PHOTOCHEMISTRY

PHOTOCHEMICAL OXIDATION OF ANTIBACTERIAL DRUGS IN THE PRESENCE OF OXYGEN-CONTAINING ADDITIVES

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The article examines the photochemical oxidation of nitrofural and tetracycline in the presence of oxygen-containing additives (hydrogen peroxide, peroxodisulfuric acid, potassium persulfate). It has been established that the addition of oxygen-containing additives significantly increases the efficiency and rate of API destruction. The highest destruction efficiency is achieved when using hydrogen peroxide, but the high cost of the reagent allows peroxodisulfuric acid and potassium persulfate to be considered as potential alternatives.

Keywords: peroxodisulfuric acid, oxidative destruction, photocatalysis, nitrofural, tetracycline

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INTRODUCTION

The issues of active pharmaceutical ingredients (hereinafter APIs) entering the environment have recently been receiving increasing attention. Traces of APIs are already being detected in almost all natural water bodies in any part of the globe [1-3]. The main cause of API entry into the hydrosphere is the discharge of insufficiently treated wastewater [4]. It is important to note that this concerns not only the production of various APIs but also domestic sewage where partially metabolized APIs of various purposes enter with patient excretions.

Even in insignificant (1-10 ng/dm ^{3}) concentrations, APIs can lead to disruptions in the vital activity of aquacultures, disturbance of species, gender, and age compositions of species, and have mutagenic and carcinogenic effects [5]. The danger of natural water bodies contamination with APIs is also due to their persistence, ability for bioaccumulation, and the possibility of decomposition with the formation of toxic metabolites [6-8].

For the treatment of wastewater containing APIs (Active Pharmaceutical Ingredients), biological, chemical, and physicochemical methods are used. High efficiency can be achieved through sorption and membrane separation methods, however, they only allow for separation and concentration of the pollutant, creating the need for subsequent neutralization of concentrates and spent sorbents [9, 10].

Chemical methods, such as ozonation, often lead to the formation of toxic by-products from API degradation [11]. Biological treatment is usually ineffective for APIs due to their high stability and possible eliminating effect on microorganisms, for example, in the case of antibiotics [12].

The severe negative impact of APIs on the environment and the drawbacks of existing wastewater treatment methods necessitate the development of new methods for their destruction. Due to their high efficiency and absence of toxic by-product formation, Advanced Oxidation Processes (AOPs), whose oxidative action is based on free radicals, are promising [13-16].

High-intensity oxidative processes based on photolysis represent a promising direction in water purification from organic ecotoxicants. Among the many AOPs, special attention has recently been given to processes based on sulfate radicals ($SO_4 \bullet$). Compared to the hydroxyl and superoxide radicals commonly formed in AOPs, sulfate radicals are characterized by a longer half-life and oxidative potential, which accounts for the greater efficiency in the destruction of organic pollutants [17, 18]. One of the most common sources of sulfate radicals is peroxodisulfuric acid ($H_2S_2O_8$).

The main objective of this study was to evaluate the possibility of using peroxodisulfuric acid in the photooxidation of tetracycline and nitrofural in wastewater.

MATERIALS AND RESEARCH METHODS

Due to its simplicity of implementation, the main method for obtaining $H_2S_2O_8$ is electrolysis of concentrated sulfuric acid solutions (equations (1), (2)). During electrolysis, the formation of a peroxodisulfuric bond occurs, the rupture of which is accompanied by the generation of sulfate radicals.

$$2HSO_4^- \rightarrow S_2O_8^{2-} + 2H^+ + 2e \qquad (1)$$

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e \qquad (2)$$

In this work, peroxodisulfuric acid obtained at D.I. Mendeleev University of Chemical Technology of Russia by electrochemical oxidation of concentrated sulfuric acid solution was used.

The decomposition of peroxodisulfuric acid with the formation of sulfate radicals can be initiated by various methods: thermal activation, electrolysis, alkalinization of the medium, photocatalysis, etc. [19]. Due to the successful application of photocatalytic methods for the destruction of APIs, the photocatalytic method was chosen to intensify the decomposition processes of peroxodisulfuric acid [20]. The formation of sulfate radicals under ultraviolet light is described by equation (3) [21].

$$S_2O_8^{2-} + hv \rightarrow 2SO\cdot_4^- \qquad (3)$$

Research on photooxidative destruction of APIs was carried out on a laboratory quasi-parallel beam setup manufactured by NPO "Melitta" (Russia), described in detail in [22]. Photodestruction of APIs was conducted using a pulsed xenon lamp (FP-05/120) and a continuous mercury lamp (LRU-V-36-001). The characteristics of the lamps used are presented in Table 1.

Experiments on photooxidation of APIs were conducted on model systems, for which nitrofural and tetracycline were selected. The choice of substances is due to their widespread use and large production volumes [23-25]. An equally important selection criterion is their high risk to biocenoses (including the potential development of resistant cultures) due to pronounced bactericidal properties. For the preparation of API solutions, corresponding preparations manufactured by OJSC "Avexima" were used. The initial concentrations of nitrofural and tetracycline were 20 mg/dm ^{3}.

The concentrations of model pollutants were determined by photometric methods using ZOMS KFK-3-01 (Russia).

RESULTS AND DISCUSSION

At the first stage of the study, photodestruction of APIs was carried out without introducing oxygen-containing additives into the system. The results of the experiment are presented in the graph of Fig. 1.

As can be seen from the presented data, regardless of the type of lamp used or the API studied, the highest degree is achieved with an irradiation time of 45 minutes and amounts to 12.4% for tetracycline when using MSLD and 80.5% when using IRL, for nitrofural 35.1% when using MSLD and 99% when using IRL. Further increase in processing time did not lead to a significant (more than 5%) increase in the degree of photodestruction, but significantly increased energy consumption for the process and reduced the productivity of the installation. The increased degree of photodestruction using IRL is explained by the peculiarity of wave radiation transmission and its higher energy.

At the next stage of the study, an assessment was made of the effect of adding peroxodisulfuric acid (6μg $H_2S_2O_8$/mg API) on the effectiveness of API photodestruction. The data obtained as a result of the experiment are presented in the graph in Fig. 2.

The main disadvantage of the proposed reagent is its instability and short shelf life. In this regard, an assessment was made of the possibility of using peroxodisulfuric acid salts for photocatalytic destruction of APIs. Potassium persulfate ($K_2S_2O_8$) was used as an oxidizer. Data on the photocatalytic destruction of nitrofural and tetracycline in the presence of potassium persulfate are presented in Fig. 3.

The provided data show that the introduction of microadditives of peroxodisulfuric acid or its potassium salt allows:

1. For the acid, to increase the maximum efficiency of API photodestruction by 10% and 57% for tetracycline using IRL and MSLD respectively, by 12% for nitrofural using MSLD.

2. For the salt, to increase the maximum efficiency of API photodestruction by 13 and 66% for tetracycline using IRL and MSLD, respectively, by 2% for nitrofural using MSLD.

The significant increase in efficiency is explained by the participation of sulfate radicals in the destruction process, formed as a result of the decomposition of peroxodisulfuric acid (equation (3)).

Experimental data demonstrate that the addition of peroxodisulfuric acid or its salt accelerates the destruction of model pollutants.

The final stage of the experiments was the assessment of the effect of hydrogen peroxide addition (the most common oxidizing reagent) on the photodegradation degree of the model API. The data obtained as a result of the experiment are presented in the graph in Fig. 4.

From the presented data, it can be seen that the addition of hydrogen peroxide can significantly increase the efficiency of API mineralization. The destruction degree was 99.3% for tetracycline using LNDD and 100% for all other cases.

It is important to note that hydrogen peroxide is an expensive and highly hazardous reagent, which significantly affects the cost of the purification process. The use of peroxodisulfuric acid solutions or its salts, obtained including from various wastes (hydrolysis acid, battery acid, etc.), will not only reduce the cost of the reagent but also organize a system for processing certain wastes, which will certainly allow making a step towards implementing a circular economy.

To assess the influence of various additives on the photooxidation of nitrofural and tetracycline, the rates of the corresponding processes were calculated. The kinetic curves of API photodestruction were analyzed using OriginPro 8.0 software. Approximation of experimental dependencies was carried out according to equation (4):

$$\mathrm{y} = a \cdot \exp\left(-x/b\right) \tag{4},$$

where a , b , c are approximation constants.

The initial rate of API oxidation reaction (υ_0) was determined as the value of the derivative of this function at $t = 0$.

$$\frac{\mathrm{d}y}{\mathrm{d}x} = -\frac{a}{b} \cdot \exp\left(-x/b\right) \tag{5}$$

$$\upsilon_0 = \frac{a}{b} \cdot \exp(0/b) = \frac{a}{b} \tag{6}$$

The calculated rates of API photodestruction are presented in Table 2.

The rate of photooxidation of any organic compounds is primarily determined by the kinetics of chemical reactions involving oxygen-containing radicals or oxidants with impurity molecules. This process can proceed via two different pathways:

1) direct reaction of the oxidant molecule with APS:

$$\text{APS} + \text{oxidant} \rightarrow \text{oxidation products} \tag{7}$$

2) or reaction with oxygen-containing radical (OCR) molecules:

$$\text{APS} + \text{OCR} \rightarrow \text{oxidation products} \tag{8}$$

From the data in Table 2, it can be seen that the highest rate of photodestruction of the considered APS is observed with combined UV exposure and hydrogen peroxide, regardless of the type of lamp used. Tetracycline proved to be a more stable compound to photooxidation compared to nitrofural. Tetracycline is more actively oxidized during photooxidation in the presence of peroxodisulfuric acid or its salt.

CONCLUSION

The results obtained during the study confirmed the prospects of using peroxodisulfuric acid as a catalyst for the photochemical destruction process of nitrofural and tetracycline.

It has been proven that irradiation of model water allows mineralizing 100% of nitrofural and 80% of tetracycline using ICL, 35% of nitrofural and 12% using RLND.

It was established that micro-additions of peroxodisulfuric acid can increase the maximum destruction efficiency by 10 and 57% for tetracycline using ICL and RLND respectively, by 12% for nitrofural using RLND. Salts of peroxodisulfuric acid increase the degree of tetracycline photodestruction by 13 and 66% when using ICL and RLND respectively, by 3% for nitrofural using RLND. In the presence of hydrogen peroxide, the photodestruction efficiency of tetracycline increases by 20 and 87% when using ICL and RLND respectively, for nitrofural when using RLND by 65%.

It has been established by calculation that the rate of photodestruction of nitrofural and tetracycline in the presence of $H_2S_2O_8$ increases by 1.2 and 3.4 times, respectively, when using ICL, and by 11.4 times for tetracycline when using HLND. In the presence of $K_2S_2O_8$ the photodestruction of tetracycline is accelerated by 6.6 and 11.4 times for ICL and HLND, respectively. Micro-additions of H_2O_2 increase the rate of mineralization of nitrofural and tetracycline by 2.4 and 5.7 times, respectively, for ICL and by 1.5 and 19.5 times for HLND. The increase in reaction rate will allow reducing the purification time, and consequently, the size of treatment facilities.

In some cases, the rate of nitrofural photodestruction decreases: by 1.6 and 8 times for oxidation in the presence of $K_2S_2O_8$ using ICL and HLND, respectively, and by 11.5 times for photodestruction using HLND in the presence of $H_2S_2O_8$.

Despite the increased efficiency of hydrogen peroxide as a catalyst, this reagent is extremely expensive and highly dangerous, which leads to the conclusion that there are significant prospects for using inexpensive and more stable peroxodisulfuric acid or its salts in the processes of oxidative destruction of APIs.

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Figure Captions

Fig. 1. Degree of photodestruction of individual API solutions: *1* – nitrofural, IKL lamp, *2* – tetracycline, IKL lamp, *3* – nitrofural, RLND lamp, *4* – tetracycline, RLND lamp.

Fig. 2. Photodestruction of APIs in the presence of $H_2S_2O_8$: *1* – nitrofural, IKL lamp, *2* – tetracycline, IKL lamp, *3* – nitrofural, RLND lamp, *4* – tetracycline, RLND lamp.

Fig. 3. Photodestruction of APIs in the presence of $K_2S_2O_8$: *1* – nitrofural, IKL lamp, *2* – tetracycline, IKL lamp, *3* – nitrofural, RLND lamp, *4* – tetracycline, RLND lamp.

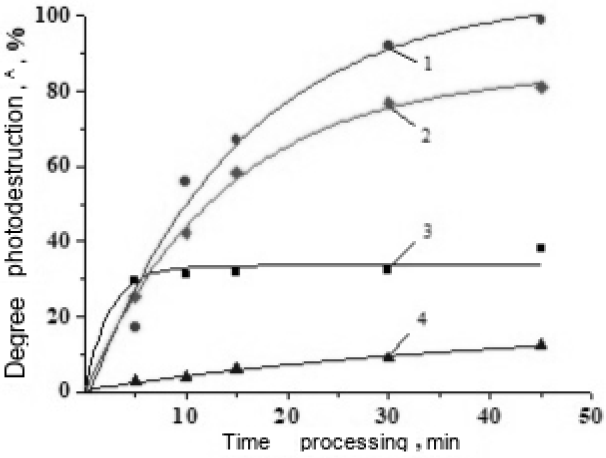
Fig. 4. Photodestruction of APIs in the presence of H_2O_2: *1* – nitrofural, IKL lamp, *2* – tetracycline, IKL lamp, *3* – nitrofural, RLND lamp, *4* – tetracycline, RLND lamp.

Table 1. Characteristics of ultraviolet lamps

Characteristics/lamp	ICL	RLND
Operation mode	pulsed	continuous
Frequency, Hz	6.6	Spectrum,
nm	Continuous	254
Energy in the range 200–500 nm, J	9.8	Average
power consumption, W	400	36×2
Average radiation power, W	65	11×2
Efficiency, %	16	30

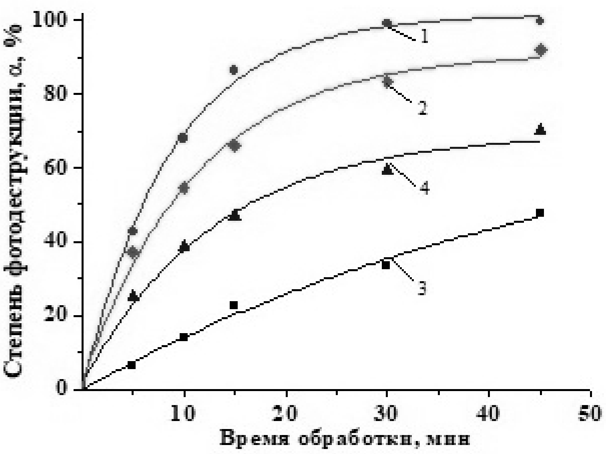
Table 2. Rate of photooxidation (υ_0) of APS depending on the type of lamp and catalytic additive

Lamp type	ICL				RLND			
Additive	No additive	$H_2S_2O_8$	$K_2S_2O_8$	H_2O_2	No additive	$H_2S_2O_8$	$K_2S_2O_8$	H_2O_2
Nitrofural								
υ_0, mg/dm^3 ×min	1.68	2.12	1.06	4.07	3.34	0.29	0.42	5.25
Tetracycline								
υ_0, mg/dm^3 ×min	0.94	3.15	6.21	5.37	0.13	1.49	1.48	2.54



Degree photodestruction, ^, %
100
80
60
40
20
0
10
20
30
40
50
Time processing , min
1
2
3
4

Fig. 1



Степень фотодеструкции, α, %
100
80
60
40
20
0
10
20
30
40
50
Время обработки, мин
1
2
4
3

Fig. 2

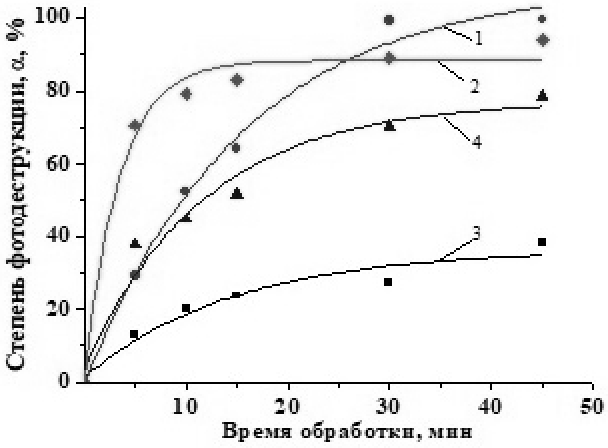

Степень фотодеструкции, α, %
100
80
60
40
20
0
10
20
30
40
50
Время обработки, мин
1
2
3
4

Fig. 3

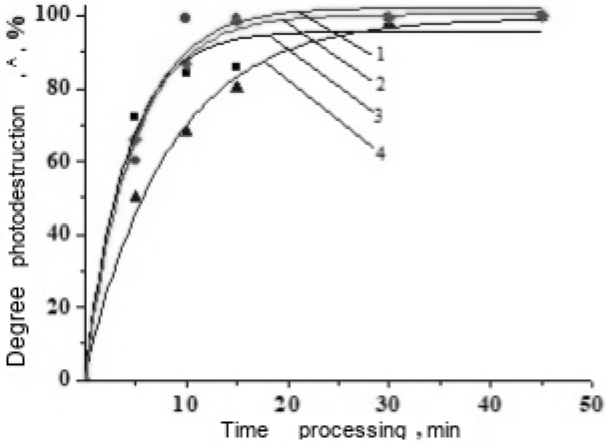

Degree photodestruction , ^, %
100
80
60
40
20
0
10
20
30
40
50
Time processing , min
1
2
3
4

Fig. 4