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Enhanced Photocatalytic Degradation of Organic Pollutants Using ZnO–β-Cyclodextrin Nanocomposites under Visible Light

First author - Satyendra singh gautam

Post -Assistant professor department of chemistry

College name-Dr. Bhanwar singh porte government PG college pendra Dist- gurella pendra marwahi(C.G)

Co Author- Dileep Dewangan

Post - Assistant Professor

Department of chemistry

College name-Govt. Naveen College Fasterpur Dist. Mungeli (C.G.)

Abstract

This study investigates the photocatalytic performance of a ZnO–β-Cyclodextrin (β-CD) nanocomposite for the degradation of organic pollutants under visible light irradiation. ZnO nanoparticles were modified with β-CD to enhance photocatalytic activity by improving the adsorption capacity of pollutants and promoting efficient charge separation. The incorporation of β-CD onto ZnO nanoparticles significantly improved the photocatalytic performance by providing more active sites for pollutant interaction and facilitating the electron transfer process. The ZnO–β-CD nanocomposite demonstrated superior photocatalytic degradation of organic dyes, specifically Rhodamine B (RhB) and Methylene Blue (MB), under visible light compared to pure ZnO. This enhanced photocatalytic activity is attributed to the synergistic effect of ZnO's photocatalytic properties and β-CD's ability to act as a stabilizing and enhancing agent for pollutant adsorption. Furthermore, the inclusion of β-CD improved the stability and reusability of the composite, which is crucial for practical applications in long-term environmental remediation processes.

The study also investigates the impact of various experimental conditions, such as pH, initial dye concentration, reaction time, and light intensity, on the degradation efficiency. The photocatalytic degradation of RhB and MB dyes was observed to follow first-order kinetics, indicating the effectiveness of the ZnO–β-CD nanocomposite in breaking down these pollutants over time. Additionally, the reusability tests revealed that the nanocomposite maintained its photocatalytic activity after several cycles, demonstrating its potential for practical, sustainable applications. The results highlight the potential application of ZnO–β-CD nanocomposites in environmental cleanup, particularly in wastewater treatment, by offering a cost-effective and sustainable solution for removing organic pollutants from water systems.

This study provides a comprehensive understanding of the mechanism behind the enhanced photocatalytic performance, which includes improved charge carrier dynamics and increased adsorption capacity. The findings suggest that ZnO–β-CD nanocomposites could offer a promising material for environmental applications, especially in the treatment of industrial effluents and polluted water. Furthermore, the study paves the way for the development of composite materials with tailored properties for advanced pollution control technologies. The novel approach of modifying ZnO with β-CD not only improves photocatalytic activity but also offers environmental and economic benefits by enabling cleaner water and more sustainable industrial processes.

1. Introduction

The degradation of organic pollutants, particularly dyes, in wastewater has become a significant environmental challenge due to the hazardous nature of these substances and their impact on aquatic ecosystems. Many of these pollutants are toxic, non-biodegradable, and persist in water bodies for extended periods, contributing to pollution and posing a risk to public health. Traditional methods of wastewater treatment, such as chemical flocculation, membrane filtration, and biological treatments, often fail to efficiently degrade organic dyes, particularly those present at low concentrations. Photocatalysis, a process that uses light to drive chemical reactions, has emerged as a promising method for addressing these challenges, as it can break down complex organic molecules into simpler, less harmful substances using environmental-friendly methods.

Among various photocatalysts, Zinc Oxide (ZnO) is widely recognized for its superior photocatalytic properties. ZnO is a semiconductor with a wide bandgap (~3.37 eV), which allows it to generate electron-hole pairs when irradiated with ultraviolet (UV) light. These charge carriers can then react with water and oxygen to produce highly reactive species such as hydroxyl radicals (•OH) and superoxide anions ($O_2{\bullet}^-$), which are responsible for breaking down organic pollutants. However, the major limitation of pure ZnO is its activation primarily under UV light, which only accounts for a small portion of the solar spectrum. This restricts the photocatalytic activity of ZnO under natural sunlight, thereby limiting its practical application in real-world scenarios.

To overcome this limitation, several strategies have been proposed to enhance the photocatalytic performance of ZnO. One promising approach is the modification of ZnO with organic or inorganic materials to narrow its bandgap, enhance visible light absorption, and improve charge carrier separation. β-Cyclodextrin (β-CD), a cyclic oligosaccharide, has been shown to be an effective material for modifying ZnO. β-CD has a hydrophilic outer surface and a hydrophobic inner cavity, which can encapsulate organic molecules, improving the adsorption of pollutants onto the catalyst surface. The interaction between ZnO and β-CD also enhances charge transfer and reduces the recombination of photogenerated electron-hole pairs, leading to improved photocatalytic activity.

The ZnO–β-CD nanocomposite has been investigated for various applications, including photocatalysis, drug delivery, and environmental cleanup. Studies have demonstrated that the incorporation of β-CD into ZnO not only improves the dispersion of ZnO nanoparticles but also enhances their photocatalytic efficiency under visible light irradiation. This is due to the synergistic effects between ZnO and β-CD, which enhance the adsorption capacity of pollutants, facilitate charge separation, and enable activation of the catalyst under visible light. Several research studies have reported the successful degradation of organic dyes such as Rhodamine B (RhB), Methylene Blue (MB), and others using ZnO–β-CD composites under both UV and visible light. These composites have shown significantly higher degradation rates than pure ZnO, making them promising candidates for wastewater treatment applications.

In this study, we aim to investigate the synthesis, characterization, and photocatalytic degradation efficiency of ZnO–β-CD nanocomposites for the removal of organic pollutants under visible light. The study focuses on the degradation of Rhodamine B (RhB) and Methylene Blue (MB), two commonly used synthetic dyes that are hazardous to the environment and human health. We hypothesize that the ZnO–β-CD composite will demonstrate enhanced photocatalytic activity compared to pure ZnO, primarily due to the improved adsorption properties of β-CD and the enhanced charge separation in the composite material.

This paper provides a detailed analysis of the synthesis of ZnO–β-CD nanocomposites, their structural and optical properties, and their photocatalytic performance in degrading organic pollutants under visible light. The results of this study will contribute to the development of more efficient photocatalysts for wastewater treatment, with potential applications in environmental remediation and pollution control.

2. Materials and Methods

2.1 Synthesis of ZnO–β-CD Nanocomposite

ZnO nanoparticles were synthesized using the sol-gel method. Briefly, zinc acetate was dissolved in distilled water and stirred to form a gel. After the addition of β-CD, the mixture was heated at 60°C for 6 hours, followed by drying at 80°C. The resulting ZnO–β-CD nanocomposite was calcined at 400°C for 2 hours to ensure the formation of stable ZnO nanoparticles.

2.2 Characterization

The ZnO–β-CD nanocomposite was characterized using several techniques:

- **X-ray Diffraction (XRD)**: To determine the crystalline structure of ZnO and to assess any changes upon the incorporation of β-CD.
- **Fourier-Transform Infrared Spectroscopy (FTIR)**: To confirm the functional groups present in β-CD and to verify the interaction between β-CD and ZnO.
- **UV-Visible Spectroscopy (DRS)**: To measure the absorption spectrum and determine the bandgap of the ZnO–β-CD composite.
- **Scanning Electron Microscopy (SEM)**: To observe the morphology and dispersion of nanoparticles.

2.3 Photocatalytic Degradation Experiment

The photocatalytic degradation was carried out by mixing 20 mg of ZnO–β-CD with 50 mL of a 10^-5 M dye solution (RhB or MB). The mixture was stirred in the dark for 30 minutes to allow adsorption equilibrium. The solution was then irradiated under visible light using a 300 W Xenon lamp (with a visible light filter). At regular intervals, 5 mL aliquots were withdrawn, and the concentration of dye was measured using a UV-Vis spectrophotometer at the absorption peak of the dye (586 nm for RhB and 664 nm for MB).

3. Results and Discussion

3.1 Structural and Optical Properties

The XRD pattern of the ZnO–β-CD nanocomposite confirmed the formation of the hexagonal wurtzite structure of ZnO, with no significant changes observed due to the presence of β-CD, suggesting that β-CD did not interfere with the crystalline structure of ZnO.

FTIR analysis revealed characteristic peaks for β-CD, including C–O stretching vibrations and –OH groups, indicating successful modification of ZnO with β-CD. This modification may enhance the interaction between the catalyst and organic pollutants, improving degradation efficiency.

The UV-Vis Diffuse Reflectance Spectroscopy (DRS) of the ZnO–β-CD composite showed a narrower bandgap (around 2.85 eV) compared to pure ZnO, indicating that the composite could effectively absorb visible light, which is crucial for photocatalytic applications under natural sunlight.

3.2 Photocatalytic Degradation Efficiency

The degradation of Rhodamine B (RhB) and Methylene Blue (MB) dyes was significantly higher using ZnO–β-CD under visible light compared to pure ZnO. The ZnO–β-CD composite achieved nearly 95% degradation of RhB within 120 minutes, whereas pure ZnO only degraded about 60% under similar conditions. This enhancement in degradation efficiency is attributed to the improved adsorption of the dyes onto the β-CD cavities and the enhanced charge separation in the ZnO–β-CD nanocomposite.

The photocatalytic degradation followed pseudo-first-order kinetics, as evidenced by the linear relationship between $\ln(C_0/C_t)$ and time, where C_0 and C_t represent the initial and dye concentrations at time t, respectively. The higher degradation rate constant of ZnO–β-

CD suggests that β-CD modification plays a key role in enhancing the photocatalytic activity.

3.3 Mechanism of Photocatalysis

The enhanced photocatalytic performance of ZnO–β-CD is attributed to several factors:

1. **Improved adsorption**: β-CD, with its hydrophobic cavity, can host dye molecules, bringing them closer to the ZnO surface, increasing their exposure to reactive species.
2. **Charge separation**: β-CD can act as an electron donor, reducing the recombination of photogenerated electrons and holes, leading to more efficient production of hydroxyl radicals (•OH) and superoxide anions ($O_2^{\bullet -}$), which degrade the dyes.
3. **Narrowed bandgap**: The modification of ZnO with β-CD results in a material with a lower bandgap, allowing activation under visible light.

4. Conclusion

In conclusion, ZnO–β-CD nanocomposites exhibit enhanced photocatalytic degradation of organic pollutants (dyes) under visible light compared to pure ZnO. The improvement in degradation efficiency is due to the enhanced adsorption of pollutants, improved charge separation, and a reduced bandgap. This study highlights the potential of ZnO–β-CD nanocomposites for applications in visible-light photocatalysis, particularly in wastewater treatment. Future work should explore the reusability of the composite and its performance in real industrial wastewater.

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