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The Influence of Ultrasound Cavitation on the Process of Degradation of Organic Substances in Wastewater of Pharmaceutical Production

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Abstract

The influence of ultrasound cavitation in the atmosphere of different gases, namely oxygen, air, and nitrogen, on the destruction of impurities of butanol and ethanol found in wastewater from the pharmaceutical plant "Galichpharm" was investigated. The effect of the corresponding gases (oxygen, nitrogen, and air) without ultrasound cavitation on the destruction of ethanol and butanol impurities in wastewater was comparatively investigated. The degree of oxidation of organic matter, effective rate constants, and approximation coefficients were calculated. It was found that the air supply is the least effective for both ethanol and butanol impurities. Degradation of ethanol by air contributed to the reduction in the organic matter content by 14.6 %, while oxidation of butanol was not observed. Ultrasound cavitation enhanced the effect of air and in common action with air the ethanol impurity content reduced by 32.58 %, and butanol impurity by 4.05 %. Nitrogen bubbling produced mediocre results for the destruction of ethanol and butanol impurities giving a decrease by 17.04 % and 0.67 %, respectively. The highest results were obtained with oxygen. Ethanol impurities decreased by 22.47 % and butanol impurities by 1.75 %. With the common action of oxygen and ultrasound, much higher results were obtained, 44.32 % for ethanol impurities and 7.43 % for butanol impurities.

Keywords

Wastewater, ultrasound cavitation, pharmaceutical industry, butanol, ethanol, chemical oxygen demand

1 Introduction

The pharmaceutical industry is an integral part of modern human development. The pharmaceutical wastewater composition is complex, with high concentrations of organic substances. Currently, about 3000 different substances are used in drugs such as painkillers, antibiotics, and contraceptives.[1]

Ethanol and butanol are mainly used as solvents.[2,3] Due to their wide use in the pharmaceutical industry, it is important to efficiently clean wastewater for its reuse as industrial water.

The wastewater of the pharmaceutical industry needs to be comprehensively treated. Applying adsorption methods (with various adsorbents) to purify contaminated wastewater showed good results.[4] The methods of membrane filtration and reverse osmosis have practical application in water purification.[5] However, these methods are appropriate for usage at lower initial chemical oxygen demand (COD) values. Therefore, we propose looking for more effective methods of water purification at much higher initial COD values or the possibility of complex uses of ultrasound cavitation (UC) with other existing methods of water treatment.

Innovative technologies and developed water purification equipment must fully meet the requirements of energy and resource conservation, environmental security, and be competitive in today's market economy. One of these innovative areas is the effective use of UC phenomena.

Due to their propagation in gases, liquids, and solids, ultrasonic waves have unique features, many of which have found practical application in various fields of science and technology. UC is one of the most important factors contributing to the intensification of various chemical and technological processes in the chemical, pharmaceutical, and food industries. The advantages of using ultrasonic cleaning in industry include: high level of safety; possibility of application for purification from dangerous substances;[6] improvement of water purification with its disinfection, deodorization, discolouration; and no environmental pollution.[7] UC is used for the degradation of polycyclic aromatic hydrocarbons, phenols, and substituted phenols.[8] The phenomenon of cavitation can occur either at an increase in fluid velocity (hydrodynamic cavitation), or at passing of an acoustic wave of great intensity during the semi-period of dilution (acoustic cavitation).[9]

One of the main features of UC chemical reactions is that they occur in an aqueous medium saturated with gas. Water is not only the most favourable environment for the formation of cavitation, but also the environment that better provides the possibility of electronic breakdown of the cavitation cavity. From the chemical aspect, not only is the occurrence of excited molecules and atoms of different gases (N_2, O_2, $N_2 + O_2$, *etc.*) interesting, but so is the participation of a water molecule in this process, which is the source of $H^{\cdot}$ and OH radicals initiating most chemical reactions. The radicals partially recombine, and the com-

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position of the final radical and molecular products of the decomposition of water in the ultrasound field depends on the nature of the dissolved gases in the water. The process of excitation of water molecules, the rate of their dissociation, is largely controlled by the presence of certain gases in the excited state in the cavity.[10] For acoustic cavitation in the frequency range of 5–50 kHz, magnetostrictive emitters, operating in the resonance mode, are used. The geometric dimensions of a wave-like system, optimal in terms of structures of emitters and components from a few centimetres to tens of centimetres contribute to this.[11] It is common that acoustic cavitation excites and evolves in the same separated area of fluid, which is called a cavitation area or a cavitation cloud. Thus, the element is repeatedly influenced by the volume of gas-liquid medium, which leads to gradual changes in certain properties (gas saturation, bubble dimensions, temperature), and these changes are practically uncontrollable.[12]

The use of the cavitation phenomenon for various industries is now developing intensively, and existing cavitation technologies have been improved.[13]

By investigating the degradation of bisphenol A under the influence of UC in the presence of gases of different nature, it was found that the best results were achieved in the presence of air. The following results were obtained in the presence of oxygen and argon.[14]

However, the effect of gases of different nature on different types of chemical and biological pollution has not been sufficiently studied. Therefore, it is advisable to investigate their effect on the process of sewage treatment with different types of pollution.

The purpose of the research is to study the efficiency of UC in the atmosphere of various gases – nitrogen, oxygen, and air on ethanol and butanol impurities found in industrial wastewater.

2 Methodology

The experiments were carried out at temperature of 20 °C, atmospheric pressure, and frequency of ultrasonic vibrations of 22 kHz.

The experiments were carried out on real wastewater from the Galichfarm pharmaceutical plant, and due to the unstable chemical composition of the real wastewater, we were unable to achieve reproducibility of the experiments. Therefore, in order to investigate the kinetics of UC, it is proposed to create one-component model mixtures with a high content of dominant harmful substances previously detected in wastewater. Dilution of pilot solutions was carried out in the following proportions: water – 20 % solution ethyl alcohol – 100 : 1 ml (mixture 1); water: 20 % solution butanol – 300 : 1 ml (mixture 2). The duration of the experiments was 120 min.

Studies of the oxidation of organic substances in aqueous solutions were conducted in three ways:

1. passing through a gas solution (oxygen, air, nitrogen);
2. influence of ultrasonic irradiation on the test mixture;
3. combined action of UC in the atmosphere of the above gases.

The oxidation value of organic impurities in water was determined by calculating the chemical oxygen demand (COD). The most common method for the determination of COD in both natural water and wastewater is the dichromate method, in which the oxidation of substances is carried out with a mixture of $K_2Cr_2O_7$+ H_2SO_4 at boiling.

$$3C + 2K_2Cr_2O_7 + 8H_2SO_4 \rightarrow 2Cr_2(SO_4)_3 + 2K_2SO_4 + 3CO_2\uparrow + 8H_2O \quad (1)$$

The excess dichromate was titrated with a solution of the Mohr's salt ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$) in the presence of *N*-phenylanthranilic acid, as a redox indicator:

$$Cr_2O^{2-} + 6Fe^{2+} + 14H^+ \leftrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \quad (2)$$

COD was calculated by the equation:

$$COD = \frac{\left(1000 \cdot \left(V_1 - V_2\right) \cdot K \cdot T\right)}{V_{sample}},\ mgO_2/dm^3 \quad (3)$$

where V_1 is the volume of Mohr's salt solution spent on the single experiment, cm^3; V_2 is the volume of Mohr's salt spent on the titration of the sample, cm^3; V_{sample} – the volume of the water sample taken for analysis, cm^3; T = 1.6 mg is the mass of oxygen equivalent to 1 cm^3 of 0.2 mol l^{-1} $K_2Cr_2O_7$ solution; K is the correction factor for the Mohr's salt concentration.

The degree of destruction of organic substances (degree of oxidation) is an indicator of the efficiency of water purification from organic substances by their oxidation (in this case, under the action of UC in the presence of gas and without it), expressed as a percentage. The degree of destruction of organic matter (D) was calculated by the equation:

$$D = 100 - \frac{COD \cdot 100}{COD_0},\ \% \quad (4)$$

where COD_0 is the initial value of COD, mgO_2/dm^3, and COD is the current value of COD at a time, mgO_2/dm^3.

3 Results and discussion

Since the initial values of the COD were in different ranges, for the sake of clarity of the experimental data, it was proposed to represent the COD/COD_0 ratio as graphs. The initial values of COD for mixture 1 were in the range (1280–1408) mgO_2/dm^3, and for mixture 2 (2372–2545) mgO_2/dm^3.

Fig. 1 shows the comparison of the indicators of COD/COD_0 under the action of the gases themselves. Ac-

cording to the obtained data, the most effective oxidizing agent is oxygen and the final COD value is 1092 mgO_2/dm^3. The effect of UC without gas was also investigated. After two hours, the value of COD decreased from 1408 mgO_2/dm^3 to 1152 mgO_2/dm^3. Nitrogen lowered COD from 1408 mgO_2/dm^3 to 1168 mgO_2/dm^3, and air dropped it from 1410 mgO_2/dm^3 to 1203 mgO_2/dm^3.

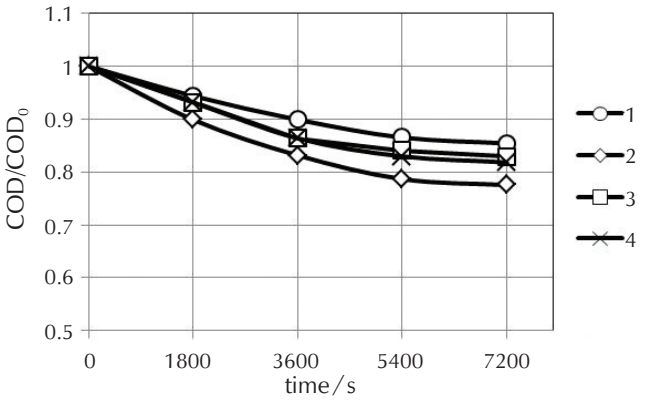

Fig. 1 – Dependence of COD/COD_0 ration *vs*. time for mixture 1 at different experimental conditions: 1 – air; 2 – O_2; 3 – N_2; 4 – UC

Analysing the graphical dependencies in Fig. 2 showed that within 30 min of the experiment the best result was obtained with the combined action of nitrogen with UC. Compared with the combined effect of oxygen and UC, the difference was 1.05 times, and with the combined effect of air and UC, 1.08 times. At the 60th min, the UC with nitrogen and the UC with oxygen showed almost the same results – 982 and 992 mgO_2/dm^3, respectively, while the UC with air reduced the COD to 1077 mgO_2/dm^3. In the third and fourth segments, the oxygen with UC continued to more actively oxidize organic matter in water than did the nitrogen or air. The COD at the end of the experiment for oxygen with UC was 784 mgO_2/dm^3, air with UC 950 mgO_2/dm^3, and nitrogen with US 887 mgO_2/dm^3.

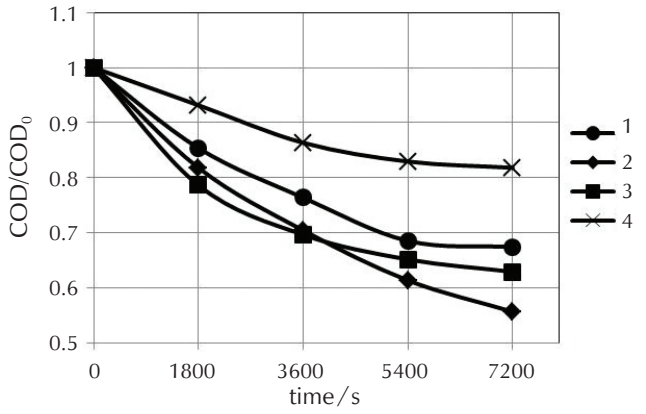

Fig. 2 – Dependence of COD/COD_0 ration *vs*. time for mixture 1 at different experimental conditions: 1 – US/air; 2 – US/O_2; 3 – US/N_2; 4 – UC

The best performance throughout the process was achieved with the combined action of UC and oxygen, reducing the COD by 1.8 times relative to the original value.

3.1 Determination of effective rate constant for mixture 1

Direction in semi-logarithmic coordinate's $\ln COD/COD_0$ over time allowed determining the effective rate constant of ethanol oxidation in the wastewater of a pharmaceutical plant. The kinetic equation enabled determination of the effective rate constant for the first-order reaction (*k*):

$$\ln\frac{C(A)}{C(A0)} = -kt \tag{5}$$

The result of this operation is a linear dependence, which means that the process can be described by a first-order kinetic equation, Fig. 3 and Fig. 4.

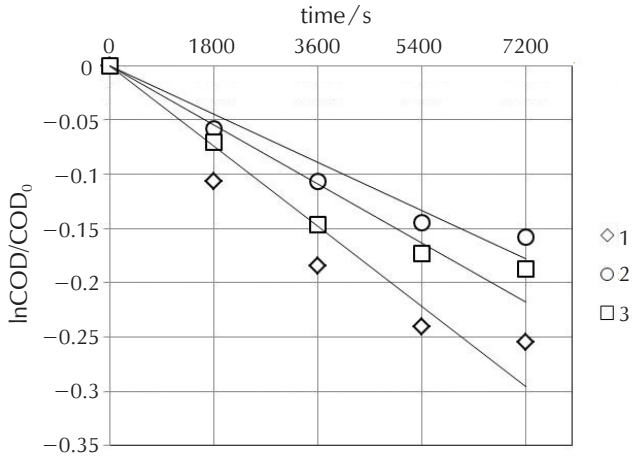

Fig. 3 – Dependence of $\ln COD/COD_0$ *vs*. time for mixture 1 at different experimental conditions: 1 – O_2; 2 – air; 3 – N_2

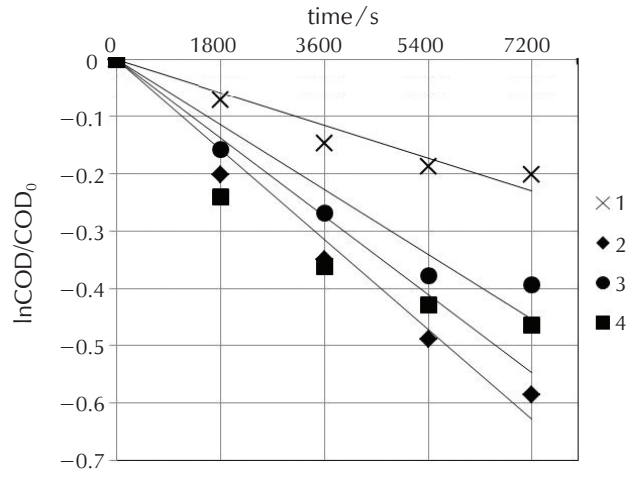

Fig. 4 – Dependence of $\ln COD/COD_0$ *vs*. time for mixture 1 at different experimental conditions: 1 – UC; 2 – O_2/UC; 3 – air/UC; 4 – N_2/UC

As Table 1 shows, the combined action of the UC with investigated gases provides higher values of effective rate constants than the results achieved by bubbling of the gases themselves.

Table 1 – Comparison of effective rate constants for mixture 1 in the presence of different gases

Process conditions	without UC		with UC	
	$k \cdot 10^5$, s^{-1}	R^2	$k \cdot 10^5$, s^{-1}	R^2
O_2	4.0	0.89	9.0	0.98
N_2	3.0	0.89	8.0	0.82
air	2.0	0.94	6.0	0.92
UC	–	–	3.0	0.92

Relative efficiency of gases is as follows:

$$O_2/UC > N_2/UC > air/UC > O_2 > N_2 > air$$

In the above series, a similar sequence of influence of the nature of the bubbled gas was traced both under cavitation conditions and without them. The action of the UC field almost doubles the effect of gases, where the combined action of O_2 with UC took leading position.

3.2 Comparison of the organic substances destruction degrees of mixture 1

Fig. 5 shows the efficiency of using different gases for the process of destruction of ethanol impurities. The lowest oxidation rate (14.6 %) was obtained by applying air to mixture 1. Slightly better results (17.04 %) were achieved using nitrogen as a gas. Higher oxidation properties were shown by oxygen, the use of which increased the oxidation rate to 22.47 %.

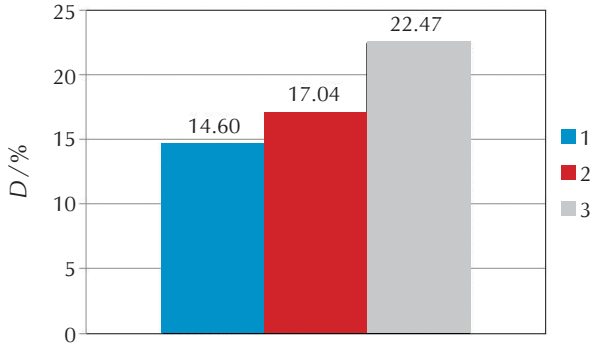

Fig. 5 – Degree of organic substances degradation in 7200 s for mixture 1 at different experimental conditions: 1 – air; 2 – N_2; 3 – O_2

The use of UC in the atmosphere of gases of different nature significantly accelerated the process of degradation of ethanol impurities, as it was evidenced by higher degree of degradation. However, the use of UC alone produced no desirable results, as may be observed from Fig. 6, where the degree of degradation of organic substances for mixture 1 on the UC is 18.18 %. The combined action of UC with air provided mediocre results, the organic substances degradation degree being 32.58 %, but using UC in the atmosphere of nitrogen caused an increase in the degradation degree of organic substances by 37.08 %. The most effective oxidizing properties were found with oxygen from the UC, increasing the rate of destruction to 44.32 %.

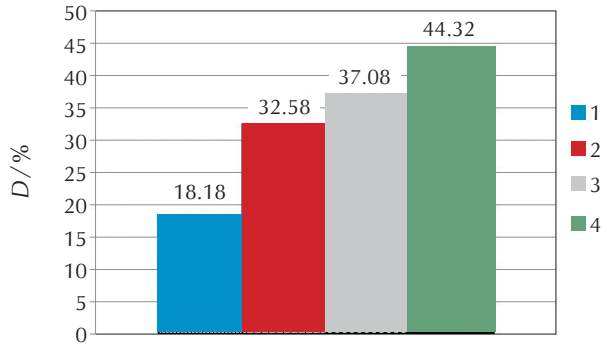

Fig. 6 – Degree of organic substances degradation in 7200 s for mixture 1 at different experimental conditions: 1 – UC; 2 – air/UC; 3 – N_2/UC; 4 – O_2/UC

Comparative graphical dependences of the effect of gas and UC on mixture 2 are presented further herein.

Analysing the curves in Fig. 7 revealed that, among the gases used for the destruction of butanol impurities, oxygen manifested itself the best, reducing the value of the COD to 2500.8 mgO_2/dm^3, and the COD for nitrogen became 2528.4 mgO_2/dm^3. Air showed no positive influence on the butanol oxidation process.

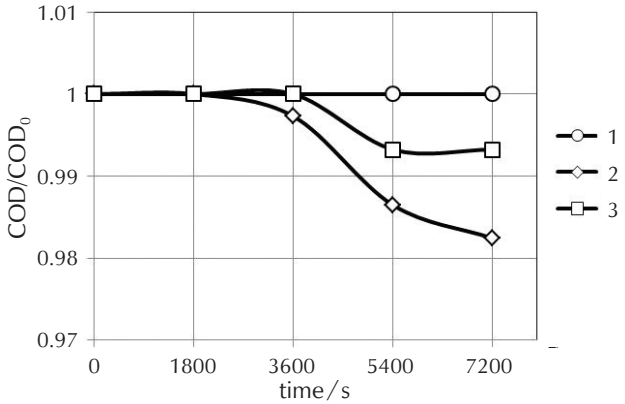

Fig. 7 – Dependence of COD/COD_0 ration *vs.* time for mixture 2 at different experimental conditions: 1 – air; 2 – O_2; 3 – N_2

Summarizing the results, it may be said that the use of the gases themselves for the destruction of butanol impurities in the aqueous medium had not produce the desired results. Therefore, in order to enhance their action, a study was conducted using common action gases with UC.

Fig. 8 shows the effect of the combined action of UC in the atmosphere of gases of different nature (oxygen, air, and nitrogen), as well as the effectiveness of the UC itself on the destruction of butanol impurities. The lowest levels of the COD were achieved by the use of UC in an oxygen atmosphere, the final value of the COD being 2356.4 mgO_2/dm^3. UC with nitrogen decreased the COD to 2408 mgO_2/dm^3, and the combined effect of UC with air on the test solution reduced the COD to 2442.4 mgO_2/dm^3. The influence of the UC itself contributed slightly to the reduction of the COD, while the UC with gas reduced the COD to 2476.8 mgO_2/dm^3.

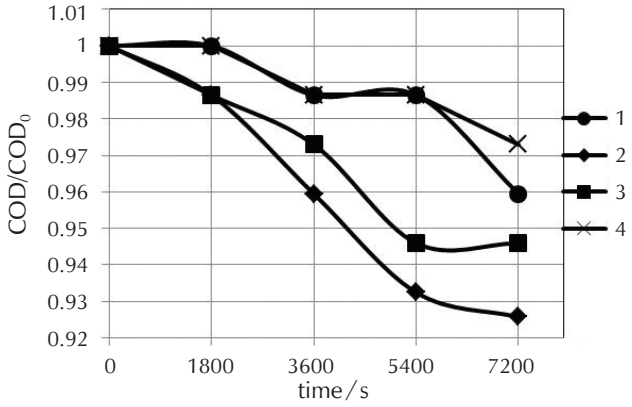

Fig. 8 – Dependence of COD/COD_0 ration *vs*. time for mixture 2 at different experimental conditions: 1 – air/UC; 2 – O_2/UC; 3 – N_2/UC; 4 – UC

Therefore, it may be said that, under these conditions, the process of butanol is weakly susceptible to destruction.

3.3 Determination of effective rate constant for mixture 2

The determination of the effective rate constant was carried out in the same way as for mixture 1, and is shown in Fig. 9 and Fig. 10.

According to the obtained constants listed in Table 2, the highest performance was achieved by influencing the solution of ultrasound with gas, namely oxygen.

The bubbling air itself failed to purify the wastewater. The bubbling of nitrogen produced a mediocre result, the constant being $0.2 \cdot 10^{-5}$, s^{-1}. The best purity was achieved with oxygen bubbling, rate constant being $0.3 \cdot 10^{-5}$, s^{-1}.

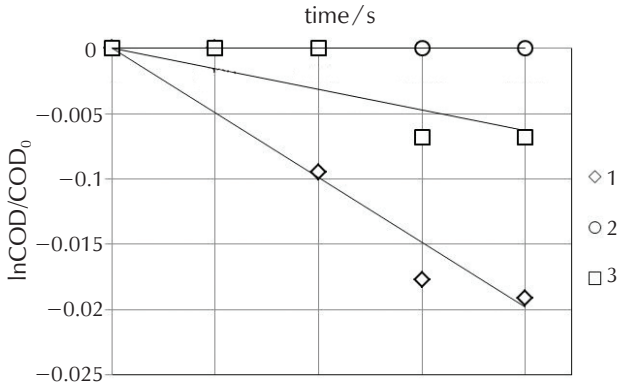

Fig. 9 – Dependence of $\ln COD/COD_0$ *vs*. time for mixture 2 at different experimental conditions: 1 – O_2; 2 – air; 3 – N_2

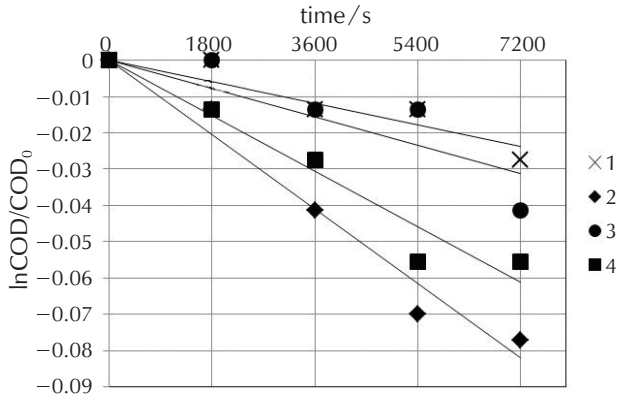

Fig. 10 – Dependence of $\ln COD/COD_0$ *vs*. time for mixture 2 at different experimental conditions: 1 – UC; 2 – O_2/UC; 3 – air/UC; 4 – N_2/UC

Table 1 – Comparison of effective rate constants for mixture 2 in the presence of different gases

Process conditions	without UC		with UC	
	$k \cdot 10^5$, s^{-1}	R^2	$k \cdot 10^5$, s^{-1}	R^2
O_2	0.3	0.86	1.0	0.976
N_2	0.2	0.69	0.8	0.94
Air	–	–	0.4	0.76
UC	–	–	0.3	0.86

Relative efficiency of gases was as follows:

$$O_2/UC > N_2/UC > air/UC > O_2 > N_2$$

This series is common both in and outside the cavitation field. That is, the action of gases is enhanced by the action of UC, similarly as for mixture 1.

In order to determine the effectiveness of the destruction of butanol impurities in aqueous solution, calculations were made to find the degrees of destruction of organic substances for mixture 2 under different experimental conditions.

Fig. 11 shows the efficiency of using gases of various nature for the process of degradation of butanol impurities which are in aqueous solution. In general, the diagram shows that no significant effect on the destruction of butanol impurities by passing through it the aqueous solution of gases of different nature was obtained. Air passing through mixture 2 failed to give the desired results, so it was omitted from the figure. When nitrogen was used, the degree of organic substances destruction was 0.67 %. Oxygen, in turn, increased this to 1.75 %.

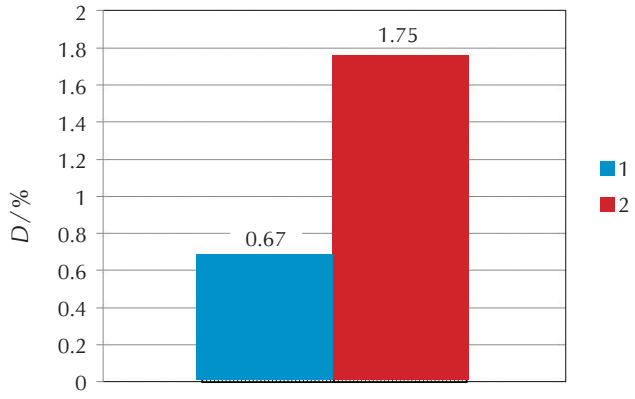

Fig. 11 – Degree of organic substances degradation in 7200 s for mixture 2 at different experimental conditions: 1 – N_2; 2 – O_2

According to Fig. 12, the degree of organic substances destruction for mixture 2 in UC conditions using gases of different nature also failed to provide the desired results. The lowest value of the degree of organic substances destruction (2.7 %) was obtained with the use of UC. The use of air with UC increased the oxidation rate of the test mixture to 4.05 %. A slightly better effect (5.4 %) was achieved with the combined action of UC with nitrogen. Among all the tested gases, oxygen with UC has the best indicator of the degree of oxidation – 7.43 %.

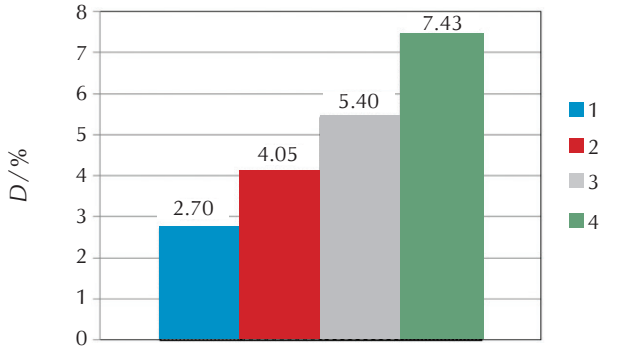

Fig. 12 – Degree of organic substances degradation in 7200 s for mixture 2 at different experimental conditions: 1 – UC; 2 – air/UC; 3 – N_2/UC; 4 – O_2/UC

3.4 Comparative characteristics of wastewater treatment of a pharmaceutical plant with a high content of ethanol and butanol impurities

Based on the obtained data, a comparative analysis of the destruction rate of ethanol and butanol in aqueous solution influenced by ultrasonic radiation, as well as sonication of an aqueous solution in the atmosphere of gases of different nature, was carried out.

As may be seen from Fig. 13, the use of gases of different nature failed to produce the expected results of destruction of butanol impurities. The obtained results are similar, with an average reduction in the COD from 2545 mgO_2/dm^3 to 2528 mgO_2/dm^3, which are very low. Ethanol impurities, in turn, are more actively destroyed. The best effect was achieved by passing oxygen, reducing the COD to 1092 mgO_2/dm^3.

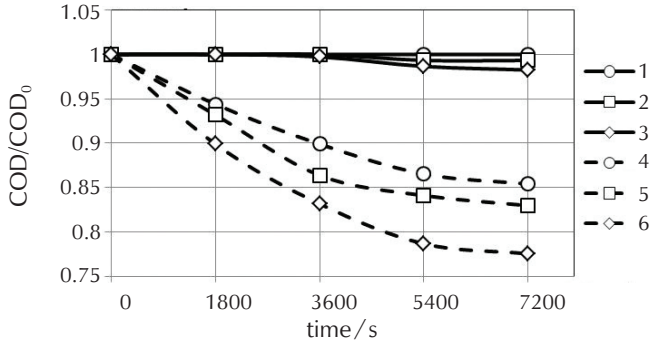

Fig. 13 – Dependence of COD/COD_0 ration *vs.* time for mixture 1(1) and mixture 2(2) at different experimental conditions: 1 – air(2); 2 – N_2(2); 3 – O_2(2); 4 – Air(1); 5 – N_2(1); 6 – O_2(1)

Fig. 14 shows the curves of the effect of gases of different nature in the process of UC. As a result of the combined action of gas with UC for the destruction of butanol impurities, a slight decrease in organic pollution was observed. The best result was achieved by the combined action of oxygen with UC, reducing the COD to 2356.4 mgO_2/dm^3. The effect of UC itself is also insignificant, the COD being decreased to 2476.8 mgO_2/dm^3.

Much better results were achieved with the combined action of gases of different nature with UC on ethanol impurities contained in wastewater. The worst data were obtained with the action of UC itself (COD decreased to 1152 mgO_2/dm^3). Among the tested gases, the least effective was the use of air and UC, where the final value of COD (120 min of the experiment) was 950.4 mgO_2/dm^3. The best oxidizing effect was achieved with the combined action of oxygen and UC, providing a final COD value of 784 mgO_2/dm^3.

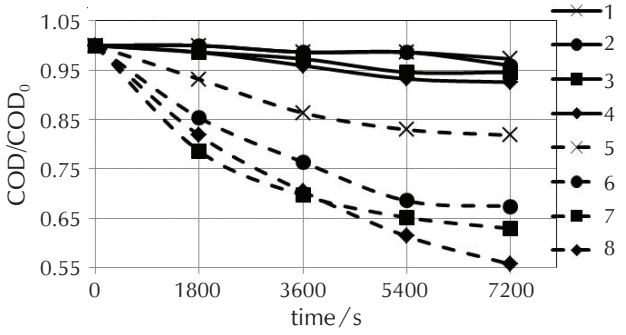

Fig. 14 – Dependence of COD/COD_0 ration *vs*. time for mixture 1(1) and mixture 2(2) at different experimental conditions: 1 – UC(2); 2 – air/UC(2); 3 – N_2/UC(2); 4 – O_2/UC(2); 5 – UC(2); 6 – Air/UC(1); 7 – N_2/UC(1); 8 – O_2/UC(1)

4 Conclusions

Among the studied gases (nitrogen, oxygen, and air), oxygen was found to be the most efficient. During the bubbling of oxygen itself, it was possible to reduce the amount of ethanol impurities by 22.47 %, while the amount of butanol by only 1.75 %. According to the law of Ukraine №56/31508,[15] the permitted COD value for wastewater in Lviv is 500 mgO_2/dm^3. The lowest COD value for butanol impurities was obtained by the combined action of oxygen with UC, the final COD value being 2356.4 mgO_2/dm^3. The obtained value indicates that the common effect of UC with oxygen is insufficient to destroy the impurities of butanol. Further studies with elevated temperatures and pressure should be performed to obtain better results. The lowest COD value for ethanol impurities was obtained by the combined action of oxygen with UC, the final COD value being 784 mgO_2/dm^3. Due to the two-stage process of the wastewater treatment plant, the use of the combined action of gas and UC allows achieving the desired results and replacing this process with one stage. The presence of a purification stage is a mandatory stage of the treatment plant, depending on the further purpose of the purified water. Therefore, the use of oxygen with UC as an intermediate stage of water purification, allows directing the purified stream (COD = 700mgO_2/dm^3) to the refining stage, and achieving a final COD within 500 mgO_2/dm^3.

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SAŽETAK

Utjecaj ultrazvučne kavitacije na razgradnju organskih tvari iz otpadnih voda farmaceutske industrije

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Ispitan je utjecaj ultrazvučne kavitacije u atmosferi različitih plinova (kisika, zraka i dušika) na razgradnju onečišćujućih tvari butanola i etanola farmaceutskih otpadnih voda tvornice "Galichpharm". Usporedno je ispitan i utjecaj kisika, dušika i zraka bez ultrazvučne kavitacije na uklanjanje onečišćujućih tvari etanola i butanola u otpadnim vodama. Izračunati su stupanj oksidacije organskih tvari, efektivne konstante brzine i koeficijenti aproksimacije. Otkriveno je da je dovod zraka najmanje učinkovit za onečišćujuće tvari etanola i butanola. Oksidacija etanola zrakom doprinosi smanjenju sadržaja organskih tvari za 14,6 %, dok oksidacija butanola nije promatrana. Ultrazvučna kavitacija pojačala je učinak zraka i u zajedničkom djelovanju sa zrakom sadržaj nečistoća etanola smanjen je za 32,58 %, a butanola za 4,05 %. Uvođenje mjehurića dušika kod razgradnje nečistoća etanola i butanola dalo je osrednje rezultate te je utjecalo na smanjenje od 17,04 % i 0,67 %. Najviši rezultati postignuti su kisikom. Nečistoće etanola smanjile su se za 22,47 %, a nečistoće butanola za 1,75 %. Uobičajenim djelovanjem kisika i ultrazvuka dobiveni su znatno viši rezultati – za nečistoće etanola 44,32 %, a za nečistoće butanola 7,43 %.

Ključne riječi
Otpadne vode, ultrazvučna kavitacija, farmaceutska industrija, butanol, etanol, kemijska potrošnja kisika

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