CATALYSTS, MAGNETIC COMPOSITES FOR REMOVAL OF PHENOL-CONTAINING COMPOUNDS FROM WASTEWATER

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ABSTRACT
Currently, the problem of creating effective technologies and highly active stable catalysts for the complete purification or post-treatment of industrial wastewater from phenols is one of the most urgent and difficult to solve. Phenols contained in wastewater are called “phenolic wastewater”. Phenol is one of the industrial pollutants, toxic to animals and humans, and destructive to many microorganisms. Deep catalytic oxidation of toxic substances is one of the most effective methods of purification of natural and wastewater from toxic impurities of phenol-containing compounds. Among modern catalytic systems in the field of fine organic synthesis and solving environmental problems, systems based on nanomagnetic particles have become of great interest in the last years. They are characterized by multivariate production and simple particle design. The relative safety of a number of magnetic materials, for example, iron oxides, attracts the attention of researchers. Magnetic nanoparticles have high magnetic susceptibility and therefore they are easily controlled by an external magnetic field. They have found demand in the field of catalytic reactions, electrochemistry, ecology, medicine, and pharmaceuticals. The data of various authors including our study clearly demonstrate the uniqueness and prospects of using magnetic nanocomposites to remove polluting phenol-containing toxic substances with their subsequent catalytic processing.

Keywords: Water Treatment, Highly Toxic Organic Compounds, Technology, Nanostructured Catalysts, Transition Metals, Polymer Matrices, Enzymes, Biocatalysts.

INTRODUCTION
Throughout the existence of civilization, mankind has largely polluted the environment with effluents. The need to improve the efficiency of environmental protection measures is associated, first of all, with the urgent need to introduce resource-saving, low-waste, and waste-free technological processes that reduce environmental pollution, including water resources. The choice of optimal treatment methods is possible only after a qualitative quantitative analysis of wastewater. The degree of purification, the selection of effective equipment, and filter elements depend on the composition of pollution and the volume of wastewater. Wastewater from industrial enterprises is very complex in its composition. The content of components in industrial water effluents depends on the characteristics of production, process operations, equipment, initial reagents, and technological regime (temperature, pressure, feedstock flow rate, and whether a catalyst is used). The maximum amount of wastewater is generated in the oil refining, metallurgical, chemical, and pulp and paper industries. As parts of wastewater from these enterprises contain a wide range of organic substances: carboxylic acids, alcohols, phenols, pesticides, surfactants, and oil products. Oil refineries and petrochemical plants, various mining and metallurgical enterprises, wood and paper processing factories, etc. are characterized by high water consumption and a high degree of pollution of industrial wastewater with toxic substances, among which a large proportion belongs to phenol-containing compounds. The ingress of phenolic compounds into water resources provokes the formation of volatile compounds with synergistic effects, and this, in turn, has a negative effect on both hydrobionts and the nature of processes occurring inside reservoirs. Phenol is especially dangerous because of its relatively good solubility in water. Phenol is one of the industrial pollutants, quite toxic to animals and humans, and destructive to many microorganisms, therefore, industrial wastewater with a high content of phenol is poorly amenable to biological treatment. Phenol is a toxic substance and it causes burns on contact with the...
skin, while it is absorbed through the skin and causes poisoning. Therefore, the problem of creating effective technologies and highly active stable catalysts for the complete purification or post-treatment of industrial wastewater from phenols is one of the most urgent and difficult to solve.

1. Phenolic wastewater
1.1. Basic information
Traditionally, the greatest attention is paid to phenols contained in wastewater, which are called “phenolic wastewater”. This is due to the fact that, compared with other components of wastewater, phenol-containing compounds have the greatest toxicity, and the ability to form chlorophenols during chlorination of water, which have increased toxicity and a sharp unpleasant odor even at negligible concentrations in water. Phenol in the degree of effect on the body refers to highly hazardous substances (the 2nd hazard class according to the State Standard 12.1.005). The maximum permissible concentration (MPC) in the air of the working area is 0.3 mg/m$^3$. The most single MPC in the atmospheric air of populated places is 0.01 mg/m$^3$, the average daily - 0.003 mg/m$^3$, and in water – MPC – 0.001 (Table-1).

<table>
<thead>
<tr>
<th>No</th>
<th>Harmful substances</th>
<th>Maximum permissible concentrations, mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>in water</td>
</tr>
<tr>
<td>1</td>
<td>Benzene</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>Oil and oil products</td>
<td>0.3</td>
</tr>
<tr>
<td>3</td>
<td>Pentane</td>
<td>0.2</td>
</tr>
<tr>
<td>4</td>
<td>Carbon disulphide</td>
<td>10.0</td>
</tr>
<tr>
<td>5</td>
<td>Toluene</td>
<td>5.0</td>
</tr>
<tr>
<td>6</td>
<td>Phenol</td>
<td>0.001</td>
</tr>
</tbody>
</table>

If the MPC is exceeded, poisoning, irritation of the mucous membranes, and skin burns are possible. Acute poisoning with phenol occurs mainly when it gets on the skin. With general poisoning, there is an increase in temperature, and a violation of the functions of the nervous system, and respiration. Chronic poisoning - irritation of the respiratory tract, indigestion, nausea, weakness, itching, conjunctivitis. Phenol has no cumulative properties. For volatile alkylphenol (simple phenol, cresols, guaiacol, ethylphenol), a generalized indicator is introduced – “the phenolic index”. The phenolic index differs from the actual content of phenols in their model mixture by 3-5 times.

Currently, coke production is one of the most polluting industries, including the water basin of the earth. This production is also the main source of phenol effluents, environmental pollution with phenol, benzo(a)pyrene, other organic compounds, ammonia, carbon monoxide, nitrogen and sulfur compounds, and dust. Most of these substances, including phenolic compounds in wastewater, are highly toxic or can be converted to toxic compounds when interacting with other substances. Phenols of wastewater from coke’s chemical production are mainly represented by monatomic phenols. The phenols of the gas collector cycle water contain 0.2–0.3% of two-atomic phenols (mainly resorcinol). The highest yield of phenols is formed during the hydrogenation of coal. In the case of thermal processing of coal, especially high-temperature processing, the content of phenols is lower. The older the fuel and the higher the temperature of its processing, the lower the content of phenols in wastewater. The coal processing temperature determines both the amount and composition of phenolic wastewater. All waste waters of coke chemical production are characterized by a very high content of toxic substances and need complex cleaning. Any purification processes should include the removal of ammonia, the extraction of phenols, and the post-treatment of wastewater by a biological method, but other purification methods have also been developed and applied. For the extraction of phenols in the by-product coke industry, the steam circulation (“evaporation”) method is mainly used, which is suitable specifically for the extraction of phenols and cresols with low boiling points (Fig.-1).

One of the simplest and most rational ways to remove phenol residues in wastewater is their oxidation to produce CO$_2$ and H$_2$O. At low-power plants, it is reasonable to use ozone and some other oxidizing agents, such as hydrogen peroxide. However, these methods are very energy intensive and do not guarantee the complete oxidation of phenols to CO$_2$ and water. For very large volumes of wastewater to be treated, aerobic
biochemical treatment is the preferred method of deep wastewater treatment, which guarantees the removal of the bulk of phenols, thiocyanates, and cyanides. In the case of production facilities for processing hydrocarbon systems, more than 50% of the contribution to the total pollution of wastewater with phenol is made by: installation of purification of process condensate and sulfur-alkaline effluents - 47%, installation of catalytic cracking G-43-107- 5 %, electric desalting plant and primary oil refining plant - 3%, hydrotreating plant 24/5- 1.8%. The largest amount of phenol at the primary oil refining plants comes from the waters of the drainage tanks of the columns of the column: partial topping of the raw materials C-1 and the main column C-2.

![Diagram](image1.png)

Fig.-1: Coke Production: a- Coke Oven: 1- a Hopper for Loading Coal Charge, 2- a Riser for Removing Volatile Products, 3- an Entrance Door, 4- a Back Door, 5- a Coke Dispenser; b- Installation of Steam Circulation Removal of Phenols from Coke Production Wastewater: 1 - Upper Section of the Scrubber; 2 - Fan; 3 - Lower Section of the Scrubber; 4 – Heater

1.2. The Analysis of Phenolic Wastewater
The certified methodology for the analysis of wastewater processed in accordance with the current regulatory and technical documents for phenol is photocolorimetry. Colorimetric determination of volatile phenols with steam is carried out. The method is based on distilling volatile phenols with steam from the sample, followed by photo colorimetric determination of them in the resulting distillate. The range of measured concentrations is more than 0.05 mg/dm$^3$. In the analysis of phenolic pollution of surface waters, the main attention is paid to the most toxic group of volatile phenols with steam. It should be noted that widely used photometric techniques do not give a complete picture of the qualitative composition of phenolic toxins and do not allow us to determine their true toxicity, whereas chromatography-based analysis methods require expensive equipment.

One of the reliable indicators of pollution of aquatic ecosystems with phenolic compounds is the determination of the content of bacteria resistant to phenolic pollution, but this cannot be a criterion for the self-cleaning ability of aquatic ecosystems. An objective assessment of the environmental risk of pollution of aquatic ecosystems with phenolic compounds requires an integrated approach: identification of zones with a high content of phenols, study of the composition of toxic phenols and determination of factors that reduce the self-purification of ecosystems.$^{2,7,16-19}$ The composition of waste water is usually characterized by the content of impurities of oil products and chemical compounds in it, as well as by the indicators of the oxidizability of organic compounds in it - biochemical (BOC) and chemical (COC) oxygen consumption (Table-2).$^{2,7,16}$ Various methods and combinations of methods are used to clean industrial wastewater. Among the effective methods of purification of natural and wastewater from toxic impurities, the use of catalytic oxidation of toxic substances is very promising. Catalysts significantly intensify the process of wastewater treatment, and also avoids the disadvantages of traditional technologies, and provide significant advantages with the minor reconstruction of facilities.$^{18}$

2. Reaction of Oxidation
In organic chemistry and technology, oxidation processes are understood as the processes of transformation of substances under the action of various oxidizing agents. Oxidation may be complete or incomplete. Under conditions of complete oxidation, combustion of any organic substances occurs with the formation
of carbon dioxide and water. For selective organic synthesis, the most valuable is incomplete (or partial) oxidation, while complete oxidation is an undesirable side process. When catalysts based on transition metal salts are used for such oxidation reactions, high process rates are achieved. The highest rates are achieved for bimetallic catalysts. The researchers note the emergence of a synergistic phenomenon, in which even very small amounts of one of the additional components of the catalyst leads to unexpected disproportionate increases in the speed of the process.

Table-2: Indicators of Biochemical (BOC) and Chemical (COC) Oxygen Consumption for Some Organic Substances and Phenol Compounds

<table>
<thead>
<tr>
<th>No</th>
<th>Substance</th>
<th>BOC, mg O₂/g</th>
<th>COC, mg O₂/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzene</td>
<td>1.150</td>
<td>3.020</td>
</tr>
<tr>
<td>2</td>
<td>Gasoline (cracking)</td>
<td>0.110</td>
<td>3.540</td>
</tr>
<tr>
<td>3</td>
<td>Fuel oil</td>
<td>0.330</td>
<td>3.300-3.660</td>
</tr>
<tr>
<td>4</td>
<td>Oil (Tuimazy field, Russia)</td>
<td>0.430</td>
<td>3.580-4.300</td>
</tr>
<tr>
<td>5</td>
<td>Toluene</td>
<td>1.100</td>
<td>1.870</td>
</tr>
</tbody>
</table>

Phenolic compounds

<table>
<thead>
<tr>
<th></th>
<th>Substance</th>
<th>BOC, mg O₂/g</th>
<th>COC, mg O₂/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Phenol</td>
<td>1.180</td>
<td>2.380</td>
</tr>
<tr>
<td>2</td>
<td>n-octyl phenol</td>
<td>1.103</td>
<td>2.520-2.950</td>
</tr>
<tr>
<td>3</td>
<td>Copper trichloro phenolate</td>
<td>0.700</td>
<td>0.843</td>
</tr>
<tr>
<td>4</td>
<td>Cresols</td>
<td>1.560</td>
<td>2.520</td>
</tr>
<tr>
<td>5</td>
<td>Pyrocatechin</td>
<td>1.405</td>
<td>1.890</td>
</tr>
<tr>
<td>6</td>
<td>Resorcinol</td>
<td>1.495</td>
<td>1.890</td>
</tr>
<tr>
<td>7</td>
<td>Hydroquinone</td>
<td>0.458</td>
<td>1.890</td>
</tr>
</tbody>
</table>

Mercaptans

| | Tert-dodecyl mercaptan     | 2.250        | 3.190        |

2.1. Catalysts for Catalytic Purification of Waste Waters

The most common catalysts for the majority of industrial processes are heterogeneous catalysts. Much more profitable and efficient to use catalysts based on nanoscale particles, while most of the catalyst atoms are available to reagents and the efficiency of catalysis increases tenfold. Numerous studies have shown that nanoparticles of many substances have amazing properties that allow them to be used as catalysts. The first studies to clarify the dependence of the rate of chemical reactions on the particle size were carried out by Soviet scientists: N.I. Kobozev (the 30s of the 20th century), G. K. Boreskov (the 50s of the 20th century). It was concluded that the rate of many catalytic reactions depends on the degree of dispersion of the active component of the catalyst. Such reactions are called structurally sensitive reactions.18-20

I. Structurally insensitive reactions - G.K. Boreskov, 1956: hydrogenation of aromatics and olefins, dehydrogenation of hydrocarbons, oxidation of H₂ with oxygen, CO + O₂ on Rh. The specific catalytic activity of the active component does not depend on the size of its particles and is approximately constant in a number of catalysts with the same chemical and phase composition.

II. Structurally sensitive reactions - M. Budar, 1969: hydrogenation of nitro compound, skeletal isomerization, dehydrocyclization; hydrolysis of C-C, C-N, C-S bonds, any oxidation reactions. For these reactions, specific catalytic activity depends on the size of its particles (1-10-100 nm), the crystal chemistry of their surface, microstructures (interblock boundaries, structural and chemical defects), phase composition, and interaction with the carrier.18

Liquid-phase oxidation with atmospheric oxygen at elevated temperature (150-350 ºC) and pressure (1.0-15 MPa) is a promising method for treating large volumes of wastewater with high concentrations of hazardous and non-biologically degradable toxic wastewater impurities, including phenolic compounds. This method was proposed in the 50s. 20th century in the United States and by the end of the 1990s. The use of catalysts can significantly reduce the temperature and pressure of aerobic oxidation and achieve a high degree of mineralization of organic ecotoxics. To facilitate the aerobic oxidation of various organic compounds, various heterogeneous catalysts have been investigated, including noble metals and oxides of some transition metals (Fe, Mn, Cu, Cr, Co, Ni, Mo, and Ce). The most active and stable catalysts are finely dispersed noble metals on carriers that are stable in an aggressive aqueous medium (TiO₂, ZrO₂, CeO₂, polymers, carbon materials). It is promising to use ruthenium-containing catalysts that have sufficient
activity and selectivity and lower cost compared to catalysts based on noble metals.\textsuperscript{18-23} The development of catalysts for the catalytic oxidation of phenols to ensure efficient purification or post-treatment of industrial wastewater is an urgent task. Among modern catalysts, catalytic systems based on nanomagnetic particles are also attractive as supported catalysts. Such systems have shown their uniqueness and high efficiency in the field of medicine, biology, and fine organic synthesis, and according to various authors, they can be very useful for solving environmental problems, and in particular for treating phenolic industrial effluents.

\subsection*{2.2. Nanoparticles Magnetic Nanocomposites}

When using nano-materials, the properties of substances and materials change dramatically. It is important to find out at what sizes of nanoparticles the catalytic properties begin to manifest.\textsuperscript{23-44} The basis of the chemical synthesis of nanoparticles is the initiation of a chemical reaction and further control of the processes of nucleation and growth of the resulting product. Modern methods of obtaining nanoparticles of magnetic materials can be divided into two groups: 1) methods based on the production of nanoparticles from compact materials; 2) methods based on the assembly of nanoparticles from atoms, ions, molecules (Fig.-2).

\begin{figure}[h]
\centering
\includegraphics[width=\columnwidth]{Fig.-2.png}
\caption{The Basic Methods for Synthesis Nano-Magnites Particles}
\end{figure}

The technology of obtaining nanoparticles of magnetic composites provides more opportunities for controlling the size, shape, composition, structure, self-organization processes, and physical characteristics of the resulting nanoparticles. The Ferromagnetic matter has a special magnetic order, which is absent in ordinary substances. Magnetic nanoparticles: 1. Metal oxides: Nickel oxides, cobalt oxides; Iron oxide nanoparticles: magnetite Fe\textsubscript{3}O\textsubscript{4}, maghemite γ-Fe\textsubscript{2}O\textsubscript{3}. 2. Metal ferrites: Cobalt ferrite, nickel ferrite, copper ferrite (Fig.-3).

Magnetic nanoparticles are magnets, they obey Coulomb’s law and can be controlled by an applied external gradient of magnetic field strength. During the transition to the nanoscale, completely unusual properties appear. For example, gold that has no magnetic properties becomes magnetic. Tamm surface states play an important role, and the density of the electronic states of γ in nanoobjects differs significantly from their volumetric counterparts. Consequently, magnetism can manifest itself in an increasing number of new nanomaterials.\textsuperscript{23-42}

The relative safety of a number of magnetic materials, for example, iron oxides, attracts the attention of researchers. Common modifications of iron oxides are hematite, maghemite, and magnetite. Taking into account the magnetic and toxicological properties of the modifications, it can be concluded that nanoparticles based on iron oxides are characterized by effective magnetic properties and significantly lower toxicity in comparison with similar compounds of nickel, cobalt, or other elements. Magnetite (the name may have come from the name of the historical region of Magnesia, in Thessaly, Greece) is a mineral of the subclass of complex iron oxides. Its composition and properties are variable and depend on the conditions of formation. Ferrites (or oxypheres) are compounds of iron oxide Fe\textsubscript{2}O\textsubscript{3} with more basic oxides of other metals, which are ferrimagnets. Magnetic nanopowders based on Fe\textsubscript{3}O\textsubscript{4} magnetite coated with citrate ions and silicon dioxide were synthesized and showed good results as sorbents for the sorption of organic and inorganic compounds from aqueous solutions.\textsuperscript{31} The maximum sorption capacity of magnetite powders modified with silicon dioxide is 22.3 mg/g for Ni\textsuperscript{2+}, 14.7 mg/g for methylene blue, and 18.8 mg/g for doxorubicin. The authors have shown the possibility of modeling the processes of sorption of organic, and inorganic substances, and drugs in the processes of water treatment and disposal of chemical
REMOVAL OF PHENOL-CONTAINING COMPOUNDS at pharmaceutical enterprises and cancer centers. In our previous study, it was shown that magnetic composites based on iron oxide demonstrate good efficiency in the oxidation of phenol with oxygen for wastewater treatment processes from phenol-containing toxicants.24

CONCLUSION

High-quality purification of water from phenol of various objects is an extremely urgent task. Among modern catalysts, both supported catalysts and catalytic systems based on nanomagnetic particles are attractive. Taking into account the magnetic and toxicological properties of the modifications, it can be concluded that nanoparticles based on iron oxides are characterized by effective magnetic properties and significantly lower toxicity in comparison with similar compounds of nickel, cobalt, or other elements. Such systems have shown their uniqueness and high efficiency in the field of medicine, biology, and fine organic synthesis, and according to various authors, they can be very useful for solving environmental problems, and in particular for treating phenolic industrial effluents.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

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All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:
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