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Використання кавітаційних технологій для процесів очищення стічних вод жиркомбінату один із перспективних методів для покращення показників якості води. Було запропоновано подачу в кавітаційну зону газів різної природи, а саме: азоту, кисню, повітря, суміші азоту та кисню у співвідношенні 1:1.

Досліджено вплив природи барботованих газів, як в умовах дії УЗ так і без нього, на зміну хімічного споживання кисню та мікробного числа. Розраховано ефективні константи швидкості руйнування органічних сполук та біологічних забруднень. Встановлено, що найвищого значення ефективної константи швидкості знезараження води від МО (5,13·10–4 с–1) було досягнуто при барботуванні азоту. Найвищого значення ступеня знезараження води в кавітаційних умовах (99,9 %) було досягнуто в атмосфері азоту, а ступеня руйнування органічних сполук – 64,3 % при одночасній дії повітря та УЗ.

Визначено, що процес руйнування органічних домішок та знезараження стічних вод жиркомбінату можна описати застосувавши кінетичне рівняння першого порядку. Встановлено відносні ряди впливу природи досліджуваних газів на кавітаційне очищення води.

Показано, що очищення стічних вод жиркомбінату при одночасному барботуванні газів у кавітаційне поле при руйнуванні органічних сполук на 5–35,7 %, при знезараженні води від МО на 1–90,5 % ефективніше, ніж дія самого УЗ.

Використання запропонованої кавітаційної технології для очищення стічних вод жиркомбінату дозволяє повністю знезаразити воду від шкідливих МО та одночасного руйнування органічних речовин. Це дозволяє усунути негативний вплив шкідливих речовин, які містяться у стічних водах для збереження навколишнього середовища та водного басейну України

Ключові слова: стічні води, кавітація, очищення, природа газів, органічні сполуки, мікробіологічні забруднення

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RESEARCH INTO EFFECTIVENESS OF CAVITATION CLEANING OF WASTEWATER OF A FAT-AND-OIL PLANT FROM ORGANIC AND BIOLOGICAL CONTAMINATION IN THE PRESENCE OF VARIOUS GASES

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1. Introduction

One of the relevant issues in the production of food is the disposal of wastewater or subsequent use of water that was already cleaned. Wastewater of oil-fat production is characterized by a high content of organic and biological contamination of different nature. The main pollutants of wastewater of extraction and refining workshops are organic substances (neutral fats, phospholipids, organic acids, etc.) that are in a dissolved form, as well as in the form of suspended solids and emulsions. Such emulsions are colloidal structures, in which dispersed phase is a fluid. The two fluids are non-soluble or poorly soluble in one another. Stability of such emulsion is caused by the ratio of densities of the phases. Density of dispersion medium is close to the density of dispersed phase, which is why such emulsion is stable in terms of sedimentation.

One of the modern technologies of water cleaning from harmful contamination is the use cavitation phenomena in the water medium. Industrial use of cavitation processes in various industries proves high effectiveness of this method for cleaning the water medium. It was found that an effective method for reducing the amount of pollutants in wastewater is the use of gases of different nature under conditions of cavitation [1]. The use of acoustic cavitation allows intensifying the processes of water cleaning from organic and biological contaminants. Ultrasound waves have a harmful effect on different microorganisms: cause decomposition of high-molecular compounds, coagulation of proteins, inactivate enzymes, toxins, cause a rupture of the cell wall, etc.

The use of acoustic cavitation that successfully improves decontamination and cleaning wastewater depending on a correct combination of cavitation cleaning of various gases in the atmosphere is effective nowadays. It is the use of such new technologies of cleaning food production wastewater that is a relevant problem of today.

2. Literature review and problem statement

Cavitation (from lat. *Cavitas* – void, cavity) is formation of cavities, filled with gas, steam or an appropriate mixture (cavitation bubbles), inside fluid, i. e. disruption of fluid integrity.

Cavitation occurs as a result of a local decrease in pressure in a fluid up to a certain critical value p_{cr} (in actual fluid the value of p_{cr} is close to pressure of saturated vapor of this fluid at a given temperature) [2]. 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) [3].

In other words, depending on the method for cavitation creation, it is possible to enhance effectiveness of the expected cavitation effect for various chemical and biochemical processes.

The use of the cavitation phenomenon for various industries is now developing intensively and existing cavitation technologies are improved [4]. Cavitation equipment, based on the phenomenon of hydrodynamic cavitation, is effective mixing, activating, dispersing and homogenizing equipment of the new generation, capable to significantly intensify and accelerate technological processes in liquid media. The drawbacks of this cavitation are the absence of the "after effect" and power consumption of the process [5].

At 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 centimeters to tens of centimeters contribute to this [6]. It is common for acoustic ways of cavitation creation that cavitation is excited 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 of certain properties (gas saturation, bubble dimensions, temperature), and these changes are practically uncontrollable [7].

The phenomenon of cavitation has been widely used in petrochemical industry, particularly the use of ultrasound (US), to remove water from emulsions of crude oil without the use of chemical reagents – demulsifiers. The experiments were carried out in the ultrasound bath at frequency of 35 kHz. Separation of water from the emulsion of crude oil was observed for all the studied emulsions. Effectiveness of demulsification of up to 65 % was obtained for the emulsion with water content of 50 %. A higher demulsification effect was obtained at temperature of 45 °C, US power of 160 W and a cleaning time of 15 min [8].

The optimal frequency of US for cleaning of crude oil was examined in paper [9]. Experiments were conducted using ultrasound baths that worked at the following frequencies: 25, 35, 45, 130, 582, 862 and 1,146 kHz and synthetic water-oil emulsions with 12 %, 35 % and 50 % of water. Demulsification of crude oil was achieved in the frequency range of 25–45 kHz for all studied emulsions. At a frequency that is above 45 kHz, no changes in characteristics of crude oil were observed. Effectiveness of the emulsion of around 65 % was achieved at the frequency of 45 kHz after 15 minutes of the US application.

Modern development of cavitation technology allows using a constant wave in high US frequencies of more than 400 kHz to facilitate separation of oil from solids [10]. At frequencies of more than 400 kHz, large constant waves at low amplitudes are formed. This provides additional segregation of particles based on such properties as density and compression. Moreover, ultrasound waves have the ability to change the relationship of fat globe through acoustic pressure. In appropriate conditions, an aggregation of globules is observed.

When cleaning oil from oil sludge [11], individual effects of five different factors on the combined process (US and freezing/melting) were studied. They are the following factors: US power, duration of US action; the ratio of water and sludge in a suspension, as well as concentration of bio-surfactants (ramnolipids) and food salt (NaCl). The rate of oil production of up to 80 % was observed at US power of 66 Watt and duration of US cleaning of 10 min, when the ratio of sediment and water was 1:2 without adding biological surface-active substances and salt. The study of certain factors revealed that addition of low concentration of ramnolipids (<100 mg/dm^3) and salt (<1 %) to sludge improves oil cleaning while using the combined method.

US influence on oil viscosity was studied in article [12], particularly the influence of US waves at frequencies of 25, 68 kHz and different powers of 100, 250 and 500 Watts on viscosity of paraffin, synthetic oil and kerosene was explored. The experiments were conducted both under controlled and uncontrolled temperature conditions in a smooth capillary tube. The results showed that fluid viscosity decreases under the influence of US, and it is associated with induced heat generation and cavitation in fluid.

Industrial wastewater is the most powerful man-made source of pollution of natural waters. Large volumes of formation and instability of chemical composition are typical of these pollutants. In addition, industrial wastewater can be formed non-systematically, which complicates the problem of disposal.

At cleaning wastewater of an alcohol plant from organic wastes using cavitation in the presence of various gases, it was shown that the joint action of gases and US is by 22–44 % more effective than the action of the US alone and by 12–25 % more effective than only bubbling of gases [13]. The identified synergistic effect of the joint application of gas and US for cleaning wastewater of an alcohol plant proves feasibility of gas supply to the cavitation zone.

Destruction of microorganisms (MO) under the influence of physical-chemical and biological factors is observed in several studies. The US is used to sterilize water, substrates [14], to destroy cells during the manufacture of vaccines, to release enzymes [15], toxins, and nucleic acids [16].

Industrial wastewater of a fat-and-oil plant is contaminated mainly by production waste and emissions. Such industrial wastewater is mostly polluted with organic substances, due to which cleaning plants are not able to clean contaminated water to the level of sanitation requirements. If the biological component is added to such water composition, it is necessary to use combined methods for water cleaning. Carrying out research to decontaminate water of a fat-and-oil plant using US and fortifying its action in atmospheres of various gases would make it possible to increase effectiveness of these processes and is a relevant problem of today.

3. The aim and objectives of the study

The aim of this research is to study effectiveness of the processes of cavitation cleaning of wastewater of a fat-and-oil plant from organic and biological contaminants in the atmosphere of different gases.

To achieve the set aim, the following problems were solved:

– to determine the influence of the nature of air, nitrogen, oxygen and the mixture of nitrogen and oxygen in the ratio of 1:1 on the process of cleaning water of a fat-and-oil plant both under cavitation conditions and without them;

– to establish kinetic regularities and features of influence of ultrasonic cavitation on the process of cleaning wastewater of a fat-and-oil plant depending on the nature of the bubbled gas.

4. Materials and methods to study the influence of gases on the cavitation wastewater cleaning

4. 1. Examined materials and equipment used in the experiment

When studying the influence of the nature of the bubbled gas on the process of cavitation cleaning of wastewater, the following gases were used: air, nitrogen, oxygen, the mixture of nitrogen and oxygen in the ratio of 1:1.

As supplementary substances, we used: potassium dichromate $K_2Cr_2O_7$, Mohr's salt, concentrated sulfuric acid, solution of N-phenylanthranil acid, distilled water, sterile water, meat-peptone agar (MPA: meat (1 dm^3), peptone (10 g), agar (15 g)).

The object of the study was the actual wastewater from JSC "Lviv Fat-and-Oil Plant" (Ukraine). Water sampling was conducted before the cleaning system of this production. This wastewater is characterized by a high content of both organic substances and biological contaminants, specifically, the original values of COD_0 were in the range of 470.4–1116.16 mg O_2/dm^3, the original values of MN_0 were in the range of $726 \cdot 10^3$–$10{,}188 \cdot 10^3$ CFU/cm^3, the content of solids was 1.5–1.7 %, acidity 0.12–0.15 %, pH was 6.3.

Research into influence of cavitation on the process of destruction of organic and biological contaminants in wastewater of a fat-and-oil plant was held in the reactor from stainless steel of grade H18N9T. US oscillations of frequency of 22 kHz from a low-frequency generator USDN-2 (Ukraine) (power 90 W) were passed with the help of magnetostrictive emitter, immersed in the volume of the studied water. The initial values of chemical consumption of oxygen and of microbial number were previously established. The fittings for sampling, supply and exit of gases were mounted in the reactor.

4. 2. Procedure for determining wastewater quality indicators

The following basic indicators are used in the process of studying the quality of water cleaning: biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC) and microbial number (MN).

In the world practice, there are numerous standards for determining BOD, such as SFS-EN 1899-1 (SFS-EN 1899-1), APHA standard 5210 B (APHA, 1998) and OECD 301 F-Guide (OECD, 1992). For wastewater sampling, the measurement standard is five days (BOD_5) at 20 °C, but other time and temperature can also be used. In Finland, for example, the typical measuring time is seven days (BOD_7) (Karttunen, 2003). The value of *COD* is determined according to the standard APHA 5220 "Chemical oxygen demand (COD)" [17].

In the study of wastewater of a fat-and-oil plant, the main indicators of the wastewater quality were the values of BOD and MN. In parallel with determining BOD and MN, effective constants of the rate of destruction of organic compounds and biological contaminants (k) and degree of destruction of organic compounds D (COD) and degree of water disinfection D (MN) were determined.

COD was determined by the bichromatic method. COD is the amount of oxygen (in mg), which is required for chemical oxidation of all organic and inorganic reducing agents in 1 dm^3 of water. The initial values of COD_0 were in the range of 470.4–1,116.16 mg O_2/dm^3. To visualize the experimental data, the original values were represented in the form of COD/COD_0.

Effective constant of the rate of destruction of organic compounds was determined using a kinetic equation of the first order.

Degree of destruction of organic compounds (in %) was calculated from the formula:

$$D(\text{COD}) = 100 - \frac{\text{COD} \cdot 100}{\text{COD}_0}, \quad (1)$$

where COD_0 is the initial value of COD, mg O_2/dm^3; COD is the current value of COD at moment τ, mg O_2/dm^3.

Determining MN implies determining the total number of microorganisms (MO), able to grow on meat-peptone agar at temperature of 37±0.5 °C for 24±2 h in 1 ml of water. Subsequently, we kept record of colonies that grew up in this medium. Cultivation of the studied MO was carried out using the depth method.

MO were grown in the thermostat at constant temperature of 37 °C and duration of 48 hours for bacteria [18]. Original values of MN_0 were in the range of $726 \cdot 10^3$–$10,188 \cdot 10^3$ CFU/cm^3. For better visualization of the experimental data, original values were presented in the form of MN/MN_0.

Degree of water disinfection (%) was calculated from formula:

$$D(\mathrm{MN}) = 100 - \frac{\mathrm{MN} \cdot 100}{\mathrm{MN}_0}, \quad (2)$$

where MN_0 is the original value of MN, CFU/cm^3; MN is the current value of MN at moment τ, CFU/cm^3.

5. Results of studying the wastewater quality indicators

Results of determining COD of wastewater of a fat-and-oil plant depending on cleaning duration in the presence of gases of different nature: nitrogen, oxygen, air and the mixture of nitrogen and oxygen in the ratio of 1:1 are shown in Fig. 1.

At the influence of the four above mentioned gases, the least effective is bubbling of the mixture of nitrogen and oxygen and only nitrogen. We observe a decrease to 718.08 mg O_2/dm^3, which is by 1.1 times smaller in comparison with the initial value when using gas mixtures. When using nitrogen, we observed a decrease to 672 mg O_2/dm^3, which is by 1.2 times less as compared to the initial value.

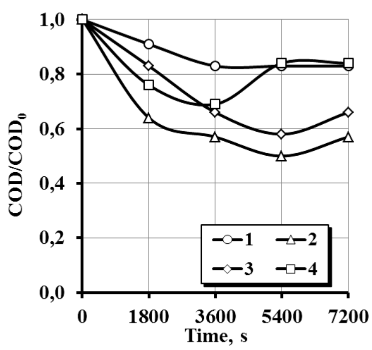

Fig. 1. Character of dependence of ratio COD/COD_0 on time of cleaning wastewater of a fat-and-oil plant in presence of gases of different nature: 1 – N_2; 2 – air; 3 – O_2; 4 – N_2+O_2

The influence of oxygen is mediocre; a decrease is up to 563.2 mg O_2/dm^3, which is by 1.5 times less than the original value.

While studying wastewater in terms of destruction of biological contamination (Fig. 2), we obtained the data that indicate that during one hour of nitrogen bubbling and at the action of oxygen, the similar effect of an increase in MN is achieved. However, further influence of nitrogen bubbling contributes to a sharp decrease in MN within the last 30 min of the experiment, a decrease in MN by 1.5 times, which corresponds to the final value of MN – $1,596 \cdot 10^3$ CFU/cm^3. During bubbling the air and a gas mixture for one hour, we observe better results – MN decreases from $4,080 \cdot 10^3$ CFU/cm^3 to $2,840 \cdot 10^3$ CFU/cm^3 for the air and from $6,300 \cdot 10^3$ CFU/cm^3 to $2,702 \cdot 10^3$ CFU/cm^3 for the gas mixture, which is by 1.4 and 2,3 times less than the original value, respectively. At subsequent water cleaning, air and oxygen bubbling within the next hour of experiment contributed to an increase in MN, which indicates inexpediency of decontamination of wastewater of the fat-and-oil plant in the atmospheres of these gases. The best result of water disinfection was obtained when using the gas mixtures – a decrease in MN is by 2.1 times of the original value.

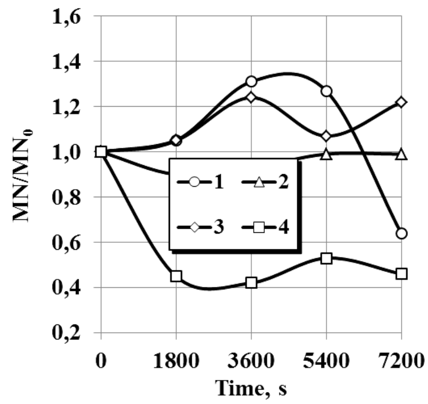

Fig. 2. Character of dependence of ratio of MN/MN_0 on duration of cleaning wastewater of fat-and-oil plant in presence of gases of various nature: 1 – N_2; 2 – air; 3 – O_2; 4 – N_2+O_2

Comparing the influence of the above gases under cavitation conditions for destruction of organic compounds, we observe a decrease in COD within all time of research depending on the nature of bubbled gas (Fig. 3).

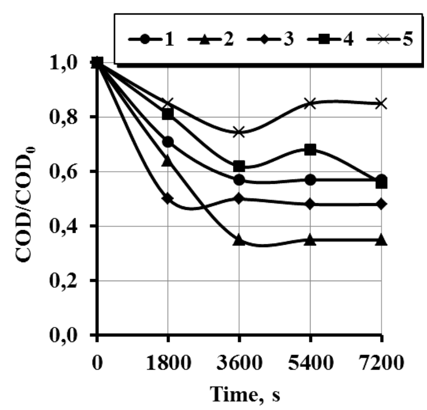

Fig. 3. Character of sound and chemical dependence of ratio COD/COD_0 on duration of cleaning wastewater of fat-and-oil plant under different conditions of the process: 1 – N_2/US; 2 – air/US; 3 – O_2/US; 4 – N_2+O_2/US; 5 – US

Some of the best results were obtained at US water cleaning in the atmosphere of nitrogen – a decrease in the concentration of organic compounds by 1.75 times was observed.

The best effect was achieved when using the air in the sonicated medium. Within two-hour cleaning, the value of COD decreased to 336 mg O_2/dm^3 of the initial value, which corresponds to the decrease by 2.8 times and indicates a decrease in the concentration of organic compounds. Simultaneous action of oxygen with US, the gas mixture with US showed the desired results – COD decreased by 1.6 and 2 times respectively.

Fig. 4 shows comparative characteristics of the influence of cavitation on the process of water disinfection in the atmosphere of the studied gases. The influence of US alone and the joint influence of the air with US on the studied water have the smallest effect of a decrease of MN up to

$4{,}672{\cdot}10^3$ CFU/cm^3 and $3{,}696{\cdot}10^3$ CFU/cm^3 respectively. At the action of the gas mixture with US within the first 30 minutes of the experiment, a decrease in the value of MN of up to $3{,}740{\cdot}10^3$ CFU/cm^3 was achieved. MN did not change significantly till the end of the experiment, and at the 120 min it decreased by 1.01 times at the action of the air and by 0.66 times at the action of the gas mixture and US.

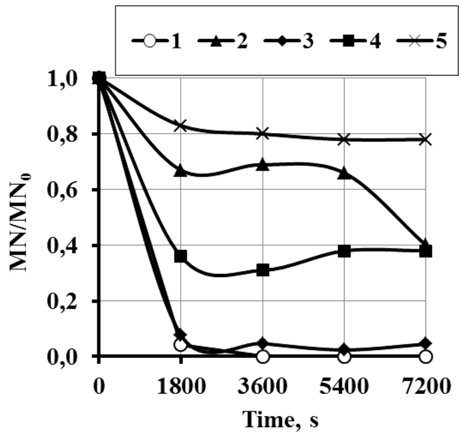

Fig. 4. Character of sound and chemical dependence of ratio MN/MN_0 on duration of cleaning wastewater of fat-and-oil plant under different conditions of the process: 1 — N_2/US; 2 — air/US; 3 — O_2/US; 4 — N_2+O_2/US; 5 — US

However, the desired and almost identical effect was achieved within the first 30 min during bubbling nitrogen and oxygen in the sonicated medium. The joint action of oxygen with US made it possible to decrease MN from $2{,}014{\cdot}10^3$ CFU/cm^3 to $92{\cdot}10^3$ CFU/cm^3, which corresponds to a decrease by 21.89 times from the original value. As far as the action of nitrogen in the sonicated medium is concerned, we managed to achieve the decrease in MN from $1{,}357{\cdot}10^3$ CFU/cm^3 to $7{\cdot}10^3$ CFU/cm^3, which corresponds to the decrease by 193.8 times of the original value. Eventually, the highest germicidal effect was achieved during the joint action of nitrogen and US after minute 12 of the study, MN is $1{\cdot}10^3$ CFU/cm^3, which in by 1,357 times less than the original value. The influence of US in the atmosphere of oxygen reaches an insignificant decrease in the value of MN to 418·103 CFU/cm^3.

To determine the order of the reaction and effective constant of the rate of destruction of organic substances and water decontamination on the MN, the kinetic equation of the first order was used.

Straightening in coordinates ln (COD/COD_0) – τ (Fig. 5) and ln (MN/MN_0) – τ proves that the process of cleaning wastewater of the fat-and-oil plant from organic and biological contaminants can be described by a kinetic equation of the first order.

When studying the kinetics of the process of wastewater cleaning in the US conditions under the influence of various gases (Fig. 5), we observe that the highest effective constant of the rate of destruction of organic compounds is reached when using the air and US – $1.5{\cdot}10^{-4}$ s^{-1}.

Analytical determining of effective constants of the rates of destruction of organic compounds and of decontamination of wastewater of the fat-and-oil plant from MO was carried out using the integral method from the relevant equations:

$$\ln\frac{COD}{COD_0} = -k\tau, \quad (3)$$

$$\ln\frac{MN}{MN_0} = -k\tau, \quad (4)$$

where k is the effective constant of rate, c^{-1}; τ is the time of destruction of organic substances or MN in wastewater, s.

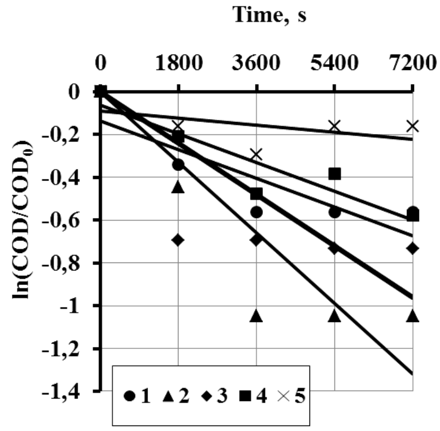

Fig. 5. Semi-logarithmic dependence of COD/COD_0 of wastewater of fat-and-oil plant on duration of sonication: 1 — N_2/US; 2 — air/US; 3 — O_2/US; 4 — N_2+O_2/US; 5 — US

Table 1 shows that in order to destroy organic contaminants, the atmosphere of the air contributed to achievement of the highest value of effective constant of the rate, it was achieved at the joint action of the air with US (k= =$1.5{\cdot}10^{-4}$ s^{-1}), and without US, k=$0.76{\cdot}10^{-4}$ s^{-1}, which is 2 times lower. The action of all gases under cavitation conditions contributed to an increase in effective constant of the rate of destruction of organic substances compared to the influence of the US itself.

Table 1

Comparative characteristic of effective constants of the rates of the process of cleaning wastewater of the fat-and-oil plant from organic and biological contaminants in presence of gases of different nature

Conditions of the process	COD				MN			
	With US		Without US		With US		Without US	
	$k{\cdot}10^4$, s^{-1}	R	$k{\cdot}10^4$, s^{-1}	R	$k{\cdot}10^4$, s^{-1}	R	$k{\cdot}10^4$, s^{-1}	R
N_2	0.74	0.74	0.26	0.77	5.13	0.17	–	–
O_2	0.64	0.55	0.66	0.74	3.79	0.53	–	–
air	1.5	0.79	0.76	0.65	1.03	0.80	–	–
N_2+O_2	0.85	0.84	0.14	0.58	1.05	0.40	1.40	0.61
US	0.18	0.17	–	–	0.34	0.80	–	–

The lowest value of effective constant of rate, which contributed to destruction of MO, was obtained during the action of the US (k=$0.34{\cdot}10^{-4}$ c^{-1}). Approximated values were achieved by bubbling the air and the mixture of gases (nitrogen and oxygen in the ratio of 1:1) in sonicated medium, specifically, $1.03{\cdot}10^{-4}$ s^{-1} and $1.05{\cdot}10^{-4}$ s^{-1} respectively. Joint action of oxygen with US and nitrogen with US showed the best values of effective constant of rate – $3.79{\cdot}10^{-4}$ s^{-1} and $5.13{\cdot}10^{-4}$ s^{-1}, which is by 11 and by 15 times higher than during the action of the US alone.

During bubbling of the studied water with nitrogen, air or oxygen, the number of MO and respectively of MN in wastewater increases, which makes calculation of effective constants of the rate of bacteria disinfection impossible. But the joint action of nitrogen with US allowed decreasing the number of MN with effective constant of rate of $1.4\cdot10^{-4}$ s^{-1}.

To study wastewater of the fat-and-oil plant with high content of organic substances and microbiological contamination, degree of destruction of organic contaminants and degree of water disinfection were calculated from equations (1) and (2) under different conditions of the process. Degrees of cleaning were calculated for final values of COD and MN (in 120 min of the experiment).

Analyzing the studies that were conducted under cavitation conditions (Fig. 6), we can conclude that the influence of US alone in the US field (the degree of destruction of organic compounds is 28.57 %). The degree of cleaning from organic contaminants during oxygen bubbling shows a mediocre result – 33.3 %. Joint action US with nitrogen and US with the mixture of gases (nitrogen and oxygen in the ratio of 1:1) showed similar results that are better than during the joint action of US with oxygen and the action of US alone (destruction degree is 42.85 % and 43.75 %, respectively).

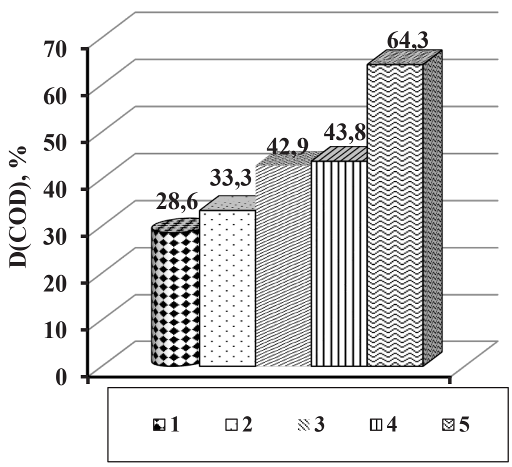

Fig. 6. Degree of destruction of organic substances in wastewater of fat-and-oil plant in 7200 s of the experiment under cavitation conditions: 1 — US; 2 — O_2/US; 3 — N_2/US; O_2/US; 4 — N_2+O_2/US; 5 — air/US

However, the joint action of US with the air appeared most effective, the degree of destruction of organic compounds reached 64.28 %, which is by 2.2 times better than the action of US alone and by 1.5 times better than the action of air (42.85 %).

For wastewater disinfection under cavitation conditions, the action of US alone and bubbling the air with US showed similar values (9.41 % and 10.28 %, respectively), which was presented in Fig. 7. Joint action of the mixture of gases (nitrogen and oxygen in the ratio of 1:1) and US is much more effective; degree of decontamination reached 53.36 %, which is almost by 5.2 times higher than the action of the air with US.

But the most worthwhile is the joint action of oxygen with US and nitrogen with US, at which degree of water decontamination of 95.43 % and 99.9 %, respectively, was achieved, which is by 4.2 and 2.8 times higher than the action of gases without sonication. The obtained data allowed establishing relative series of effectiveness of influence of the gases' nature on the process of destruction of organic compounds and bacteria disinfection in wastewater of the fat-and-oil plant both under cavitation conditions and without them (Table 2).

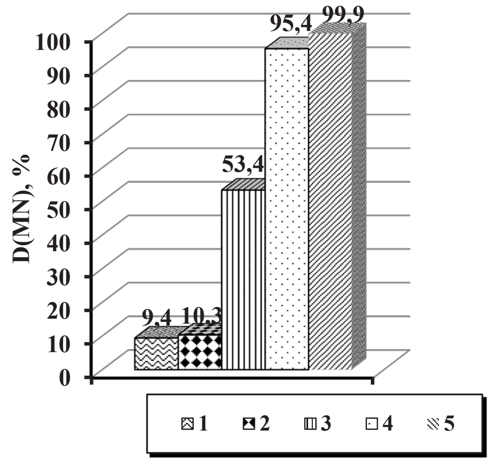

Fig. 7. Degree of decontamination of wastewater of fat-and-oil plant at 7,200 s of the experiment under cavitation conditions: 1 — US; 2 — N_2+O_2/US; 3 — N_2/US; 4 — air/US; 5 — O_2/US

Table 2

Relative series of effectiveness of the influence of gases' nature on the process of destruction of organic compounds and bacteria disinfection in wastewater of fat-and-oil plant

Conditions of the process	Relative series of effectiveness of impact of gases' nature on COD	Relative series of effectiveness of impact of gases' nature on MN
With US	air.>N_2+O_2>N_2>O_2>US	N_2>O_2>N_2+O_2>air.>US
Without US	air.>O_2>N_2>N_2+O_2	N_2+O_2

The atmosphere of the air, both in the presence of US, and without it, demonstrated highest effectiveness for destruction of organic compounds. The US in the presence of air contributes to an increase in degree of water cleaning by 1.5 times compared with the action of the air. To decontaminate wastewater of the fat-and-oil plant without the US, it is advisable to use only the mixture of nitrogen and oxygen in the ratio of 1:1. Complete wastewater cleaning from bacterial contamination (99.9 %) was achieved under cavitation conditions in the presence of nitrogen.

6. Discussion of results of studying the influence of the nature of the examined gases on the processes of cavitation water cleaning

While studying the influence of nitrogen, air, oxygen and the mixture of nitrogen and oxygen in the ratio of 1:1 on the process of cleaning wastewater of the fat-and-oil plant from organic contaminants, which is shown in Fig. 1, we see a decrease in COD during the first hour of the experiment for all the above-mentioned gases. However, bubbling of nitrogen and the mixture of nitrogen and oxygen gases in the ratio of 1:1 an hour after the beginning the experiment was inappropriate, since an increase in COD was observed. The largest cleaning effect is achieved at bubbling of the air. Bubbling of the mixture of nitrogen and oxygen in the reaction medium, in which both organic and bacterial contamination existed simultaneously, during the action of the gas within an hour contributed to an increase in COD due to emergence of new organic substances that can be formed as a result of destruction of bacterial contamination. The influence of the nature of oxygen is less favorable for decreasing COD in comparison with the action of the air due to existence of aerobic bacteria in the medium. In other words, the atmosphere of the given gases was a favorable environment for living of bacterial contamination.

In parallel with determining water cleaning from organic compounds, the studies on water decontamination from MO at the action the same gases were carried out (Fig. 2). Supply of the mixture of nitrogen and oxygen contributed to the greatest effect of disinfection of water of the fat-and-oil plant, whereas the action of nitrogen and oxygen had little impact on the process of water disinfection.

After analyzing the existing influence of the mentioned above gases on the process of water cleaning, it was discovered that during bubbling of gases alone, a high degree of destruction of organic contaminants and water disinfection was not achieved. That is why in order to intensify the action of these gases, the joint use of ultrasonic waves and mentioned above gases would be appropriate, which is presented in Fig. 3. A comparative analysis of the impact of gases in the presence of the US field proves appropriateness of cavitation influence on the process of destruction of organic compounds in wastewater of the fat-and-oil plant. The highest effect was achieved at bubbling of the air under the cavitation conditions.

Given the data presented above (Fig. 4), it follows that the joint influence of US and gases simultaneously is most effective in the process of disinfection of water of the fat-and-oil plant. Nitrogen showed the greatest disinfection effect at minute 30 of the experiment almost up to complete water disinfection, which proves high effectiveness of supply of this gas to the cavitation area in comparison with the effect of nitrogen alone. The similar pattern is observed at bubbling of oxygen and other used gases. Saturation of the sonicated medium with this or that gas contributes to an increase in the rate of reaction both at destruction of organic compounds (Fig. 5), and water disinfection from MO (Table 1), which was proved by calculated values of effective constants of reaction rates. Thus, the nature of the gas, which saturates water during cavitation, plays a significant role. Gas solubility significantly affects the rate of gas diffusion to the cavity and, respectively, gas content in it. Depending on thermodynamic properties of the gas, chemical yield of radicals increases with an increase in effective temperature of splashed bubbles but decreases at an increase in heat conductivity of surrounding gases [2].

The most important result of cavitation is initiation of free radical reactions. Electric charges occur in cavitation cavities during sonication, due to which water molecules are exposed to strong ionization. Chemical products, which are strong oxidizers, occur in the sonicated aqueous medium:

$$H_2O \rightarrow H + \bullet OH,$$

$$H\bullet + O_2 \rightarrow HO_2\bullet.$$

It is the oxidizers that determine many chemical reactions, which are caused by the ultrasonic field.

At simultaneous presence of both organic substances and bacterial contamination in the medium and passing a certain gas through this water in the presence of US oscillations, there occurs simultaneous influence of cavitation on contaminated water, intensified by the nature of certain gas. Inactivation of bacteria and bacterial agglomerates during sonication is associated with physical, mechanical and chemical effects that occur during acoustic cavitation. Energy, which is sufficient for weakening or strengthening of bacterial cells, is created at the collapse of a cavitation bubble; chemical effect of cavitation is formation of radicals H• and •OH. These radicals attack the chemical structure of the walls of bacterial cells and weaken it, causing destruction.

At the stage of formation of cavitation cavity, molecules of carbohydrate and dissolved oxygen get inside and the concentration of the latter in a bubble is by two or three orders of magnitude larger than that in the fluid. Inert gases and the mixture of gases in the cavitation field manifest themselves as gases, capable to react, since the rate of cavitation decomposition of water is determined by the rate of formation of •ON radical that is capable to react and by thermodynamic properties of the gas. At splashing up the cavitation cavity, the nature of bubbled gas actually contributes to the concentration of accumulation of dissolved oxygen from water to a bubble, and this in turn affects the process of destruction of both organic and bacterial contamination.

A molecule of water in this process is the source of formation of free radicals, which in turn initiate most of chemical reactions. Gas, dissolved in water, shows a dual action. On the one hand, gas provides an excess of germs for formation of cavitation bubbles. Existence of gas contributes to improvement of conditions for destruction of bubbles due to an increase in temperature at compression. This leads to an increased cleaning effect. On the other hand, it increases pressure in bubbles and decreases cavitation rate.

The presence of the cavitation cavity or gases that are in the excited state affects the rate of dissociation of water molecules. Radicals partially recombine, but the composition of final radical and molecular products of water decomposition in the cavitation field depends on the nature of gases, dissolved in water.

Thus, the rate of gas diffusion to the cavity and gas content in it are significantly affected by thermodynamic properties of gases, specifically: solubility, thermal conductivity, and specific heat capacity. The highest value of temperature that is achieved in a cavitation bubble depends on thermal conductivity of gas under cavitation conditions, the ratio of specific heat capacities (C_P/C_V) of gas. At an increase in thermal conductivity of surrounding gases, chemical yield of radicals decreases. But an increase in chemical yield of radicals occurs with an increase in the ratio C_P/C_V, i. e. at an increase in effective temperature of bubbles that are splashed [2].

It was found that the joint use of US and gas provides an increase in degree of destruction of organic compounds in wastewater of the fat-and-oil plant (Fig. 6). The highest value of 64.28 % was achieved at the joint action of the air and US, which is by 2.2 times better than the action of US alone and by 1.5 times better than bubbling of the air alone. The atmosphere is nitrogen in the US field (Fig. 7) contributes to complete water disinfection of up to 99.9 %, which again proved the impact of gas nature under cavitation conditions, in particular, the rate of intensification of the process of formation of free radicals H• and •OH. These radicals are strong oxidizing agents in the processes both of destruction of organic compounds and of water decontamination from MO. This is proved by the established relative series of activeness of gas influence on the process of cleaning wastewater of the fat-and-oil plant under cavitation conditions and without them (Table 2).

7. Conclusions

1. It is shown that cleaning wastewater of the fat-and-oil plant during simultaneous bubbling of gases to the cavitation field at destruction of organic compounds is by 5–35.7 % and at water disinfection by 1–90.5 % more effective than the action of the US alone. The relative series of effectiveness of the impact of the nature of the studied gases on the process of cavitation cleaning of wastewater of the fat-and-oil plant were established.

2. It was determined that effective constants of the rate of cavitation destruction of organic compounds and water decontamination depend on the nature of bubbled gas. The air demonstrated the best cleaning effect on cavitation destruction of organic compounds, and nitrogen – on biological pollution. The effect of nitrogen in the cavitation field allows achieving the degree of water disinfection of 99.9 %.

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