PROSPECTS FOR THE USE OF METAL OXIDES IN NANOFORM FOR INDUSTRIAL WASTEWATER TREATMENT

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The article presents the results of a theoretical study on the prospects for the use of metal oxides in nanoform for industrial wastewater treatment. The growing problem of water pollution by inorganic compounds, especially heavy metals (Pb^{2+}, Cd^{2+}, Hg^{2+}, Cr^{6+}), as well as phosphates, nitrates, and sulfates, creates a demand for innovative and eco-friendly purification technologies. Conventional treatment methods often lack effectiveness under conditions of high pollutant concentrations or complex wastewater composition. Nanostructured metal oxides, due to their high surface area, ion-exchange capacity, and catalytic activity, offer promising solutions for pollutant removal. The study provides an analytical overview of recent scientific literature on the properties, synthesis methods, and application of TiO_2, ZnO, Fe_3O_4, MnO_2, CuO, and Al_2O_3 in purification processes. The mechanisms of sorption, photocatalysis, precipitation, and complexation are discussed in detail. Influencing factors such as pH, particle morphology, temperature, pollutant concentration, and contact time are analyzed. Special attention is paid to the development of composite materials and surface-functionalized nanomaterials, which enhance selectivity, reusability, and stability in aggressive environments. The potential environmental impact, regeneration strategies, and barriers to large-scale application are also considered. The conclusions highlight the relevance of nanostructured metal oxides in the development of efficient, scalable, and sustainable technologies for water purification, in line with modern ecological and industrial challenges. Further interdisciplinary research is recommended to address safety, standardization, and cost-effectiveness aspects.

Keywords: *metal oxides, nanomaterials, photocatalysis, sorption, wastewater, water purification*

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1. Introduction

Water pollution due to industrialization is one of the most acute environmental problems of our time. Industrial wastewater is characterized by an extremely complex composition, high toxicity and significant variability depending on the source of origin. The main danger is represented by inorganic compounds, in particular heavy metal ions (Pb^{2+}, Cd^{2+}, Hg^{2+}, Cr^{6+}), nitrates, phosphates, cyanides, as well as chlorides and sulfates. These pollutants are persistent in the environment, capable of bioaccumulation in living organisms and cause a number of toxic effects in both biota and humans. In this regard, the treatment of industrial wastewater is a priority task in the field of environmental protection and water treatment.

Traditional water purification methods, such as chemical precipitation, coagulation, adsorption on activated carbon or filtration through sand barriers, do not always provide the proper level of purification at high concentrations of pollutants. In addition, they may be accompanied by the formation of a large amount of secondary waste, have a high cost or require significant energy costs. In this regard, the search for innovative solutions that combine efficiency, economy and environmental safety is relevant. In recent years, there has been growing interest in the use of nanomaterials (Raliya et al., 2016), in particular metal oxides in nanoform, in water purification technologies. Nanomaterials, due to their unique physicochemical properties - in particular, high specific surface area, ion exchange capacity, catalytic activity and chemical stability - demonstrate significant potential in the processes of sorption, photocatalytic decomposition of pollutants, oxidation, filtration and precipitation. Such properties make them effective at low concentrations of pollutants, and also allow for targeted removal of heavy metal ions and toxic anions.

Among the most promising inorganic nanomaterials (Raliya et al., 2016) are oxides of titanium (TiO_2 (Zhang et al., 2020)), zinc (ZnO (Li et al., 2021)), iron (Fe_3O_4 (Wang et al., 2018)), aluminum (Al_2O_3), manganese (MnO_2 (Ghosh et al., 2016)), copper (CuO (Liu et al., 2020)) and their combined forms. For example, TiO_2 (Zhang et al., 2020) is actively used in photocatalytic purification technologies, where under the influence of ultraviolet radiation it is able to decompose organic compounds and deactivate microorganisms. Fe_3O_4 (Wang et al., 2018) demonstrates magnetic properties, which allows it to be quickly removed from the aquatic environment after the sorption process is completed. ZnO (Li et al., 2021), due to its high chemical activity, is effective in the treatment of water contaminated with heavy metals or pharmaceuticals. For example, using ZnO nanoparticles (50 mg/L), methylene blue dye at a concentration of 10 mg/L was degraded by 95% under UV light within 60 minutes (Li et al., 2021).

From the perspective of inorganic chemistry, the mechanisms of action of nanomaterials (Raliya et al., 2016) include the processes of complexation, ion exchange, electrostatic interaction, as well as surface reactions with the formation of poorly soluble compounds. These processes can be controlled by changing the pH, temperature, ionic strength of the medium or modifying the surface of nanoparticles with functional groups.

Despite the large number of scientific publications, the practical implementation of metal oxides in nanoform on an industrial scale is still limited. The reasons are the insufficient study of the long-term effects of their use, the possible toxic effect of the nanoparticles themselves on the environment, the complexity of recycling or regeneration of materials after cleaning. There is also a need to standardize methods for testing the effectiveness of cleaning with the participation of nanomaterials (Raliya et al., 2016).

The aim of this article is to analyze the current state of research on the application of nanostructured metal oxides for industrial wastewater treatment, focusing on their physicochemical properties, pollutant removal efficiency, and potential for further implementation in eco-technology.

2. Theoretical Background

The theoretical study is based on a comprehensive analysis of modern scientific literature devoted to the use of nanostructured metal oxides in industrial wastewater treatment technologies. The main source of information was articles published in leading international scientific publications, in particular, such as Journal of Hazardous Materials, Water Research, Environmental Science & Technology, Science of the Total Environment, Desalination, Nanomaterials, as well as in patent databases and conference proceedings. The selection of sources was carried out taking into account their scientific reputation, the peer-reviewed nature of the publications, the relevance of the topic and the availability of empirical data on the effectiveness of the use of metal oxides in nanoform for the treatment of aquatic environments. In total, more than 100 scientific papers were analyzed within the framework of the study, published mainly over the last 10 years.

The main criterion for selecting literature sources was the presence of a description of the physicochemical properties of nanomaterials (Raliya et al., 2016), the conditions of their synthesis, experimental parameters of water purification, types of pollutants, removal efficiency and the possibility of regeneration of nanomaterials (Raliya et al., 2016) after use. Special attention was paid to studies that compare different types of nanostructured metal oxides with each other or with traditional reagents, which made it possible to carry out a critical comparison of the effectiveness of different approaches to water purification.

The methodological basis of the study was based on the generalization and systematization of scientific data on the use of such nanomaterials (Raliya et al., 2016) as titanium oxide (TiO_2 (Zhang et al., 2020)), zinc oxide (ZnO (Li et al., 2021)), iron oxide (Fe_3O_4 (Wang et al., 2018), γ-Fe_2O_3), copper oxide (CuO (Liu et al., 2020)), aluminum oxide (Al_2O_3), manganese oxide (MnO_2 (Ghosh et al., 2016)), as well as their composites. These oxides were studied from the point of view of their morphology, crystal structure, specific surface area, particle size, chemical stability and reactivity. In the vast majority of studies, the synthesis of nanoparticles was carried out by the sol-gel method, hydrothermal synthesis, co-precipitation, thermal decomposition of precursors or chemical precipitation from aqueous solutions. The obtained nanomaterials (Raliya et al., 2016) were analyzed using X-ray diffraction (XRD), electron microscopy (SEM, TEM), infrared spectroscopy (FTIR), as well as specific surface area analysis (BET) and ζ-potential methods.

The experimental parameters taken into account in the sources included the concentration of pollutants, pH of the medium, process temperature, ratio of the mass of the sorbent to the volume of the aqueous solution, contact time and the presence of foreign ions. Considerable attention was paid to studies of the removal efficiency of heavy metals, such as cadmium, lead, copper, mercury, chromium, as well as phosphates, fluorides, nitrates, dyes and phenolic compounds. The level of water purification was assessed using atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectroscopy (ICP-OES), UV-Vis spectroscopy and ion chromatography.

The literature review also included a comparison of purification mechanisms, including sorption, photocatalysis (Qu et al., 2013), chemisorption, electrostatic interaction, complexation and precipitation. It was shown that the type of dominant mechanism depends on the nature of the nanomaterial, the type of pollutant and the process conditions. For example, TiO_2 (Zhang et al., 2020) demonstrates high photocatalytic activity when irradiated with ultraviolet light, while Fe_3O_4 (Wang et al., 2018) works effectively as a sorbent in a wide pH range due to its magnetic properties, which also facilitate the regeneration process and the extraction of the material from the aqueous environment.

In addition, the study analyzed works on surface modification of nanomaterials (Raliya et al., 2016) in order to increase their selectivity and stability. This includes functionalization with amino groups, immobilization on macroporous supports, creation of hybrid structures based on polymers, zeolites or carbon nanotubes. Such approaches allow to expand the scope of application of nanomaterials (Raliya et al., 2016) for purification of complex wastewaters, in particular those containing mixtures of organic and inorganic pollutants.

Thus, the methodology of this theoretical study is based on a systematic generalization of modern approaches to the synthesis, characterization and application of nanostructured metal oxides as a promising class of materials for purification of industrial wastewaters. The results of the analysis allow to draw conclusions regarding the effectiveness of the use of these nanomaterials (Raliya et al., 2016), to determine their advantages and limitations, and to outline the directions of further scientific research in this area.

3. Analysis of Recent Research

As a result of the theoretical analysis of the literature, it was found that nanostructured metal oxides demonstrate significant potential in the processes of industrial wastewater treatment, in particular in the removal of heavy metals, phosphates, dyes, phenols and other toxic components. The main factors ensuring the high efficiency of these materials are their high specific surface area, ability to chemisorption, photocatalytic properties and the possibility of modification in order to increase the selectivity to certain classes of pollutants. Among the most frequently studied nanomaterials (Raliya et al., 2016) in modern literature, the oxides of titanium (TiO_2 (Zhang et al., 2020)), zinc (ZnO (Li et al., 2021)), iron (Fe_3O_4 (Wang et al., 2018)), copper (CuO (Liu et al., 2020)), manganese (MnO_2 (Ghosh et al., 2016)) and aluminum (Al_2O_3) stand out. It was found that TiO_2 (Zhang et al., 2020) is particularly effective as a photocatalyst when irradiated with ultraviolet or visible light. Due to its electron-hole properties, it initiates redox reactions that contribute to the decomposition of organic pollutants, including dyes and pharmaceutical residues. Importantly, TiO_2 (Zhang et al., 2020) is chemically stable, non-toxic and affordable, which makes it one of the most promising nanomaterials (Raliya et al., 2016) in water treatment technologies.

Fe_3O_4 (Wang et al., 2018), in turn, demonstrates powerful magnetic properties, which allows it to be used as a magnetic sorbent. Its efficiency in the removal of heavy metal ions is explained by electrostatic interactions and the possibility of forming intra- or intermolecular complexes. One of the main advantages of magnetite is the possibility of its rapid removal from purified water using an external magnetic field, which greatly facilitates the operation and regeneration of the sorbent. However, in a low pH environment, Fe_3O_4 (Wang et al., 2018) can be partially dissolved, which requires additional stabilization or surface modification.

ZnO (Li et al., 2021) is a versatile material with pronounced antibacterial activity, photocatalytic ability and high sorption coefficient. It is widely used for water purification from heavy metals, in particular cadmium and lead, as well as organic dyes. At the same time, its activity largely depends on the morphology of the particles: nanorods, nanoplates and nanospheres demonstrate different adsorption capacity depending on the openness of the crystallographic planes. In addition, it is important to take into account the tendency of ZnO (Li et al., 2021) to aggregation in an aqueous environment, which can reduce the available surface for sorption. Manganese oxides, in particular MnO_2 (Ghosh et al., 2016), are characterized by a high ability to oxidize many organic and inorganic compounds. The literature describes cases of effective use of MnO_2 (Ghosh et al., 2016) for the removal of chromium (VI) from industrial wastewater. In this case, both sorption and catalytic action are observed. The mechanism involves the reduction of Cr^{6+} ions to the less toxic form Cr^{3+} with subsequent sorption or precipitation.

Copper oxide (CuO (Liu et al., 2020)) also exhibits interesting properties in water purification systems. Due to the presence of free d-electrons, it is capable of participating in electron transfer reactions, which opens up the possibility of its application in photocatalytic and electrochemical systems. CuO (Liu et al., 2020) is active in the removal of As^{5+}, Pb^{2+} ions, as well as in the decomposition of some organic impurities. However, due to the possible toxicity of copper ions in the aquatic environment, it is necessary to ensure control over their release after purification.

It has been shown that the purification efficiency depends on a number of conditions: pH of the aqueous environment, temperature, contact time, contaminant concentration and the presence of competitive ions. Thus, at low pH values, the sorption efficiency of metal cations, as a rule, increases due to increased ionization of the nanoparticle surface, but this may be accompanied by a decrease in the stability of the oxides themselves. In an alkaline environment, the formation of hydroxide precipitates can lead to the fixation of metals in the form of insoluble phases, which is also used as an additional purification mechanism.

According to the results of a systematic analysis, one of the promising directions is the creation of composite systems in which metal oxide nanoparticles are combined with polymer matrices, natural sorbents (zeolites, clays), graphene or carbon nanotubes. Such systems provide improved stability, controlled dispersion of nanoparticles and the possibility of multiple use. In addition, composites allow for the effective combination of mechanisms of action - for example, sorption and photocatalysis (Qu et al., 2013) - in one technological solution.

It should also be noted that many studies consider the regeneration of nanomaterials (Raliya et al., 2016) as a key factor for reducing the cost and environmental risks of purification technologies. Most metal oxides retain high efficiency after several cycles of use, however, some of them, especially those modified with organic functional groups, require delicate regeneration conditions, which may limit their practical application.

Despite their numerous advantages, the widespread industrial adoption of nanostructured metal oxides is currently limited by the lack of standardized testing protocols, the potential ecotoxicological risks of the nanoparticles themselves, and the need for - adaptation of existing water treatment systems to new technologies. Therefore, it is important to conduct further interdisciplinary research with a focus on safety, long-term stability, scalability and cost-effectiveness of using such materials.

4. Conclusions

The theoretical study conducted allows us to conclude that nanostructured metal oxides are promising materials for the treatment of industrial wastewater due to the combination of high reactivity, developed specific surface area, stability and multifunctionality. The greatest scientific and practical interest is in the oxides of titanium, zinc, iron, manganese, copper and aluminum, which exhibit high efficiency in the processes of sorption, photocatalysis, precipitation and complexation.

The analyzed literature sources confirm that the effectiveness of nanomaterials largely depends on their morphology, synthesis method, application conditions and type of pollutants. In addition, the possibility of regeneration and reuse of materials plays an important role, which directly affects the economic feasibility of implementing technologies on an industrial scale.

One of the promising areas of development is the creation of composite and hybrid materials based on metal oxides, which provide increased stability, selectivity and multifunctionality of purification systems. At the same time, further research should be aimed at standardizing methods for assessing the effectiveness of nanomaterials, assessing their long-term impact on the environment, studying the mechanisms of interaction with different types of pollutants, and adapting them to the real conditions of industrial enterprises.

In general, metal oxides in nanoform have significant potential for the development of new, effective and environmentally friendly water purification technologies that meet the objectives of sustainable development and modern challenges in the field of water resources protection. This is also confirmed in the works.

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ПЕРСПЕКТИВИ ВИКОРИСТАННЯ ОКСИДІВ МЕТАЛІВ У НАНОФОРМІ ДЛЯ ОЧИЩЕННЯ ПРОМИСЛОВИХ СТІЧНИХ ВОД

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У статті представлено результати теоретичного дослідження щодо перспектив використання оксидів металів у наноформі для очищення промислових стічних вод. Загострення проблеми забруднення водного середовища неорганічними сполуками, зокрема іонами важких металів (Pb^{2+}, Cd^{2+}, Hg^{2+}, Cr^{6+}), а також фосфатами, нітратами та сульфатами, зумовлює необхідність упровадження інноваційних та екологічно безпечних технологій очищення. Традиційні методи водоочищення часто виявляються малоефективними за умов високої концентрації забруднювачів або складного складу стічних вод. Наноструктуровані оксиди металів завдяки високій питомій поверхні, здатності до йонного обміну та каталізу демонструють перспективні властивості для видалення токсичних компонентів. У дослідженні здійснено аналітичний огляд сучасної наукової літератури, присвяченої властивостям, методам синтезу та застосуванню TiO_2, ZnO, Fe_3O_4, MnO_2, CuO та Al_2O_3 у процесах очищення. Детально розглянуто механізми сорбції, фотокаталізу, осадження та комплексоутворення. Проаналізовано чинники, що впливають на ефективність очищення, зокрема pH середовища, морфологію частинок, температуру, концентрацію забруднювачів і тривалість контакту. Особливу увагу приділено створенню композитних матеріалів та функціоналізованих наноматеріалів, які підвищують селективність, відновлюваність і стабільність в агресивних умовах. Розглянуто також екологічні ризики, методи регенерації та обмеження впровадження у промисловому масштабі. У висновках підкреслено значущість наноструктурованих оксидів металів для розробки ефективних, масштабованих і сталих технологій очищення води, що відповідають сучасним екологічним і техногенним викликам. Рекомендовано подальші міждисциплінарні дослідження, спрямовані на вирішення питань безпечності, стандартизації та економічної доцільності.

Ключові слова: *наноматеріали, оксиди металів, стічні води, очищення води, сорбція, фотокаталіз*