Abstract— Ozonation is a wide used technique for waste water treatment at the final stage. However, among other concerns, it is considered to be one of the most expensive treatment methods and, hence, cost optimization together with the increase of treatment efficiency is desirable. This paper aims development of a novel approach in water ozonation intensification by exposure it to vibration at certain resonant frequencies. During such treatment specific processes arise, which are called vibroresonant effects. The experiments were carried out on a lab bench that consisted of a simple column was installed on a shaker. They have showed that exposure to vibration at certain resonant frequencies makes the ozone bubbles smaller, while increasing their total quantity in water and improving their even distribution among water column. This increases specific phase boundary area and improves treatment efficiency without adding any extra impact factor. It was found, that at certain treatment modes COD reduction has increased by 30% compared to sole ozonation without vibration and reached 57% in total.

Index Terms—Wastewater treatment, ozonation, vibration, vibroresonance.

I. INTRODUCTION

OZONE appears to be a strong oxidizer, which possesses the ability to destroy many organic substances and impurities in aqueous solutions at normal temperatures [1,2]. Oxidizing ozone allows to essentially ensure water discoloration, elimination of flavors and odors, as well as disinfection. Oxidized ozone both inorganic and organic substances dissolved in waste water. Ozonation could be used to purify waste water from phenols, petroleum products, hydrogen sulphide, arsenic compounds, SAS, cyanides, dyes, cancerogenic aromatic hydrocarbons, pesticides, etc. However, ozonation is characterized by a number of disadvantages [3]:

--Ozone is a toxic gas, and that is why any use of it requires careful safety and security control.
--Due to water saturation with the ozone and air mixture, the water acquires high oxidizing ability and becomes corrosion-active, which requires the use of equipment and materials resistant to ozone.
--In case the water ozonation mode and the ozone dose are incorrectly selected, oxidation byproducts could be formed that are poorly removed during the purification process and could be more toxic than the original contaminants.
--Short duration of exposure.
--When the water ozonation is carried out, many organic contaminants are exposed to destruction; and, as a result, the amount of biodegradable compounds is increasing, and favorable conditions for the repeated bacterial contamination of purified water are created.
--and the most important thing: the technique is expensive, since it consumes a lot of electricity per unit of water to be purified.

In this regard, the issues of intensification of this purification technique are particularly acute.

A. Methods for Ozonation Enhancement

The process of wastewater purification is significantly improving with the combined usage of ultrasound and ozone, ultraviolet irradiation and ozone, as well as of other physical factors [4].

If the tasks of ozonation intensification are concerned, scientific works could be conditionally divided into two groups:

--studying the increase in the ozone treatment efficiency;
--studying the destruction of hardly oxidizable by-products formed within the process of ozonation.

The technique of activating the oxidative processes at the interface of the gas and liquid phases under the action of a pulsed electric discharge, which allowed to reduce the content of oil products in water from 2 mg/l to 0.07 mg/l was considered in [5].

The method of simultaneous action of ozone and electrochemical processing was considered in [6]. The efficiency of processing based on the real runoff of surface melted waters in the City of Ivanovo was 76% for oil products and the same for phenol.

Another version of the ozonation intensification process was presented in [7]. Increasing the degree of wastewater purification was achieved by adding the 60-70% ozone to wastewater, removing the oxidized oil products and processing the filtrate with the remaining amount of ozone.

In [8], ozonation in a column with the multi-diaphragm perforated walls was investigated. As a result, the size of bubbles was decreasing (down to several hundred microns); therefore, transfer and retention of gas and liquid appearing,
when small fluid pulses and diaphragm walls were present, improved. The experiments were carried out by continuous introduction of ozone at the 23 g/m³ concentration and at varying gas flow rates (2.1 – 4.7 l/min). The installation efficiency results were assessed using two criteria:

-20% increase in the rate of the hydroxybenzoic acid vapor decomposition;
--75% increase in the hydroxybenzoic acid vapor decomposition, when the number of walls increased up to 5 pieces.

In [9], the efficiency of ozonation in combination with magnetic treatment was proved. According to the results of the experiment, in 60 minutes the oxalic acid under normal conditions was oxidized by 75%. The use of magnetic treatment allowed to increase this indicator up to 81%.

Another technique aimed at intensifying the ozonation process was the hydrodynamic cavitation [10] carried out with the use of the most common devices ensuring the efficient process of mixing gas with processed with treated water and their further contact, which included: mixers, columns filled with granular material; mechanical turbines; hydraulic emulsifiers; liquid spray contactors; diffusor tubes; and porous disks. The work was carried out using model solutions prepared with distilled water and containing the ammonium ion, which source was the ammonium nitrate salt.

The efficiency of ozonation usage in combination with the heterogeneous photocatalysis was proved in [11]. The study was carried out on formic acid with bromide ions. As a result of processing with only the photocatalysis, the formation of by-products, such as bromate ions, was registered. When the runoff was treated with heterogeneous photocatalysis in combination with ozonation, the by-products decomposition was registered, and the runoff treatment efficiency increased.

It was determined in [12] that the use of spark and barrier discharges allowed ensuring deep oxidation of aromatic and aliphatic compounds contained in the industrial wastewater. The results of the oxidation process intensification were obtained: with the initial values of the COD water indicator nearly of 1,200 mg O/l, the electric discharge plasma technique allowed to achieve a decrease in the indicator ranging from 45% to 98%. The range of the COD operating values constituted up to 2,500 mg O/l.

The usage of ozone in combination with nonthermal plasma is also widely known [13]. The study demonstrated that the 2,4-dichlorophenoxyacetic acid decomposition by plasma in combination with ozonation was twice as fast compared to ozonation only. Almost complete decomposition of the 2,4-dichlorophenoxyacetic acid was registered after 60 minutes of ozonation using the plasma treatment.

Work [14] describes the experience of using ozonation in combination with exposing the runoff to the ultrasound. The study demonstrated that the ultrasound treatment increased the efficiency of reaction. Reduction in the content of 1,3-dinitrobenzene and 2,4-dinitrotoluene constituted up to 55% - 57%. The efficiency of the ozonation only did not exceed 15%. The increase in the effect was due to the enhancement of diffusion and mass transfer.

Other possible reasons for the intensification of the ozonation process are presented in [15]. The work demonstrated that ozonation of oils could by itself reduce the surface tension to values of 0.05 mN/m. In addition, when performing ozonation, the total porosity was increasing, and the pore distribution in size was changing. Vibration possessed a similar effect. Put together both these two effects allow the effect to be multiplied. In this regard, it was decided in the given paper to study the technique of vibroacoustic effect on ozonation.

II. METHODS AND MATERIALS

The device (Fig. 1) designed to ensure ozonation in combination with the vibroacoustic action appeared to be a 250 ml volume cylindrical beaker (column) mounted on a 4808-type vibration table produced by Brüel and Kjær. A signal from the Vibration Research VR9500-type vibration controller and from the Brüel and Kjær 2719-type power amplifier was provided to the vibration table. The vibration controller generated a sinusoidal signal of predetermined frequency and vibration acceleration level; and the accuracy of the signal assignment was determined using a feedback accelerometer. Ozone was provided into the beaker through the aerator from the ozone generator with the 1 g/h capacity.

The experiments were carried out on a model runoff, prepared from tap water and engine oil, and also at the runoff of a car wash facility. In order to prepare a model runoff, 1,000 cm³ of water (CODₐ = 27.7 mg/L) and 0.5 ml of a machine oil were mixed. The solution was stirred to a steady state, using a paddle stirrer at 750 rpm for 30 minutes at room temperature of 20°C.

The efficiency of treatment was determined using the COD. The COD determination was carried out using the HACH DR 6000 visible area UV spectrophotometer with the 15 - 150 mg/l certified range.

The efficiency of the treatment could be determined using the efficiency coefficient criterion:

\[
\varepsilon = \frac{\text{COD}_{\text{in}} - \text{COD}_{\text{t}}}{\text{COD}_{\text{in}}} \cdot 100\%
\]

where: CODᵢ is the chemical oxygen consumption after treatment; CODᵢ₀ is the initial chemical oxygen consumption at the model runoff.

A. Determination of Vibroresonant Modes

The main hypothesis in this paper appears to be the necessity to execute vibration effect on the waste water purification processes using the resonance frequencies.

In order to identify technological conditions differing in parameters and effects result, a study was carried out of the natural (resonant) frequencies of the installation, which combined expansion table, column, and model runoff of the predetermined volume. For this purpose additionally an accelerometer was added, which was measuring the actual value of vibration acceleration and passing the signal to the controller.

The natural frequencies are determined using the spectra successive measurements method in different system configurations. First, the spectrum is taken on the empty
vibration table, and the vibration table natural frequencies are obtained. Then the spectrum is taken on the vibration table with the expansion table installed on it; and the natural frequencies of the expansion table with the vibration table are obtained. However, since the vibration table frequencies were already determined previously, frequencies are distinguished characteristic only for the expansion table using the received values. In a similar way, the frequencies of other system components are determined, including column and fluid column of a given volume. Results of the given analysis are summarized in Table 1.

After analyzing the obtained data, it could be asserted that the natural resonant frequency of the expansion table is 107 Hz, the column is 280 Hz, and the model runoff is 885 Hz. The difference between the frequencies obtained could be justified by the increasing system mass, which leads to a decrease in the natural frequency.

On the basis of the analysis carried out, a conclusion could be made that it is necessary to carry out vibroacoustic runoff treatment at the above-mentioned frequencies. The maximum levels of vibration acceleration were determined on the basis of the extreme technical capabilities of the test facility; and then for each frequency mode several experiments were conducted at the maximum level and at several fractions of the maximum level.

Study of the Ozonation Processes Vibration Intensification Principles

In the course of studying the principles of the ozonation processes vibration intensification, an additional installation was assembled for photo and video registration of processes occurring during the vibrational ozonation. It was found that the effect of vibration at the resonance frequencies significantly influenced the processes of ozone flowing out through the aerator [16]; and the ozone bubbles dispersed composition in the purified water was changing. An example of the aeration change is presented in Fig. 2 [17].

The bubbles dispersion and size were determined using the Dynamic Studio 2016 software, which allows to process images and to display measurement results in quantitative or visual form. The results are presented in Fig. 3. It was established that when vibration was applied at the resonant frequencies, the volume content of the gas phase in the water was increasing significantly. In particular, the specific volume fraction increased from 0.28 mm³/mm³ to 0.55 mm³/mm³. At the same time, an increase in small size bubbles (up to 1 mm) was especially noticeable. This effect was caused by a decrease in the aerators hydraulic resistance, when the vibrational and acoustic effect was applied to it [18].

III. RESULTS AND DISCUSSION

Efficiency of the model runoff ozonation without employing vibration is presented in Fig. 4. Obviously, after 60 minutes of ozonation, it was possible to ensure the COD content reduction in the model runoff from 135 to 98 mg/l, which constitutes the 28% efficiency in accordance with the formula (1).

The given experiment was repeated 3 times; and the average values indicated above were obtained.

Above, the technological modes differing in parameters and effect results were established, which were subsequently used to carry out the testing: - 885 Hz, 10 g; - 290 Hz, 5g; - 107 Hz, 2g.

The levels of vibration acceleration were limited by the maximum permissible power of the power amplifier of 180 W, and the reduction thereof accompanied by the frequency decrease could be explained by the high-energy capacity of low-frequency oscillations.

In all cases, the initial COD in the model runoff constituted 107 mg/l.

Results of processing the model runoff at all the above modes are presented in Fig. 5.

Data presented demonstrate the positive results of vibroacoustic effect on the ozonation of the model runoff. The highest processing efficiency is achieved at the resonance frequency of the fluid column and constitutes 57%. That means, when using the proposed method, the processing efficiency could be increased up to 2 times.

Fig. 6 demonstrates the change in the COD extraction with time, when operating at the fluid column resonance frequency and using the vibration acceleration of 10 g.

Fig. 7 demonstrates variation in the COD extraction, when operating at the fluid column resonance frequency (885 Hz) under different vibration acceleration values.

After analyzing the data, it could be asserted that the higher is the vibration acceleration, the higher is the efficiency. However, in practice, setting a high mode leads to an increase in the noise component of the signal and higher energy consumption. Taking into consideration the logarithmic nature of the processing efficiency variation, it would be sufficient to set the mode within the 4 – 8 g range.

In the course of the experiment, the dependence of the processing efficiency upon the ozone consumption was established. Water ozonation was carried out for an hour in combination with vibroacoustic exposure at the frequency of 885 Hz and vibration acceleration of 5 g. During the first experiment, ozone consumption was equal to 1.8 g/hour, and the processing efficiency did not exceed 7%. During the last experiment, the ozone consumption was equal to 11 g/hour, and the processing efficiency reached 57%.

Accordingly, on the basis of a number of experiments carried out, a conclusion could be made that using the vibroacoustic effect is highly efficient for intensifying the model runoff ozonation process.

A. Car Wash Facility Runoff Treatment

In order to confirm the results obtained, treatment of a car wash facility runoff was carried out. The COD initial value on the runoff constituted 1,520 mg/l. Before starting the vibration ozonation, resonance frequencies search was performed, and it was established that the fluid column resonance frequency in the column with the same volume of runoff in it (250 ml) constituted 923 Hz. The difference of this frequency from the resonant frequency of the model runoff column was in the lower runoff mass of the car wash facility and higher content of light oil products.

In all other respects, the treatment was carried out
according to the technique described above.

Results of the treatment are presented in Fig. 9.

As a result, it was determined that when using the resonance mode, the cleaning efficiency at the 60 minutes treatment constituted 56%, which is comparable with previous experiments; while similar treatment without vibration allowed to purify waste water only by 27%.

IV. CONCLUSION

Influence of the vibroresonant effect on the ozonation efficiency was established. Laboratory tests demonstrated that the proposed technology allows reducing the COD level in a model runoff by 2 times. Vibroresonant effect helps to additionally disperse gas in the fluid providing better transfer and dissolution in the runoff. Bubble fragmentation occurs as a result of acoustic cavitation. The use of the new ozonation intensification method could allow the use of lower ozone concentrations in water treatment technologies.

Table and Figure

<table>
<thead>
<tr>
<th>SYSTEM COMPONENTS NATURAL RESONANT FREQUENCIES</th>
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<td><strong>System component</strong></td>
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<td>Fluid column, 250 ml</td>
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Fig. 1. A scheme of lab bench for ozone treatment intensification by exposure to vibration

Fig. 2. Ozone bubbles disperse composition in purified water. Left: runoff treatment using ozonation; right: runoff treatment using ozonation in combination with vibroacoustic effect

Fig. 3. Change in the air bubbles volumetric quantity depending on the size thereof with and without vibration
Fig. 4. Model runoff ozonation efficiency without using vibration

Fig. 5. Efficiency of processing using the natural resonance frequencies

Fig. 6. Efficiency of processing the model runoff in time at 885 Hz with 10 g vibration acceleration

Fig. 7. Dynamics of the model runoff processing efficiency variation at the 885 Hz frequency vibration acceleration change

Fig. 8. Dynamics of the variation in the model runoff processing with a change in the ozone consumption at 5g vibration acceleration and at 885 Hz frequency

Fig. 9. Efficiency of car wash facility runoff treatment time at 923 Hz and 10g vibration acceleration

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