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Ozonation as a means of increasing the ecological safety of agrosystems: Purification of soils and irrigation water from toluene and its derivatives

Abstract. The aim of the study was to evaluate the effectiveness of liquid-phase ozonation of methylbenzenes as a method for neutralising aromatic xenobiotics in surface waters and soils of agroecosystems. Spectrophotometric, iodometric, chromatographic, and elemental analysis methods were used to study the dynamics of aromatic ring destruction, the formation of intermediate and final products, and to determine the reactivity of arene derivatives. It was established that the main pathway for the conversion of methylbenzenes is the ozonolytic cleavage of the benzene ring, with the formation of aliphatic ozonides. The yield of benzoic acid did not exceed 5.8%, which indicates insignificant stabilisation of the aromatic fragment. For p-xylene, the degree of mineralisation reached over 70% after 30 minutes of ozonation. The presence of donor substituents in the benzene ring ($-CH_3$, $-OH$, $-NH_2$) contributed to deep core destruction, while acceptor substituents ($-NO_2$, $-COOH$) reduced its reactivity, changing the direction of the reaction to the side alkyl chain. Derivatives with functional groups capable of nucleophilic attack ($-OH$, $-NH_2$, $-SH$) were characterised by a significantly higher reaction rate (up to 25 times) compared to toluene. The acylation of such groups with acetic anhydride lowered the reaction rate and increased the selectivity for the formation of stable products. Particular attention was paid to the composition and structure of the reaction products. Peroxides formed as a result of the destruction of the aromatic ring have different structures, ranging from monomeric to oligomeric forms. They were highly soluble in acetic acid but were easily precipitated or removed from the solution, which was a key advantage of the process in water and soil purification applications. The data obtained demonstrated the potential of liquid-phase ozonation as an effective tool for the selective and controlled neutralisation of aromatic compounds in soils and waters for agricultural use. The results obtained can be used by ecologists, agrochemists, and water purification specialists to increase the ecological safety of agricultural areas and irrigation systems contaminated with aromatic compounds

Keywords: ozone; methylbenzenes; destruction; peroxides; water purification; kinetics

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INTRODUCTION

Modern agriculture faces the urgent problem of pollution of agroecosystems with organic pollutants, in particular toluene derivatives, which enter the soil and water resources through the use of pesticides, herbicides, fuels and lubricants, and industrial emissions. These compounds have high resistance to biodegradation, which leads to their accumulation in the soil environment, a decrease in the biological activity of soils and a deterioration in crop quality. Given the importance of preserving soil fertility and water resource safety, the development of effective, environmentally safe methods for cleaning up such pollutants is a pressing task for agricultural science.

The authors S. Lim *et al.* (2022) emphasise in their work the promise of liquid-phase ozonation as a method for the deep destruction of aromatic pollutants in water systems. They note that ozone in the liquid phase forms highly active hydroxyl radicals that are capable of effectively breaking down sTable organic structures, including toluene and its derivatives. B. Liao *et al.* (2022) investigated the mechanisms of ozone oxidation of methylbenzenes and found that the electronic properties of substituents in the benzene ring significantly affect the selectivity and reaction rate. The work of H. Luo *et al.* (2021) shows that the nature of substituents determines the decomposition pathways of aromatic compounds and influences the formation of oxidation products, which is of particular importance for Ukrainian agroecosystems.

Research by A. Salnikova & S. Salnikov (2021) confirmed the effectiveness of the combined use of ozonation and solar sterilisation to reduce the concentration of pesticides in irrigation water, while minimising the negative impact on soil microbiota. O. Chayuk (2019) points out the importance of analysing the formation of peroxide compounds in the process of aromatic substance destruction, as they can have both a positive effect on oxidative potential and be potentially toxic to some members of the microflora. M. Tahamolkonan *et al.* (2022) draw attention to the need to optimise ozone dosing, as excessive concentrations can inhibit soil microbial activity and disrupt natural biogeochemical cycles.

The work of S. Lim *et al.* (2022) emphasises the importance of the spatial arrangement of substituents in aromatic molecules, as this directly affects the kinetics of ozonation reactions and the formation of minor products. A recent study by X. Li *et al.* (2021) demonstrated that enhanced ozonation with the addition of mechanical stirring provides over 90% degradation of benzo[a]pyrene in soil in just 90 minutes, while improving the bioavailability of residual products for further microbial degradation. An analysis of bioremediation methods that complement ozonation is presented in a review by C. Rusănescu *et al.* (2024), which justifies the combination of physicochemical and biological technologies to complement effective strategies for the restoration of contaminated soils.

Based on current research, it has been established that ozonation is a promising and environmentally safe method for the degradation of toluene and related aromatic compounds in agroecosystems. This approach demonstrates high efficiency in cleaning soils and water environments from persistent organic pollutants. At the same time, for practical implementation, it necessary to study in depth the mechanisms of ozonolysis under different soil conditions, in particular its impact on soil fertility, enzymatic activity and microbiota structure. The aim of this work was to conduct a comprehensive analysis of the effectiveness of liquid-phase ozonation of toluene and its derivatives, as well as to determine the optimal conditions for environmental safety and restoration of the fertility of agricultural systems.

LITERATURE REVIEW

The contamination of agricultural ecosystems with organic toxicants, among which toluene derivatives occupy a special place, poses a serious environmental threat to the sustainable development of agriculture. These compounds enter soil and water resources mainly through the excessive use of agrochemicals, such as herbicides and pesticides, as well as through the use of petroleum products and technical fluids containing aromatic hydrocarbons. Sources of pollution also include untreated industrial wastewater. Due to their high chemical stability and low susceptibility to natural decomposition, these substances accumulate in the soil environment. This, in turn, leads to a decrease in the enzymatic activity of soil biota, disruption of the microbial balance and a general deterioration in fertility, which negatively affects the quality and safety of agricultural products (Aidoo *et al.*, 2023).

Against this backdrop, innovative methods of detoxifying the agricultural environment deserve increasing attention. One of the most promising technologies is ozonation, a process based on the use of a strong oxidant, ozone, which is capable of destroying complex organic molecules. Ozone oxidation is accompanied by the generation of secondary active agents, in particular hydroxyl radicals, which demonstrate high reactivity towards aromatic hydrocarbons, including benzene and toluene structures. The results of laboratory and field studies show that ozone, acting directly in the soil, promotes the decomposition of heavy organic compounds into less toxic intermediate products that are more accessible for further biological degradation. This significantly enhances the ability of soil microorganisms to mineralise hydrocarbon residues (Yu *et al.*, 2024).

The combined use of ozonation with other physical, chemical or biological methods is particularly effective. For example, the combination with soil solarisation demonstrates a synergistic effect on the decomposition of persistent pesticides, while maintaining the overall microbial viability and bioactivity of the soil at an accepTable level (Díaz-López *et al.*, 2021). However, along with the positive results, a number of studies have found that excessive or improperly regulated ozonation can have a suppressive effect on soil microflora, in particular through the oxidation of beneficial metabolites or the destruction of cell structures (Garrido *et al.*, 2023). This highlights the need to optimise ozone exposure regimes according to soil type, degree of contamination and agroecosystem specifics.

In a study by E. Potapenko *et al.* (2021), the kinetics and mechanism of ozonolysis of arenes were investigated. It was shown that ozone can interact with both the side methyl radical and the aromatic ring, resulting in the formation of a wide range of products, from benzoic acid to unsTable peroxides. The authors proved that the solvent significantly influences the direction of the reaction. The study of the ozonolysis of 2,4-dinitrotoluene deserves special attention. It was found that in the presence of electron-accepting substituents (–NO_2), ozone attacks both the benzene ring and the side chain. The formation of hydroperoxides indicates a radical mechanism, with the temperature regime influencing the predominant direction of the reaction: at lower temperatures, ring attack prevails. The work of A. Galstyan *et al.* (2018) considers the reactions of ozone with aminotoluenes. It is shown that electron-donating groups activate the aromatic system to electrophilic attack by ozone. In acetic anhydride, with the participation of mineral acid, acylation of amino groups occurs, which changes the reactivity of the molecule. Even without catalysts, the reaction is selective and produces sTable aliphatic products. These works are an important basis for further research in the field of pollutant processing, organic synthesis and environmental chemistry. In addition to soil purification, ozonation is also actively being introduced for post-harvest processing of vegetables and fruits. In particular, the use of ozonated water for washing products significantly reduces the residual concentrations of agrochemicals, unlike conventional water washing, which has limited effectiveness in removing hydrophobic compounds (Singh *et al.*, 2022). This approach not only improves food safety but also extends the shelf life of products.

Another interesting area of research is the effect of ozonation on physiological and biochemical processes in plants. For example, ozone treatment of seeds causes changes in the profile of volatile organic compounds, which can serve as biomarkers of germination or stress response (Khanashyam *et al.*, 2021; Dong *et al.*, 2022). Such effects open up new possibilities in pre-sowing seed treatment as a method of stimulating growth processes.

Separately, it should be mentioned that there are studies investigating the interaction of ozone with the processes of microbial degradation of organic pollutants. For example, hybrid systems combining ozonation with biological treatment have shown high efficiency in destroying polycyclic aromatic hydrocarbons in soil, even under conditions of increased pollution (Olak-Kucharczyk *et al.*, 2023, Malek & Choudhary, 2023). Such results confirm the potential of combined methods as tools for restoring the functional state of degraded agricultural landscapes.

Given the accumulated results, there was a clear need for further study of the possibilities of ozonation as a means of remediating agricultural systems. In particular, research into the kinetics and mechanism of ozonolysis of methylbenzenes, the effectiveness of their neutralisation with ozone, and the impact of this process on long-term soil fertility, their microbiological balance and the ecological stability of the agrosphere as a whole remain relevant.

MATERIALS AND METHODS

Laboratory studies were conducted at the Research Laboratory of Ozonolytic Transformations of the National University of Life and Environmental Sciences of Ukraine (Kyiv) between January and April 2025. High-purity chemical reagents were used for the experiments: sulphuric and glacial acetic acids from Sigma-Aldrich ("chemically pure" grade), toluene and its substitutes from Acros Organics ("chemically pure" grade). The water for the solutions was demineralised.

Acylation of hydroxy- and aminotoluenes was carried out according to a method in which 0.4 mol·l-1 of aminotoluene and 30 ml of 80% acetic acid were loaded into a 50 ml round-bottom flask. When the solution was gradually heated to 130-140 °C, the water was distilled off, after which the resulting product was separated into 30 ml of water cooled to 5 °C, filtered and dried. Ozone oxidation was carried out in a cylindrical glass reactor with a volume of 30 ml (height – 8 cm, diameter – 2.2 cm) with a perforated diaphragm for better contact between the gas and liquid phases. 20 ml of solvent and the calculated amount of arenes were loaded into the reactor. The ozone generator was model OZ-100 (manufacturer: OzoneTech Ltd., Ukraine). Ozone was produced by corona discharge at a voltage of 7 kV, a current of 20 mA, water cooling, with constant regulation of the generator temperature at 25 ± 1 °C. The ozone concentration in the gas mixture was controlled using a built-in spectrophotometric analyser with an accuracy of ± 0.02% by volume and was automatically stabilised by a feedback system.

The kinetics of the reactions were studied as follows. The ozone-air mixture was fed into the reactor at a rate of 20 l/h, with an ozone concentration of 0.8-1.2% by volume. Ozonation lasted from 15 to 120 minutes, depending on the experimental conditions. During the reaction, magnetic stirring at a speed of 300 rpm was used to ensure uniform distribution of ozone in the liquid. The process was controlled by gas chromatography on an Agilent 7890B chromatograph with a flame ionisation detector (FID), HP-5 column (length 30 m, diameter 0.32 mm, film thickness 0.25 μm) (Potapenko *et al.*, 2021). The evaporator temperature was 250 °C, and the column temperature was programmed from 120 to 175 °C with a rise rate of 8 °C/min. The carrier gas is nitrogen, flow rate: 2.0 l/min, hydrogen – 1.8 l/min, air – 18 l/min.

The ozone concentration in the gas phase was measured spectrophotometrically using a SF-46 LOMO spectrophotometer with a Teflon flow cell (optical path length 10-100 mm). The optical density of the gas flow was recorded automatically by a potentiometer with a error of ≤ 5%. The ozone concentration was calculated using the Lambert-Beer equation with molar extinction coefficients.

Quantitative analysis of peroxides was performed by iodometric titration: 1 ml of the reaction mass was added to 10 ml of a 5% potassium iodide solution, acidified with 2.5 ml of 0.1 M sulphuric acid, kept for 1 and 24 hours at 20 ± 2 °C, and then titrated with 0.05 M sodium thiosulphate solution. The concentration of peroxides was calculated using the formula (1):

$$[oz] = \frac{V_T M_T}{n\mathrm{Vp}}, \mathrm{mol} \cdot \mathrm{l}^{-1}, \qquad (1)$$

where V_T is the volume of sodium thiosulphate for titrating the iodine solution, ml; V_p is the volume of the reaction mass, ml; M_T is the molar concentration of thiosulphate, mol · l^{-1}; n is the number of transferred electrons.

The relative measurement error was ±8%.

The rate constant for the new substance, knowing the constant for toluene and the ratio of products in the reaction mixture, was determined by the formula (2):

$$K_{sub}/k_{st} = [P_{sub}]/[P_{st}], \quad (2)$$

where k_{sub} – the desired value of the constant; k_{st} – the known constant for the standard substance; $[P_{sub}]$, $[P_{st}]$ – the concentrations of the corresponding reaction products.

Statistical data processing was performed using the program OriginPro 2023. For each experiment, at least three parallel determinations were performed. The results are presented as the mean arithmetic value ± the standard deviation. Statistical significance was determined using the Student's t-criterion at a significance level of $p < 0.05$.

RESULTS AND DISCUSSION

To determine the possibility of cleaning surface water and soil from aromatic compounds, the kinetics of the liquid-phase ozonation reaction of methylbenzenes was investigated. As it turned out, the main products of toluene oxidation by ozone are ozonides – aliphatic products of aromatic ring destruction, which is also described in the work of R. Samsami *et al.* (2023). In trace amounts, benzyl alcohol and benzaldehyde, CO_2 accumulate as intermediate products, while benzoic acid is the final product of the aromatic reaction, the yield of which does not exceed 6% (Table 1).

Table 1. Oxidation of methylbenzenes with ozone in acetic acid at 293 K.
$[O_3]_0 = 4.7 \cdot 10^{-4}$; $[ArCH_3]_0 = 0.4\ mol \cdot l^{-1}$; Vp = 0.01 l

Compounds	Selectivity, %	
	oxidation via the side chain	oxidation via the aromatic ring
Toluene	5.9	93.6
1,4-Dimethylbenzene	5.1	92.3
1,3-Dimethylbenzene	4.6	92.5
1,2-Dimethylbenzene	0.0	99.5
1,3,5-Trimethylbenzene	0.0	100.0
2-Nitrotoluene	6.2	89.0
3-Nitrotoluene	12.4	82.0
4-Nitrotoluene	14.2	81.5
3-Chlorotoluene	13.1	84.2
4-Toluenesulfonyl chloride	26.3	72.1

Source: developed by the author

The composition of the products of the ozonation of methylbenzenes in the liquid phase indicates the following: the reaction proceeds in two directions: mainly via the benzene ring with the formation of its degradation products, and via the side chain of the substrate with the formation of aromatic products; with an increase in donor substituents in the aromatic ring, the selectivity of oxidation along the side chain decreases; the stability of the benzene ring in the reaction with ozone increases with the introduction of acceptor substituents. During ozonation of 1,3- and 1,4-dimethylbenzenes, 96% of the substrate is subject to destructive ozonation, while 1,2-dimethylbenzene and 1,3,5-trimethylbenzene are completely converted to ozonides. The stability of the aromatic ring increases with the introduction of acceptor substituents. When ozonising 4-nitrotoluene, the yield of 4-nitrobenzoic acid reaches 14.2%. Similar results were obtained during the oxidation of 3-nitrotoluene. In the case of the 2-isomer, the selectivity for the methyl group is significantly reduced, which is due to the steric effect of the substituent (Table 1).

The results of the study demonstrate that ozonation of methylbenzenes in the liquid phase can effectively neutralise toxic aromatic pollutants through complete or partial destruction of the benzene ring. Of particular importance is the ability of the formed ozonides and peroxides to be easily removed from the solution – these compounds precipitate or break down into volatile components, which greatly simplifies the purification of water and soil from reaction residues.

The values of the ozone absorption rate constants in reactions with methylbenzenes given in Table 2 indicate a satisfactory correlation between the reactivity of substituted toluenes (with the exception of hydroxy-, amino- and mercapto-toluene) and the substituent constants (σ). The calculated ρ for this series is -2.25, which indicates an electrophilic mechanism for the reaction of ozone with methylbenzenes.

Table 1. Rate constants for the reaction of ozone with methylbenzenes at 293 K

Compound	$[O_3]_o \cdot 10^4$, mol · l^{-1}	[ArH]o · 10^2, mol · l^{-1}	Keff, l · mol^{-1} · s^{-1}	
			AcOH	Ac_2O
Toluene	0.28 ÷ 0.57	7.7 ÷ 28.3	0.80 ± 0.08	0.88 ± 0.08
1,2-Dimethylbenzene	0.18 ÷ 0.33	5.4 ÷ 7.3	0.88 ± 0.08	3.08 ± 0.30
1,3-Dimethylbenzene	0.18 ÷ 0.33	5.4 ÷ 7.3	4.15 ± 0.40	4.56 ± 0.50
1,4-Dimethylbenzene	0.18 ÷ 0.33	5.4 ÷ 7.3	5.00 ± 0.50	5.61 ± 0.50
1,3,4-Trimethylbenzene	0.18 ÷ 0.33	2.4 ÷ 5.3	29.60 ± 3.00	32.54 ± 3.00
1,3,5-Trimethylbenzene	0.18 ÷ 0.33	2.4 ÷ 5.3	45.10 ± 0.45	50.56 ± 5.00
4-Hydroxytoluene	0.24 ÷ 0.51	0.2 ÷ 0.6	2.22 · 103	2.43 · 103
4-Aminotoluene	0.14 ÷ 0.41	0.2 ÷ 0.6	2.42 · 103	2.66 · 103
4-Acetamidotoluene	0.18 ÷ 0.45	10.1 ÷ 25.9	0.81 ± 0.07	0.85 ± 0.05
4-Acetoxytoluene	0.28 ÷ 0.57	15.1 ÷ 35.9	0.59 ± 0.05	0.66 ± 0.06
4-Nitrotoluene	0.38 ÷ 0.55	25.5 ÷ 48.0	0.035 ± 0.004	0.083 ± 0.006
3,4-Dinitrotoluene	0.38 ÷ 0.55	25.5 ÷ 48.0	0.020 ± 0.002	0.022 ± 0.002
2,4-Dinitrotoluene	0.38 ÷ 0.55	25.5 ÷ 48.0	0.016 ± 0.002	0.018 ± 0.002

Source: developed by the author

A different kinetic picture is observed upon ozonation of methylbenzenes that have substituents with lone electron pairs ($-OH$, $-NH_2$, $-SH$). Firstly, under these conditions, oxidation via the methyl group does not occur, the main reaction products in the case of hydroxytoluenes are ozonides, and for aminotoluenes – ozonides, nitrotoluenes, and polymeric products. Secondly, their reactivity is three orders of magnitude higher ($k_{eff} = 2.22 \cdot 10^3$ l · mol^{-1}·s^{-1}) than the reactivity of methylbenzenes ($k_{eff} = 0.8$ l · mol^{-1} · s^{-1}). All of this is explained by the fact that ozone attacks not the methyl group or the aromatic ring, but primarily the lone pair of electrons of the heteroatom (Galstyan *et al.*, 2009). A change in the direction of ozone attack and its partial redirection to the methyl group is achieved under the conditions of prior acylation of the hydroxy- and amino groups with acetic anhydride. The effective rate constant decreases by three orders of magnitude and approaches the value for methylbenzene (Table 2). The direction of the reaction becomes typical for the ozonation of methylbenzenes – via the double bonds of the aromatic ring and, to a lesser extent, via the methyl group with the formation of acetamido- and acetoxybenzoic acids (Table 3). Corresponding aromatic alcohols and aldehydes were identified as intermediate oxidation products. It is not possible to stop the process at the stage of their predominant formation, as is the case with methylbenzenes, under these conditions.

Table 3. Dependence of the selectivity of methylbenzene oxidation with ozone on the substrate structure at 293 K

Compound	Selectivity, %		
	Via the methyl group	Via the aromatic ring	Unidentified products
Toluene	5.9	80.3	3.7
2-Acetamidotoluene	5.1	92.9	2.0
3-Acetamidotoluene	14.2	84.7	1.1

Table 3, Continued

Compound	Selectivity, %		
	Via the methyl group	Via the aromatic ring	Unidentified products
4-Acetamidotoluene	15.5	83.5	1.0
2-Acetoxytoluene	7.5	90.5	2.0
3-Acetoxytoluene	17.3	80.5	2.2
4-Acetoxytoluene	19.8	78.6	1.6

Note: $[O_3]_0 = 4.7 \cdot 10^{-4}$; $[ArCH_3]_0 = 0.4$ mol·l^{-1}; Vp = 0.01 l
Source: developed by the author

To clarify the chemical structure of ozonides – products of aromatic ring destruction – after oxidation under a vacuum of 5 mm Hg, the solvent was distilled off. The isolated compounds were oily, viscous, light yellow liquids, highly soluble in acetic acid and its anhydride, but poorly soluble in dichlorethane. They reacted with potassium iodide, but in different ways. Toluene, di- and trimethylbenzene peroxides interact with potassium iodide in two stages: the first being rapid, during which molecular iodine is released in an amount equivalent to one peroxide group, and the second being slow (≈ 24 hours) with the release of iodine in an amount equivalent to one or two more peroxide groups. These facts, as well as the stoichiometric coefficient for ozone (n ≈ 2-3), indicate that the specified peroxides are formed through ozonides and are oligomers of linear structure (Galstyan *et al.,* 2009).

Peroxides of nitro-, acetoxy- and acetamidotoluene react with potassium iodide within 1 hour, and molecular iodine is released in an amount equivalent to one peroxide group, i.e. they have a monomeric structure (scheme). These data are consistent with the literature, according to which it is the hydroperoxide groups that easily react with potassium iodide, and the reduction of dialkyl peroxide groups is completed in ≈ 20-24 hours (Potapenko *et al.*, 2021). Thus, depending on the nature of the substituents, peroxides can be monomers or oligomers, but regardless of their structure, they are easily removed from the solution, which contributes to the rapid purification of the agricultural system.

The results confirm the effectiveness of liquid-phase ozonation as a method for deep purification of natural waters and soils from alkyl aromatic pollutants. It has been established that the selection of conditions (environment, temperature, type of substituents) allows the selectivity of the process to be regulated, directing it either towards the preservation of the aromatic ring (for synthetic purposes) or towards its destruction (for ecological neutralisation). The ability of the formed ozonides to precipitate provides a simple scheme for removing reaction products, which is especially valuable in water purification technologies without the need for complex filtration.

The results obtained indicate the effectiveness of liquid-phase ozonation as a method for the disposal of alkyl aromatic compounds in an aqueous environment, which is extremely important in terms of improving the environmental safety of agricultural systems. It has been established that the main direction of methylbenzene oxidation is the destruction of the benzene ring with the formation of ozonides, which is consistent with the results of R. Samsami *et al.* (2023), who described a similar destruction of aromatic rings under the action of ozone. The low yield of aromatic products, such as benzoic acid, indicates the predominance of complete cycle cleavage reactions over partial side chain oxidation.

A comparative analysis of substituted methylbenzenes demonstrated a significant influence of the electronic nature of substituents on the direction and depth of oxidation. The presence of acceptor groups, such as $-NO_2$ and $-SO_2Cl$, contributes to an increase in the stability of the aromatic ring and, accordingly, a decrease in side chain selectivity. This confirms the conclusions made earlier in the work of A. Galstyan *et al.* (2009), where attention was focused on the change in electron density in the ring as a key factor in the interaction with electrophilic ozone. The determined value of $\rho = -2.25$ further confirms the electrophilic nature of the mechanism of interaction of ozone with methylbenzenes, which correlates well with the Hammett parameters of the substituents.

The observation of a change in the reaction mechanism in the presence of substituents with a free electron pair (–OH, $-NH_2$, –SH) deserves special attention. In such cases, the main target of attack is not the aromatic ring, but the heteroatom, which leads to a significant increase in reactivity and a change in the product composition. This opens up the potential for selective modification of the structure of aromatic pollutants prior to their oxidation, in particular by means of preliminary acylation, which "blocks" active groups and changes the course of the reaction. The decrease in the reaction rate after acylation also meets expectations and demonstrates the possibility of regulating the kinetic parameters of the process.

A separate place is occupied by the study of the composition of reaction products: the identification of oligomeric peroxides as destruction products for unsubstituted and weakly substituted arenes and monomeric hydroperoxides in the case of substituted derivatives is a significant contribution to the understanding of the ozonation mechanism. The degree of reaction with potassium iodide, the duration of iodine release, and the behaviour of peroxide compounds confirm the literature data of E. Potapenko & I. Isaenko (2023), which describe the two-stage nature of peroxide reduction depending on their structure.

Thus, the results of the study deepen the understanding of the mechanisms of liquid-phase ozonation of aromatic compounds, allow the classification of reaction products according to structural features, and form the scientific basis for the creation of effective technologies for the purification of water and soil from alkyl aromatic xenobiotics. The practical value is confirmed by the possibility of selective destruction of toxic components with the formation of products that are easily separated from the environment. Since the literature, such as the work of H. Einaga & X. Zheng (2024), focuses mainly on gas-phase ozonation or ultraviolet activation of ozone, the data obtained expand the understanding of the effectiveness of the liquid-phase approach without the need for complex installations.

CONCLUSIONS

Research has shown that liquid-phase ozonation of methylbenzenes is a highly effective method for the destruction of aromatic xenobiotics in the aquatic environment. The main transformation pathway is the destruction of the aromatic ring with the formation of unsTable ozonides, which further decompose into aliphatic products. Side-chain oxidation was observed only in the case of substrates with electron-accepting substituents. It has been established that the electronic nature of substituents in the aromatic ring significantly influences the direction and depth of ozonation. Donor substituents promote ring destruction, while acceptor substituents, on the contrary, reduce the reactivity of the aromatic system, directing oxidation to the side methyl radical. The most pronounced selectivity for the formation of benzoic acid and its derivatives was observed for 4-nitrotoluene and 4-toluenesulphochloride. The rate constants of ozone absorption by substrates show a clear dependence on the Hammett parameter σ, with a correlation coefficient $\rho = -2.25$, which confirms the electrophilic nature of the interaction of ozone with arenes. It has been established that the reaction products are both monomeric and oligomeric peroxide structures, which depend on the nature of the substrate. Peroxides are precipitated from the reaction medium or easily extracted, which enables their effective removal from the aquatic or soil environment. The practical significance of the study lies in confirming the feasibility of using ozonation as a technology for cleaning agroecosystems. The method allows to neutralise residual amounts of herbicides and pesticides in irrigation water; reduce the content of aromatic xenobiotics in soils, increasing biological activity; reduce the toxicity of agrochemical effluents; and promote the creation of closed water systems in agriculture.

From a scientific point of view, the results indicate the possibility of controlled selection of ozonation products by changing the reaction conditions (temperature, ozone concentration, pH of the medium, type of solvent, etc.), which makes the method universal for implementation in environmentally safe technologies for the destruction of organic pollutants. Prospects for further research include the development of scalable ozonation technologies for the treatment of agricultural wastewater; assessment of the impact of ozonation products on soil microbiota; investigation of combined destruction methods (ozonation + bioremediation/photolysis); and study of the toxicological profile of intermediate reaction products.

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Озонування як засіб підвищення екологічної безпеки агросистем: очищення ґрунтів і поливної води від толуену та його похідних

Анотація. Метою дослідження було оцінити ефективність рідиннофазного озонування метилбензенів як способу знешкодження ароматичних ксенобіотиків у поверхневих водах та ґрунтах агроекосистем. У роботі використано спектрофотометричні, йодометричні, хроматографічні методи аналізу та елементний аналіз для вивчення динаміки руйнування ароматичного ядра, утворення проміжних та кінцевих продуктів, а також визначення реакційної здатності похідних аренів. Встановлено, що основним шляхом перетворення метилбензенів є озонолітичне розщеплення бензенового ядра з утворенням аліфатичних озонідів. Вихід бензойної кислоти не перевищував 5,8 %, що свідчить про незначну стабілізацію ароматичного фрагмента. Для п-ксилолу ступінь мінералізації сягав понад 70 % за 30 хв озонування. Наявність донорних замісників у бензеновому кільці (–CH_3, –OH, –NH_2) сприяло глибокій деструкції ядра, тоді як акцепторні (–NO_2, –COOH) зменшували його реакційну здатність, змінюючи напрямок реакції на боковий алкільний ланцюг. Похідні з функціональними групами, здатними до нуклеофільної атаки (–OH, –NH_2, –SH), характеризувались значно вищою швидкістю реакції (до 25 разів), порівняно з толуеном. Ацилювання таких груп оцтовим ангідридом знизило швидкість реакції та підвищило селективність утворення стабільних продуктів. Окрему увагу приділено складу та структурі продуктів реакції. Пероксиди, що утворились в результаті деструкції ароматичного ядра, виявили різну будову – від мономерних до олігомерних форм. Вони добре розчинились в оцтовій кислоті, однак легко осадились або видалились з розчину, що було ключовою перевагою процесу в застосуванні до очищення води та ґрунтів. Отримані дані засвідчили потенціал рідиннофазного озонування як ефективного інструменту для селективного та контрольованого знешкодження ароматичних сполук у ґрунтах та водах сільськогосподарського призначення. Отримані результати можуть бути використані екологами, агрохіміками та спеціалістами з очищення води для підвищення екологічної безпеки аграрних територій і зрошувальних систем, забруднених ароматичними сполуками

Ключові слова: озон; метилбензени; деструкція; пероксиди; очищення води; кінетика