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Photooxidative Post-Treatment of Pharmaceutical Wastewater

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Abstract

The results of laboratory studies on the additional treatment of model wastewater from pharmaceutical production with the help of the combined effect of UV radiation and hydrogen peroxide are presented. Literature data on the existing purification technological schemes were analyzed, with the determination of their main advantages and disadvantages. Experimental results were obtained on the treatment of model solutions of acetylsalicylic acid, tetracycline and sulfadimezin after passing through three stages of purification: photooxidation, coagulation, and sorption. The values of chemical oxygen demand (COD) and concentration of active pharmaceutical ingredients (API) were determined. The combined action of photooxidation and hydrogen peroxide makes it possible to achieve purification efficiency up to 80 % for COD and up to 99 % for API. A technological scheme for the treatment of pharmaceutical wastewater is proposed.

Keywords: photooxidation, purification, pharmaceutical wastewater

INTRODUCTION

The pharmaceutical industry is distinguished by high water consumption and, therefore, by a substantial amount of the formed wastewater containing a great amount of specific pollutants. The production of medicinal preparations includes several stages, and waste waters with different concentrations of mineral and organic substances, as well as the products of incomplete decomposition formed in incomplete reactions are generated at each stage. The total wastewater amount is formed as a sum of all wastes from different stages of production based on process changes and is distinguished by periodicity [1]. The composition of waste waters may be diverse. In the majority of cases, wastewater from the production of medicinal preparations contains multicomponent mixtures of either inorganic or organic substances in the dissolved state.

At present, the amounts of medicinal preparations and the products of their metabolism polluting the water resources of our planet are increasing all over the world. The medications get mainly into rivers and then into drinking water from household drainage and cattle farms. The biological decomposition of pharmaceutical preparations is often hindered due to their high toxicity with respect to microorganisms, so only a few pharmaceuticals can be relatively easily biodegraded in the environment. An alternative method against biodegradation may be chemical destruction/oxidation, providing complete mineralization of pollutants. Initially, wastewater had been purified in the pharmaceutical production with the help of aerobic treatment in aeration tanks. However, this

method is inefficient for removing all potentially dangerous pollutants from wastewater, so it is necessary to use other up-to-date technologies.

The main stages of the technological scheme of pharmaceutical wastewater purification are mechanical purification, neutralization, physicochemical purification unit, additional purification and decontamination. Additional purification of these kinds of wastewater may involve biological methods, thermal decomposition, or a number of improved oxidation-based methods. Traditional purification methods sometimes are insufficiently effective due to the presence of specific and difficult-to-decompose compounds in solution. Modern schemes are based on oxidation processes involving the action of several factors. These methods include the treatment with Fenton's reagent, cavitation, photocatalytic oxidation, plasmachemical oxidation, the combined action of ozone and hydrogen peroxide, oxidation with humid air, supercritical oxidation [2–6]. In particular, photochemical and photocatalytic oxidation is widely used in the processes involved in the additional purification of wastewater [7–9]. Improved oxidation-based methods are characterized by rather high rate constants of chemical reactions – 10^7–10^{10} L/(mol · s), and high (up to 100 %) efficiency of purification with respect to a broad range of organic pollutants.

So, the goal of the present work was to evaluate the possibility of using photooxidation as a method for additional purification of wastewater from pharmaceutical production.

EXPERIMENTAL PROCEDURE

The objects of the investigation were the model solutions of active pharmaceutical substances (APS); these active substances were acetylsalicylic acid (ASA), tetracycline and sulfadimezin. The active substance, or pharmaceutical substance, APS is a chemical compound or unique biological substance as a drug component with the physiological action providing the therapeutic effect of the drug.

The initial concentration (C_{in}) of ASA and sulfadimezin was 0.5 g/L, tetracycline – 0.1 g/L. Investigation of the photooxidative destruction of the model solutions of APS was carried out with the help of the UV radiation in a coil reactor with a low-pressure mercury quartz lamp DRB-8 with a power of 8 W, described in more detail in [10, 11]. The scheme of the set-up is shown in Fig. 1.

The APS solution is admitted into the UV set-up with the help of a peristaltic pump (*1*).

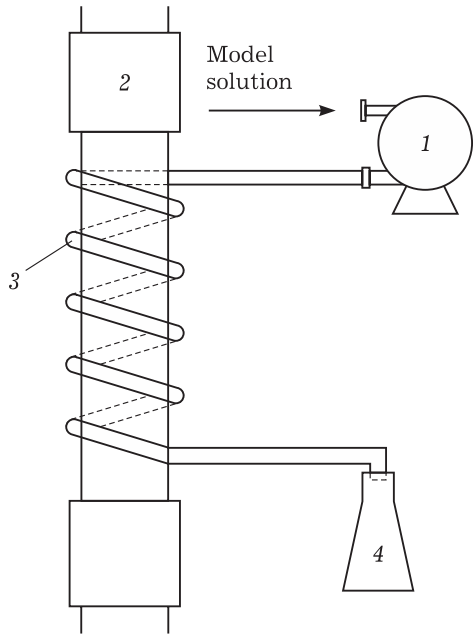

Fig. 1. Scheme of the laboratory set-up: *1* – peristaltic pump; *2* – UV lamp DRB-8; *3* – quartz coil photoreactor; *4* – receiver.

Then the solution passes over a quartz coil (*3*) around the DRB-8 lamp (*2*), and the purified solution enters the receiving vessel (*4*). The minimal intensity of the UV lamp (E_{min}) at the wavelength of 254 nm is 0.02535 W/cm^2. The light power of the DRB-8 lamp corresponding to the resonant line at 254 nm is 2.5 W. The DRB-8 lamp is mounted coaxially with the quartz coil, the diameter of which is 45 mm, and the inner diameter of the quartz tube is 5 mm. The lamp and the coil are mounted in a case made of stainless steel. The peristaltic pump providing the flow of the irradiated solution is mounted outside the case. The advantages of this scheme are almost complete absorption of the UV radiation from the lamp, the absence of the necessity to use mixing devices, and permanent saturation of the irradiated solutions with the air, which is necessary for photooxidation of organic compounds. The time of contact of the liquid with the irradiation zone (τ) was 160 s. To intensity photooxidation, hydrogen peroxide (H_2O_2) was introduced into the solutions of APS under treatment in the stoichiometric amount, with the concentration for ASA 50 mmol/L, for tetracycline 10.8 mmol/L, and for sulfadimezin 56 mmol/L.

The concentrations of APS, monocarboxylic acids and aldehydes were determined by means of spectrophotometry. Determination of the concentration of ASA in the solution under investigation

is based on the formation of a nitro compound: its alkaline solution is yellow [12]. The method of tetracycline determination in water is based on the formation of a complex compound of tetracycline; its alkaline solution is yellowish-green [13]. The method to determine the concentration of sulfadimezin is based on the formation of diazonium salts in a solution containing hydrochloric acid, and this process is participated by sodium nitrite. A bright scarlet azo compound is formed in the presence of chromotropic acid and diazonium salt [14]. The mass concentration of formaldehyde was determined using a photometric method, which is based on its distillation with water vapour from a water sample, followed by the interaction with acetyl acetone in the presence of ammonium ions, resulting in the formation of a yellow reaction product [15]. The concentration of monocarboxylic acids (calculated for formic acid) was determined relying on a colour-producing reaction of these compounds with ammonium metavanadate [16]. The chemical oxygen demand (COD, mg O/L) in water was determined by titration according to PND F 14.1:2.100–97 [17].

A 5 % solution of $Ca(OH)_2$ ($C(Ca^{2+})$ = 0.27 g/L) was used as a coagulating agent; Praestol (C = 0.5 g/L) was a flocculant; sorption was carried out on a BAU coal filter. To prepare a solution of APS, a tablet of tetracycline or ASA, or sulfadimezin was thoroughly crushed in an agate mortar, and then the necessary amount of the preparation was weighted. The initial solution was mixed for 10–15 min till the complete dissolution of the component to be determined, and then settled for solid inclusions to precipitate. After coagulation/ flocculation stages, the APS solution under investigation was filtered through a blue line paper filter.

The total degree of purification (α_{tot}, %) was determined using equation

$$\alpha_{tot} = (1 - (1 - \alpha_1)(1 - \alpha_2)(1 - \alpha_3)) \cdot 100\ \%$$

where α_1 is the efficiency of purification at stage No. 1, $\alpha_1 = (COD_{in} - COD_1)/COD_{in}$; α_2 is the efficiency of purification at stage No. 2, $\alpha_2 = (COD_1 - COD_2)/COD_1$; α_3 is the efficiency of purification at stage No. 3, $\alpha_3 = (COD_2 - COD_3)/COD_2$.

RESULTS AND DISCUSSION

Investigation of the oxidative destruction of the considered APS dissolved in model water under the individual action of UV radiation and the combined action of UV/H_2O_2 was presented in [11]. On the basis of those data, it was determined that the joint effect of UV radiation and hydrogen peroxide provided a high degree (up to 95 %) and a high rate of the oxidative destruction of APS in comparison with the separate action of UV or H_2O_2. In addition, it was determined both qualitatively and quantitatively that photooxidation of the considered APS involved the formation of di-monocarboxylic acids and aldehydes, which required additional purification of water.

So, previous studies allow us to propose a technological scheme for the purification of wastewater from pharmaceutical works (Fig. 2). The necessary purification degree is mainly determined by the COD and other normative physicochemical characteristics of water for the permitted discharge into the centralized drainage systems. The limiting COD value is adopted at a level of 150 mg O/L [18]. It should be stressed that experiments were carried out with individual aqueous model solutions of APS (tetracycline, sulfadimezin and ASA), and the scheme is proposed on the basis of laboratory investigations.

We suppose that the stages of purification of pharmaceutical wastewater may look like the following: wastewater enters the receiving tank, from where it is pumped through a mixer into the flocculation chamber. While the solution is pumped through the mixer, the solution of $Ca(OH)_2$ as a coagulant is introduced into the mixture. After filling the flocculation chamber, a mixer is switched on, and a small amount of a flocculant is introduced with the help of a dosing pump to enhance the efficiency of flocculation. After mixing, the pulp is fed to the mechanical filter, where it is separated into the liquid and solid phases. The solid phase is utilized and transferred to the damp of solid wastes, while the liquid phase enters additional purification.

Additional purification is carried out in the unit of photochemical (ultraviolet, UV) treatment, where the solution of H_2O_2 is introduced in dosed amounts. The unit of UV treatment should consist of connected photochemical reactors with low-pressure mercury quartz lamps. After UV treatment, water is pumped into the flocculation chamber, in which the solution of coagulant ($Ca(OH)_2$) and a small amount of flocculant solution are also introduced. After mixing, the pulp is admitted to the mechanical filter, where it is separated into the liquid and solid phases. Then the water passes through a sorption filter and is discharged into the drainage system.

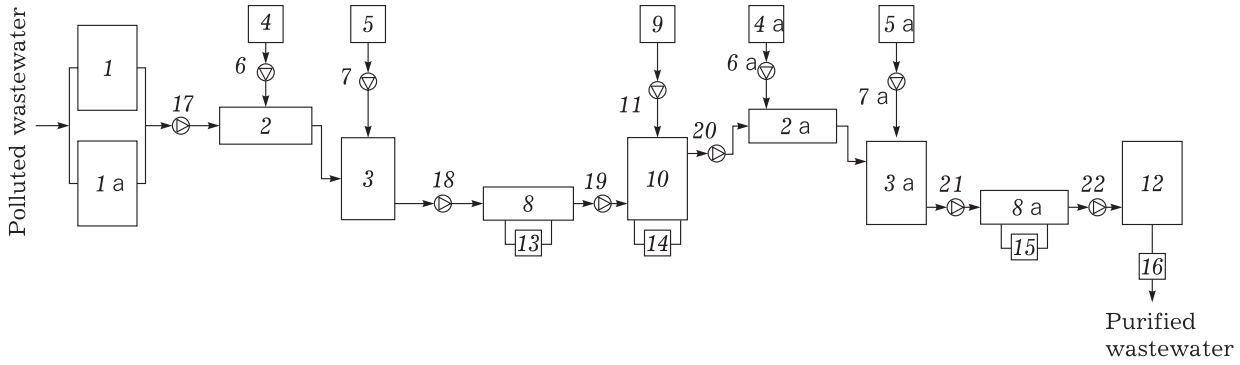

Fig. 2. Scheme of purification of wastewater from a pharmaceutical plant:
1, 1a – receiving vessels (vessel *1a* is considered to be duplicate in the case if vessel *1* is full); *2, 2a* – mixers; *3, 3a* – flocculation chambers; *4, 4a* – measuring vessels with $Ca(OH)_2$ solution; *5, 5a* – measuring vessels with the flocculant; *6, 6a, 7, 7a* – dosing pumps; *8, 8a* – mechanical filters; *9* – measuring vessel with H_2O_2; *10* – UV treatment unit; *11* – dosing pump; *12* – sorption filter; *13–16* – concentration sensors; *17–22* – pumps.

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In view of method universality, the set-up may be used for local purification of chemically polluted wastewater formed at the enterprises with a broad range of ready medicinal preparations, as well as in the case of the high initial concentrations of pharmaceutical preparations. In view of the fact that the amount of wastewater contaminated with active substances is not more than 10–15 % of the total amount of wastewater, investment into the arrangement of local wastewater purification is two orders of magnitude lower than the amount necessary for the construction of all-factory facilities of biological purification, which are used traditionally but are not always effective in APS removal.

Experimental results on the concentrations of APS, aldehydes, carboxylic acids and on COD values in model wastewater before and after purification are listed in Table 1 for each APS.

It may be determined through a calculation that the total degree of purification (α_{tot}) of model wastewater, with respect to COD, is 80 % for ASA, 60 % for tetracycline, 80 % for sulfadimezin.

At the same time, the degree of photooxidation after the 1st stage (α_{ox}, %), calculated with respect to the active APS as

$$\alpha_{ox} = ((C_{in} - C_{fin})/C_{in}) \cdot 100\ \%$$

where C_{in} and C_{fin} are the initial and final APS concentrations, g/L, was 82 % for ASA, 85 % for tetracycline, 99 % for sulfadimezin.

It should also be noted that after coagulation/flocculation and sorption stages, the residual concentrations of the compounds under determination decrease.

CONCLUSION

A technological scheme of the purification of wastewater containing APS based on the combination of reagent-based and photooxidation methods is presented in the work. The proposed scheme allows achieving a high degree of decontamination from active substrates due to photochemical destruction through UV irradiation of preliminarily clarified wastewater. The residual concentrations of destruction products are removed through sorption at the final stage. The COD of purified wastewater does not exceed the limiting value (150 mg O/L). It is determined that photooxidation may be used as one of the stages of purification of wastewater containing pharmaceutical preparations.

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TABLE 1

Parameters before and after purification of the model wastewater containing acetylsalicylic acid (ASA)/tetracycline/sulfadimezin

Concentration	Before purification	After purification at each stage		
		1	2	3
	ASA			
ASA, g/L	0.5	0.09	0.072	0.04
Formaldehyde, mg/L	0	1.57	0.56	0.56
Carboxylic acids, mg/L	0	3.89	0.43	0.19
COD, mg O/L	400	190	150	80
	Tetracycline			
Tetracycline, g/L	0.1	0.015	0.01	0.01
Formaldehyde, mg/L	0	1.9	1.3	1.1
Carboxylic acids, mg/L	0	33.5	12.4	8.6
COD, mg O/L	100	80	50	40
	Sulfadimezin			
Sulfadimezin, g/L	0.5	0.005	0.004	0.002
Formaldehyde, mg/L	0	2.2	0.7	0.7
Carboxylic acids, mg/L	0	65.1	28.6	25.5
COD, mg O/L	500	260	160	100

Notes. 1. COD is chemical oxygen demand. 2. 1 – after the UV treatment unit with the introduction of hydrogen peroxide; 2 – after coagulation and flocculation; 3 – after sorption, purified wastewater.

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