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КАВИТАЦІЙНИЙ РОЗКЛАД БЕНЗОЛУ ПІД ДІЄЮ АКУСТИЧНИХ ВИПРОМІНЮВАНЬ УЛЬТРАЗВУКОВОГО ДІАПАЗОНУ

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Досліджено розклад бензолу під дією ультразвукових випромінювань, сформованих за допомогою ультразвукового магнітострикційного випромінювача. На основі спектрофотометричного аналізу розчинів бензолу, з застосуванням акустичних випромінювань ультразвукового діапазону встановлено зміну концентрації бензолу у часі. Встановлено, що ініціювання процесу впродовж 300 с, оброблення є достатнім для подальшого розкладу бензолу без подальшого накладання кавітаційних полів. Це дає підстави стверджувати, що застосування акустичних випромінювань ультразвукового діапазону навіть для ініціювання реакцій розкладу ароматичних сполук, зокрема бензолу, є надзвичайно ефективним.

Ключові слова: очищення стічних вод, бензол, кавітація, окиснення, спектрофотометрія.

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CAVITATION DECOMPOSITION OF BENZENE UNDER ACOUSTIC RADIATION OF ULTRASONIC RANGE

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The decomposition of benzene under ultrasonic radiation generated by ultrasound magnetostriction emitter was investigated. On the basis of spectrophotometric analysis of benzene solutions with the application of acoustic emission of ultrasonic range was found that benzene concentrations change over time. Was established that initiation of the process for processing 300 seconds is sufficient for further decomposition of benzene without further stimulation of cavitation fields. This gives reason to believe that the use of acoustic radiation of ultrasonic range even to initiate decomposition reactions of aromatic compounds, including benzene, is extremely effective.

Key words: wastewater treatment, benzene, cavitation, acoustic signal, resonance, spectrophotometry.

Introduction. Water is one of the main components of any technological processes of various industries. In particular, it serves as reagent, raw material, environment, working fluid, etc. During the course of majority of technological processes or operations water becomes polluted by other components of production, resulting in waste water formed. Much of the wastewater gets into natural water reservoirs insufficiently treated or even untreated. This is due to insufficient financing of development and organization of technological processes of waste water treatment and lack of effective technologies for their conditioning. This is especially true for waste water with high content

of organic compounds, which are mainly produced at chemical and petrochemical enterprises. State of the relevant water ecosystem greatly depends on the composition of liquid wastes and wastewaters that get into natural water bodies. Often excessive flow of pollutants causes the degradation of natural ecosystems.

Formulation of the problem and review of literature sources. Chemical industry enterprises include a complex of productions where different in nature and therefore varied in properties products are manufactured and where relevant emissions and wastes are formed. The main organic pollutants of wastewaters of chemical and petrochemical plants are emulsified and dispersed aromatic compounds as single core (benzene, toluene, phenol, xylene) and multicore (naphthalene, anthracene, phenanthrene, etc.). Such substances violate the equilibrium of natural biogeocenosis (primarily, river, sea), changing the relationship between different groups of hydrobionts and directions of metabolism and also inhibit the respiratory activity of organisms, processes of nitrification and nitrogen fixation. Local treatment facilities of chemical and petrochemical plants often do not meet requirements on the content of aromatic compounds in wastewaters that are moved to the stage of biochemical purification. Therefore the search for new methods to reduce the content of aromatic compounds in industrial wastewater is important.

There are many methods of wastewater treatment from organic contaminants, extraction, absorption, flotation, ion exchange methods and reagent methods, biological oxidation and so on. The most universal method for wastewater treatment from organic substances is biological treatment in the aeration tanks or on biofilters as an independent method and in combination with other methods of pre-treatment, post-treatment [1]. However, at present day biological treatment methods require additional costs for special equipment and its exploitation and also for intensification of the cleaning process. The methods need to be consistent with the maximum allowable concentration of pollutants in waste water (it is important to consider the load on the sludge due to number of substances-pollutants) and to ensure the absence of any toxic pollutants (they can cause the death of the microorganisms and ecosystems of biological treatment plants).

Previous studies have established the fundamental possibility of wastewaters cleaning from organic contaminants using acoustic radiation of ultrasonic range [2]. The use of ultrasonic radiation is a promising method of wastewater treatment for ensuring technical and economic efficiency of the process [3]. It was suggested that organic substances decomposition takes place because excitement of cavitation phenomenon in the aquatic environment take place. However, it is necessary to establish the optimal conditions of the cavitation treatment of wastewater for their effective cleaning in cavitation fields.

The purpose of the work is to study of the decomposition of benzene under ultrasonic acoustic radiation, which causing occurrence of the phenomenon of cavitation, in continuous and discontinuous modes.

Experimental part. Models of wastewaters that contained 530 mg/dm^3 benzene were used in the study. They were received as a result of long-term (at least two hours) intensive mixing of water-benzene emulsion at room temperature to reach equilibrium in the system in which the chemical oxygen demand (COD) value assuming constant values.

Ultrasound magnetostriction emitter type “Ultrasonic Disintegrator UD-20” with a frequency of radiation 22 kHz was used for excitation of cavitation phenomenon. The study was conducted under isothermal conditions at a temperature of $298 \pm 0.5 \text{ K}$. The reaction flask was placed in a thermostatic

bath connected to the thermostat UV-20. The temperature of the reaction medium was controlled by thermometer with precision ± 0.5 K. Thermostatic bath with the reaction flask was placed on a magnetic mixer.

Effect of cavitation on change of benzene concentration in the aquatic environment was investigated under different processing modes: continuous (constant performance of ultrasound emitter) and impulse (treatment of the environment during the first 300 s of the process). The total duration of the process in both cases is equal to 1800 s.

The concentration of benzene in the model wastewater was determined by UV/VIS-spectroscopy at intervals of 300 s throughout the study period using two-beam spectrophotometer SPECORD M40 Carl Zeiss JENA in the wavelength range of 200... 400 nm and quartz cuvettes of 10 mm thick. The calibration graph of dependence of optical density from the benzene concentration in solutions, obtained by serial dilution of the initial saturated model wastewater, was previously built.

Initial and final values of the chemical oxygen demand (COD) of model waste water, due to which the content of benzene was calculated, were determined according to known methods of ISO 6060: 2003 [4].

Results and Discussion. The absorption band in the 230-265 nm composed with three main peaks with maximums of 251.7; 254.5 and 258.4 nm was recorded in the UV spectrum of the original aqueous solution of benzene. This band is called benzene absorption band in long-wave region and characterized by well-defined vibrational structure [5]. However, it was observed that shift of the oscillating structure peaks in the short wave area occurs for the studied system. For example, the most characteristic for benzene absorption maximum 256 nm shifts and is shown at 254.5 nm. This shift can be explained by the fact that the data is related to the spectrum of benzene in organic solvents and the studied system is aqueous.

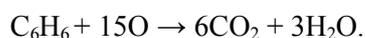
It was found that throughout the cavitation processing of environment, both in stationary and pulsed modes, the intensity of the peaks of UV spectrum of benzene decreases. The typical spectrums of benzene at different times of the process for all modes of cavitation processing of environment are shown in Fig. 1. The oscillating absorption band structure has identical form and position of main peaks corresponds to the same values of wavelengths at different periods of the process. It can be identified only main peaks at the end of the process, when the degree of conversion of benzene exceeds 85... 90 % (Fig. 1 b).

Consequently it can be argued that a gradual transformation of benzene takes place in cavitation field, namely decrease of its concentration and not its destruction with accumulation of relevant organic fragments in the environment. This is confirmed by the absence of any absorption spectra in a long-wave region. Therefore, it can be assumed that oxidation of benzene to stable products – water and carbon (IV) oxide occurs in cavitation field, which was confirmed by determining the COD of the environment.

Probably a series of parallel-sequential processes occurs in the aquatic environment. Firstly, sonoliz of water, that is prevailing in the system, according to the general scheme



with the formation of strong oxidants – mostly radicals [6]. Secondly, cavitation decomposition of benzene with the formation of short-living organic fragments of radical nature. Thirdly, the interaction of products of water sonoliz with benzene and products of cavitation destruction that can be represented by gross equation



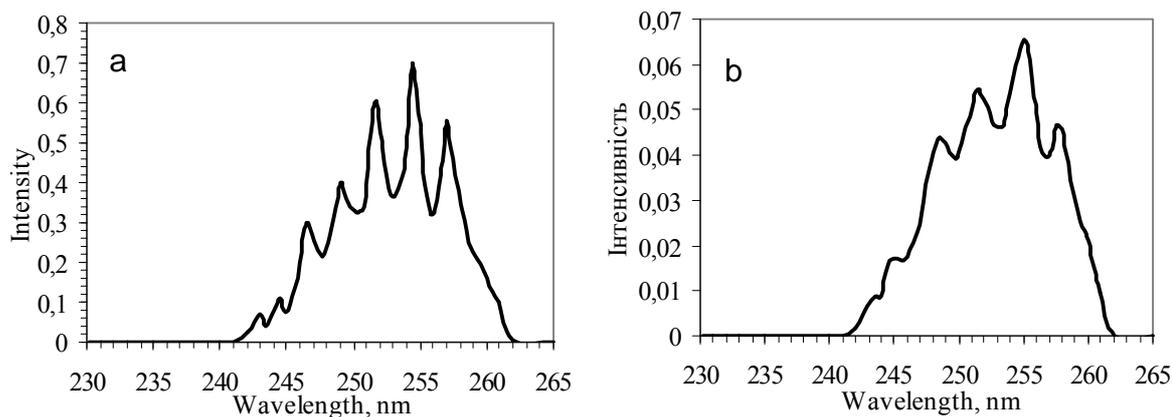


Fig. 1. UV spectrums of benzene in aqueous solution at different periods of the process:
a – in the beginning; b – at the end

Concentration of benzene in the model during 300 s decreased from 6.79 to 3.64 mol/dm³, that is 46 %, under constant excitation in the environment medium of cavitation phenomena. The rate of oxidation of benzene during this period amounted to 1,0510⁻² mol/dm³s. Further reduction in the concentration of benzene occurs in monotonic mode and this change was almost rectilinear during 1500 s (Figure 2, curve 1). This means that further oxidation of benzene occurs at a constant speed equal to 1.9110⁻³ mol/dm³s.

It was established that generally under constant cavitation action within 1800 s the concentration of benzene in the model environment decreased to 0.78 mol/dm³, which is 88 %. The COD value of the reaction medium is reduced almost proportionally to the decrease of the concentration of benzene during the process duration. Thus, the initial COD value for model wastewater is equal to 454 mg O²/dm³ and for the environment treated by acoustic radiation – 63 mg O²/dm³, which is 86 % less than the original value. Due to obtained results, changes in concentration of benzene (on 88 %) and COD value (86 %) are very close, that confirms suggested assumption about the mechanism of oxidation of benzene under ultrasonic radiation.

Since the oxidation of benzene in cavitation field most likely occurs by radical mechanism, the following studies were performed not at continuous excitation of cavitation phenomenon, but only during initial stages of the process. In this case, the phenomenon of cavitation could cause formation of radicals, namely initiation of radical chain processes.

The intensity changes of concentration over time is greater in the case of cavitation use only for initiation of benzene oxidation process than under constant action of ultrasonic radiation. The rate of oxidation of benzene was slightly higher during the first 300 seconds, when cavitation was excited in environment, than in the previous case and equal to 1,2610⁻² mol/dm³s, and benzene conversion degree reached 56 %. It was established that after the termination of ultrasonic radiation, which excites cavitation in the reaction medium, benzene oxidation process continued. The rate of the process was higher than at a constant action of acoustic radiation. For example, rate of the process was equal to 5.23·10⁻³ mol/ dm³·s in the range between 300 and 600 s. This is 2.7 times more than at constant action of acoustic radiation. Thereafter, the process rate decreased to 1.42·10⁻³ mol/ dm³·s.

It was established that concentration of benzene in the model solution was close to zero already after 1200 s from beginning of the study and after 1500 s from experiment start the relevant reflections on the spectrogram were not found. Thus, the degree of oxidation of benzene was approaching to 100 %.

Obtained results can be explained by peculiarities of the course of processes system in aqueous-benzene medium under cavitation field.

Duration of the process of full benzene oxidation was calculated from the regression equation – it is about 2700 s.

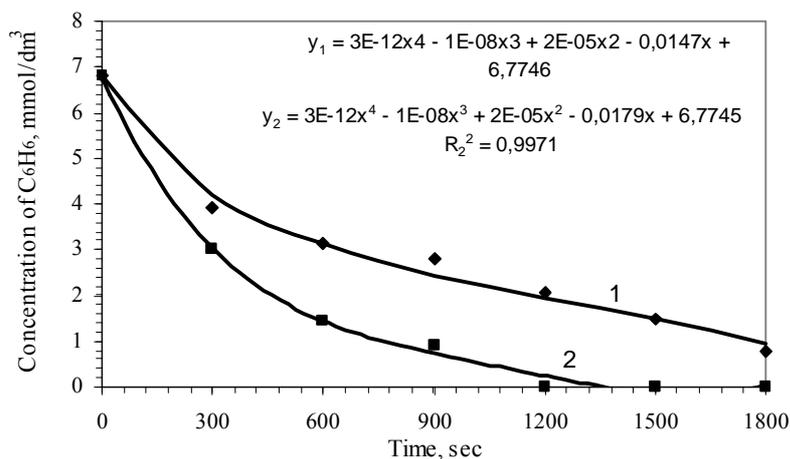


Fig. 2. The dependence of benzene concentration change in time: 1 – under constant action of acoustic radiation; 2 – under initiating of the process by acoustic radiation within the first 300 s

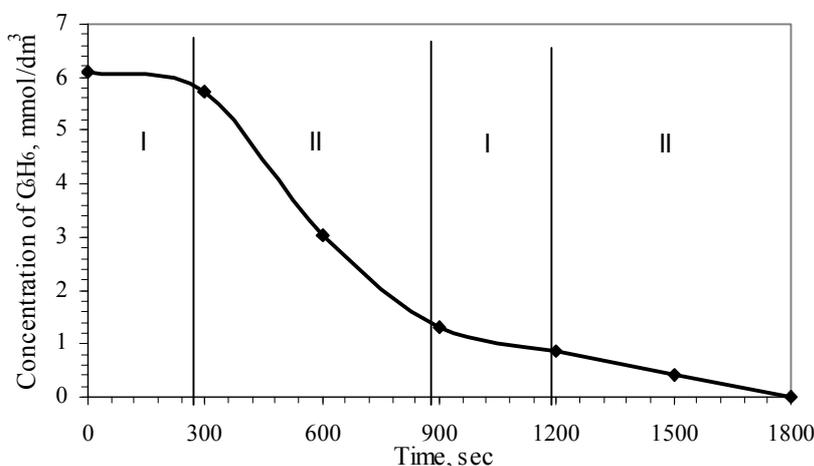


Fig. 3. The dependence of changes in the concentration of benzene in time under periodic action of acoustic radiation: periods: I – cavitation processing; II – without cavitation

The obtained results can be explained by peculiarities of progress of system processes in aqueous-benzene medium in cavitation fields under conditions of research. A sequence of radical processes arises during the comparatively short time (300 s) in case of initiation of the process by using acoustic radiation of ultrasonic range, that stimulates cavitation. First of all it is due, as was mentioned above, to sonolysis of the water, which is the predominant component in the system. Thereafter products of sonolysis of the water with oxidative character interact with benzene, which belongs to the reducing agents. Consequently, the oxidation degradation of benzene with the emergence of radical nature related products is possible – continuation of the chain occurs. Then there is a further development of the chain process.

Constant generation of radicals, which concentration increases in the environment, occurs during the continuous stimulation of cavitation. The probability of recombination of radicals increases, especially for those, which were formed as a result of water sonolysis. It is clear that formed relevant products, even with oxidizing properties, such as hydrogen peroxide, have much lower oxidative resolution than the particles of a radical nature. Accordingly, the rate of oxidation of benzene decreases.

These considerations are confirmed by the data obtained during periodic cavitation stimulation (Fig. 3): every 300 s of the treatment following 600 seconds – without the action of acoustic radiation.

The total duration of the process to achievement of 100 % oxidation of benzene is less than during constant stimulation of cavitation, but less than in the case of initiating of the process within 300 s.

Conclusions. This study established fundamental possibility of use of ultrasonic range acoustic radiation for decomposition of benzene in aqueous environments. In particular, it was found that the fullness of benzene decomposition is achieved in the case of short-term action of ultrasonic radiation over 300 s. Completeness of benzene decomposition decreases in the case of increase in the duration of ultrasonic treatment.

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