

Z. O. Znak¹, Y. V. Sukhatskyi¹, P. R. Gogate², R. V. Mnykh¹, P. Thanekar²

¹Lviv Polytechnic National University,

Department of Chemistry and Technology of Inorganic Substances,

²Institute of Chemical Technology, Mumbai, India,

Department of Chemical Engineering

zenovii.o.znak@lpnu.ua

OXIDATIVE DESTRUCTION OF BENZENE IN THE CONDITIONS OF UNSTATIONARY CAVITATION EXCITATION

<https://doi.org/10.23939/ctas2023.01.038>

The threshold value of the energy required for the decomposition of benzene after the cessation of cavitation has been established. The regularities of the oxidative destruction of benzene in the cyclic mode “cavitation-exposure” were established. The possibility of destruction of benzene in case of initiation of the process by introducing a certain amount of its cavitationaly activated part into the water-benzene medium is shown. The role of oxygen in the cavitation decomposition of benzene was experimentally confirmed.

Key words: benzene; ultrasound; cavitation; initiation; “threshold” energy; periodic excitation of cavitation.

Introduction

Wastewater from many chemical and petrochemical enterprises contains a considerable amount of aromatic compounds, both mono- (benzene, toluene, phenol, cresols) and polycyclic (anthracene, naphthalene, pyrene, phenanthrene) [1]. These compounds exhibit carcinogenic, mutagenic and teratogenic effects on living organisms. They are characterized by high bioresistance and, accordingly, slight biodegradability, which naturally decreases with an increase in the number of benzene rings in the structure of the aromatic compound. This ensures their stability in the environment and the possibility of transmission through the trophic chain. Therefore, the search for effective energy-saving methods of neutralizing aromatic compounds, in particular, benzene, is an urgent task within the framework of the implementation of the “zero emissions” policy.

The destruction of benzene in aqueous media was studied using processes that differed significantly in their physical and chemical nature. In particular, these were the following processes: aerobic-anaerobic degradation [2], photocatalysis based on TiO₂ [3] or nanocomposites [4] and cavitation [5–9]; benzene extraction was also carried out by two-phase extraction [10]. Wu et al. [11] investigated the

degradation of benzene under the influence of ultrasonic radiation at a power of 40 W. It was established that the rate of destruction of benzene was lower than that of cyclohexene. Under the action of acoustic cavitation, the degree of benzene destruction reached 88 % [5]. In the mode of stationary cavitation, the degree of benzene conversion of 89...91 % was achieved [6]. The application of the combined treatment of the water environment with the effect of ultrasound radiation and Fenton’s reagent [9] made it possible to achieve a degree of benzene decomposition of 93.4 %. Research conducted using a hydrodynamic cavitator with a 1.1 kW pump [12] established a high efficiency of benzene decomposition – the degree of its conversion reached 98.9 %. The results of the study of cavitation destruction of aromatic compounds are also given in [13–15].

Previous studies have established that the introduction of air in the amount of 2 % (by volume) into the water-benzene medium made it possible to increase the speed of the process by at least two times. Based on the obtained results, a conclusion was made about the radical mechanism of benzene oxidation [5]. Therefore, it was proposed to conduct a study of the destruction of benzene under

conditions of non-stationary cavitation excitation, in which the decomposition of benzene was predicted even after the cessation of cavitation excitation after the generation in the reaction medium of a certain critical concentration of products of a radical nature, which would further contribute to the continuation of the chain radical process. It was also assumed that such a process can occur after the introduction of a certain amount of energy into the reaction medium, at which the course of the benzene oxidation process is possible even after the cessation of cavitation excitation.

The purpose of the work: to study the process of benzene destruction under conditions of non-stationary cavitation excitation.

Materials and research methods

The research used a model benzene solution (MBS), which was prepared by mixing benzene (purity 99.9 %, Deza Company, Czech Republic) with distilled water; initial concentration of benzene – 0.67...0.73 g/dm³ (8.60...9.35·10⁻³ mol/dm³); the last value corresponded to the maximum solubility of benzene at a temperature of 20 °C.

Research was conducted on laboratory installations in which the phenomenon of cavitation was excited by fundamentally different methods. The first is with the help of an ultrasonic magnetostrictive emitter “Ultrasonic UD-20” (radiation frequency 20 kHz, power – 10.2 W) (Fig. 1). In addition to an ultrasonic emitter 3 with a concentrator 2 and a power supply unit 4, the installation contained a reaction tank 1; The UTU-4 ultra-thermostat 6 is equipped with a removable bath 7, which was placed on a magnetic stirrer 8. The temperature in the reaction vessel 1 was determined by a thermometer 8.

The volume of MBS medium, which was placed in flask 1, was 150...250 cm³.

In the second laboratory installation (Fig. 2), a hydrodynamic jet type cavitator 8 was used to excite cavitation. The installation also included: circulating tank 1 with temperature control system 2 and agitator 3, circulating centrifugal pump 6. The MBS consumption and the pressure, which was determined by the manometer 15, were regulated by valves 5, 7, 16. The air in the MBS was supplied by the compressor 13 through the rheometer 12 and aerator 4.

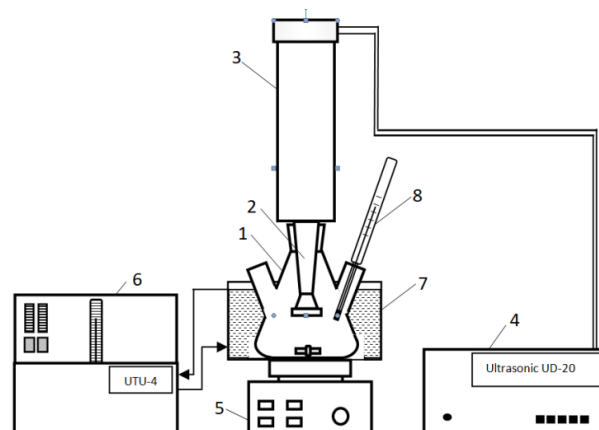


Fig. 1. Scheme of the installation for the study of cavitation neutralization of benzene:

- 1 – reaction flask; 2 – ultrasound concentrator;
- 3 – magnetostrictive emitter; 4 – power supply unit of the ultrasound emitter;
- 5 – magnetic stirrer; 6 – thermostat;
- 7 – thermostatic bath; 8 – thermometer

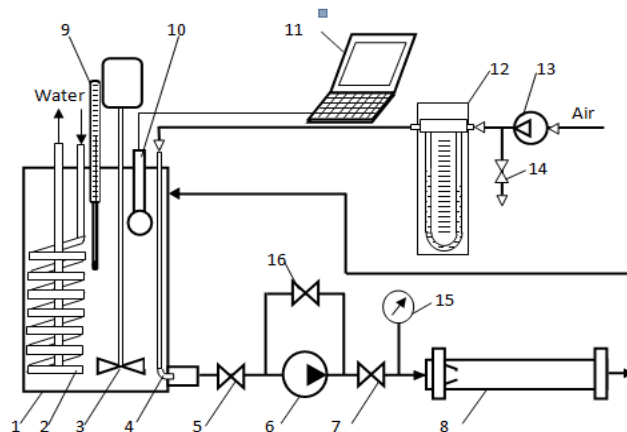


Fig. 2. Installation scheme with cavitation reactor:

- 1 – circulation tank; 2 – cooling system; 3 – stirrer;
- 4 – air inlet; 5, 7, 14, 16 – taps; 6 – circulation pump;
- 8 – cavitator; 9 – thermometer; 10 – hydrophone;
- 11 – PC; 12 – rheometer; 13 – compressor;
- 15 – manometer

The body of the cavitator 8 is made of quartz glass, which made it possible to visually observe the formation of the cavitation area. The cavitation area was formed due to the collision of the MBS jets, which were formed at the exit from the profiled nozzles: the number of nozzles is 3; the diameter of the nozzles at the exit is 2 mm, the angle of attack (the angle between the axes of adjacent nozzles) is 160...165 degrees.

The volume of MBS in the system was equal to 17.5 dm³. The consumption of MBS at a certain pressure was determined by the volumetric method

at the entrance to the circulation tank 1. The nominal power of the centrifugal pump was 1.1 kW. The pressure at the entrance to the cavitator 8 was varied in the range of 0.2...0.36 MPa.

Research at the first installation was performed in adiabatic and isothermal (at a temperature of $293 \pm K$) conditions, at the second – in adiabatic conditions. Analysis of the water environment for benzene content during the research was carried out using spectrophotometers “Specord M40” (in the range of 200...900 nm) and ULab 102 (at a wavelength of 254 nm, which corresponds to the maximum absorption of benzene).

The amount of energy (W), which is introduced into the reaction system by the ultrasound emitter, was determined according to the equation

$$W = \frac{N \cdot \tau}{V},$$

where N – power of the ultrasound emitter, W; τ – duration of cavitation treatment, sec; V – volume of the reaction medium that was subjected to processing, dm^3 .

Taking into account the radical mechanism of oxidative destruction of benzene, the research was carried out in the following modes of non-stationary cavitation excitation: 1) periodic in the mode “cavitation – exposure – cavitation – exposure ...”; 2) introducing a certain volume of pre-cavitationally treated model solution into the water-benzene medium.

Results and discussion

The studies were carried out with the power of the ultrasound emitter of 10.2 W and with constant turbulent mixing of the MBS. It was established that after cavitation treatment of the solution for at least 300 sec, benzene destruction occurs (initial content $8.6 \cdot 10^{-3} \text{ mol/dm}^3$) even after cessation of cavitation excitation. During this time, 51 kJ/dm^3 (68 W/dm^3) of energy was introduced into the solution. This value of energy was taken as a “threshold”, which is necessary to create conditions in the environment for further destruction of benzene even without cavitation. However, the main condition for this is the presence of oxygen in the system, which is absorbed from the air under conditions of intensive mixing of the liquid phase. Therefore, in the future, research in the non-stationary mode of cavitation excitation was carried out under the condition that the amount of energy introduced into the liquid-

phase medium should not be less than the “threshold” value.

Investigation with periodic excitation of cavitation were carried out in adiabatic ($T_0 = 293 \text{ K}$) conditions and the power of ultrasound radiation was 10.2 W; the duration of cavitation was equal to 300 sec, and exposure – 600 sec (accepted on the basis of the results of previous studies). In adiabatic conditions, the reduction of the C_6H_6 concentration to the MPC was achieved in three periods of “excitation – exposition” (Fig. 3).

A greater angle of inclination of individual areas corresponding to the cavitation mode meant an increase in the speed of the process; at the same time, the temperature of the solution increased by 4.5...5 degrees. During exposure, the temperature decreased due to heat transfer to the environment. The average rate of benzene destruction during cavitation was almost twice as high as during solution exposure in the corresponding periods. Thus, in periods I and II, the rate of benzene decomposition during cavitation was $11.63 \cdot 10^{-3}$ and $3.50 \cdot 10^{-3} \text{ mol/sec} \cdot \text{m}^3$, while during exposure it was $1.71 \cdot 10^{-3}$ and $1,31 \cdot 10^{-3} \text{ mol/sec} \cdot \text{m}^3$. At the same time, it is worth noting that during exposure, the destruction of benzene continued, albeit at a slower rate. Interestingly, in the III period, the rate of benzene decomposition during cavitation was higher than in the II period and was $5.52 \cdot 10^{-3} \text{ mol/s} \cdot \text{m}^3$. This can be explained by an increase in the temperature of the reaction medium to 307 K under adiabatic conditions. An increase in the temperature of the solution contributes to an increase in the rate of benzene destruction during cavitation. During 30 min. a degree of benzene conversion of ~70 % was achieved. The total duration of the process until the maximum permissible concentration (MPC) of benzene is reached is ~50 min. The energy consumption for the decomposition of benzene under periodic excitation of cavitation in adiabatic conditions is about 9000 kJ/mol.

The obtained results convincingly testify to the radical mechanism of oxidative destruction of benzene, which is initiated by cavitation phenomena.

In the future, the decomposition of benzene was studied after mixing certain volumes of MBS: pre-activated by cavitation and initial. The research was carried out at different ratios of cavitationally activated (CAMBS) and initial (IMBS) model benzene solution; duration of cavitation treatment of MBS was 10 and 30 min.

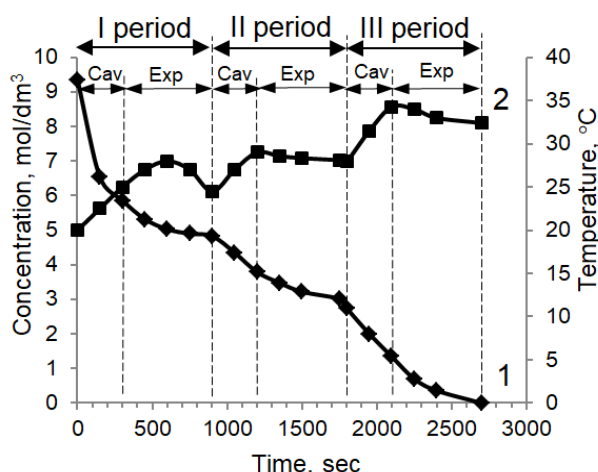


Fig. 3. Dependence of benzene concentration (1) and medium temperature (2) on time in adiabatic conditions: mode: Cav – cavitation; Exp – exposures (without cavitation)

During 10 min under the influence of ultrasound radiation with a power of 10.2 W, the concentration of C_6H_6 (volume of MBS 100 cm^3) decreased from 9.35 to 4.58 mol/m^3 (section A_1B_1 in Fig. 4). After that, 25 cm^3 of CAMBS was quickly taken from the reaction mixture and added to 75 cm^3 of IMBS with intensive stirring (CAMBS content in the mixture was 25 %) and in contact with air. The concentration of C_6H_6 in the mixture was calculated based on the content of C_6H_6 in CAMBS and IMBS and their volumes – it was equal to 7.52 mol/m^3 (point C_1 , Fig. 4). After that, the benzene content in the reaction mixture was periodically determined under constant intensive stirring (section D_1E_1 , Fig. 4). After 30 min (after mixing CAMBS and IMBS) the degree of C_6H_6 conversion was equal to 72 %. The estimated duration of the process until reaching the MPC was about 80 min.

Similar studies were conducted with preliminary cavitation activation of simulated wastewater for 30 minutes. The ratio between CAMBS and IMBS was the same – 1:3. Changes in the concentration of C_6H_6 in MBS during cavitation treatment and in a mixture of CAMBS and IMBS are shown in Fig. 4 (sections A_2B_2 and C_2E_2). Within 600 sec after mixing CAMBS with IMBS, the degree of conversion was ~66 %, and the duration of the process was ~95 min. Therefore, increasing the duration of cavitation treatment of MBS slightly reduces the efficiency of benzene decomposition. This confirms the conclusion about the radical mechanism of the

process: with an increase in the concentration of radicals formed during cavitation in the solution, the probability of their recombination increases and the probability of interaction with benzene decreases. In addition, an increase in the duration of wastewater treatment will lead to an unproductive increase in energy consumption for the implementation of the process. Therefore, further studies were carried out with the processing of MBS for 600 sec and the content of CAMBS in a mixture with IMBS 15; 10; 5 %. It is interesting that the dependences of the change in the concentration of C_6H_6 for the above-mentioned content in the mixture differed very little from those for 25 % of the CAMBS content, which led to conducting research at an even lower (0.25–1.00 %) CAMBS content in the mixture with IMBS (Fig. 5).

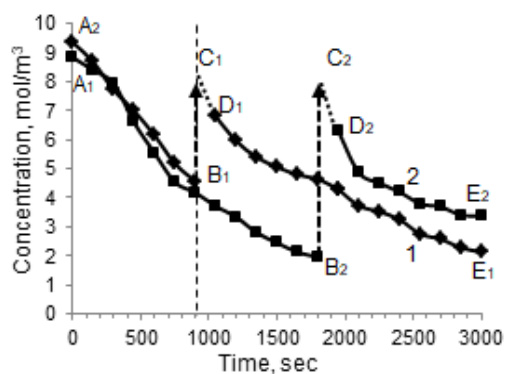


Fig. 4. Dependence of benzene concentration on time: during cavitation activation of MBS (areas A_1B_1 and A_2B_2); after mixing CAMBS and IMBS (areas C_1E_1 and C_2E_2) with a volume ratio of CAMBS and IMBS = 1 : 3; duration of cavitation treatment of MBS, sec: 1 – 600; 2 – 1800 (the moment of addition of CAMBS is shown by an arrow)

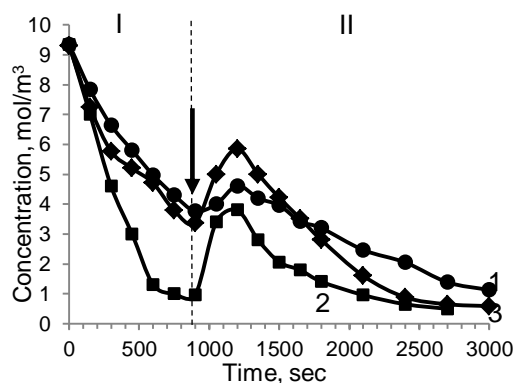


Fig. 5. Dependence of benzene concentration on time during MBS processing and after mixing CAMBS and PMBS (introduction of CAMBS is shown by an arrow); the content of CAMBS in the mixture, %: 1 – 0.5; 2 – 0.75; 3 – 1.0

The change in the degree of conversion of benzene from the moment of mixing CAMBS with IMBS is shown in Fig. 6 (the initial concentration of C_6H_6 in the mixture of CAMBS with IMBS was taken to be equal to its concentration in the original solution).

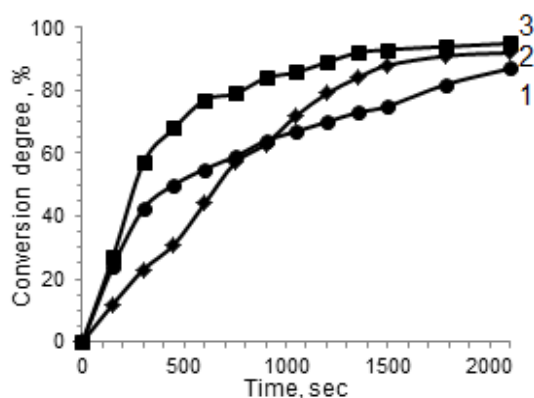


Fig. 6. Dependence of the degree of benzene conversion on time after mixing CAMBS with IMBS; the content of CAMBS in the mixture, %: 1 – 0.5; 2 – 0.75; 3 – 1.0

For the content of CAMBS in a mixture with IMBS 1.00; 0.75; 0.50 % time to reach MPC is about 52, 47 and 67 minutes respectively (Fig. 7). A further decrease in the content of CAMBS causes a sharp decrease in the rate of benzene destruction and, accordingly, an increase in the duration of the process.

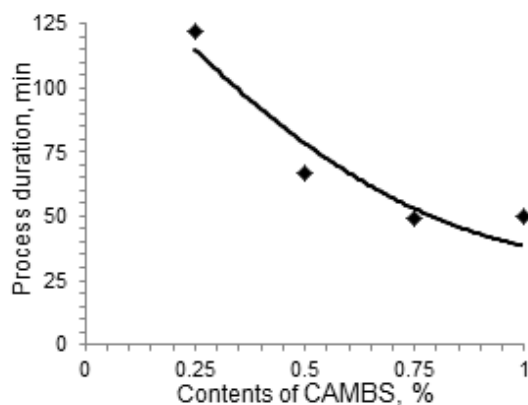


Fig. 7. Dependence of the duration of benzene transformation on the volume content of CAMBS in the mixture

Therefore, for effective benzene removal, it is advisable to activate about 1 % of wastewater by cavitation and then mix it with untreated water. The specific energy consumption for the destruction of benzene will be about 10 kJ/m^3 (0.17 kW/m^3).

To confirm the role of oxygen in the destruction of benzene, its decomposition was investigated after mixing CAMBS with IMBS both under constant stirring, which ensured oxygen absorption, and without stirring (Fig. 8).

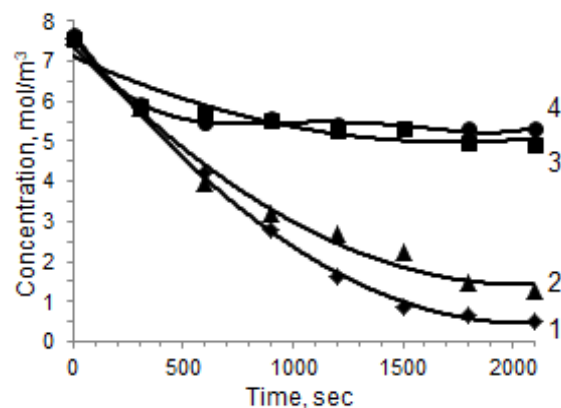


Fig. 8. Dependence of benzene concentration on time in a mixture of CAMBS with IMBS; the content of COI in the mixture, %: 1 – 1.0; 2 – 0.25; hydrodynamic conditions: 1, 2 – with mixing; 3, 4 – without mixing

As expected, without mixing, that is, practically without oxygen absorption, the destruction of benzene practically does not occur (Fig. 8, curves 3 and 4). In addition, the change in the concentration of benzene (in contrast to the mixing process) with the content of CAMBS in the mixture of 1.0 and 0.25 % is practically the same. This confirms the role of oxygen in the destruction of benzene as a radical process. The decrease in the concentration of benzene during the first 600 sec of the process is due to the absorption of oxygen from the air during the preparation of the model solution. Therefore, in all cases during this time, the rate of benzene destruction was the same and equal to approximately $5.7 \cdot 10^{-3} \text{ mol/sec} \cdot \text{m}^3$. But with limited oxygen access, the process of benzene decomposition quickly subsides (Fig. 8, curves 3 and 4). With intensive absorption of oxygen, oxidation occurred according to patterns similar to those given above. This convincingly confirms the very important role of oxygen in the destruction of benzene precisely as an oxidative process.

The results obtained on a laboratory setup with an ultrasonic emitter were confirmed during technological studies using a hydrodynamic cavitator (Fig. 9). After the cessation of cavitation excitation for 30 min (the pressure in front of the cavitator was equal to 0.39 MPa, air consumption $80 \text{ cm}^3/\text{min}$), the

solution was still circulated in the installation with constant mixing and air supply for another 40 min. Circulation of the environment is necessary for uniform and constant absorption of oxygen. There was a kind of exposition of MRB (the pressure in front of the cavitator was equal to 0.1 MPa, under these conditions cavitation is not excited). At the same time, a further decrease in the concentration of benzene was observed (Fig. 9). The total degree of benzene conversion after 70 min (30 min – cavitation, 40 min – exposure) was equal to 92.8 %.

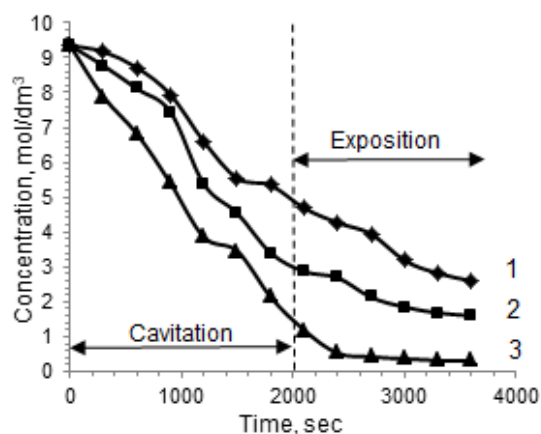


Fig. 9. Dependence of benzene concentration on time: air consumption, cm^3/min : 1 – 40; 2 – 60; 3 – 80

An increase in the flow of air, which is supplied to the water environment in front of the hydrodynamic cavitator, contributes to the destruction of benzene.

If the benzene solution was subjected to continuous cavitation treatment for 70 minutes (thousand 0.39 MPa, air flow rate $80 \text{ cm}^3/\text{min}$), the degree of benzene conversion decreased by 15 %. This is probably due to the intense recombination of radicals that are formed during cavitation.

In the case of a hydrodynamic cavitator, the pump consumes a large amount of energy to circulate the reaction solution for a longer period of time, say 70 min. However, limiting cavitation to the first 30 minutes reduces the pump power consumption required for the total treatment time, which reduces the total treatment cost. Therefore, the use of cavitation within a limited treatment time can be considered a cost-effective approach to benzene degradation. However, a necessary condition for the decomposition of benzene in this mode is the presence of oxygen in the reaction system.

Conclusions

The process of cavitation destruction of benzene takes place by a radical mechanism with the participation of oxygen absorbed from the air.

Oxidative destruction of benzene is characterized by the presence of a “threshold” energy value equal to $51 \text{ kJ}/\text{dm}^3$ ($68 \text{ W}/\text{dm}^3$), after its introduction into the water-benzene solution, the destruction of benzene can occur even after the cessation of cavitation, but with the mandatory presence in the oxygen system.

Reduction of energy consumption for the destruction of benzene is achieved by carrying out the process in the periodic “cavitation–exposure” mode, provided that the duration of the cavitation mode ensures the introduction of energy, the value of which is not less than the “threshold”.

To neutralize benzene, it is not advisable to treat the entire volume of wastewater – it is enough to initiate the process by treating only part of it (about 1 % of the total volume).

The work was carried out with the support of the Ministry of Education and Science of Ukraine within the framework of the joint Ukrainian-Indian research project “Hydrodynamic cavitation as the basis of an energy-saving technology for cleaning wastewater of industrial enterprises from toxic organic compounds and solid-phase dispersed particles”.

References

1. Rahman, W., Khan, M. D., Khan, M. Z., Halder, G. (2018). Anaerobic biodegradation of benzene-laden wastewater under mesophilic environment and simultaneous recovery of methane-rich biogas, *Journal of Environmental Chemical Engineering.*, 6 (2), 2957-2964. doi.org/10.1016/j.jece.2018.04.038.
2. Atashgahi, S., Hornung, B., Van Der Waals, M. J., Da Rocha, U. N., Hugenholtz, F., Nijse, B., Molenaar, D., Van Spanning, R., Stams, A. J. M., Gerritse, J., Smidt, H. (2018). A benzene-degrading nitrate-reducing microbial consortium displays aerobic and anaerobic benzene degradation pathways. *Sci. Rep.*, 8, 1–12. doi: 10.1038/s41598-018-22617-x.
3. Gomathi, Devi, L., Krishnaiah, G.M. (1999). Photocatalytic degradation of p-amino-azo-benzene and p-hydroxy-azo-benzene using various heat treated TiO_2 as the photocatalyst. *J. Photochem. Photobiol. A: Chem.*, 121, 141–145.
4. Yu, H., Ming, H., Zhang, H., Li, Pan, H. K., Liu, Y., Wang, F., Gong, J., Kang, Z. (2012). Au/ZnO nanocomposites: Facile fabrication and enhanced photocatalytic activity for degradation of benzene. *Mater. Chem. Phys.*, 137, 113–117. doi.org/10.1016/j.matchemphys.2012.02.076.

5. Zin, O., Sukhatskiy, Yu., Znak, Z., Lysenko, A. V. (2017). Cavitation decomposition of benzene under acoustic radiation of ultrasonic range. *Visnyk Natsionalnoho universytetu "Lvivska politekhnika"*. *Khimiia, tekhnolohiia rehovyn ta yikh zastosuvannia*, 868, 273–278.
6. Znak, Z. O., Sukhatskiy, Yu. V., Zin, O. I., Khomyak, S. V., Mnykh, R. V., Lysenko, A. V. (2018). The decomposition of the benzene in cavitation fields. *Voprosy Khimii i Khimicheskoi Tekhnologii*, 1(116), 72–77.
7. Braeutigam, P., Wu, Z. L., Stark, A., Ondruschka, B. (2009). Degradation of BTEX in aqueous solution by hydrodynamic cavitation. *Chem. Eng. Technol.*, 32(5), 745–753. doi:10.1002/ceat.200800626.
8. Dhanke, P. B., Wagh, S. M. (2020). Intensification of the degradation of Acid RED-18 using hydrodynamic cavitation. *Emerg. Contam.*, 6, 20–32. doi: 10.1016/j.ultsonch.2022.106144.
9. Ramteke, L. P., Gogate, P. R. (2015). Treatment of toluene, benzene, naphthalene and xylene (BTNXs) containing wastewater using improved biological oxidation with pre-treatment using Fenton/ultrasound based processes. *J. Ind. Eng. Chem.*, 28, 247–260. doi.org/10.1016/j.jiec.2015.02.022.
10. Weschayanwivat, P., Kunanupap, O., Scamehorn, J. F. (2008). Benzene removal from waste water using aqueous surfactant two-phase extraction with cationic and anionic surfactant mixtures. *Chemosphere*, 72, 1043–1048. DOI: 10.1016/j.chemosphere.2008.03.065.
11. Wu, Z., Lifka, J., Ondruschka, B. (2004). Aquasonolysis of selected cyclic C₆H_x hydrocarbons. *Ultrason. Sonochem*, 11, 187–190. DOI: 10.1016/j.ultsonch.2004.01.028.
12. Thanekar, P., Gogate, P. R., Znak, Z., Sukhatskiy, Y., Mnykh, R. (2021). Degradation of benzene present in wastewater using hydrodynamic cavitation in combination with air. *Ultrasonics Sonochemistry*, 70, 105296. doi.org/10.1016/j.ultsonch.2020.105296.
13. Barik, A. J., Gogate, P. R. (2016). Degradation of 4-chloro 2-aminophenol using a novel combined process based on hydrodynamic cavitation, UV photolysis and ozone. *Ultrason. Sonochem*, 30, 70–78. DOI: 10.1016/j.ultsonch.2015.11.007.
14. Goel, M., Hongqiang, H., Mujumdar, A. S., Ray, M. B. (2004). Sonochemical decomposition of volatile and non-volatile organic compounds – A comparative study. *Water Res.*, 38, 4247–4261. DOI: 10.1016/j.watres.2004.08.008.
15. Weavers, L. K., Ling, F. H., Hoffmann, M. R. (1998). Aromatic compound degradation in water using a combination of sonolysis and ozonolysis. *Environ. Sci. Technol*, 32, 2727–2733. DOI: 10.1021/es970675a.

З. О. Знак¹, Ю. В. Сухацький¹, П. Р. Гогейт², Р. В. Мних¹, П. Танекар²

¹ Національний університет "Львівська політехніка",
кафедра хімії і технології неорганічних речовин,

² Інститут хімічної технології, Мумбаї, Індія,
кафедра хімічної інженерії

ОКИСНА ДЕСТРУКЦІЯ БЕНЗЕНУ В УМОВАХ НЕСТАЦІОНАРНОГО ЗБУДЖЕННЯ КАВІТАЦІЇ

Встановлено порогове значення енергії, необхідної для деградації бензену після припинення збудження кавітації. Визначено закономірності окисної деградації бензену в циклічному режимі "кавітація–експозиція". Показано можливість деградації бензену у разі ініціювання процесу введенням до водно-бензенового середовища деякої кількості попередньо кавітаційно активованої його частини. Експериментально підтверджено роль кисню в процесі кавітаційної деградації бензену.

Ключові слова: бензен; ультразвук; кавітація, ініціювання, "порогова" енергія, періодичне збудження кавітації.