Solar-powered Elimination of Ciprofloxacin Utilizing Binary ZnO-based Nanomaterial from Aquatic Environment

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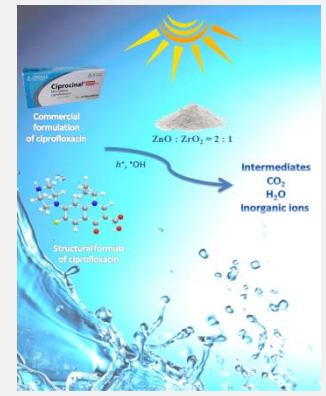

Ciprofloxacin (CIP) is a widely used fluoroquinolone antibiotic prescribed for treating respiratory, urinary tract, gastrointestinal, and abdominal infections. Due to intensive use, CIP often occurs in the environment. This study examined ZnO/ZrO_2 binary photocatalyst for CIP photocatalytic degradation under simulated sunlight. Mineralization and release of inorganic ions during CIP degradation were assessed. Furthermore, an investigation was conducted to understand the mechanism behind the photodegradation and to determine the potential for reusing the photocatalyst. Results showed that ZnO/ZrO_2 outperformed pristine ZnO and ZrO_2 photocatalysts in CIP removal using simulated sunlight. Chemical oxygen demand removal efficiency reached 54.9% after 120 min of photocatalytic degradation. Analysis revealed fluoride, nitrite, and nitrate ion formation during photodegradation. Photogenerated holes were found to be crucial in the CIP degradation mechanism. Also, photocatalyst reutilization maintained an 86% removal efficiency after each 120-min cycle.

Introduction

Presently, there is a significant production of medications, leading to their widespread presence in the environment. This occurs due to inadequate disposal methods for unused drugs and their limited biodegradability during wastewater treatment processes [1]. Ciprofloxacin (CIP), is a fluoroquinolone antibiotic extensively utilized in the treatment of respiratory and urinary tract infections, along with gastrointestinal and abdominal infections [2]. Rodrigues-Mozaz et al. conducted a study of monitoring the presence of 53 antibiotics in wastewater in various European countries and CIP was detected in Portugal in 1,435.5 ng/l concentration [3]. Over the recent years, there has been a tightening of environmental standards aimed at decreasing pollutant emissions. Hence, there is a pressing need to devise methods for effectively removing pollutants from contaminated aquatic environments. One potential solution lies in employing advanced oxidation processes, which, under moderate experimental conditions, have the capacity to generate highly reactive hydroxyl radicals, facilitating pollutant elimination [4].

In this work, activity of novel binary photocatalyst ZnO/ZrO_2 in photocatalytic degradation of CIP under simulated sunlight (SS) was investigated. The level of mineralization during photocatalysis was assessed, as well as the release of various inorganic ions during the photocatalytic degradation of CIP. Additionally, a study was conducted to investigate the mechanism of photocatalytic degradation and the potential for reutilization of photocatalyst.

Material and Methods

The removal processes were carried out in a photochemical cell [5]. A 20 mL aqueous solution containing 0.05 mmol/L of CIP (CAS No 85721-33-1, ≥ 98% purity, Sigma-Aldrich) was measured in the mentioned cell. The photocatalyst ZnO/ZrO_2 (synthesized using threestep mechanochemical-assisted calcination procedure) was added (0.5 mg/mL) to the solution, followed by sonication in an ultrasonic bath for 15 min to reach adsorption-desorption equilibrium. Subsequently, the cell was thermostated at 25 °C, and stirring was initiated with an oxygen stream, 3.0 mL/min, throughout the removal process. The examinations under SS irradiation were conducted using a 50 W halogen lamp (Philips). Direct photolysis experiments were carried out under the same conditions, with no added photocatalyst. The investigations aimed at identifying the active species involved in the degradation mechanism of CIP were carried out by employing EDTA × 2Na, *p*-BQ, NaF, or t-BuOH (3.0 mmol/L). The photocatalytic degradation process were conducted under identical conditions as previously described. The procedure of reutilization study of ZnO/ZrO_2 was as follows: after 120 min of CIP degradation, the ZnO/ZrO_2 suspension was left overnight in darkness to allow the precipitation of ZnO/ZrO_2 nanoparticles. Subsequently, the supernatant was removed, and the photocatalyst was dried in an oven at 60°C for 2 h. After drying, the photocatalyst was added to a fresh solution of CIP, and photocatalytic degradation was carried out under identical experimental conditions. To evaluate the efficiency of the newly synthesized catalyst in degrading CIP, an ultra-fast liquid chromatograph with diode array and fluorescence detector (UFLC-DAD/RF, Shimadzu Nexera) was employed. The chromatographic conditions as follows: 20: 80 (ACN: H_2O, *v*/*v*), flow rate 0.8 mL/min, injection volume 10 µL, column temperature 25 ^oC, absorption maximum at 279 nm. Ion chromatographic determinations were performed on a Dionex ICS 3000 Reagent-Free IC system with conductometric detector. For the anion determinations was used an IonPac AS18 analytical column (250 mm × 4 mm i.d., bead diameter 8 µm). The mobile phase was a solution of KOH (20–40 mmol/L) at a flow rate of 1 mL/min.

Results and Discussion

The efficacy of the newly synthesized binary photocatalyst ZnO/ZrO_2 was compared to that of pristine ZnO and ZrO_2 photocatalysts, as well as direct photolysis of CIP. This comparison aimed to evaluate and potentially validate the enhanced photocatalytic activity. As depicted in Fig. 1, ZnO/ZrO_2 emerged as the most effective photocatalyst for CIP removal. This underscores the enhancement in photocatalytic efficiency achieved by coupling different photocatalysts, particularly in the visible region.

In the successful application of photocatalysis, crucial information pertains to the extent of mineralization attained during the process. To evaluate the degree of mineralization during the photocatalytic degradation of CIP, chemical oxygen demand removal efficiency was determined and after 120 min of photocatalytic degradation it was 54.9%. Additionally, the monitoring of nitrate, nitrite, and fluoride ions through ion chromatography yields valuable data for evaluating the degradation of CIP. Evolution of different ions formed during photocatalytic degradation of CIP was shown in Table 1. To explore the potential mechanism underlying the photocatalytic degradation of CIP, EDTA × 2Na, *p*-BQ, NaF, and *t*-BuOH were employed to scavenge photogenerated holes, superoxide radical ions, adsorbed, and free hydroxyl radicals, respectively. Obtained results showed that the addition of EDTA × 2Na resulted in the most significant inhibition of CIP degradation, indicating that photogenerated holes play a crucial role in the photocatalytic degradation mechanism of CIP. Considering that photocatalyst reutilization is a crucial factor in heterogeneous photocatalysis, the experiments were carried out in two consecutive runs under unchanged experimental conditions. The removal efficiency remained consistent at 86% after 120 min of photodegradation in each cycle, demonstrating that the photocatalyst remained effective even after two uses.

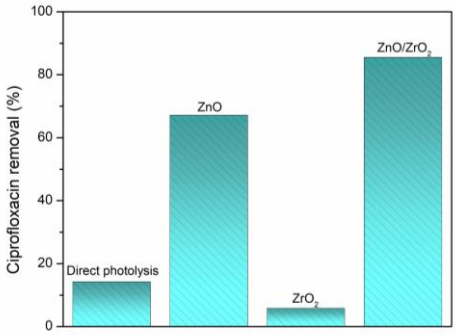

Figure 1. Percentage of CIP removal in the presence/absence of different photocatalysts.

Table 1. Ion chromatography results for CIP compared to ultrapure water.

Ions (mg/L)	Ultrapure water	CIP
Fluoride	< 0.1	0.55
Nitrite	0.31	1.8
Nitrate	< 0.1	3.82

Conclusions

ZnO/ZrO_2 emerged as the most potent photocatalyst for the removal of CIP using simulated sunlight compared to pristine ZnO and ZrO_2 photocatalysts. The assessment of chemical oxygen demand removal efficiency revealed a significant mineralization degree, reaching 54.9% after 120 min of CIP photocatalytic degradation. Furthermore, the investigation included the analysis of the formation of different ions during the photocatalytic degradation of CIP, revealing the presence of fluoride, nitrite, and nitrate ions. The analysis of the potential mechanism showed that photogenerated holes play a crucial role in the photocatalytic degradation of CIP. Finally, regarding the study on photocatalyst reutilization, it was noted that the removal efficiency of CIP remained consistent at approximately 86% after 120 min of photodegradation in each cycle.

Acknowledgments

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