APPLICATION OF NANOMATERIALS AND NANOTECHNOLOGIES IN CONSTRUCTION

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Research of the wastewater treatment method for the production of wood-chip building materials in the presence of nanostructured heterogeneous catalys

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ABSTRACT: Introduction. Phenols and petroleum products are common wastewater contaminants in many industries. Due to their persistence and toxicity in the natural environment, an efficient waste disposal technology is needed. Ozonation in the presence of heterogeneous catalysts is one of the advanced methods for treating wastewater from these toxicants. Since most catalysts are expensive, they are being sought on the basis of transition metals and their oxides, which have high activity and relatively low cost. In this regard, the Scientific and Educational Center for Innovative Technologies (SECIT) of USPTU carried out work on the search for an effective and affordable catalyst for the deep oxidation of phenol and petroleum products in wastewater under the influence of ozone. **Methods and materials.** To study catalytic ozonation, we used model waste water containing phenol and oil products at concentrations of 8 and 30 mg/dm^3, respectively. Ozonation was carried out in the presence of fresh (1) and spent (2) NiO–MoO_3 catalyst deposited in the form of a film on cylindrical Al_2O_3 granules weighing 0.5 – 2 g. **Results.** Optimal conditions of ozonation have been found (1), within 10 min of the decomposition process in its presence, COD decreased by 25% compared to the oxidation process with a catalyst (2), and by 40% compared to classical ozonolysis. It was found that the optimal loading of catalyst (1) is 1 g, duration is 35 min, pH = 8.5, temperature – 22 – 30°C, ozone dose – 5 g/dm^3. Discussion. At catalyst dosages of less than 1 g/dm^3, the low efficiency of removing phenol and hydrocarbons is probably due to a lack of the adsorption surface of the catalyst. **Conclusion.** The studied method of purification allows to reduce the content of phenol and oil products to the standard indicator of drinking water quality (0.001 and 0.05 mg/dm3, respectively), COD by 96% and solve the problem of the harmful effects of these toxicants on ecosystems.

KEYWORDS: Phenol, oxidation method, catalytic ozonation, nanostructured heterogeneous catalyst, waste water, woodchip construction materials.

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INTRODUCTION

The continuous growth and development of the industrial sector of the economy leads to a constant increase in environmental pollution. Water resources are experiencing one of the highest environmental pressures, with an increasing number of highly toxic compounds entering the waters of water basins used by humans for household needs. Therefore, the primary task of modern ecology is to solve the problem of water pollution with highly toxic organic compounds.

Phenols and petroleum products are common pollutants of wastewater from many industrial sectors. Phenol-formaldehyde resins are widely used as binders in the woodworking industry for the manufacture of various building materials (plywood, chipboard, oriented chipboard, fiber board).

The group of phenolic waters includes wastewater from gas, coke-gas and coke-chemical plants for semi-coking of coal and brown coal, distillation and hydrogenation plants of coal and brown coal tar, some enterprises for the production of plastics (phenoplastics), some enterprises of the organic synthesis industry associated with the production or processing of phenols of toleruberoid plants.

The concentration of phenols in wastewater, depending on the industry, can vary from 5 to 30 mg/l. If the

phenol content is higher than 1 g/l, the aqueous solution is considered toxic.

With the joint presence of oil hydrocarbons and phenols, the decomposition of the latter slows down, since the biodegradation of petroleum hydrocarbons produces an additional amount of phenolic compounds, which leads to an increase in the degree of pollution. These compounds have harmful effects on human health and ecosystems [1]. So, for example, when swimming in water bodies, there is a risk of skin diseases. When contaminated fish is eaten, phenolic compounds are not excreted from the human body, they react with other substances. Phenol is a potent poison, has carcinogenic and mutagenic properties. Drinking water with a high content of petroleum products increases the risk of developing cancer of the internal organs, diseases of the digestive and endocrine systems. Oil products envelop fish eggs, and subsequently they cannot produce offspring.

Methods of wastewater treatment from phenols can be conditionally divided into two groups: destructive and regenerative. The main destructive methods of wastewater treatment from phenols include thermo-oxidative, oxidative methods, as well as electrochemical oxidation and hydrolysis. Destructive methods are used if it is impossible or economically inexpedient to extract impurities from wastewater that does not require the return of phenol to production. The use of regenerative methods in wastewater treatment at chemical plants makes it possible to neutralize wastewater and extract phenols with their subsequent application. There are the following regenerative methods of phenol extraction: extraction purification, distillation, rectification, adsorption, ion exchange purification, reverse osmosis, ultrafiltration, esterification, polymerization, polycondensation, biological purification and conversion of phenols into poorly soluble compounds.

Due to the resistance of phenols and petroleum products to biodegradation and toxicity in the natural environment, an effective technology for the disposal of wastewater is needed. Ozonation is widely used for wastewater treatment from these toxicants.

Ozonation is a widely used method of deep purification of water from phenols, as well as from other petroleum products. Ozone has a great oxidizing ability, has a strong bactericidal effect, eliminates unpleasant odor and taste and returns the water to its natural color. The oxidizing properties of ozone in water can manifest themselves in reactions of direct oxidation, ozonolysis, catalysis, radical oxidation and polymerization. Some organic compounds undergo direct oxidation. The catalytic effect of ozone is to initiate oxidation reactions with oxygen dissolved in water. Ozone oxidation occurs at the site of the double bond of the benzene ring, and a hydroxyl radical is oxidized in parallel with the subsequent recombination of peroxyradials, hydrogen peroxide reacts with ozone to form water and oxygen. To accelerate the initiation process, it is advisable to carry out oxidation in an alkaline environment. The higher the pH value of the medium, the greater the degree of ozone oxidizability. For example, the optimal pH value for the oxidation of phenols with a concentration of less than 50 mg/l is 11.4. The ozonation process is carried out in reaction baths or mixers in which water is mixed with ozonized air or oxygen. To produce 1 kg of ozone, 15 kW of electricity is required. The power consumption per 1 kg of oxidized phenol is 50 – 100 kWh in pure aqueous solution.

The efficiency of water purification by ozonation is increased by carrying it out in combination with ultraviolet irradiation, hydrogen peroxide, biological purification, activated carbon, sonolysis, electrochemical oxidation and catalysis [2–15]. In our opinion, ozonation in the presence of available and best studied homogeneous and heterogeneous catalysts is the most effective of the considered methods [15–18].

The use of catalytic ozonation does not require other energy costs (for example, UV) or the cost of maintaining a certain pH value, since it is effective in a wide range of acidity values of the reaction medium. In addition, in most cases, catalytic ozonation systems have shown good efficiency and a higher degree of mineralization of various organic compounds in water purification compared to classical ozonation.

Catalytic ozone oxidation is recommended to be used for the treatment of wastewater generated during the washing of printed circuit boards in the electronics industry [19]. The catalyst is a mixture of copper and chromium oxides. Five-minute treatment of these effluents at an ozone dose of 90 – 100 mg/l containing highly alkaline solutions of organic compounds increased their conversion rate from 70-80 to 92 – 95%.

For wastewater treatment of dyeing and finishing industries of the wool industry, catalytic oxidation with ozone on the surface of a catalyst made of activated carbon AG-3 coated with MnO_2 manganese dioxide was proposed. The maximum effect of dye discoloration was 96% [20].

Catalytic oxidation with ozone can be used to purify phenol-formaldehyde wastewater, where crushed pyrolusite ore serves as a catalyst [21]. However, a significant disadvantage of this method is that with repeated use of pyrolusite, its catalytic activity is significantly reduced. Regeneration of pyrolusite is achieved when it comes into contact with a 1.5 – 2% solution of sulfuric acid, which is consumed at the same time to dissolve the surface layers of manganese dioxide.

Extensive studies indicate the high efficiency of homogeneous catalysts; however, their use leads to secondary water pollution, which limits their use. Therefore, researchers are paying more and more attention to heterogeneous catalysis.

A number of heterogeneous catalysts have been proposed: metal oxides, minerals, carbon materials, and supported metals.

An increase in the efficiency of oxidation of phenol-containing wastewater with ozone was observed when iron oxide Fe_2O_3 applied to γ-alumina by soaking the granules of γ-Al_2O_3 in a solution of $Fe(NO_3)_3 \cdot 9H_2O$ was used as a catalyst. As a result of ozonation, COD decreased from 240 to 83 mg/l at an ozone dose of 1.54 mg/mg of COD, which is 3 times less than without a catalyst [22, 23].

Heterogeneous catalysts produced by the research and production enterprise "Catalyz" with the use of transition metal complexes have been commercially introduced. The developed catalysts based on ceramics are characterized by high mechanical strength (crushing, abrasion), acid and alkali resistance, low moisture capacity [24].

In order to increase the catalytic activity of a metal or its compound during ozonation, they are deposited in a thin layer on an inert material with special surface properties, which increases both the surface area and the number of active sites of the catalyst [16, 25]. However, most catalysts are expensive, which limits their industrial application. Therefore, a search is underway for catalysts based on transition metals and their oxides for the deep oxidation of stable compounds with high activity and relatively low cost. Of particular interest are nanocatalysts. Due to their small size and large surface area, which provides good adsorption and has special mechanical, optical and magnetic properties, nanocatalysts exhibit high reactivity in the treatment of toxic pollutants from wastewater. The development of nanomaterials in wastewater treatment technology is economically viable, environmentally friendly and meets the growing demands of water quality standards, so ozonation with nanocatalysts is the most promising advanced process known. Previously, we studied the efficiency of wastewater treatment of a plywood-board plant by ozonation in the presence of available and best-studied heterogeneous catalysts [16]: Fe_2O_3 deposited in the form of a nanofilm on 0.5 – 1.0 mm particles of γ-Al_2O_3; Al_2O_3 deposited as a nanofilm on 2.5 – 3.0 mm TiO_2 particles; MnO_2 deposited as a nanofilm on 2.5 – 3.0 mm TiO_2 particles. The results of the experiments on catalytic ozonation of wastewater indicate a high treatment effect: COD decreased by 1.7 (TiO_2/Al_2O_3, TiO_2/MnO_2) and 3 times (γ-Al_2O_3/Fe_2O_3) compared with ozonation without a catalyst.

In this regard, the Scientific and Educational Center for Innovative Technologies (SECIT) of the Institute of Architecture and Civil Engineering of USPTU carried out work on the search for an effective and affordable catalyst for the deep oxidation of phenol and oil products in wastewater under the influence of ozone.

METHODS AND MATERIALS

For the study of catalytic ozonation, a model solution was used, the composition of which, in terms of the content of phenol and petroleum products, is similar to wastewater from the production of woodchip construction materials (Table 1).

An ozone generator OGVK-02K was used to produce ozone; to ensure the introduction of an ozone-oxygen mixture into water and contact with impurities, a reactor with a volume of 1 dm^3 was used; ozone concentration control device in water – photometer "Expert-003". Waste water preliminarily filtered through the Blue Ribbon filter was poured into the reactor. The catalyst weighing 0.5 – 2 g was loaded into the ozonator tank in the form of cylindrical particles. NiO-MoO_3 oxides deposited in the form of a film on cylindrical Al_2O_3 granules with a diameter of 1.2 – 1.4 mm and a length of 4 – 5 mm were used as a catalyst. Ozone was supplied to the treated water using a porous ceramic dispersant at a constant gas flow rate. Oxidation was carried out in a non-flow mode with intensive stirring of the catalyst on a magnetic stirrer in a fume hood. The concentration of ozone in the air of the working area was controlled using TI-[O_3-0.003] indicator tubes; it should not exceed 0.0001 mg/dm3. After 5 – 40 minutes of stirring in the presence of ozone, the waste water was separated from the catalyst. At certain time intervals, sampling and analysis of the residual concentration of phenol (TsV 1.04.04-91 "A") and COD

Table 1
Wastewater characteristics

№ п/п	Water quality indicators	Analysis result		Normative document on the procedure (method) of measurements
		Source waste water	Wastewater after O_3 treatment (catalyst No.1)	
1	Hydrogen index (units pH)	5.5±0.3	8,5±0,2	ERD F 14.1:2:3:4. 121-97
2	COD, mgO_2/dm^3	203±41	<10	ERD F 14.1:2:4.210-2005
3	Phenol, mg/dm^3	8.0±1.3	<0,001	TsV 1.04.04-91 «A»
4	Oil products, mg/dm^3	30.0±2.3	0,05±0,01	ERD F 14.1:2:4. 5-95

by the photometric method (ERD F 14.1:2:4.210-2005) were carried out. PH was measured on an ANION 4100 pH meter. The concentration of nickel and molybdenum ions in wastewater was monitored on a PB2201 spectrophotometer (ERD F 14.1.46-96, ERD F 14.1:2.47-96).

RESULTS AND DISCUSSION

At the first stage, to assess the activity of the catalyst, the efficiency of the oxidation process was studied in terms of the change in COD over the reaction time in the presence of fresh catalyst (1), spent catalyst (2) and without it (Fig. 1). The results indicate the highest efficiency of the catalyst (1). Already after 10 minutes of the decomposition process in its presence, COD decreased by 25% compared to oxidation with a catalyst (2), and 40% less compared to classical ozonolysis.

At the second stage, the optimal conditions for ozonation with catalyst (1) were selected using the "experiment-point" method. Good results of phenol decomposition were achieved at pH = 8.5 – 11.0 (Fig. 2). Therefore, before oxidation, the model solution was alkalized to pH = 8.5. The influence of the temperature of the aqueous solution (Fig. 3) and the dose of ozone (Fig. 4) on the effect of ozonation was also studied. The lowest residual concentration of phenol was achieved at 22 – 30°C, and the optimal dose of ozone was 5 g/dm³.

To achieve the maximum efficiency of the oxidation of organic substances at the next stage, the optimal catalyst loading (1) was selected under the best process conditions: duration – 35 min, pH = 8.5, temperature – 22 – 30°C, ozone dose – 5g/dm³. The dependence of COD on the catalyst dose is shown in Figure 5.

It can be seen from the data obtained (Fig. 5) that the optimal catalyst dose is 1 g/dm³. At catalyst dosages less than 1 g/dm³, the low efficiency of phenol and hydrocarbon removal is probably due to the lack of an adsorption

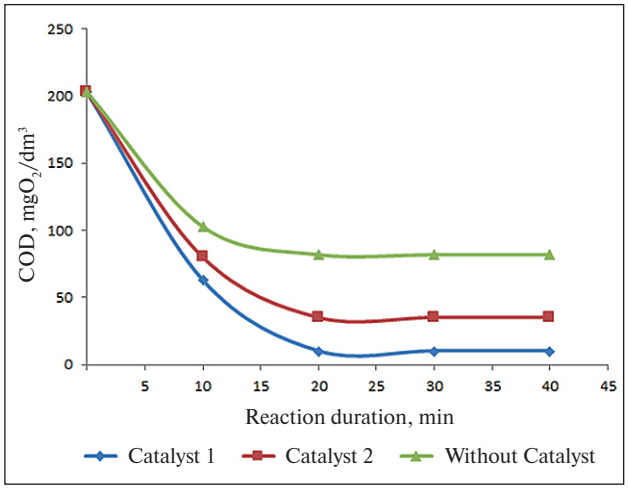

Fig. 1. **Dependence of COD on the duration of ozonation**

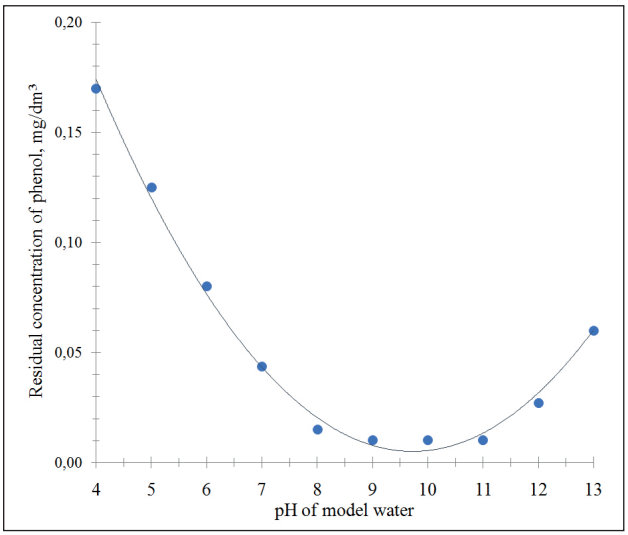

Fig. 2. **Influence of pH on the residual concentration of phenol in an aqueous solution during catalytic (catalyst No. 1) ozonation** (duration – 35 min, temperature – 22°C, ozone dose – 5 g/dm³)

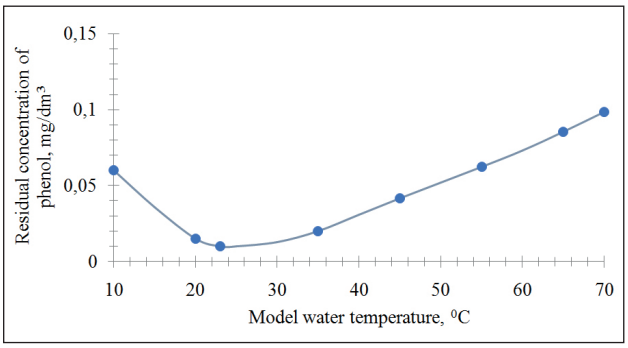

Fig. 3. **Effect of model solution temperature on the residual concentration of phenol during catalytic (catalyst No. 1) ozonation** (duration – 35 min, pH = 8.5, ozone dose – 5 g/dm³)

surface of the catalyst. According to available literature data, in many cases it is believed that dissolved ozone and organic compounds are adsorbed on the catalyst surface. After that, the adsorbed ozone molecules are involved in the initiation of radical reactions on the surface-active sites of the catalyst. The resulting reactive radicals ·OH and HO_3· subsequently react with ozone to form more ·OH or attack organic pollutants directly. The ability to transfer electrons between metal ions of different valences Ni (II) and Mo (VI) of the catalyst we use facilitates the decomposition of O_3 to free active radicals, increasing the efficiency of oxidation [19].

The results of purification of the model solution are given in the table. The content of phenol and the COD index correspond to the standard values for water for drinking and domestic purposes.

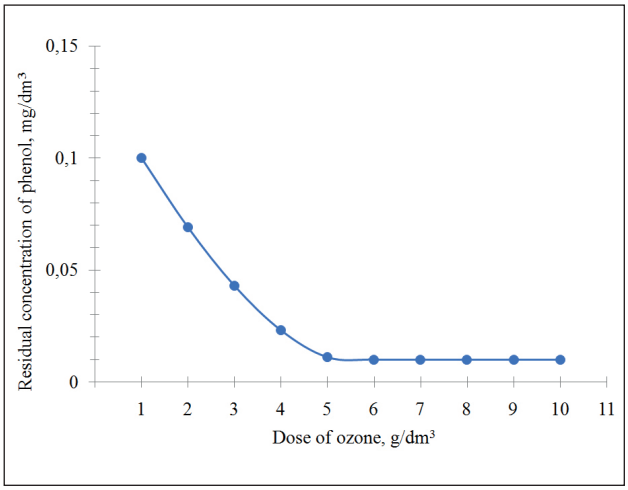

Fig. 4. **Effect of ozone dose on the residual concentration of phenol during catalytic (catalyst No. 1) ozonation** (duration – 35 min, pH = 8.5, temperature – 22°C)

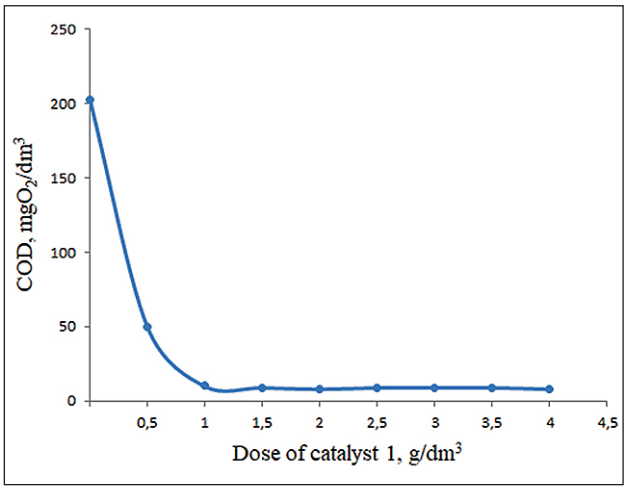

Fig. 5. **Dependence of COD on catalyst dose (1)**

CONCLUSIONS

The conducted studies have shown that ozonation should be carried out in the presence of fresh heterogeneous $NiO\text{-}MoO_3/Al_2O_3$ catalyst, which is used in a small amount (1 g/dm³). The studied method of purification allows to reduce the content of phenol and oil products to the standard indicator of drinking water quality (0.001 and 0.05 mg/dm³, respectively), COD by 96 % and solve the problem of the harmful effects of these toxicants on ecosystems.

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Aliya K. Mazitova – scientific guidance; research concept.

Irina A. Sukhareva – performing experiments; writing the text of the article; final conclusions.

Georgy M. Sidorov – final conclusions.

Rustem A. Talipov – performing experiments; writing the text of the article.

Alfiya F. Aminova – performing experiments.

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