Modern Physical Chemistry Research (2025)
Clausius Scientific Press, Canada

DOI: 10.23977/mpcr.2025.050103
ISSN 2616-1702 Vol. 5 Num. 1

ZnO Analysis of the Effect of Nanostructure Photocatalytic Antibiotic Wastewater Treatment

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Keywords: ZnO nanomaterials; photocatalysis; antibiotic wastewater; degradation mechanism; catalyst stability

Abstract: With the widespread use of antibiotics, the pollution problem of antibiotic wastewater is becoming more and more serious, and it is difficult for traditional water treatment methods to completely remove antibiotics and their metabolites in water. ZnO Because of its excellent photocatalytic performance, nano-photocatalytic technology has become an effective way to solve the antibiotic wastewater treatment. This paper summarizes the application progress of ZnO nanophotocatalysts in antibiotic wastewater treatment, and analyzes the basic properties of ZnO nanostructures and their photocatalytic degradation mechanisms. We mainly explored the effect of ZnO photocatalytic degradation of antibiotic wastewater, compared the treatment effect of different antibiotic wastewater, and evaluated the key factors affecting the photocatalytic performance of ZnO, such as light intensity, pH value, etc. The stability and regeneration properties of ZnO photocatalysts are further discussed, and the long-term properties and regeneration ability of the catalysts are improved through material optimization and surface modification are proposed. The challenges and future directions of ZnO nano-photocatalytic technology in antibiotic wastewater treatment are summarized.

1. Introduction

With the wide application of antibiotics, the discharge of antibiotic wastewater is increasing, which contain antibiotics and their metabolites that have not been completely metabolized or degraded, which pose a serious threat to the water ecological environment and human health. Traditional water treatment technologies, such as physical adsorption, chemical precipitation and biodegradation, can remove some pollutants, but they have poor removal effect on refractory organic matter such as antibiotics. As a new type of environmental purification technology, photocatalytic technology has gradually become an effective means to solve the problem of antibiotic wastewater treatment with its high efficiency, environmental protection and sustainability. ZnO Nanomaterials have become one of the research hotspots because of their excellent photocatalytic properties, low cost and non-toxicity. This paper will systematically review the application progress of ZnO nanophotocatalyst in antibiotic wastewater treatment, focus on the key issues such as degradation mechanism, performance optimization, stability and regatability, and explore the future research direction.

2. Characteristics and treatment requirements of antibiotic wastewater

2.1 The sources and types of antibiotic wastewater

Antibiotic wastewater mainly comes from pharmaceutical production, hospital wastewater, aquaculture industry and human daily use of wastewater discharge [1]. In the process of pharmaceutical production, a large number of antibiotic apis and their derivatives are not completely recovered in the manufacturing, cleaning, packaging and other links, and finally enter the sewage system. Hospital wastewater contains the antibiotics and their metabolites left in the patient, which often contains a variety of drug components. Antibiotics in the breeding industry are mainly used for the prevention and control of animal diseases, but a large number of drugs not absorbed by animals will enter the environment through the excrement, forming a high concentration of antibiotic wastewater [2]. With the widespread use of antibiotics, wastewater after personal consumption may also become a source of antibiotic contamination. Common antibiotics include tetracycline, penicillin, chloramphenicol, sulfonamides, etc. These drugs have strong stability in the environment and are difficult to be degraded naturally. The long-term residue will pose a serious threat to the ecological environment and human health [3]. Therefore, the effective treatment of the antibiotic wastewater is very urgent.

2.2 Environmental impact of antibiotic wastewater

Antibiotic wastewater has a profound impact on the environment, mainly reflected in its harm to the water ecosystem, soil and biology [4]. After antibiotics enter the water, it may lead to change the structure of microbial communities in the water. Chronic exposure to low concentrations of antibiotics may confer resistance to aquatic microorganisms, which may affect the stability of the ecological chain and species diversity [5]. The drug composition in antibiotic wastewater is difficult to be completely removed by conventional sewage treatment methods, leading to its accumulation in water bodies, and then affecting the safety of drinking water and the quality of farmland irrigation water sources. Long-term residues of antibiotics may be transmitted through the food chain to higher organisms, especially humans, increasing the risk of transmission of resistant pathogens [3]. The discharge of antibiotic wastewater not only damages the ecological environment, but also may bring a serious threat to human health. Therefore, it is urgent to develop efficient treatment technology to reduce its negative impact on the environment.

2.3 The current status and challenges of wastewater treatment technology

The treatment efficiency of antibiotic wastewater is limited by traditional physical chemical method. It for example, the removal rate of tetracycline by activated carbon adsorption is only 40% - 60%, and its metabolite [6] cannot be completely degraded. Photocatalytic technology has become a research hotspot because of its efficient degradation ability, but the stability of the catalyst is still a key bottleneck. Wang Chao et al. (2018) found that the degradation efficiency of unmodified ZnO nanoparticles to chloramphenicol decreased by 35% after three consecutive applications, indicating that their cyclic stability was insufficient for [7]. Traditional physicochemical methods, such as activated carbon adsorption, ozone oxidation and chemical precipitation, can remove some pollutants, but often fail to effectively degrade antibiotics and their metabolite [8]. These methods have problems such as high treatment cost, secondary pollution and unstable treatment effect. Although biological treatment technology has some advantages in degrading organic matter, the high concentration of drugs in antibiotic wastewater often inhibit the activity of microorganisms and reduces the treatment efficiency [9]. Recently, photocatalytic oxidation, as an emerging environmental protection technology, has attracted wide attention due to its ability to rapidly degrade organic pollutants under ambient temperature and pressure. However, the stability, regenerability and catalytic efficiency of photocatalysts are still the bottleneck of current research. Therefore, the development of efficient, economical and long-term stable wastewater treatment technology has become a key task to solve the antibiotic wastewater pollution.

3. ZnO Application of nanophotocatalysts in antibiotic wastewater treatment

3.1 Photocatalytic degradation mechanism

We show that the morphology of ZnO nanomaterials significantly affects their catalytic efficiency. The degradation rate of ZnO nanorods prepared by Yang Honghong et al. (2023) reached 92%, while the traditional nanoparticles only reached 68%, which is attributed to the larger specific surface area of the nanorods and the better carrier separation efficiency of [10]. The development of composites further improved the performance. For example, the degradation rate constant (k value) of ZnO / TiO_2 heterojunction was 0.045 min-1, which was 1.8 times [11] higher than that of a single ZnO. The application of ZnO nano-photocatalyst in antibiotic wastewater treatment mainly depends on its photocatalytic degradation mechanism. In the process of photocatalytic degradation, ZnO nanomaterials can absorb light energy and excite electrons to transition to the conduction band, producing free electrons (e) and holes (h). These free electrons and holes can react with water molecules and dissolved oxygen molecules to generate reactive oxygen species (such as · OH, · O2, etc.). These reactive oxygen species have strong oxidation capacity and can effectively degrade the organic substances in antibiotic molecules. Specifically, holes (h) react with water molecules to form · OH radical, while free electrons (e) react with dissolved oxygen to form superoxide anion (· O2). Under the combined action of the two, they can break the chemical bonds of antibiotic molecules, destroy their molecular structure, and finally convert them into harmless simple compounds such as CO2 and H2O [12].

ZnO The high specific surface area and good electron conductivity of the nanophotocatalyst enhance its photocatalytic activity, which can effectively promote the separation of electrons and holes and reduce the composite phenomenon, thus improving the degradation efficiency. The band structure of ZnO also determines its high photocatalytic activity under UV light, which is especially suitable for treating UV-exciting organic pollutants. ZnO Nanophotocatalyst, through the excitation of light electron-hole pair, generates strongly oxidized free radicals, effectively degrade the harmful components in antibiotic wastewater, and provides a new technical path for environmental pollution control[13].

3.2 Research progress in the application of ZnO nanomaterials in antibiotic wastewater treatment

Metal doping can significantly improve the optical response range of ZnO. Ma Yun et al. (2022) found that the degradation efficiency of Ag-doped ZnO (Ag-ZnO) on sulfonamide antibiotics increased to 85% under visible light, while the undoped ZnO was only 52%, attributed to the surface plasmon resonance of Ag effect of nanoparticles. Moreover, N element doping can promote the generation of · OH radical by introducing oxygen vacancies, increasing the degradation rate of chloramphenicol by 40%. With its excellent photocatalytic properties, high stability and environmental protection, ZnO is ideal for antibiotic wastewater treatment. Researchers have prepared different shapes and structures of ZnO nanomaterials (such as nanorods, nanosheets, nanoparticles, etc.), in order to improve their catalytic efficiency of [14]. In particular, the specific surface area, crystal structure and defect regulation of ZnO nanomaterials directly affect their photocatalytic properties.

Several studies have shown that ZnO nanomaterials can effectively degrade the pollutants in a variety of antibiotic wastewater, including tetracycline, penicillin, chloramphenicol, etc. By adjusting the morphology and size of ZnO, the researchers found that nanostructured ZnO materials have higher photocatalytic activity and better stability than large-size ZnO particles. For example, ZnO nanorods exhibit better degradation than ZnO nanoparticles due to their large surface active sites. In order to further improve the catalytic performance of ZnO, many scholars have developed a composite photocatalyst [15,16] through surface modification or composite with other semiconductor materials (such as TiO2, CuO, etc.). These composite catalysts can effectively improve the separation efficiency of photogenerated electron-hole pairs and reduce the composite phenomenon, thus significantly enhancing the application effect of ZnO in antibiotic wastewater treatment.

3.3 The performance optimization and improvement of the ZnO catalyst

The molecular complexity of antibiotics directly affects the degradation efficiency. Zhou Shuai et al. (2022) found that tetracycline contained benzene ring and amino group, and its degradation rate (k=0.025 min-1) was significantly lower than that of simple penicillin (k=0.038 min-1) [17]. In addition, the effect of the initial concentration was significant: when the tetracycline concentration increased from 10 mg/L to 50 mg/L, the degradation efficiency of ZnO decreased from 89% to 47%, mainly due to the aggravation of [18] at high concentration. ZnO The performance optimization and improvement of the catalyst is the key to improve its application efficiency in antibiotic wastewater treatment. In order to overcome some limitations of ZnO in practical applications, such as low photocatalytic activity, slow reaction rate, and poor stability of the photocatalyst, the researchers have carried out various optimization work. Modified ZnO nanocatalysts are a common method to improve their catalytic properties. Common modification methods include surface doping, crystal structure adjustment, and morphology control. For example, by doping with metal ions (such as Ag, Cu, Fe, etc.) or non-metallic elements (such as N, C, etc.), the electronic structure of ZnO can be effectively changed, and its optical absorption performance and electron conductivity can be improved, thus improving the photocatalytic efficiency. Doped metallic or non-metallic elements can provide additional energy levels, promote the separation of electron-hole pairs, reduce the electron-hole recombination, and then enhance the catalytic activity of [10]. The recombination of ZnO with other semiconductor materials is also an important way to improve its catalytic performance. ZnO The recombination with TiO2, CuO, SnO2 and other materials can not only broaden the light absorption range, but also enhance the separation efficiency of light-generated electron-hole pair, so as to improve the photocatalytic degradation performance. Through synergy, the composite material can improve the stability and regeneration of the catalyst, reduce the inactivation of ZnO in the reaction process, and prolong the service life of the catalyst. The morphology regulation of ZnO is also an important means to improve its performance. It have shown that one-or two-dimensional ZnO materials such as nanorods and nanosheets are more conducive to improve the reaction rate than conventional nanoparticles. This is because 1-or 2-D ZnO materials provide more active sites and larger surface area, thus facilitating the contact of the antibiotic molecule with the catalyst and improving the degradation efficiency.

The performance of ZnO catalyst is significantly improved by doping, recombination and morphology regulation. These optimization measures provide a more efficient and stable solution for the application of ZnO in antibiotic wastewater treatment.

4. Analysis of the effect of ZnO nanostructure photocatalytic treatment of antibiotic wastewater

4.1 Evaluation criteria for the photocatalytic treatment effect

The effect evaluation criteria of photocatalytic treatment of antibiotic wastewater are mainly based on the degradation efficiency, the reaction rate and the degree of water quality improvement of the treated wastewater [19]. Degradation efficiency is one of the core indicators to evaluate the photocatalytic effect, usually taking the removal rate or concentration change of antibiotics as the measure. In practical studies, the removal rate of antibiotics in water samples is often calculated by measuring the ratio of the initial concentration and the treated concentration, so as to evaluate the effect of photocatalytic degradation [20]. The higher removal rate means that the photocatalyst can effectively degrade the antibiotic pollutants and reduce the drug residues in the water body. Reaction rates are often used to reflect the reaction efficiency of the photocatalytic process. Reaction rate is usually measured by building kinetic models to calculate the rate constants (k values) of the degradation reaction. For photocatalytic degradation reactions, pseudo-first order reaction kinetic models are often fitted, and larger rate constants indicating faster photocatalytic degradation. The reaction rate is an important basis for evaluating the catalyst activity and the overall efficiency of the system. The improvement of water quality after wastewater treatment is also one of the evaluation criteria, especially the removal effect of major pollutants such as COD (chemical oxygen demand), BOD (biochemical oxygen demand) and TOC (total organic carbon) in water. The ideal photocatalytic treatment should not only remove the antibiotic itself, but also effectively reduce the content of organic matter in the water and avoid secondary contamination.

The evaluation criteria of the effect of photocatalytic treatment mainly include multiple dimensions, such as antibiotic removal rate, reaction rate and water quality improvement degree, which can fully reflect the application effect of ZnO nanophotocatalyst in antibiotic wastewater treatment.

4.2 Comparison of different antibiotic wastewater treatment effects

The treatment effect of different antibiotic wastewater showed significant differences in the ZnO nano-photocatalytic process, which is closely related to the chemical structure, polarity, hydrophilicity of antibiotics and their stability in water. Studies have shown that widely used antibiotics such as tetracycline, chloramphenicol, and penicillin have significantly different removal effects in photocatalytic degradation [21]. Tetracycline molecules contain abundant amino groups and carboxyl groups, and their complex ring structure makes it relatively stable and slowly degraded during photocatalysis. In contrast, antibiotics such as chloramphenicol and penicillin can usually be degraded rapidly under ZnO photocatalysis due to their simple molecular structure. In particular, penicillin antibiotics usually have higher degradation rates in photocatalytic reactions due to their smaller molecules and strong chemical activity. The initial concentration of antibiotics also significantly affected the treatment effect. In high concentration wastewater, the reaction efficiency of ZnO nanophotocatalyst may be suppressed due to the aggravation of photogenerated electrons and holes, which leads to reduced catalytic activity. Low-concentration wastewater is relatively easy to treat, and the ZnO catalyst can efficiently degrade the antibiotic molecules in a short time. Further research showed that the degradation efficiency of the wastewater and the treatment efficiency of different antibiotics can significantly improve the treatment effect of ZnO nanophotocatalyst.

ZnO There are different effects of different antibiotics, and the molecular structure, wastewater concentration and reaction conditions of antibiotics are the key factors affecting the efficiency of photocatalytic degradation. Targeted treatment optimization of different types of antibiotic wastewater will help to improve the performance of ZnO photocatalysts in practical applications.

4.3 Factors affecting ZnO photocatalytic performance (such as light intensity, pH value, etc.)

ZnO In the treatment of antibiotic wastewater, its catalytic performance is affected by a variety of factors, among which light intensity, pH value and catalyst dosage are the most critical influencing factors. Light intensity has a direct effect on the properties of ZnO photocatalysts. The efficiency of the photocatalytic reaction is closely related to the irradiation of ultraviolet light. The greater the light intensity, the more opportunities the ZnO nanomaterials has to absorb light energy, thus stimulating more electron and hole pairs and enhancing the rate of the photocatalytic reaction. It is found that in a certain range, with the increase of light intensity, the degradation rate of antibiotics also shows an increasing trend, but when the light intensity is too high, the reaction system may be unstable [22] due to thermal effect and excessive activation of the photocatalyst surface. The pH value is another important factor affecting the photocatalytic performance of ZnO. The surface charge properties of ZnO nanomaterials change with pH, which affects the interaction between antibiotic molecules and the catalyst. Usually, under acidic conditions, the ZnO surface shows positive charges, while the antibiotic molecules may have negative charges, and this charge attraction helps to improve the adsorption capacity of the antibiotic molecules, thus promoting photocatalytic degradation. However, in an alkaline environment, the ZnO surface may change to a negative charge, affecting its interaction with the antibiotic molecules, leading to a decrease in the degradation efficiency. The factors such as the catalyst dosage, the solution temperature and other ionic components in the wastewater also have an influence on the photocatalytic performance of ZnO. For example, the low amount of catalyst may lead to insufficient catalytic site and low reaction rate; when the catalyst is excessive, it may cause the aggregation between the photocatalysts, reduce its effective surface area, and instead reduce the degradation efficiency. Optimizing the light intensity, pH value and catalyst dosage are of great significance to improve the effect of ZnO photocatalyst in antibiotic wastewater treatment.

5. Study on the regeneration and stability of ZnO photocatalysts

5.1 Stability assessment of the catalyst

Wang Wenliang (2021) found that the degradation efficiency of tetracycline by unmodified ZnO on tetracycline decreased from 92% to 58%, while Fe3 + -doped ZnO (Fe-ZnO) only decreased to 83%, attributed to Fe3 + inhibited photocorrosion and enhanced structural stability [23]. The stability of ZnO photocatalyst is one of the key factors for its long-term application effect in antibiotic wastewater treatment. Stability assessment is usually achieved through multiple recycling experiments, focusing on whether the catalyst has performance decay or structural changes during the reaction process [24]. It is shown that the photocatalytic activity of ZnO photocatalyst gradually decreases without effective repair or regeneration, and this phenomenon is usually related to the loss of the surface active site of the catalyst, the destruction of the crystal structure and the generation of aggregation phenomenon. To evaluate the stability of ZnO, it is often performed by detecting changes in its photocatalytic degradation capacity, usually using the degradation removal rate of standard antibiotic wastewater as a measure. The characterization methods of catalysts, such as X-ray diffraction (XRD), scanning electron microscopy (SEM) and specific surface area analysis, are also often used to observe the structural changes and crystal form stability of ZnO nanomaterials after multiple cycles. The study shows that by optimizing the synthesis process of ZnO, doped metal or recombination with other materials, the ZnO can effectively improve its stability and delay the inactivation process of the catalyst, thus improving its long-term effect and economy in practical application. Therefore, the stability of ZnO photocatalyst is an important evaluation index for its commercial application, which directly determines its practical application potential in environmental governance.

5.2 Regeneration and reuse of the catalyst

Regeneration and reuse of ZnO photocatalysts are important indicators of their sustainability in practical applications. Because the catalyst may gradually lose its activity due to the treatment process of pollutant adsorption, surface poisoning or crystal structure change, studying the regeneration performance of the catalyst is crucial to reduce the operating cost and improve the resource utilization. Regeneration is usually performed by physical or chemical methods such as heat treatment, acid-base washing or solvent extraction to remove organic contaminants and other impurities accumulated on the surface of the catalyst. Heat treatment (400℃, 2 h) effectively restored the catalytic activity of the inactivated ZnO. The experiments showed that the degradation rate of regenerated ZnO recovered from 89% in the first to 82% in the third, while the efficiency of the unregenerated catalyst was only 45% [25]. Experimental studies have shown that the ZnO photocatalyst can restore some catalytic activity after regeneration, but its efficiency usually gradually decreases with the number of cycles, especially in the high intensity pollution environment.

In order to improve the regenerative properties of ZnO catalysts, many researchers have adopted the strategies of composite materials or surface modification to enhance the pollution resistance and stability of the catalysts. By doping with metal or non-metal elements and recombining with other materials, the inactivation of ZnO catalyst can be significantly delayed and improve its reuse performance. Overall, the good regeneration and reuse performance of ZnO photocatalyst are key for its long-term application in antibiotic wastewater treatment, which can effectively reduce the treatment cost and improve the economic benefits.

6. Conclusion

ZnO Nanophotocatalytic technology has shown a good application prospect in the field of antibiotic wastewater treatment. Its excellent photocatalytic performance and low environmental burden make it ideal for the treatment of antibiotic wastewater. However, ZnO nanophotocatalysts still face some challenges in practical applications, including catalyst stability, regeneration, and adaptability to different types of antibiotic wastewater. By optimizing the synthesis process, surface modification and the development of composite materials, the photocatalytic efficiency and stability for long-term applications can be effectively improved. Optimizing the reaction conditions, such as light intensity, pH value and catalyst dosage, is also the key to improving the photocatalytic degradation efficiency of ZnO. In the future, the further development of ZnO nano-photocatalytic technology will rely on the optimization of the catalyst performance, the improvement of the treatment process, and the large-scale application of wastewater treatment systems. With the continuous progress of technology, the application prospect of ZnO photocatalyst in antibiotic wastewater treatment is worth expecting.

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