

SELF-PURIFICATION OF AQUATIC MEDIA FROM HEXACHLOROCYCLOHEXANE IN A RADICAL PROCESS

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Abstract. It is known, that highly toxic pesticide hexachlorocyclohexane (HCH) is resistant to decomposition and has a long-term accumulating capacity. Nevertheless, it undergoes complete degradation in reactions with hydroxyl radicals in Fenton-like systems. The goal of this work was to study the influence of HCH on the processes of radical self-purification of water bodies and to explain the mechanisms of chemical transformation of substances occurring in natural waters, as well as to reveal the kinetic characteristics of the processes of radical self-purification of water bodies. It was found, that HCH plays a dual role for aquatic ecosystems – it is not only a scavenger of free radicals, but also an additional initiator. Under the influence of light in the surface layer of water, HCH generates radicals, thus contributing to the self-purification processes.

Keywords: hexachlorocyclohexane, natural water, radical self-purification, kinetic characteristic.

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Introduction

The ability of self-purification of natural waters is understood as a set of hydrodynamic, physical, biological and chemical processes aimed at restoring their original properties and composition. The course and rate of the processes of self-purification depend on a number of conditions: on the nature of incoming pollutant chemicals, on the volume and rate of pollution, on the hydrodynamic conditions of the aquatic environment, on the chemical composition and biological state of water masses and bottom sediments, water temperature, oxygen regime. The intensity of self-purification can be calculated on the basis of the results of hydrological and hydrochemical observations carried out on water objects [1-3].

The self-purification ability of natural water consists of a sum of processes of mass transfer, biochemical and chemical transformation.

The most significant for the self-purification of the aquatic environment are: (a) physical processes of mass transfer: dilution, evaporation, sorption (by suspended particles and bottom sediments), bioaccumulation; (b) microbiological transformation; (c) chemical transformation: hydrolysis, photolysis, oxidation.

An important place in the system of self-purification of the natural water environment is held by the processes of oxidation of organic substrates, as well as catalytic and photochemical transformations of substances, accompanied by the formation of highly reactive particles [1-9]. In the course of reduction of oxygen to water (H₂O or OH⁻) four redox equivalents are consumed. The product of the two-electron reaction is a relatively stable molecule or anion of hydrogen peroxide (H₂O₂ or HO₂⁻), whereas products of the odd-electron reduction are reactive free radicals. The most aggressive intermediate on the route of O₂ to H₂O is the hydroxyl radical OH⁻, the most powerful oxidant of non-specific action. The establishment of thermodynamic equilibrium concentration of OH⁻ radicals in natural water is excluded, since its reactivity in relation to the vast majority of organic substances is characterized by a diffusion controlled rate constant. So at all conditions and regimes the steady-state concentration of OH⁻ radicals is several orders lower, than the thermodynamic equilibrium, corresponding to the redox potential of the medium.

It is obvious that for the assessment of processes occurring in natural water the most

advantageous method is the use of model systems, that is, the study in the laboratory of mechanisms similar to those occurring in natural water. The study of the mechanisms of transformation of various substances in such systems will explain and regulate the processes occurring in the real environment. In practical terms, the task is to assess the impact on the water model system of various substances constantly present in the natural environment and their impact on the processes of radical self-purification. This requires: (a) to simulate a system containing various components of natural water; (b) to investigate, on their basis, chemical transformations of pollutants in laboratory conditions, both separately and in their joint presence; (c) to establish the kinetic parameters and regularity of the process of chemical self-purification with free radicals.

Hexachlorocyclohexane (HCH) is a representative of organochlorine pesticides, which have toxic properties, are resistant to decomposition and have storage capacity. The Aarhus Protocol (1988) on persistent organic pollutants stated that technical hexachlorocyclohexane (mixture of isomers HCH) is on the list of restricted substances. Technical HCH is a mixture of five HCH isomers: α -HCH (50-70%), β -HCH (3-14%), γ -HCH (11-18%), δ -HCH (6-10%) and ε -HCH (3-5%). The α -, β - and γ -HCH isomers are the most common in the environment. The α -isomer prevails in atmospheric air and waters of the world ocean [13].

The influence of HCH on the processes of radical self-purification of water bodies was studied on model systems, which allowed to explain the mechanisms and processes of chemical transformation of substances occurring in natural water, as well as to reveal the kinetic characteristics of the processes of radical self-purification of water bodies.

Experimental

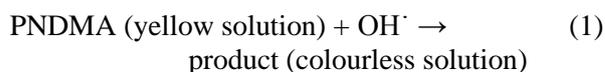
Materials

Humic acid sodium salt of technical grade, *p*-nitrosodimethylaniline (PNDMA), H₂O₂ and HCH were purchased from Sigma-Aldrich (Germany); FeCl₃·6H₂O from Stanchem, (Poland); KH₂PO₄, Na₂HPO₄·2H₂O from Chem-Lab (Belgium).

Method for determination of free OH[·] radical

The method is based on the interaction of OH[·] radicals with *p*-nitrosodimethylaniline (PNDMA) resulting in solution discoloration (Eq.(1)), thus allowing indirect determination of

the free radicals using UV-Vis spectroscopy. For the same purpose PNDMA dye is used in radiation chemistry.



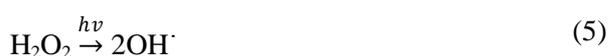
In case of natural water samples, the gradual discoloration of PNDMA acts as an indicator of the chemical-biological processes that take place, and the process is described by Eqs.(2-5) [1-3,10-12].



where, W_i - rate of radicals initiation

$\Sigma k_i[S_i]$ - inhibitory capacity of the medium.

The OH[·] radicals are generated as a result of H₂O₂ photolysis (Eq.(4)).



The reaction rate constant of various substances with OH[·] radicals is almost always in the range of $10^8 \div 10^{10} \cdot \text{M}^{-1} \cdot \text{s}^{-1}$, and is usually considered as $k_i = 10^9 \cdot \text{M}^{-1} \cdot \text{s}^{-1}$.

The effective concentration of PNDMA is estimated by the value of the inhibitory capacity (Eq.(6)):

$$\Sigma k_i S_i \approx 10^9 \cdot \Sigma [S_i] \quad (6)$$

where $[S_i]$ is the concentration of radical scavengers;

$\Sigma k_i[S_i]$ is the inhibitory capacity of the medium.

For:

$\Sigma k_i[S_i] < 10^4 \cdot \text{s}^{-1}$, the water should be classified as very clean;

$\Sigma k_i[S_i] > 10^6 \cdot \text{s}^{-1}$, the water should be classified as highly contaminated;

$\Sigma k_i[S_i] = 10^5 \cdot \text{s}^{-1}$ the water is in its normal state with respect to the flow of free radical self-purification processes.

The dimension and physical meaning of the parameter $\Sigma k_i[S_i]$: it can be regarded as an effective pseudo-first order rate constant of the OH[·] radicals destruction in the aqueous medium.

Knowing the rate of radicals initiation W_i and constant of destruction rate, it is possible to

determine the stationary concentration of OH[•] radicals (Eq.(7)):

$$[\text{OH}] = W_i / \sum k_i [S_i] \quad (7)$$

The lower is the value of $\sum k_i [S_i]$, the greater is the contribution of the radical mechanism to the self-purification of the aquatic environment.

Experimental procedure

The solutions were prepared using twice distilled water and the reaction was carried out at pH 7, which was set by the 0.0013 M phosphate buffer. Additionally, the pH was periodically monitored (before and after the photolytic session) using the WTW Inolab pH 720 pH-meter. All measurements were carried out under thermostated conditions, at a temperature of 20°C. The solutions were contained in aerobic conditions, bringing the modeling conditions closer to the natural ones.

Hydrogen peroxide was used as a source of OH[•] radicals. Such important parameters as the rate of photochemical discoloration of the PNDMA in the absence and in the presence of a pesticide, the rate of initiation of free radicals, the “inhibitory ability” of the medium, as well as the steady-state concentration of OH[•] radicals were calculated in the course of this research.

In this study, the photolytic reactions were induced by irradiating the solution samples using a DRSH-100 mercury lamp for 30 minutes, with a time step of 5 minutes, the absorbance was measured at $\lambda = 440$ nm. The constancy of the light flux and its intensity were checked with a standard ferrioxalate actinometer.

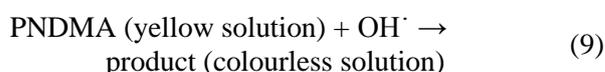
The samples (50 mL) were placed in a thin-walled quartz glass with a volume of 100 mL and exposed to irradiation. Given the absorption spectrum of hydrogen peroxide and the low concentration of this reagent, the illumination throughout the volume could be considered uniform. However, solutions were mixed with a magnetic stirrer during irradiation, for additional averaging.

The concentration of the initial hydrogen peroxide ($1 \cdot 10^{-2}$ M) that was used to model the systems ($1 \cdot 10^{-3}$ M) was determined by the iodometric method. The solutions of HCH and humic acid sodium salt were prepared by weighing. Our goal was to study their influence on the processes of radical self-purification of water systems. PNDMA was chosen as an indicator, being a trap of OH[•] radicals formed during the photolysis of hydrogen peroxide.

Results and discussion

The influence of hexachlorocyclohexane on the processes of radical self-purification of water

In the present study, the principle from-simple-to-complex was used, which implies a step-by-step complication of the investigated model systems. The simplest model system used in the study consisted of phosphate buffer–PNDMA–H₂O₂, artificially exposed to UV radiation. After a certain amount of time, the absorbance of the system was measured periodically. Oxidation of PNDMA occurs as a result of its interaction with OH[•] radicals generated by H₂O₂ under the action of light (Eqs.(8,9)).



Consecutive absorbance measurements allowed plotting the kinetic curve of the dye oxidation (Figure 1). The rate of PNDMA interaction with OH[•] radicals W_0 was calculated, which turned out to be equal to $2.54 \cdot 10^{-8}$ M·s⁻¹.

By modelling a system consisting of the same components as the previous one, but complicating its composition by introducing different elements of natural water, for example HCH, a more complex model system was obtained: buffer solution-PNDMA-H₂O₂-HCH, which included a variation of the initial concentration of the pesticide.

Kinetic parameters for the model systems containing different concentrations of HCH were calculated (Table 1).

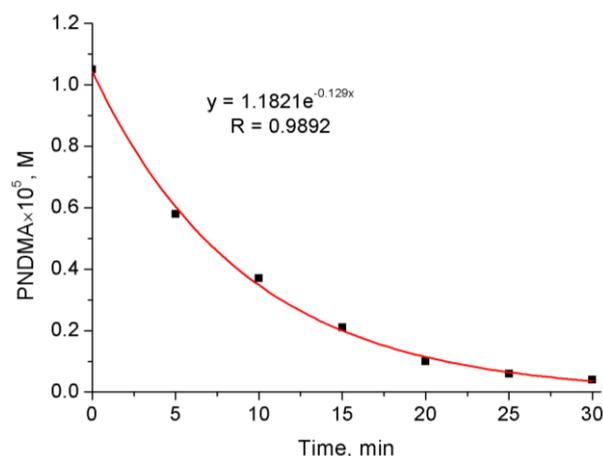


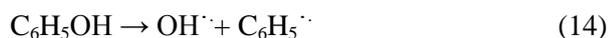
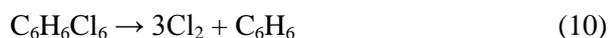
Figure 1. The kinetic curve of the photochemical discoloration of PNDMA in the system PNDMA-H₂O₂. Experimental conditions: pH 7, t = 20°C, [H₂O₂] = 10⁻³ M.

Table 1

Kinetic characteristics of PNDMA discoloration in the presence of different HCH concentrations.				
$[HCH] \cdot 10^5, M$	$W_0 \cdot 10^8, M \cdot s^{-1}$	$W_i \cdot 10^{11}, M \cdot s^{-1}$	$\sum k_i [S_i] \cdot 10^{-5}, s^{-1}$	$[OH] \cdot 10^{16}, M$
0.5	1.3	0.14	4.61	0.03
1.0	1.4	0.14	1.21	0.12
1.5	1.5	0.37	0.18	2.05
2.0	1.5	0.61	0.13	4.65
2.5	1.4	1.10	0.49	2.25

Experimental conditions: pH 7, $t = 20^\circ C$, $[H_2O_2] = const = 10^{-3} M$, $[PNDMA]_0 = 1.05 \cdot 10^{-5} M$.

Based on the obtained data, one can see that in the presence of different HCH concentrations, the rate of discoloration of PNDMA increases, which suggests that, along with hydrogen peroxide, HCH is a generator of an additional amount of free radicals (Eqs.(10-15)):



In addition, the presented data show that the inhibitory ability of the environment parameter ($\sum k_i [S_i]$) decreases with increasing the amount of pesticide and is in the range $(0.13-4.6) \cdot 10^5 s^{-1}$, which is characteristic for the normal state of the water environment in relation to processes of radical self-purification.

Another important kinetic parameter of the radical process of self-purification is the stationary concentration of free OH^\cdot radicals. A reasonable increase in the concentration of free radicals is a favourable phenomenon in the water system, as this fact contributes to the active process of radical self-purification. For this system, the stationary concentration of hydroxyl radicals varies within $10^{-16} M$, which has a positive effect on the process of self-purification. Thus, HCH has a dual role for aquatic ecosystems. On one hand, it is a hardly degradable substance that can accumulate in living organisms and sediments. From another point of view, in the surface water layer under the influence of light and in the case of oxidizing components (*i.e.* the presence of hydrogen peroxide in the water), this pesticide is capable to generate additional free radicals, which is a

favourable factor for the unfolding of chemical self-purification processes involving free radicals.

The influence of humic substances on the processes of radical self-purification of water

Further increasing the complexity of the studied model systems must take into account one of the components of natural waters, the humic substances. They play an important role in many physico-chemical and biochemical processes occurring in natural systems, and are characterized by the presence of a large number of functional groups, as well as a high ability to form complexes. Humic substances have a number of important features such as participation in the regulation of ion-exchange reactions, influence on the acid-base and redox regimes, and increase in the productivity of hydrobionts, thereby contributing to the improvement of the ecological state of water systems. Thus, the influence of HCH on the process of radical self-purification in the presence of humic substances was studied. Initially, a simple system was modelled in the absence of HCH, the so-called "blank" consisting of buffer solution- H_2O_2 -PNDMA-humic substances, which had also been exposed to UV light. For the blank system we calculated the rate of photochemical interaction traps (PNDMA) produced by the photolytic decomposition of H_2O_2 with OH^\cdot radicals. The results of the experiments demonstrated that the concentration of PNDMA decreased due to the oxidation of hydroxyl radicals formed in the system, which could also be generated by humic substances present in the system at a concentration of $50 mg \cdot L^{-1}$. It is well known that in sunlit surface waters, the humic substances act as sensitizers or precursors for the production of photoreactants such as singlet oxygen, humic-derived peroxy radicals, hydrogen peroxide, solvated electrons, and OH^\cdot radicals [14]. Numerous studies [15] have provided unequivocal evidence that OH^\cdot is generated in natural waters by the photolysis of nitrite and nitrate, and in waters containing sufficiently high metal ion concentrations, through ligand-to-metal

charge-transfer reactions and photo-Fenton chemistry. However, Zhou, X. and Mopper, K. reported that the total OH[·] production rate in seawaters was significantly larger than that expected from the sum of these processes [16]. They concluded that there was a “missing source” of hydroxyl radical production and that source was most likely due to the direct photolysis of colored dissolved organic matter – humic substances.

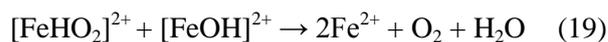
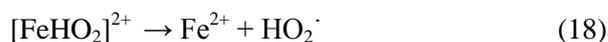
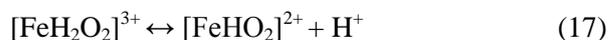
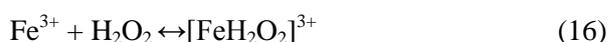
By complicating the composition of the studied system, a series of experiments were carried out for the buffer solution system-PNDMA-H₂O₂-humic substances-HCH, for which the corresponding kinetic parameters were calculated (Table 2). Data analysis demonstrates that the rate of photochemical discoloration of PNDMA added into the system is reduced in the presence of the different HCH concentrations, indicating the interaction of matter-dye with the formation of free OH[·] radicals.

An important parameter for assessing the process of radical self-purification is the rate of initiation of free radicals, which are involved in the transformation of many dissolved pollutants in the aquatic environment. The increase in the W_i suggests that humic substances can generate free radicals. At the beginning of this series (Table 2) inhibition does not occur – this suggests that the presence of humic substances (HS) contributes to a more effective flow of self-purification processes [2]. Then, with increasing levels of HCH, the inhibitory capacity begins to increase. This may be due to the fact that HS are able to form intermediate products such as complex compounds that do not generate free radicals. Thus, HS play a dual role in water systems, which negatively affects the radical self-purification processes. The steady-state concentration of OH[·] radicals in the studied system is reduced, which leads to ending of the processes of radical self-purification, because of to the lack of free radicals for oxidation reactions.

Thus, the combined presence of the pesticide HCH and HS has a dual role in the implementation of the process of radical self purification, depending on the dominance of one

of the chemicals - HCH or HS. The interaction product has the ability to capture free radicals and, as a result, their stationary concentration in the system decreases.

The studies took into account that transition metal ions (Cu(II), Fe(III), etc) play an important role in the generation of free radicals. Transition metal ions are indispensable components of natural waters. Depending on the environmental conditions, transition metal ions exist in different degrees of oxidation and are part of a variety of inorganic and organometallic compounds. The Fe(III)-compounds are most commonly found in surface natural waters and under the influence of UV light in the presence of H₂O₂ the reactions (Eqs.(16-21)) may occur:



Taking into account all mentioned above, it becomes clear that it is necessary to study the effect of trivalent iron compounds on the processes of radical self-purification of the aquatic environment in the presence of the pesticide HCH.

As in previous experiments, we followed the method of modelling the system to identify the kinetic parameters of the radical process of self-purification of the aqueous medium in the presence of Fe(III) ions. Thus was modelled the following system: phosphate-buffer solution-H₂O₂-PNDMA-Fe(III) for which was calculated the reaction rate of the dye with free radicals. Further, the complexity of the system was increased by the addition of pesticide and the basic kinetic parameters were calculated for each case.

Table 2

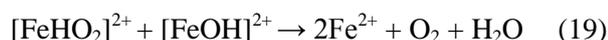
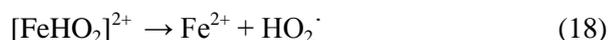
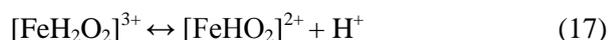
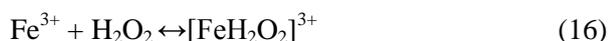
Kinetic characteristics of PNDMA discoloration in the presence of HCH and humic substances (HS).				
$[\text{HCH}] \cdot 10^5, M$	$W_0 \cdot 10^8, M \cdot s^{-1}$	$W_i \cdot 10^{11}, M \cdot s^{-1}$	$\sum k_i [S_i] \cdot 10^{-5}, s^{-1}$	$[\text{OH}] \cdot 10^{16}, M$
0.5	0.9	1.25	-	-
1.0	0.74	1.28	-	-
1.5	0.54	1.29	1.34	0.96
2.0	0.5	1.31	1.57	0.83
2.5	0.47	1.29	1.67	0.77

Experimental conditions: pH 7, $t = 20^\circ\text{C}$, $[\text{H}_2\text{O}_2] = \text{const} = 10^{-3} M$, $[\text{PNDMA}]_0 = \text{const} = 1.05 \cdot 10^{-5} M$, $[\text{HS}] = \text{const} = 50 \text{ mg} \cdot \text{L}^{-1}$.

The data demonstrate that an increase in the content of HCH in the system generates additional hydroxyl radicals. Noticeable changes in the system of self-purification were registered. When adding different pesticide content, the inhibitory capacity parameter of the medium is reduced and is of the 10^5 s^{-1} order that is characteristic to the normal state of the water body. The decrease in inhibitory capacity of the studied system is related to the formation of OH^\cdot radicals which interact with the PNDMA dye inducing its oxidation. A significant increase in the content of OH^\cdot radicals in the system, the steady-state concentration of which is of the 10^{-16} M magnitude, contributes to the self-purification processes. Thus, the combined presence of HCH and iron compounds in such a system has a positive effect on radical self-purification.

To study the effect of HCH on the self-purification process involving free radicals in the combined presence of Fe(III) and humic substances (HS), a corresponding model system was simulated. Initially, the kinetics of the transformation of these substances without HCH was studied to assess their impact on the processes of radical self-purification. Applying the method of traps of free radicals by which the concentration of the PNDMA dye was measured, it was found that the rate of its discoloration indicates the appearance of additional amounts of OH^\cdot radicals in the system, which are generated by both Fe(III) ions and HS [1]. A comprehensive review of possible stages involved in Fenton-like systems is suggested in a recent review [17]. We suppose that the mechanism includes the following reactions:

by Fe(III) ions (Eqs.(16-22))



by humic substances (Eqs.(23,24))



The introduction into the system of different concentrations of HCH, where free radicals are deliberately generated, leads to a partial increase in the formation of new free radicals, the rate of initiation of free radicals in the system increases, and the inhibitory capacity of the medium decreases. Consequently, there are more free radicals in the system, which enhances the process of radical self-purification. The increase in the rate of formation of new radicals can be explained by the fact that besides hydrogen peroxide, Fe(III) ions, HS, as well as HCH generate additional free radicals. The role of HS [18] and iron compounds [19-21] in the generation of free radicals was already reported. Heterogeneous photo-Fenton processes using zero valent iron microspheres were studied for the treatment of waste waters contaminated with 1,4-dioxan [19]. Koppenol, W. found that the reaction characteristics of this process are completely different from those of the oxidation process of hydroxyl radicals produced by pulse radiolysis on cytochrome C, and also concluded that an intermediate species with oxidation activity may be present, such as ferric ions [20]. Pestovsky, O. *et al.* excluded the possibility of tetravalent iron existence under the conditions of $\text{pH} \leq 3$ by using different principles on reactions of $(\text{CH}_3)_2\text{SO}$ with tetravalent iron and hydroxyl radicals [21]. But under the conditions of $\text{pH} > 3$, more and more evidence has proved the existence of tetravalent iron in the system [21].

The value of the inhibitory capacity of the aqueous medium $\sum ki/Si$ decreases, for the HCH systems it is in the range of 10^5 s^{-1} that is typical for the normal state of the aqueous system. In cases of large amounts of pesticide, when radicals are in excess compared to other components, HCH generates OH^\cdot radicals, which are actively involved in chemical self-purification processes.

Conclusions

In the present study, the principle from-simple-to-complex was used, which implies a step-by-step complication of the investigated model systems.

The study of the influence of hexachlorocyclohexane (HCH) on the processes of radical self-purification of the water systems led to the conclusion that this substrate is a generator of OH^\cdot radicals. The obtained results indicated that the steady-state concentration of hydroxyl radicals is of 10^{-16} M magnitude in the presence of HCH. The inhibitory capacity of the water systems is in the range $0.13 \cdot 10^5 - 4.6 \cdot 10^5 \text{ s}^{-1}$ that is typical for the normal state of the medium.

The inhibitory capacity value of the order of 10^5 s^{-1} in the modelled water systems containing both HCH and humic substances (HS) indicates that the water is in the normal state with respect to the flow of free radical self-purification processes.

The joint presence of HCH and iron compounds in the water system leads to the formation of free radicals, as well. The steady-state concentration of OH^\cdot radicals varies within $0.15 \cdot 10^{-16}$ – $5.8 \cdot 10^{-16}$ M, which allows the effective flow of self-purification processes by radical mechanism.

The presence of HCH, HS and iron compounds from the chemical point of view enhance the process of radical self-purification, since all these substances are involved in processes accompanied by the formation of OH^\cdot radicals. The steady-state concentration of OH^\cdot radicals in modelled water systems increases significantly.

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