

USING PHOTOCATALYTIC SYSTEM UV-**нано-TiO₂-K₂Cr₂O₇** FOR DETERMINING COD IN WATER ANALYSIS

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ABSTRACT

The results of a study a photocatalytic systems UV-nano-TiO₂- K₂Cr₂O₇ is described. The oxidation process was held in a specially designed photoreactor. Glucose (readily oxidizable compound, standard substance in the arbitration method COD) and acetic acid (difficultly oxidizable substance) used for optimize of oxidation conditions. The effect of irradiation time and intensity, acidity, amount of catalyst and electron scavengers was investigated. The effect on oxidation of organic substances and its causes from amount of scavengers K₂Cr₂O₇ has been studied and explained. The oxidation of many organic compounds – hydrocarbons, alcohols, ketones, organic acids and their derivatives, amino acids, aromatic compounds, nitrocompounds, surfactants and other, which are the most common organic pollutions in waters in optimal conditions were investigated. System UV-nano-TiO₂-K₂Cr₂O₇ in the methods of determining the COD for clean waters and wastewaters was applied. The results were in good agreement with those from the conventional COD_{Cr} methods.

Keywords: photocatalytic oxidation, nano-TiO₂ catalyst, potassium dichromate, chemical oxygen demand

INTRODUCTION

Conventional COD evaluation methods had several disadvantages, such as extreme conditions of determination, long time of analysis (2–4 h), high probability of errors due to complex procedures dependent upon the operators skill, the duration of the procedure for determining and distortion results of the analysis in the presence of certain salts and consumption of expensive (Ag₂SO₄) and toxic reagents (K₂Cr₂O₇ and HgSO₄) [1]. Therefore, actual scientific task remains the search for new oxidation conditions for determining of oxidability of water.

In recent years much attention to a process for photocatalytic oxidation (mineralization) of organic substances in water is paid [2]. A lot of research oxidizing abilities systems using a heterogeneous photocatalyst – semiconductor nano-TiO₂ were held. Catalyst nano-TiO₂ has a number of advantages – it is ecologically safe, chemically inert and sufficiently stable in composition and structure in ordinary conditions, and is relatively inexpensive [3-5]. In the analytical practice nano-TiO₂ at first to determine the total organic carbon (TOC) was proposed [6], and then – for the determination of COD. Scavengers of electrons (electron absorbers) were common chemical oxidants – potassium dichromate and potassium permanganate, Ce (IV) used as [7-10]. Photocatalytic oxidation of glucose and potassium hydrogen phthalate was examined in these studies (standard substances which are used in the arbitration method determination of COD) and developed methods for determining the COD for certain types of water. The received results were comparison with the results obtained by known methods and confirmed their correctness.

In our opinion, these authors have not found out some significant patterns of behavior photocatalytic systems. For example, it has been not explained the initial concentration of the K₂Cr₂O₇, boundaries determine the amount of COD, influence sorption dichromate ions on the catalyst on the accuracy of the analysis results, the effect of a method for separating the photocatalyst. Some recommendations of the authors difficult to perform, for example, measure the pH of 0,5 with high precision in common pH-meter. In addition, a significant decrease in the initial concentration dichromate ions greatly reduces the potential for absorption of electrons

process, so at high COD values (500 ... 600 mg) violated stoichiometric ratios between the components of the process, which greatly affects the reproducibility of the results.

The aim of our study was a detailed study of all the factors that affect the completeness of oxidation and optimization of conditions for photocatalytic mineralization of organic impurities reducing agent.

METHODOLOGY OF RESEARCH

Device

The process of destruction in a specially designed photoreactor was carried out. It consisted of a quartz reaction flask 100 cm³ (4), UV-lamp (3), mounted on the base (2). Lamp was placed directly in flask. The reaction mixture was kept in suspension and heated with a magnetic stirrer (7). Temperature was measured by a thermometer (1). The flask was placed in a water jacket (5) with thermal insulation (6). (Fig. 1).

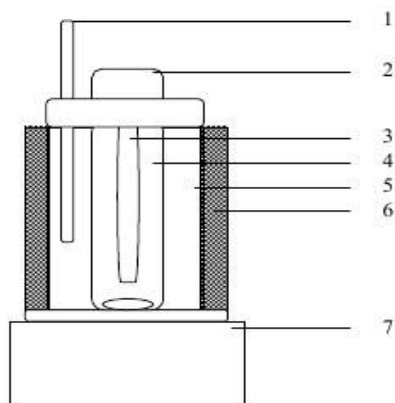


Fig.1. Photoreactor

Lamp (OSRAM) characteristics: HNS mercury lamp low pressure type, C-band, $\lambda = 253,7$ nm, capacity 9 W, the total capacity of the UV flux – 1,9 W.

The spectrophotometric measurements were carried out using spectrophotometer Beckman DU 520.

The acidity was measured by a pH-meter P-160 MI.

Reagents and solutions

Catalyst nano-TiO₂, grade P25, production companies Degussa– nonporous powder mixture of anatase and rutile in a ratio of 70:30, with a surface area 55 ± 15 m²·g⁻¹ and a crystallite size of 30 nm to 0,1 micron diameter particles [11].

All chemicals were of analytical reagent grade.

Potassium dichromate, K₂Cr₂O₇, standard solution 0,25 N; sulfuric acid, concentrated and diluted 1:10; d-glucose, a standard solution, corresponding to 1000 mg·l⁻¹ COD, was prepared by dissolving 0.9372 g of d-glucose in distilled water and diluting to 1 l with distilled water. Appropriate dilutions gave solutions of different COD values [7]; Mohr's salt, 0,25 N and 0,05 N.; ferriin (prepared by mixing batches of 1,485 g of 1,10-phenanthroline and 0,695 g FeSO₄·7H₂O and subsequent dissolution in 100 cm³ of distilled water); silver sulphate.

Organic compounds: hexane, heptane, octane, decane; methanol, ethanol, propanol, 2-butanol, 1-butanol, ethyleneglycol, glycerol, mannitol, benzyl alcohol; phenol, resorcinol; acetone, acetylacetone, methyl-ethyl ketone; tartaric acid, oxalic acid, acetic acid, lactic acid; potassium hydrogen phthalate; dioxane, amyl acetate, ethyl acetate; glucose, lactose, saccharose; aniline, nitroaniline, ethanolamine; glycine, alanine, valine, leucine, phenylalanine, proline, leucine, serine, asparagine, glutamine, histidine, arginine; acetamide, urea, thiurea, dimethylformamide; benzene, nitrobenzene, toluene, ethylbenzene; sodium lauric sulphate, cetyl pyridinium bromide; chloroform; benzotriazole.

These solutions were prepared by dissolving (or emulsification) or a certain amount of sample substance in 100 cm³ distilled water. The concentrations of substances are 0,125 mol eq·dm⁻³.

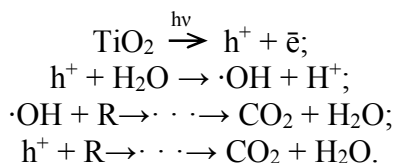
Experimental procedure

Volumetric flask of 50 cm³ were injected in stages: potassium dichromate solution, sulfuric acid, d-glucose solution or other organic reductant and distilled water to the mark. The resulting solution was transferred to the reaction flask, 100 cm³, which was placed previously catalyst charge. The solution was heated to the desired temperature. Substances oxidation began to occur with intensive mixing, when the UV-lamp was turned and was accompanied an increase of Cr(III) concentration produced by the photocatalytic reduction of Cr(VI). After a certain time

irradiation reaction, the aqueous samples were centrifuged at 800 rpm (using photocolometry). The registration of the results of experiments carried out in two ways – titrimetric and photometric.

RESULTS OF RESEARCH AND DISCUSSION

In this research a COD measurement by a photocatalytic oxidation method using nano-TiO₂ was studied [11]. It is known, that by irradiation with UV light C-band in the nano-oxide electrons valence band (\bar{e}) pass in conduction band, leaving in the valence band positively charged vacancy – holes (h^+), which are strong oxidants (their potential amount +3,5 V) [12,13]. The high oxidizing ability of such systems is also associated with the formation of various oxygenated radicals (eg, $\cdot OH$), which are formed on the TiO₂ surface illuminated with ultraviolet light [3]:



where R – organic reductant.

Simultaneously with the process photogeneration electron-hole pairs is their undesirable recombination. To prevent it a different chemical oxidizing agents – electron scavengers are using [14-17]. The potassium dichromate, K₂Cr₂O₇ ($\varphi^0(\text{Cr}_2\text{O}_7^{2-}) = 1,36 \text{ V}$) we used in our studies.

Known [7,8], that the amount of reduced absorber and oxidized reductant are stoichiometric. Indeed, the electrons that enter into the valence band are absorbed by the chemical oxidant, thus it is recovered quantitatively. The remaining positive holes oxidize stoichiometric reducing agents present in the system.

Overseeing the process of photooxidation can be determining the amount of the oxidized or reduced form dichromate ions.

To optimize heterogeneous photooxidation process glucose was carried out because it is a standard substance in arbitration method of determination COD_{Cr}. The effect of acidity, temperature, time, weight of the catalyst and the initial concentration of dichromate ions were studied.

Effect of acidity

It is known, that the isoelectric point of nano-TiO₂ P-25 is at pH 6,25 [14]. At pH < 6,25 catalyst surface becomes electropositive, which favors adsorption of Cr (VI) anions and therefore the degree of oxidation of organic substances increases with decreasing pH. The greatest oxidative capacity among the forms of Cr (VI) are dichromate ions Cr₂O₇²⁻, existing in a highly acidic environment. The direct oxidation of organic substances potassium dichromate in the system at a pH ~ 0 is not happening, because it is a weaker oxidant than holes.

It was found that the presence in the system of 2,4 cm³ 1:10 diluted solution of sulfuric acid (pH ~ 0,75) allows the oxidation of glucose at COD 100 mgO·dm⁻³ 95 ... 100%. It's confirmed by the coincidence theoretically calculated values of COD and obtained experimental data. Of these, 0,17 cm³ consumed directly by the oxidation of glucose per 100 mg O·dm⁻³, and the remainder quantity necessary to maintain the oxidation potential of dichromate ions.

Temperature effect

The process speed increases with increasing temperature up to the boiling point of the solution. According to the rule of Vant Hoff, the function $v = f(t)$ is non-linear. However, in our case we are seeing a straight. In [2] it is shown that the linear form of this dependence is determined by the Langmuir-Hinshelwood mechanism, which takes into account not only the chemicals, but also physical processes (sorption, processes in the semiconductor, etc.).

It should also be noted that at temperatures around the boiling point of the solution is increased evaporation, which leads to a decrease in reproducibility. Therefore, the temperature range was chosen by 85 ... 90 °C.

Effect of time

The time of the process greatly affects the degree of reduction of dichromate ions. The optimal time for glucose oxidation constitutes 15– 20 minutes.

Dosage of the photocatalyst nano-TiO₂

The degree of glucose oxidation increases with the concentration of TiO₂ to 4 g·dm⁻³. With a further increase concentration of the catalysis decreases the efficiency of photooxidation, which can be explained by the weakening of penetrating radiation in a suspension.

Selection of the initial concentration of K₂Cr₂O₇ and their adsorption on the catalyst

In [7] proposed initial concentration of Cr (VI) 0,01 mol·dm⁻³. The authors believe that of high concentrations the process is stabilized and explained this maximum of adsorption Cr₂O₇²⁻ on the catalyst.

We have found that this relationship is more complex. On the one-hand, the absorber should be sufficient to ensure destruction of the process, especially for water with a high content of impurities (COD > 100 mg O·dm⁻³). On the other hand, dichromate ions strongly absorb in the UV-range, almost coinciding with the lamp-conductive radiation range. Therefore, most of them will reduce the amount of energy used for photocatalysis and, in general, a useful reaction yield is significantly reduced. So it was predetermined range of COD of 0 – 100 mg O·dm⁻³ and calculate the necessary amount of scavenger with a slight excess (~ 15%). Given excess, to determine the COD unit 100 in the described conditions, must enter the reaction flask 7,5·10⁻⁴ equivalents dichromate ion.

Studying the influence of adsorption of dichromate ions on the catalyst in the absence of glucose revealed that dichromate ions in the system is spent almost exclusively on the absorption photoelectrons and their adsorbed only ~ 2,7 %. These data confirm the stoichiometry heterogeneous photocatalysis processes.

The degree of recovery dichromate ions on the amount of glucose was studied as a function $v_{eq}(K_2Cr_2O_7)_{use} = f(COD)$ and the data were compared with the COD theoretical. The method of calculation of this index is given in [18].

Register experimental results

Titration method was chosen for better comparison with the results obtained by the arbitration method definition of COD. The amount of glucose oxidized and accordingly, COD was determined by the potassium dichromate concentration difference before and after photooxidation process Mohr salt titration in the presence of ferroin indicator [1].

Ions Cr (VI) and Cr (III) are colored, so it is more precise and express photometric method can be used for the determination of COD.

It is advisable to determine the content of the ions Cr (III), because their spectrum has a peak at 610 nm and with equal concentrations of the two forms of chromium ions is more intensive.

To determine completeness recovery ions Cr (VI) in its various concentration of the reaction mixture plotted in coordinates $A - f(C_{Cr^{3+}})$, which was used in determination of the concentration of Cr(III) after photooxidation.

Remove of catalyst

When using photometric method for determining COD significant problem is the removal of nano-TiO₂ from the system. In the [19-22] it is suggested to carry out precipitation, centrifugation, and the catalyst is used immobilized solid support – glass, metal, quartz, etc. We used centrifugation.

Positive results of glucose oxidation have allowed to conduct a number of experiments on the mineralization of substances of other classes, to confirm the optimal conditions.

Table 1. The oxidation of organic substances in the system of UV-nano-TiO₂-K₂Cr₂O₇ in optimized conditions glucose

Substance	Oxidability, %	Substance	Oxidability, %
Ethanol	37	Oxalic acid	37
Isobutanol	32	Tartaric acid	71
Glycerin	100	Acetic acid	21
Resorcinol	99	Amyl acetate	38
Mannitol	100	Glycine	63
Acetone	21	Lauryl sulfate	33
Glucose	100	Benzene	28

The table shows that the conditions chosen for the glucose (easily oxidized substances) [22], are not optimal for the oxidation of many other substances, and should be optimized conditions using hard compound to be oxidized.

One of these substances is acetic acid. It is known as an intermediate in the catalytic oxidation of many organic substances and participates in the metabolism of a variety of biological systems. Therefore, to test the oxidative ability of the system of UV-nano-TiO₂-K₂Cr₂O₇, we chose acetic acid.

As shown by previous experiments, the oxidation of acetic acid is 21% in the previously selected conditions. Therefore, we studied the ability of the system to oxidation hard oxidation substances.

The experimental procedure is analogous to the method of using glucose.

To optimize the process of oxidation of acetic acid were also investigated the effect of the initial concentration of dichromate ion, acidity, time and temperature.

The influence of the initial concentration K₂Cr₂O₇.

We conducted a study of depending on oxidation of acetic acid over a wide range of concentrations of potassium dichromate.

Table 2. Dependence of the degree of oxidation of acetic acid concentration of dichromate ions

C ₀ (Cr ₂ O ₇ ²⁻), mol·dm ⁻³	ω (C ₂ H ₄ O ₂), %	C ₀ (Cr ₂ O ₇ ²⁻), mol·dm ⁻³	ω (C ₂ H ₄ O ₂), %
0,0025	32	0,01	18
0,0033	28	0,0133	16
0,0042	24	0,0166	13
0,005	21	0,02	3
0,0066	19		

It was found that under the conditions proposed by the authors of [6], oxidation acetic acid passes only 11 %, there for, we suppose that a most of amount of energy absorption of significant amount of dichromate ions. For the oxidation of acetic acid COD ≤ 100 mgO·dm⁻³ is optimal initial concentration C₀(Cr₂O₇²⁻) = 0,0025 mol·dm⁻³.

Effect of acidity

It has been found that previously set (for glucose) acidity at pH order of 0,75, is insufficient to oxidize the acetic acid.

At pH ~ 0,5, which is achieved by introducing into the reaction mixture of 5 cm³ of sulfuric acid diluted 1:10 ensured oxidation COD acid at 100 mgO·dm⁻³ at 60 ... 62% (subject to the other, previously established conditions). Lowering the degree of oxidation of acetic acid at pH <

0,5, we explained difficulties in sorption dichromate ions on the photocatalyst due to the shielding effect of protons.

Temperature effect

Degree of oxidation of acetic acid by the temperature has the same pattern as that for the oxidation of glucose. When the temperature reached 85 ° C, the degree of oxidation was 60 % and does not increase further more. So, we have an optimum temperature of 85 ° C was chosen.

Dependence of the time

Time of process significantly influence for degree of reduction of dichromate ions. As expected, for the oxidation of acetic acid needed longer exposure to UV-radiation. Optimal time of exposure to acetic acid oxidation is 60 minutes.

Thus, the optimized conditions of photocatalytic oxidation of acetic acid as follows: $C_0(\text{Cr}_2\text{O}_7^{2-}) = 0,0025 \text{ mol}\cdot\text{dm}^{-3}$, $m(\text{TiO}_2) = 4 \text{ g}\cdot\text{dm}^{-3}$, time of experiment $\tau = 60 \text{ min}$, the temperature $t = 85 \text{ }^\circ\text{C}$, the volume of H_2SO_4 (diluted 1:10), $V = 5,00 \text{ cm}^3$.

In new optimized conditions oxidizing ability of the system has been studied for a variety of organic substances, which have been selected and classified according to different functional groups. Moreover, most of them are representative of pollutants in wastewater types.

Methods of experiment

Volumetric flask of 50 cm^3 were injected in stages: a solution of potassium dichromate – 1,5 cm^3 , a sulfuric acid – 5 cm^3 , the organic substance – 5 cm^3 , distilled water – to label.

The results of photocatalytic mineralization of organic substances represented in the table 3. For comparison, the literature data and some of our data (marked with *), obtained under the conditions of the arbitration and acceleration methods.

Table 3. Comparison of oxidation of organic compounds in various oxidation systems

№	Substance	Oxidability ¹ , %	Oxidability ² , %	Oxidability ³ , %
Alkanes				
1.	Hexane	–	–	89
2.	Heptane	–	–	91
3.	Octane	–	–	83
4.	Decane	–	–	63
Alcohols				
5.	Methanol	–	–	96
6.	Ethanol	37	94	99
7.	Propanol	–	–	94
8.	2-Butanol	58	93	98
9.	1-Butanol	58	90	95
10.	Ethylene glycol	100	–	100
11.	Glycerol	100	–	99
12.	Mannitol	98	–	100
13.	Benzyl alcohol	–	–	100
Phenols				
14.	Phenol	96	99	98
15.	Resorcinol	97	–	97
Ketones				
16.	Acetone	53	93	79
17.	Acetylacetone	–	–	90
18.	Methyl-ethyl ketone	33	–	87
Acids and solts				
19.	Oxalic acid	100	–	99
20.	Tartaric acid	100	100	100

№	Substance	Oxidability ¹ , %	Oxidability ² , %	Oxidability ³ , %
21.	Lactic acid	37	81*	95
22.	Acetic acid	7	95	91
23.	Potassium hydrogen phthalate	99	101	100
Ethers and esters				
24.	dioxane	100	–	97
25.	Amyl acetate	59	95	98
26.	Ethyl acetate	24	61*	93
Carbohydrates				
27.	Glucose	97		98
28.	Lactose	–	–	100
29.	Saccharose	100	–	99
Amines				
30.	Aniline	100	113	107**
31.	Nitroaniline	–	–	100
32.	Ethanolamine	–	–	98
Amino acids				
33.	Glycine	100	100	92
34.	Alanine	–	–	97
35.	Valine	67	94	96
36.	Leucine	–	–	98
37.	Phenylalanine	–	–	100
38.	Proline	–	–	89
39.	Serine	–	–	98
40.	Asparagine	–	–	100
41.	Glutamine	–	–	100
42.	Histidine	67	–	96
43.	Arginine	–	–	97
Amides				
44.	Acetamide	7,5	36*	91
45.	Urea	0	3*	84
46.	Thiourea	–	–	100
47.	Dimethylformamide	43	60	96
Arenes				
48.	Benzene	19	19	97
49.	Nitrobenzene	20	99	98
50.	Toluene	19	56*	93
51.	Ethylbenzene	–	–	95
Surface-active agents				
52.	Sodium lauric sulphate	21	72	94
53.	Cetylpyridinium bromide	22*	56*	88
Others				
54.	Chloroform	–	–	70
55.	Benzotriazole	–	–	100

1 – Oxidation under the arbitration method without catalyst,%

2 – Oxidation in the conditions of the arbitration method with the catalyst Ag₂SO₄,%

3 – Oxidation in a photocatalytic mineralization%

* – Our results of arbitration method

** – Results based on the oxidation of the amino group to molecular nitrogen.

The table shows, that in UV-nano-TiO₂-K₂Cr₂O₇ system in optimized conditions all classes of organic compounds well oxidized.

The results of the study of oxidation of organic compounds and the determination of an optimal photocatalysis conditions enabled the development of methods for determining COD natural waters and wastewaters. To verify the results of the method in parallel with the photocatalyst, and COD was determined by an accelerated arbitration procedure described in [1] using the catalyst Ag₂SO₄ (tab. 4) or photometrically.

To verify the results from the photocatalytic method, it was determined COD by arbitration and accelerated methods, described in [1] using the catalyst Ag₂SO₄ or photometrically.

Characteristics of the working solution and photocatalytic systems for COD for relatively pure waters (1) and wastewaters (2) the following:

(1) $V(\text{K}_2\text{Cr}_2\text{O}_7) = 1,5 \text{ dm}^{-3}$ (0,5 N), $V(\text{проб}) = 30...40 \text{ dm}^{-3}$, $V(\text{H}_2\text{SO}_4, 1:10) = 2,4 \text{ dm}^{-3}$, $V_{\text{sol}} = 50 \text{ dm}^{-3}$, $m(\text{TiO}_2) = 0,2 \text{ g}$, UV-irradiation, 9 W, $\lambda = 253,7 \text{ nm}$, $\tau = 30 \text{ min}$, $t = 85^\circ\text{C} \pm 2^\circ\text{C}$, stirring on a magnetic stirrer ~ 800 rpm.

(2) $V(\text{K}_2\text{Cr}_2\text{O}_7) = 1,5 \text{ dm}^{-3}$ (0,5 N), $V(\text{проб}) = 30...40 \text{ dm}^{-3}$, $V(\text{H}_2\text{SO}_4, 1:10) = 5 \text{ dm}^{-3}$, $V_{\text{sol}} = 50 \text{ dm}^{-3}$, $m(\text{TiO}_2) = 0,2 \text{ g}$, UV-irradiation, 9 W, $\lambda = 253,7 \text{ nm}$, $\tau = 60 \text{ min}$, $t = 85^\circ\text{C} \pm 2^\circ\text{C}$, stirring on a magnetic stirrer ~ 800 rpm.

The results of the analysis of waters and wastewaters are shown in Table 5.

Table 5. The results of the determination of COD for different types of water

№	The name of the sample	COD _{Cr ac}	COD _{Cr arb}	COD _{fc}	
				value	S _r
1.	Tap water	30	33	34	0,059
2.	Bottled water “Znamenivska”	9	13	13	0,043
3.	Water after industrial cleaning	16	22	24	0,072
4.	Water of the river Yuzhny Bug in the city	118	156	154	0,021
5.	Water of the river Yuzhny Bug before the city	86	97	101	0,032
6.	Water of the river Ingul in the city	89	236	240	0,021
7.	Storm wastewater	38	52	52	0,033
8.	Domestic wastewater	179	230	256	0,020
9.	Wastewater dairy "Lactalis"	268	408	412	0,015
10.	Wastewater Bashtansky cheese plant	320	510	526	0,011
11.	Wastewater sausage manufactory	356	442	460	0,020

As can be seen from Table. 5, the results of determining COD wastewater photocatalytically method correlate well with the values of COD_{Cr} received arbitrage method for 11 samples of water. The linear regression equation and correlation coefficient were: $y = 1,0054x + 0,7063$ and 0,9756 ($n = 6$), respectively, where x and y – the results obtained by the arbitration and the proposed methods.

Conclusion

The purpose of this work is to investigate the oxidative capacity of the photocatalytic UV-nano-TiO₂-K₂Cr₂O₇ system, optimization of conditions of oxidation using of glucose and acetic acid, develop a method for monitoring COD applying this system and checking the results of the determination in real water compared to existing methods. In this system K₂Cr₂O₇ stoichiometrically interacts with photoelectrons conduction band and improves the ability of the photocatalytic degradation of organic compounds. Thus, the COD of the sample of water can be assessed by determining the concentration of Cr (III), resulting in the reduction of chromate ions. The optimization of operation conditions was studied. The method of determination of COD in different waters have a number of significant advantages – a short time of analysis, accuracy, sensitivity, simplicity, absence of expensive and toxic reagents. These results correlate well with results obtained by other methods.

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