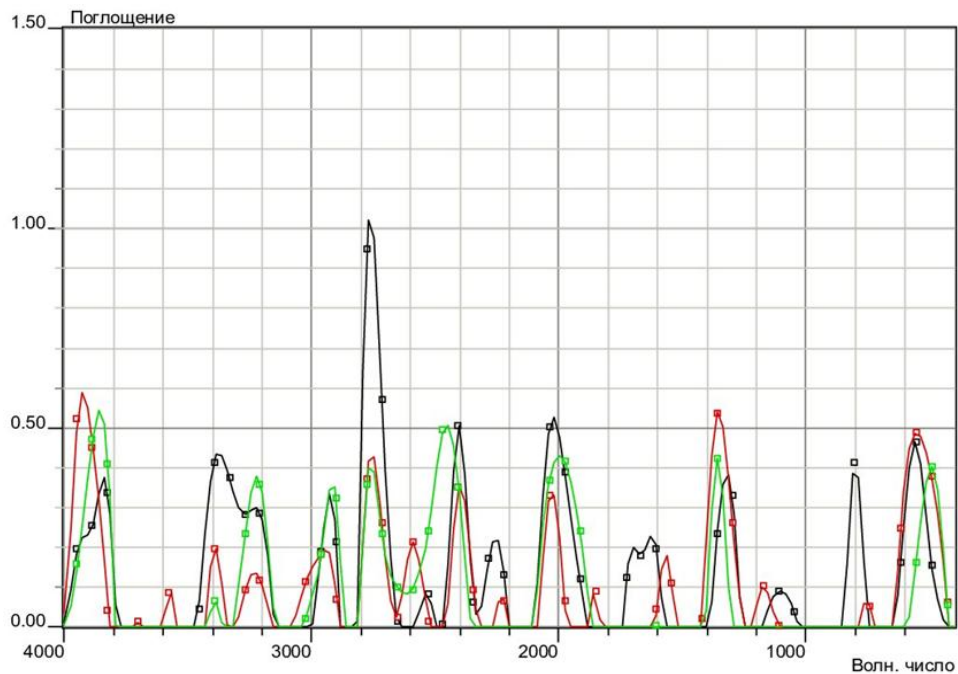


Fig. 8. Infrared spectrum of DDE solutions in the presence of Zn (II)

— - DDE initial solution; — - Solution after 30 minute of DDE photochemical oxidation by hydrogen peroxide in the presence of Zn (II); — - Solution after 120 minute of DDE photochemical oxidation by hydrogen peroxide in the presence of Zn (II)

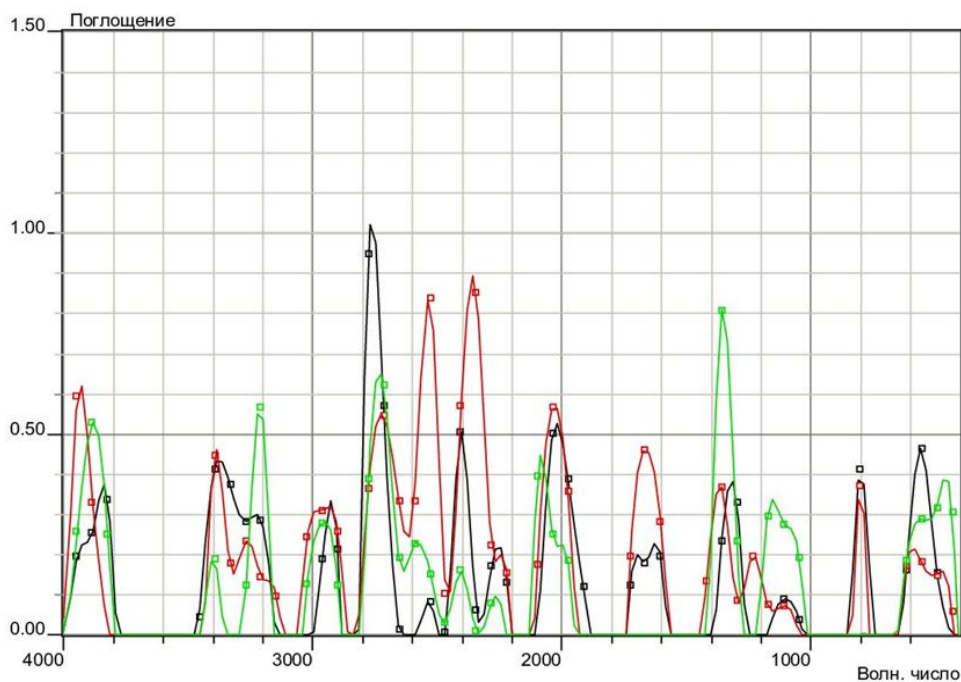


Fig. 9. Infrared spectrum of DDE solutions in the presence of Fe (III)

— - DDE initial solution; — - Solution after 30 minute of DDE photochemical oxidation by hydrogen peroxide in the presence of Fe (III); — - Solution after 60 minute of DDE photochemical oxidation by hydrogen peroxide in the presence of Fe (III)

After 120 minutes of lindane photochemical oxidation by hydrogen peroxide and after 60 minutes in the presence of Fe (III) on the infrared spectrum of solutions the band of 1700 cm^{-1} corresponding to C=O stretch vibrations in aliphatic ketones is disappeared and the band of 1130 cm^{-1} corresponding to stretch vibrations of S-O in secondary alcohols is emerged.

On the infrared spectrum of DDE initial solution, can be obtained the following main characteristic frequencies:

$\nu = 1700\text{ cm}^{-1}$ – C=C stretch vibration in alkenes;

$\nu = 1620\text{ cm}^{-1}$ – C–C stretch vibration in aromatic ring;

$\nu = 1100\text{ cm}^{-1}$ – C–H plane deformation vibrations in 1,4-substituted arena;

$\nu = 800\text{ cm}^{-1}$ – C–H out of plane deformation vibrations in 1,4- substituted arena;

$\nu = 570\text{ cm}^{-1}$ – C–Cl stretch vibration.

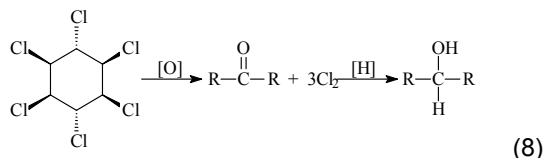
After 30 minutes of DDE photochemical oxidation by hydrogen peroxide on the infrared spectrum of

solutions both without catalysts, and in the presence of the catalysts initiating processes of H_2O_2 and H_2O photolysis is observed decreasing of intensity of stretching band of 1800, 1640 and 570 cm^{-1} corresponding to C=C stretch vibrations in alkenes, C–C in the aromatic ring and C–Cl respectively; and emergence of stretching band of 1140 cm^{-1} corresponding to S-O stretch vibrations in phenols.

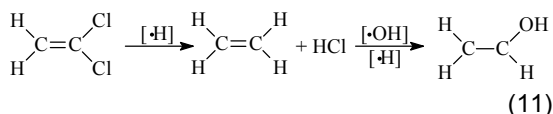
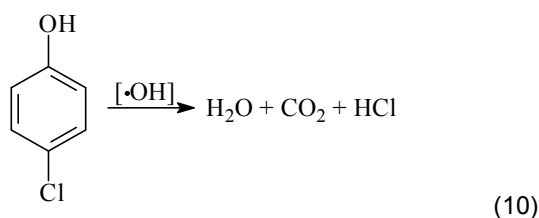
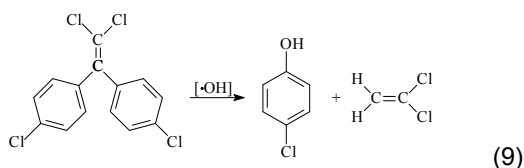
After 120 minutes of DDE photochemical oxidation by hydrogen peroxide without catalysts and in the presence of Zn (II), and after 60 minutes – in the presence of Fe (III) on the infrared spectrum of solutions the band of C=C stretch vibrations in alkenes, C–C in aromatic ring, S–O in phenols and C–Cl ($1800, 1640, 1140, 570\text{ cm}^{-1}$) are disappeared, and the bands of 1250 and 1110 cm^{-1} corresponding to deformation vibrations of OH-groups and C–O stretch vibrations in the primary alcohols, respectively.

The determined estimated products of photochemical oxidation of pesticides by hydrogen peroxide on the basis of collected IR spectrums of solutions are allowed to assume the process mechanisms.

There is a cycle rupturing in lindane leading to formation of the aliphatic ketones which are restored to secondary alcohols:



DDE has rupture of C(1) atom benzene ring (the reaction of "addition-substitution of the side-chain") has the least energy barrier among all optional versions of interaction of the hydroxyl radical with the benzene ring [23]) to formation of intermediate oxidation products (chlorophenols and alkenes). Chlorophenols are oxidized by hydroxyl radical to carbon dioxide and water, and alkenes are hydrated to primary alcohols:



4. CONCLUSION

The conducted research of photochemical oxidation of organochlorine pesticides by hydrogen peroxide in the presence of homogeneous catalysts showed high efficiency of their neutralization with formation of nontoxic products (carbon dioxide, water and primary alcohols).

FINDINGS

1. The kinetic of processes of photochemical oxidation of lindane and DDE is studied. It is observed that pesticides are completely oxidized within the first hour by hydrogen

peroxide in the presence of chloride of iron (III), which is being the initiator of the photolysis of hydrogen peroxide and water.

2. The photochemical oxidation rate of pesticides by hydrogen peroxide is calculated:

$$K_{DDE}^I = 1,532 \cdot 10^{-2} \text{ min}^{-1} \quad ; \quad K_{lindane}^I = 1,087 \cdot 10^{-2} \text{ min}^{-1}$$

Over homogeneous catalysts initiating the photolysis of hydrogen peroxide and water, the constant rates are increasing:

$$K_{DDE+ZnSO_4}^I = 1,903 \cdot 10^{-2} \text{ min}^{-1};$$

$$K_{lindane+ZnSO_4}^I = 1,901 \cdot 10^{-2} \text{ min}^{-1}$$

$$K_{DDE+FeCl_3}^I = 5,532 \cdot 10^{-2} \text{ min}^{-1};$$

$$K_{lindane+FeCl_3}^I = 6,785 \cdot 10^{-2} \text{ min}^{-1}$$

3. The analysis of pesticides photochemical oxidation products by IR spectrums allowed assuming mechanisms of photochemical oxidation of pesticides by hydrogen peroxide.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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