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Original research article

PHOTODEGRADATION OF CIPROFLOXACIN WITH COPER-MODIFIED TITANIUM(IV)-OXIDE

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ABSTRACT – In recent years, the issue of emerging pollutants, particularly antibiotics, in aquatic ecosystems has garnered significant attention due to their potential environmental and public health impacts. To address this, we synthesized TiO_2 modified with Cu at three different molar ratios (0.5%, 1%, and 2%) and applied these photocatalysts to degrade ciprofloxacin in an infusion solution. The photodegradation process was monitored over 240 minutes using UV-Vis spectroscopy. The results indicated that the degradation efficiency of all three photocatalysts was approximately 50%. However, determining the precise degradation efficiency solely through UV-Vis spectroscopy proved challenging. This is because some degradation by-products exhibited absorbance maxima similar to ciprofloxacin, leading to potential inaccuracies in measuring the true extent of degradation. Further analysis, such as high-performance liquid chromatography (HPLC) or mass spectrometry, would be required to more accurately quantify the degradation products and assess the overall efficiency of the photodegradation process. This study highlights the complexity of using UV-Vis spectroscopy alone for analyzing antibiotic degradation in aquatic environments.

Keywords: Photocatalysis, Ciprofloxacin, Rutile TiO_2, DFT Calculations, Metal Decoration.

INTRODUCTION

The environment faces increasing pollution from population growth, industrialization, and human activities, leading to the widespread detection of organic contaminants such as dyes, pesticides, and pharmaceuticals in water [1]. Antibiotics are particularly concerning due to their rising use in human and animal treatment, entering aquatic environments through wastewater from industries, households, farms, and hospitals, as well as agricultural runoff. Despite their low concentrations (micrograms to nanograms per liter), the increasing consumption of antibiotics raises concerns about bacterial resistance and health risks [2]. Annual antibiotic consumption has reached

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between 100,000 and 200,000 tons, with a 65% increase noted between 2000 and 2015, and it is projected to rise by over 200% by 2030 [3]. Commonly detected antibiotics in water include sulfamethoxazole, trimethoprim, and ciprofloxacin, with wastewater treatment plants often unable to fully remove these contaminants [2]. There are several factors that contribute to the presence of ciprofloxacin (CIP) in aquatic environments and nature. First, wastewater treatment plants are not fully capable of removing antibiotics. Additionally, ciprofloxacin (Figure 1), a synthetic fluoroquinolone derivative, is highly stable, making it more resistant to degradation. Lastly, ciprofloxacin is a widely used antibiotic for treating a variety of infectious diseases [4]. Its broad-spectrum activity targets both Gram-positive and Gram-negative bacteria by inhibiting bacterial DNA synthesis through interaction with DNA gyrase, an enzyme essential for bacterial chromosome replication [5].

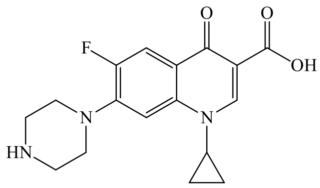

Figure 1 Structure of ciprofloxacin

There is a growing focus on developing effective methods for removing antibiotics from the environment, with UV-based photocatalysis emerging as a promising approach for degrading organic pollutants, including antibiotics [6]. This method offers key advantages such as low cost, energy efficiency, and the ability to operate at room temperature while using atmospheric oxygen for oxidation. Additionally, photocatalysts can be recovered and reused, making the process user-friendly and environmentally safe, as it requires no additional chemicals [2, 6]. However, current photocatalytic methods face limitations, particularly in industrial applications. These include limited visible light utilization (only 3–4% of sunlight is UV), rapid charge recombination, restricted migration of photogenerated electrons and holes, and potential toxicity of byproducts [2, 7]. Despite these challenges, advances in material science are promising. Studies have identified semiconductor materials like metal oxides (e.g., TiO_2, SnO_2) and metal sulfides (e.g., ZnS) as effective photocatalysts [2]. Among these, TiO_2 is noteworthy for its widespread use in degrading various organic substances, including dyes and pharmaceuticals [2, 8] . Its popularity is attributed to its excellent optical and electronic properties, stability, affordability, non-toxicity, and corrosion resistance [2, 7, 9]. However, TiO_2 has limitations, such as a large band gap and low UV light utilization [7]. Recent research aims to enhance TiO_2's performance under visible light through techniques like elemental doping, coupling with other semiconductors, and nanostructure synthesis. Doping can improve visible light absorption and photocatalytic performance by reducing the band gap and boosting charge separation [2, 7]. Furthermore, coating TiO_2 with a thin layer of noble metals (Au, Ag, Pt, and Pd) has shown improvements in photocatalytic efficiency, as these metals help trap photogenerated electrons, thereby extending the electron-hole pair lifetime and improving overall photocatalytic effectiveness [10, 11].

The aim of this study is to investigate the effect of a thin copper layer on the photocatalytic efficiency of titanium dioxide in the degradation of ciprofloxacin. Given that copper is more affordable than other noble metals, this approach presents a cost-effective alternative for enhancing TiO_2 photocatalysts. The research focuses on evaluating how copper deposition influences the rate, efficiency, and stability of TiO_2 in the photodegradation of ciprofloxacin under UV-light irradiation.

EXPERIMENTAL

Preparation of TiO_2

In this synthesis of TiO_2, 40 mL of titanium isopropoxide ($Ti(OCH(CH_3)_2)_4$) (Sigma-Aldrich, St. Louis, MO, USA, 97%) was dissolved in 6 mL of 2-propanol (Centrohem, Stara Pazova, Serbia, 99.5%) and stirred at room temperature for 10 minutes. Deionized water with a pH of 6 was then gradually added over 3 hours with vigorous stirring. The molar ratio of titanium isopropoxide, 2-propanol, and water was 5:3:10, respectively. The resulting precipitate was washed three times with ethanol (Reahem, Novi Sad, Serbia, 70%), centrifuged, and dried overnight in an oven at 100ºC. Calcination of the obtained titanium(IV) oxide was conducted at 700ºC for 5 hours, followed by cooling overnight [9].

Preparation of (Cu)TiO_2

The synthesis of titanium(IV) oxide modified with 0.5, 1, and 2% copper was performed by adding 0.5 g of titanium(IV) oxide to 50 mL of deionized water and dispersing it for 30 minutes at 90ºC in an ultrasonic bath. Then, 7.6 mg, 15.1 mg, and 30.25 mg of copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, Merck, Darmstadt, Germany, 99.5%) were added for 0.5, 1, and 2% molar fractions of copper, respectively. Afterward, 12.5 mg of solid sodium hydroxide (Lach-ner, Neratovice, Czech Republic, 99.6%) was added, followed by 5 mL (γ = 0.5, 1, and 2 $g \cdot L^{-1}$) of sodium borohydride solution (BDH Chemicals Ltd., Poole, UK, 95%), and the mixture was stirred for 2 hours. The resulting precipitates were washed, centrifuged, and dried overnight at 100ºC in an oven [9].

Photodegradation of the ciprofloxacin infusion mixture

A vial of ciprofloxacin, a commercial injection solution (Marocen®, Hemofarm, Serbia), containing 100 mg of ciprofloxacin lactate in 10 mL, was diluted in deionized water using a 250 mL volumetric flask. Subsequently, 12.5 mL of this solution was further diluted to 250 mL in another volumetric flask. The resulting solution has a final molar concentration of $4.75 \cdot 10^{-5}$ $mol \cdot L^{-1}$, which corresponds to a mass concentration of 20 $mg \cdot L^{-1}$.

Photodegradation of ciprofloxacin

Photodegradation was performed using 20 mg of bare TiO_2 and (Cu)TiO_2 (0.5, 1, and 2%) suspended in 50 mL of ciprofloxacin solution. The reaction mixture was stirred for

30 minutes in the dark, along with a blank solution, to establish equilibrium before irradiation. Following this, the samples were exposed to UV light (Philips TUV 15W UVC Disinfection, Poland) for a duration of 4 hours. Aliquots were collected at various intervals: 0, 15, 30, 60, 120, 150, 180, 210, and 240 minutes for the mixture, with hourly samples taken from the blank. The progress of the photodegradation process was monitored using UV-Vis spectrometry (LLG Labware, Detroit, USA) [9].

RESULTS AND DISCUSSION

The UV-Vis spectra for ciprofloxacin degradation over 240 minutes of UV irradiation are shown in Figure 2. These spectra provide crucial insights into the photodegradation process of ciprofloxacin under UV light. The characteristic absorption maximum at 277 nm, which corresponds to the presence of ciprofloxacin, diminishes progressively over time, indicating that the compound is undergoing photodegradation. This reduction in absorbance suggests that the molecular structure of ciprofloxacin is being altered due to exposure to UV radiation, leading to its breakdown into various degradation products. The continuous monitoring of these spectra allows us to track the rate and extent of degradation, providing valuable information about the efficiency of the photocatalytic process.

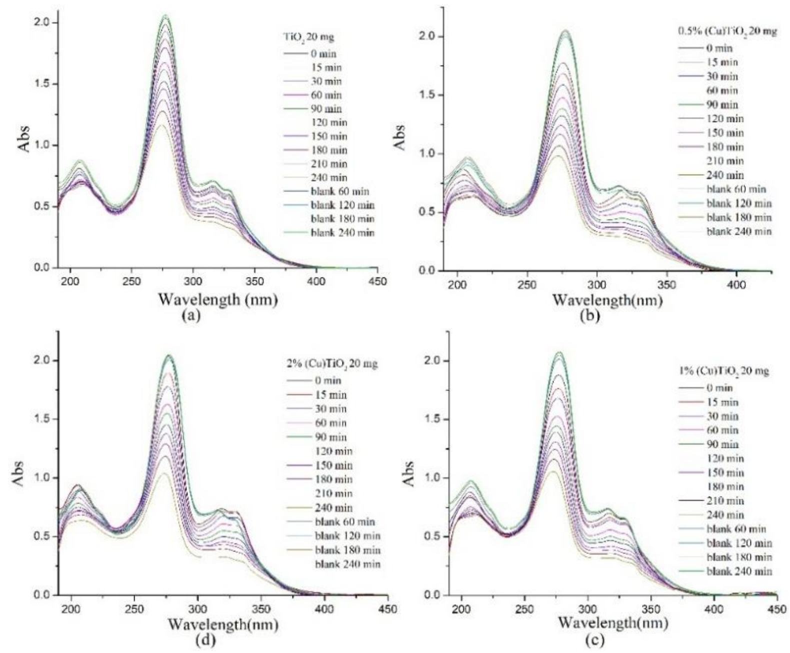

Figure 2 UV-Vis spectra of photodegradation of the ciprofloxacin solution with bare TiO2 (a), 0.5% (Cu)TiO2 (b), 1% (Cu)TiO2 (c) and 2% (Cu)TiO2 (d).

The efficiency of ciprofloxacin degradation was evaluated by measuring the decrease in absorbance at 277 nm, following pseudo-first-order kinetics described by the equation: $A=A_0 \cdot e^{-kt}$, where k is the rate constant. The linearized form $\ln(A/A0)=-kt$ was used to calculate k from the graph's slope. The kinetic curves for ciprofloxacin degradation with 30 mg of photocatalysts are shown in Figure 3.

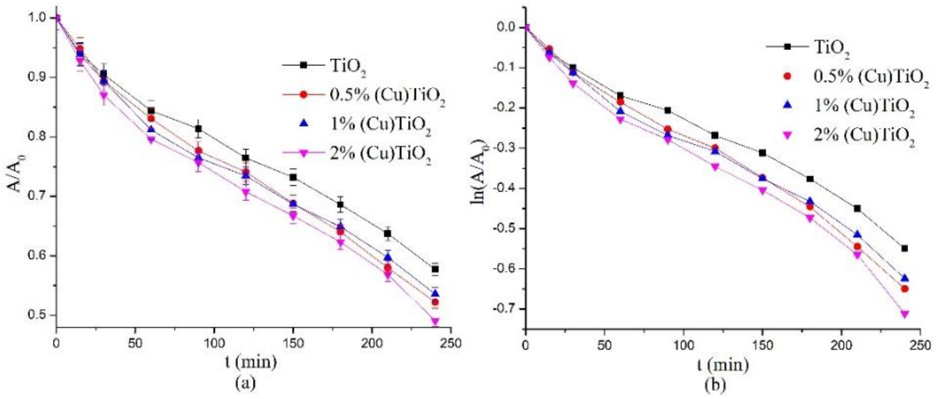

Figure 3 Degradation curves (a) and their linearized pseudo-first-order fits (b) of ciprofloxacin commercial solution for the infusion.

Table 1 presents the calculated pseudo-first-order rate constants, coefficient of determination, and percentage of degradation based on decreasing the absorbance values at 277 nm.

Table 1 Calculated pseudo-first-order rate constants of CIP degradation and percentage of degradation

Photocatalyst	k (min^{-1})	R^2	Degradation of CIP (%)
TiO_2	0.00208 ± 0.00008	0.98745	42.27
0.5% (Cu)TiO_2	0.00252 ± 0.00008	0.99102	47.81
1% (Cu)TiO_2	0.0024 ± 0.0001	0.98625	46.44
2% (Cu)TiO_2	0.0026 ± 0.0002	0.98112	50.91

The results indicate that the addition of 2% copper led to an increase in photocatalytic efficiency, achieving nearly 51% degradation over a 4-hour period. In comparison, the pure titanium(IV) oxide exhibited a lower degradation rate of 43%.

CONCLUSION

These findings highlight the potential of copper-modified titanium(IV) oxide as an effective photocatalyst for environmental applications, particularly in the degradation of organic pollutants. The enhanced performance observed with the copper addition suggests that the deposition of metal layers can improve the photocatalytic properties of TiO_2, making it a promising approach for developing more efficient catalysts. Further research could explore the underlying mechanisms of this enhancement and assess the long-term stability and applicability of the modified photocatalysts in real-world conditions.

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