

# ТЕХНОЛОГІЯ НЕОРГАНІЧНИХ РЕЧОВИН ТА СИЛКАТНИХ МАТЕРІАЛІВ

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## КАВІТАЦІЙНЕ ОЧИЩЕННЯ СТІЧНИХ ВОД ВІД ТОЛУОЛУ

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Наведено результати досліджень процесу кавітаційного очищення імітату стічних вод, що містять толуол. На підставі спектрофотометричного аналізу водних розчинів толуолу, оброблених ультразвуковим магнітострикційним випромінювачем, встановлено зменшення інтенсивності піків УФ-спектра толуолу принаймні у 7 разів та дифузний характер основних смуг поглинання толуолу. Виявлена рівність початкової швидкості процесу кавітаційного очищення імітату стічних вод від толуолу за різних режимів – стаціонарного та режиму ініціювання реакцій розкладу та окиснення, а також незначний вплив тривалості кавітаційного оброблення на величину ступеня очищення імітату внаслідок дії кавітаційних явищ. З метою зменшення енергомісткості процесу очищення у 2 рази запропоновано здійснювати його у режимі ініціювання.

Ключові слова: очищення стічних вод, толуол, кавітація, спектрофотометрія, стаціонарний режим, режим ініціювання реакцій розкладу та окиснення.

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## CAVITATION WASTEWATER TREATMENT FROM TOLUENE

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The article presents the results of studies of the process of cavitation treatment of wastewater with imitation of toluene presence. On the basis of spectrophotometric analysis of aqueous solutions of toluene treated with ultrasonic magnetostrictive emitter, a decrease in the intensity of the peaks of the UV toluene spectrum, at least 7 times, and the diffuse nature of the main toluene absorption bands were found. The equality of initial velocity of the process of cavitation treatment of wastewater with imitation of toluene presence in the different regimes – the stationary regime and the regime of initiation of decomposition and oxidation reactions, as well as the insignificant influence of the duration of cavitation treatment on the degree of treatment of the imitation due to the effect of cavitation phenomena, were found. In order to reduce the energy intensity of the process of treatment in 2 times it is proposed to implement it in the mode of initiation.

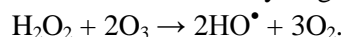
Key words: wastewater treatment, toluene, cavitation, spectrophotometry, stationary regime, regime of initiation of decomposition and oxidation reactions.

**Introduction.** Monocyclic aromatic compounds (benzene, toluene, ethylbenzene, xylene, phenol and their derivatives), which are received by rectification from coal tar, pyrolysis of petroleum fractions,

during catalytic reforming (platforming and hydroforming) of oil fuel, etc., are integral components of waste water enterprises of chemical and coke and petrochemical industry. They have a large migration potential in soil and water due to their relatively high resistance to biodegradation and water solubility [1]. The toxic effect of these compounds is associated with proven (for benzene) or hypothetical (for other compounds) carcinogenicity, disorders of the activity of the human endocrine and central nervous system [2]. The presence of aromatic compounds in biocenoses (primarily river and marine) leads to inhibition of respiratory activity of hydrobionts, processes of nitrification and nitrogen fixation, which is manifested in the change of the species and trophic structure of these natural groups.

**Problem statement and an overview of literature sources.** The high stability of monocyclic aromatic compounds to biodegradation results in low efficacy of biological methods of sewage treatment. A promising method in the processes of wastewater treatment from aromatic compounds is their cavitation treatment. Reduction of aromatic compounds content in wastewater is due to their degradation and oxidation in cavitation fields.

At the same time, the efficiency of wastewater treatment depends on the intensity of the development of cavitation phenomena, which, in turn, is determined by the technological parameters of cavitation treatment (pressure at the entrance to the cavitator, the temperature of the reaction medium, multiplicity of treatment), and the structural features of the cavitation generators (type, shape of cavitation elements, their geometric dimensions and spatial location) [3-11]. Thus, the maximum rate of cavitation degradation of phenol in sewage was achieved during 60 minutes of cavitation treatment in a generator of hydrodynamic cavitation (pressure at the entrance to the cavitator – 0.4 MPa) of a combined design consisting of a Venturi tube and plate with hole. Based on the analysis of the absorption spectrum in the ultraviolet range, it has been found that the products of cavitation decontamination of phenol are ketones or aldehydes, benzendiales and fatty acids [9]. It was found that the amount of destructured phenol depends on the multiplicity of wastewater treatment in the hydrodynamic cavitator, and on the concentration of phenol in them. The use of a cavitator without the use of oxidants can be effective and economically feasible for the wastewater treatment from phenol at its concentration up to 10 mg / dm<sup>3</sup> [10]. The use of combined technology for wastewater treatment from 2,4,6-trichlorophenol (fungicide, herbicide, insecticide, defoliant, etc.), which involves their cavitation treatment and advanced oxidation processes (H<sub>2</sub>O<sub>2</sub> + O<sub>3</sub>), has allowed to achieve the following indices, %: the degree of neutralization of 2,4,6-trichlorophenol – 100; reduction of total carbon content by 95.6; the decrease in the amount of chemical consumption of oxygen – by 80.9. Optimal conditions of the treatment process [11]: device for generating cavitation – Venturi tube; duration of cavitation treatment – 2 hours; input pressure at the cavitation generator – 0.4 MPa; temperature – 303 ± 2 K; pH 7; the concentration of 2,4,6-trichlorophenol and hydrogen peroxide (mg / dm<sup>3</sup>) – respectively, 20 and 100; mass consumption of ozone – 400 mg / hour. Significant decrease in the content of total carbon and the amount of chemical consumption of oxygen is explained by the formation of free radicals – hydroxyls due to the interaction of hydrogen peroxide with ozone



It has been established that the rate of oxidation of aromatic compounds, in particular benzene and toluene, by ozone significantly increases in the cavitation field excited by ultrasonic radiation [13]. In this paper a radical mechanism of the process initiated by the generation of hydroxyl radicals (HO<sup>•</sup>) is proposed, due to the course of cavitation phenomena.

**The purpose of the work.** The purpose of the work was to study the process of cavitation treatment of wastewater imitations of chemistry and petrochemistry enterprises from toluene under adiabatic conditions.

**Experimental part.** Investigation of the processes of cavitation wastewater treatment under adiabatic conditions was carried out on the example of wastewater imitations containing toluene. The wastewater imitations were prepared by continuous stirring (~ 2 hours) of distilled water with

an excess (relative to the solubility) of toluene at a constant temperature (289 K) until a constant concentration was achieved. The excess of toluene was separated after the bundle of water-toluene and toluene phases, respectively. The content of toluene in distilled water after reaching the saturation state was  $1.51 \text{ mol} / (\text{m}^3 \text{ of water})$ .

To generate acoustic cavitation, an ultrasonic emitter of the magnetostrictive type “Ultrasonic Disintegrator UD-20” with a frequency of 22 kHz was used. The study of the influence of cavitation phenomena on the water-toluene medium was carried out under adiabatic conditions in stationary regime and the regime of initiation. The stationary regime is the constant excitation of cavitation throughout the experiment at the constant frequency of ultrasonic oscillations. The regime of initiation of the process is to excite cavitation phenomena within 15 minutes with subsequent exposure to the medium. Specific power of cavitation treatment,  $\text{kW} / \text{m}^3$ : for stationary regime – 68; for the regime of initiation of process – 34. The studies were carried out both for stirring in turbulent mode, and without mixing; total duration of the process – 30 minutes; analysis of medium on toluene content was carried out every 5 minutes.

The concentration of toluene in the wastewater imitation was determined by UV / Viz spectroscopy using the SPECORD M40 Carl Zeiss JENA dual-beam spectrophotometer (thickness of the quartz cell – 10 mm, wavelength range 200...900 nm, medium of comparison – distilled water). During the studies, the temperature of the water-toluene medium was measured.

**Research results and their discussion.** The presence of alkyl groups (in particular, of the group –  $\text{CH}_3$ ) in the benzene ring as substituents results in the displacement of the B band (by the Braude classification of the absorption bands) [12] with a fine structure in the long-wave region (the so-called bathochromic displacement) – from 256 (for benzene) to 262 (for toluene) nm (Fig. 1). It has been established that due to cavitation treatment in different modes (stationary regime and regime of initiation of decomposition and oxidation reactions), the intensity of the peaks of the UV-spectrum of toluene is significantly reduced. Typical UV spectra of toluene in the beginning and at the end of cavitation treatment (after 30 minutes) are shown in Fig. 1.

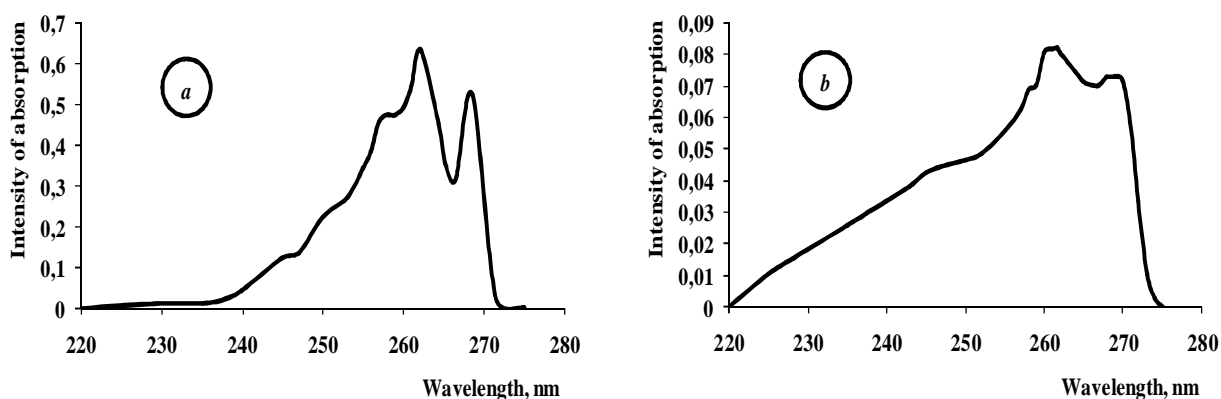
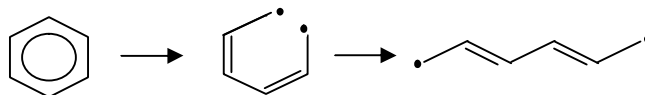


Fig. 1. UV-spectra of toluene in an aqueous medium at different periods of the cavitation treatment process: a – at the beginning; b – at the end

The intensity of the peaks of the UV-spectra of toluene is reduced, at least in 7 times, at the end of the process of cavitation treatment by the ultrasonic emitter (Fig. 1b). In this case, the main absorption bands in the toluene spectrum are characterized by a more diffuse (blurred) structure (Fig. 1b), compared with the structure of absorption bands at the beginning of the process. More intensified region in the range 220...235 nm, in comparison with the initial UV-spectrum of toluene, may indicate the presence of polygonal linear systems in the medium. They can be formed as a result of cavitation, oxidative or combined degradation of the benzene ring to form linear fragments containing several double bonds



The bathochrome displacement of this absorption region, in comparison with polydienes (the maximum absorption of 220 nm), is possibly due to the presence of the methyl group as a substituent.

At the same time, in the range 270...900 nm, other areas of absorption were not detected. This indicates that under the action of cavitation, mainly occurs the destruction of toluene with its subsequent deep oxidation to the final stable products – CO<sub>2</sub> and H<sub>2</sub>O.

The concentration of toluene in the stationary regime of cavitation treatment over 1800 sec decreased from 1.51 to 0.28 (mol of toluene) / (m<sup>3</sup> of water), ie 81.5 % (Fig. 2). This is the total degree of water treatment from toluene, which takes into account its partial desorption (treatment rate – 55 %) due to intense mixing of the imitation, and treatment due to acoustic cavitation (the degree of treatment is 26.5 %).

In the regime of cavitation initiation of the decomposition and oxidation reactions of toluene for 900 sec (with further exposure on the medium for a further 900 sec with a periodic determination of its concentration in the imitation), a decrease in the concentration of toluene from 1.51 to 0.52 (mol of toluene) / (m<sup>3</sup> of water) , which is 65.6 % (Fig. 3), of which: 45.8 % – purification due to the desulsion of toluene into the gas phase; 19.8 % – purification due to decomposition and oxidation processes caused by the action of cavitation phenomena on the reaction system.

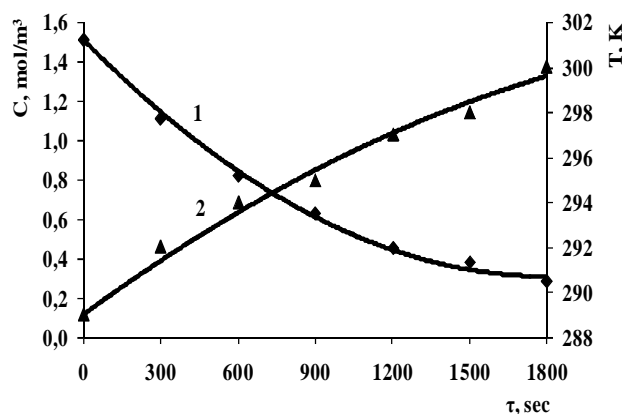


Fig. 2. The dependence of the concentration of toluene ( $C$ , mol / m<sup>3</sup>) (1) and the temperature of the imitation ( $T$ , K) (2) on the duration of cavitation treatment ( $\tau$ , sec) in stationary regime

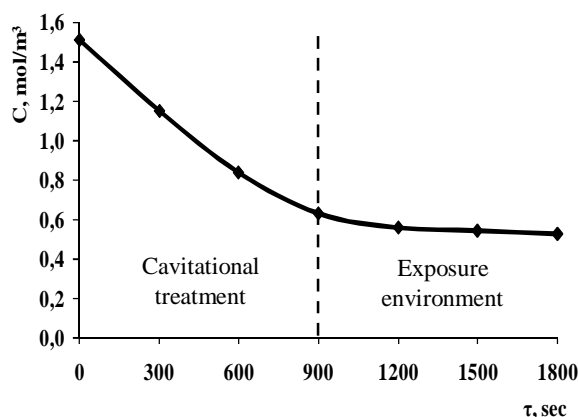


Fig. 3 Dependence of the concentration of toluene ( $C$ , mol / m<sup>3</sup>) in the imitation of wastewaters from time ( $\tau$ , sec) in the regime of cavitation initiation of decomposition and oxidation reactions during 900 sec

On the basis of experimental data, the initial velocity of the process of cavitation treatment of wastewater imitation from toluene in different regimes (Table) is calculated. The value of the initial speed of this process for different regimes of cavitation treatment is practically equal, and the degree of treatment of wastewater imitation from toluene due to cavitation differ slightly – 26.5 and 19.8 % respectively. Therefore, in order to save energy resources (reduction of the energy intensity of the process by 2 times) and, if necessary, the preliminary shallow treatment of wastewater from toluene, it is expedient to use the regime of cavitation initiation of decomposition and oxidation reactions (the effect of cavitation fields on the reaction system during 900 sec).

Table 1

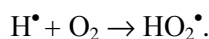
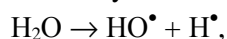
**The value of the initial velocity of the process of treatment of the wastewater imitation from toluene in the cavitation fields under different regimes**

Cavitation treatment regime	Initial velocity, $u \cdot 10^3$ , mol / (m <sup>3</sup> ·sec)
Stationary	1,15
Regime of initiation of decomposition and oxidation reactions	1,12

The difference of the decomposition of toluene and benzene in the regime of initiation of the process under the influence of ultrasonic radiation is revealed. The change in the concentration of benzene in the stationary mode of excitation of cavitation in most cases was less intense than in the mode initiation process for not less than 600 sec. This phenomenon was explained by the radical nature of the process, namely: after the accumulation in the reaction medium of the critical concentration of radicals as products of water sonolysis, degradation and oxidation of benzene occur with high speed. At the same time, in stationary regime, in which fragments of radical nature are generated continuously, it is likely that there is a local increase in their concentration and, consequently, an intensive recombination. This leads to a decrease in the degree of conversion of benzene in the stationary mode of generation of the cavitation field.

The change in the concentration of toluene is more intense in the case of stationary regime of excitation of cavitation, in comparison with the process of initiation of the cavitation. This is probably due to the influence of the methyl group as a substituent of the I generation in benzene.

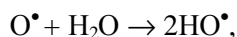
Conducting research on the constant contact of the water-toluene medium with air at a constant intensity of mixing in turbulent regime and without stirring made it possible to determine the role of oxygen in the process of toluene conversion. Thus, during the cavitation treatment of the medium without mixing, the rate of its conversion was at least three times lower than with turbulent stirring. This is due to the fact that oxygen belongs to the so-called chemically active gases involved in the reactions of the transformation of radicals arising from the water's sonolysis:



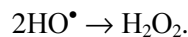
Absorbed oxygen in the cavitation cavity can dissociate with the formation of atomic oxygen



which causes the occurrence of a hydroxyl radical



which can form hydrogen peroxide



The generated particles of radical nature ( $\text{O}^\bullet$ ,  $\text{HO}^\bullet$ ,  $\text{HO}_2^\bullet$ ) help to extend the chain and by using hydrogen peroxide, lead to oxidative degradation and deep oxidation of fragments of organic compounds.

**Conclusions.** On the basis of the analysis of information sources, the effectiveness of the use of cavitation phenomena for the purification of aqueous media from monocyclic aromatic compounds is shown. Examples illustrating the presence of dependence between the efficiency of wastewater treatment from aromatic compounds and the intensity of the development of cavitation phenomena, which, in turn, is determined by the technological parameters of cavitation processing (pressure at the entrance to the cavitator, the temperature of the reaction medium, the multiplicity of treatment) and the constructive features of cavitation generators (type, form of cavitating elements, their geometric sizes and spatial placement), is given. The process of treatment of wastewater imitation from toluene is proposed to be carried out using an ultrasonic magnetostrictive emitter.

It is established that due to the cavitation treatment of the imitation in different regimes, the intensity of the peaks of the UV-spectrum of toluene substantially decreases, at least 7 times, and the structure of the main absorption bands becomes diffuse in nature (becomes blurred).

Were determined the equality of initial velocity of the process of cavitation treatment of wastewater imitation from toluene in different regimes ( $1.15 \cdot 10^{-3}$  mol / ( $\text{m}^3 \cdot \text{sec}$ ) – for stationary regime and  $1.12 \cdot 10^{-3}$  mol / ( $\text{m}^3 \cdot \text{sec}$ ) – for the initiation regime), as well as insignificant influence of the duration of cavitation treatment on the degree of treatment of the imitation due to the effect of cavitation phenomena. Therefore, in order to reduce the energy intensity by 2 times and, if necessary, the preliminary shallow treatment of wastewater from toluene, it is expedient to use the cavitation initiation regime of the decomposition and oxidation reactions (the effect of the cavitation fields on the reaction system for 900 seconds).

Further studies of the processes of cavitation treatment of aqueous media from monocyclic aromatic compounds will be aimed at studying the influence of temperature and atmosphere, in which research will be conducted, on the efficiency of treatment.

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