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# ADVANCING ENVIRONMENTAL SUSTAINABILITY: ENHANCED PHOTOCATALYTIC DEGRADATION OF CEFOPERAZONE USING ZnO AND $H_2O_2$ UNDER DIFFERENT RADIATION SOURCES

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**Abstract**: Cefoperazone is a widely utilized antibiotic from the cephalosporins group to treat bacterial infections. Nevertheless, due to its extensive use as a β-lactam antibiotic, it has been found to accumulate in aquatic environments, leading to notable adverse effects on flora and fauna. Consequently, there arises a necessity for its removal from the environment. The aim of this work was to investigate the efficiency of photocatalytic degradation of cefoperazone by ZnO and $H_2O_2$ using different types of radiation (simulated solar (SS), UV-LED, and UV). The applied nanomaterial in the presence of $H_2O_2$ showed significant efficiency in removing cefoperazone compared to direct photolysis. In the first 20 min of irradiation, 49.0% and 59.4% of cefoperazone were degraded when SS and UV-LED were used, respectively, while cefoperazone was completely degraded under UV irradiation. The reaction rate constant indicates that the degradation of cefoperazone is pseudo-first order.

**Keywords**: Antibiotics, Photocatalysis, Environmental protection.

## 1. INTRODUCTION

Water is the main and essential component of all living organisms. Freshwater makes up 3% of the total water on planet Earth, and only a small amount (0.01%) of this freshwater is available to the human population [1]. The global shortage of freshwater resources has existed worldwide for a long time. Since the second half of the 20th century, rapid economic development has caused various environmental problems. Among them, the water pollution problem has reached a severe level, further aggravated by insufficient water resources. Therefore, dealing with this problem and finding solution for water pollution is essential [2].

Pollutants in water pose a serious threat to human health and the aquatic ecosystem. There are a large number of pollutants that are categorized into inorganic, organic, pathogenic, and radioactive pollutants. Among them, organic micropollutants such as pharmaceuticals are currently the most extensive global problem because they are found in low concentrations in the environment, released uncontrollably, and for some, there is no legal regulation [3].

Cephalosporin antibiotics have been widely utilized to combat bacterial infections due to their broad antibacterial spectrum and potent efficacy against bacteria. However, over decades of ubiquitous and excessive use, these cephalosporins have been found in various aquatic environments at concentrations ranging from ng/dm$^3$ to mg/dm$^3$. Prolonged exposure to these residues has led to the proliferation of antibiotic-resistant bacteria, posing significant risks to human health through bioaccumulation. Given these concerns, developing efficient methods to remove cephalosporins from aquatic environments is crucial [4]. Among the cephalosporins, cefoperazone is a widely utilized pharmaceutical belonging to the third generation of semisynthetic antibiotics. This antibiotic is effective against a wide range of bacterial strains responsible for infections in the respiratory, urinary, skin, and female genital tracts, making it highly versatile in its antibacterial activity [5].

Traditional methods for water purification have proven to be insufficiently effective in completely removing organic micropollutants, as evidenced by their presence in wastewater [6]. Therefore, developing new, more efficient methods for water purification, which should meet the additional requirements of green chemistry, is necessary. Advanced oxidation processes (AOPs) that use the power of free radicals are an excellent choice due to the high efficiency of decomposition of organic micropollutants. Instead of simply extracting from water, this method can oxidize non-biodegradable, stable, and toxic organic pollutants under normal conditions to non-toxic compounds [7]. Various AOPs have been utilized to degrade organic micropollutants, and among them, heterogeneous photocatalysis using ZnO photocatalyst has emerged as one of the most promising technologies [8].

ZnO is a notable n-type semiconductor featuring a wide band gap of 3.37 eV and a high excitation binding energy of 60 meV at room temperature, with good electro-optical properties and high electrochemical stability. ZnO can generate electron-hole pairs when exposed to UV or visible light. These electrons and holes can then react with adsorbed $O_2$ on the photocatalyst's surface and $H_2O$ to produce $O_2^{\bullet-}$ and $^{\bullet}OH$ radicals, respectively. These radicals play a crucial role in completely reducing and oxidizing the organic contaminants into their degradation products, $CO_2$ and $H_2O$ [9]. Utilizing ZnO at the nanoscale allows modifying and enhancing its electrical, optical, and magnetic properties. ZnO proves to be an environmentally friendly material. This characteristic makes it ideal for everyday applications without risks to human health or the environment. ZnO is more cost-effective compared to $TiO_2$, which is recognized as a significant photocatalytic material. Due to its cost-effectiveness, ZnO becomes a more feasible choice for large-scale water treatment operations. ZnO's primary advantage lies in its ability to efficiently absorb a broad spectrum of solar light and more light quanta than certain other semiconducting metal oxides. However, ZnO does have its limitations, notably the wide band gap energy and susceptibility to photo-corrosion [8].

This paper investigated the efficiency of photocatalytic degradation of cefoperazone by ZnO with the addition of $H_2O_2$ under simulated solar (SS), UV-LED, and UV irradiation. The applied nanomaterial in the presence of $H_2O_2$ showed significant efficiency in removing cefoperazone compared to direct photolysis (DP). Also, the reaction rate constant, according to which the degradation of cefoperazone in the presence of ZnO and $H_2O_2$ takes place in the pseudo-first-order, was calculated. The degradation of cefoperazone was monitored by HPLC–PDA technique.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Cefoperazone sodium salt ($C_{25}H_{26}N_9NaO_8S_2$, (6*R*,7*R*)-7-[[(2*R*)-2-[(4-ethyl-2,3-dioxopiperazine-1-carbonyl)amino]-2-(4-hydroxyphenyl)acetyl]amino]-3-[(1-methyltetrazol-5-yl)sulfanylmethyl]-8-oxo-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylic acid) was used without additional purification. The standard solutions of cefoperazone (0.05 mmol/dm$^3$) were made using ultrapure water ($\kappa$ = 0.055 μS/cm). The solutions were stored in a light-free environment at a temperature of 4 °C. Chemicals such as 99.9% acetonitrile (ACN, $C_3H_3NO$, Sigma-Aldrich, pro analysis), 85% orthophosphoric acid ($H_3PO_4$, Lachema, Neratovice, Czech Republic, pro analysis), and $H_2O_2$ (30%, Sigma–Aldrich, Germany) were employed without purification. ZnO (Sigma-Aldrich, 99.9% hexagonal wurtzite structure, particle size around 41 nm, specific surface area 6.5 m$^2$/g) was used as the catalyst.

### 2.2 Degradation procedures

The photocatalytic degradation of cefoperazone was carried out using a Pyrex glass cell equipped with a plain window, onto which the light beam was focused. The total volume of the cell was approximately

40 $cm^3$. Experiments were performed using 20 $cm^3$ of 0.05 $mmol/dm^3$ cefoperazone solution containing 1.0 $mg/cm^3$ of ZnO and 3.0 $mmol/dm^3$ of $H_2O_2$. Before irradiation, the reaction mixture was sonicated for 15 min in the dark to establish adsorption/desorption equilibrium. Before irradiation, the reaction mixture was maintained at a constant temperature of 25 °C using a water circulating jacket while exposed to a stream of $O_2$ at a 3.0 $cm^3$/min rate. The solution was stirred with a magnetic stirring bar throughout the experiments under a continuous gas flow. A halogen lamp (50 W Philips) was used as SS source, UV LED Lamp (5W Enjoydeal, China, type: MR16 AC 85-265V/12) was used as LED irradiation source, and high-pressure mercury lamp (125 W, Philips, HPL-N, emission bands at 290, 293, 296, 304, 314, 335, and 366 nm, with maximum emission at 366 nm) was used as UV irradiation source. All experiments were performed at the natural pH without adjustment (c.a. 7.3).

### 2.3. Analytical procedures

To monitor cefoperazone removal's kinetics, 0.50 $cm^3$ aliquots were extracted from the reaction mixture at the beginning of the experiment and at regular time intervals. Throughout the analysis, the highest volume variation in the reaction mixture due to aliquot sampling was approximately 10%. The solutions were filtered through Millipore (Millex-GV, 0.22 µm) membrane filters. Before analysis, the potential adsorption of cefoperazone on the filters was examined and confirmed to be absent. High-Performance Liquid Chromatography with Photo Diode Array detection (HPLC–PDA, Shimadzu) equipped with an Eclipse XDB–C18 column (150 mm × 4.6 mm i.d., particle size 5 µm, 30 °C) was used for analysis. A 20 µL sample was injected and analyzed using the HPLC–PDA system, with the UV/vis PDA detector set at 205 nm, an appropriate wavelength of absorption of cefoperazone. The isocratic method of analysis was employed, utilizing a mobile phase composed of a mixture of ACN and water (30 : 70, v/v, pH = 2.42), with the water acidified using 0.1% $H_3PO_4$ and a flow rate of 0.8 $cm^3$/min. The reproducibility of repeated runs was around 3−10%, and the retention time for cefoperazone was determined to be 6.7 ± 0.1 min. A glass electrode (pH-Electrode SenTix 20, WTW) connected to a pH meter (pH/Cond 340i, WTW) was utilized to measure the reaction mixture's pH.

## 3. RESULTS AND DISCUSSION

The research investigated the heterogeneous photocatalytic degradation of cefoperazone in wa-

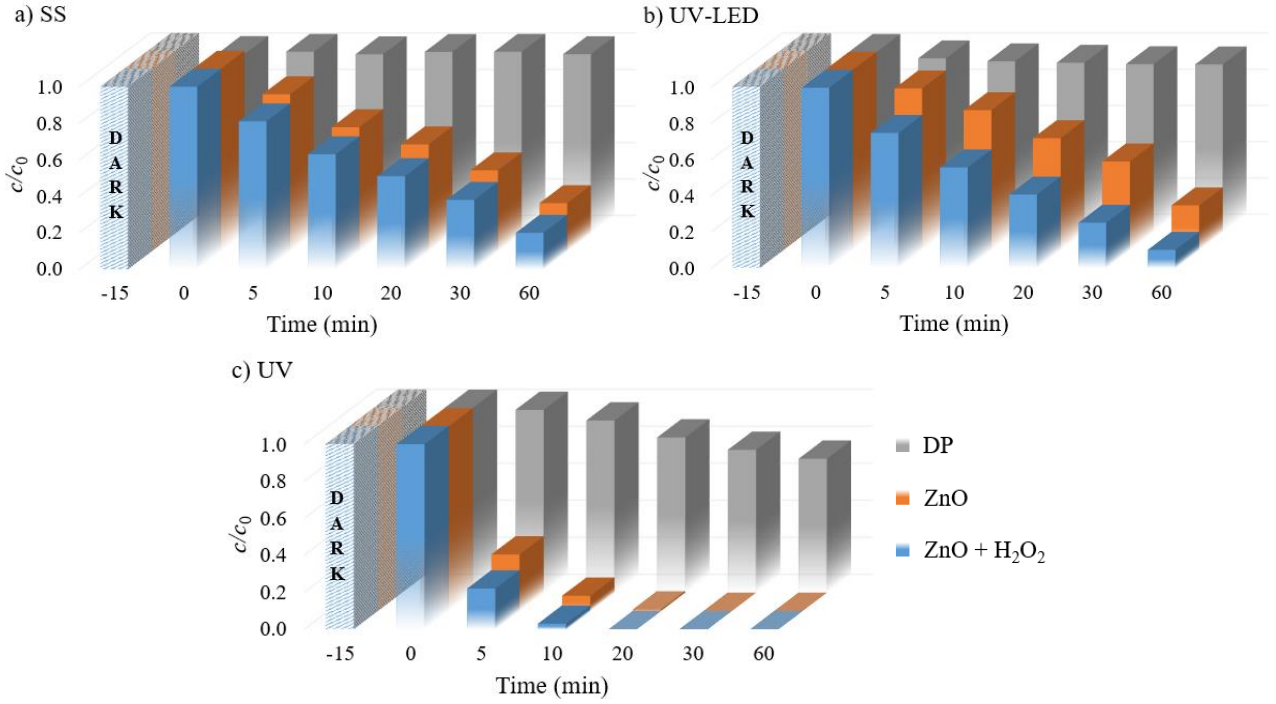

***Figure 1.*** *The kinetics of cefoperazone degradation (0.05 $mmol/dm^3$) under different conditions and irradiation sources*

ter, utilizing the photocatalyst ZnO and $H_2O_2$ under SS, UV-LED, and UV irradiation. DP efficiency was evaluated under SS, UV-LED, and UV irradiation to assess their impact on cefoperazone degradation. The results showed that using SS and UV-LED irradiation, only 1.9% and 7.5% of cefoperazone were degraded after 60 min, respectively. A higher degradation efficiency was observed under UV irradiation, whereby 29.5% of cefoperazone was degraded. The results indicated that DP was inefficient in completely removing cefoperazone from water (Figure 1). Subsequently, the effectiveness of ZnO as a photocatalyst was examined, revealing significantly higher efficiency in cefoperazone degradation compared to DP. Namely, using SS and UV-LED radiation, approximately 70% of cefoperazone was degraded after 60 min of irradiation (Figures 1a and 1b). When employing UV irradiation, complete degradation was achieved within just 20 minutes (Figure 1c). The results show that ZnO is effective as a photocatalyst for the complete degradation of cefoperazone under UV irradiation while using SS and UV-LED, more time is required to achieve the same.

In order to potentially achieve higher efficiency in the photodegradation of cefoperazone by ZnO, we added $H_2O_2$ to the system. In this way, the cefoperazone degradation efficiency was increased compared to photocatalytic degradation with ZnO. The enhancement in degradation efficiency was most pronounced employing UV-LED radiation. After 60 min, cefoperazone's degradation efficiency under SS and UV-LED irradiation was 80.0% and 90.0%, respectively (vs. 70% using just ZnO) (Figures 1a and 1b). In the presence of UV irradiation, 97.0% of cefoperazone was degraded after 10 min using ZnO and $H_2O_2$ (Figure 1c). Namely, it is known that $H_2O_2$ decomposes into •OH radicals under the influence of irradiation [10]. Therefore, the concentration of •OH radicals in the solution that can react with cefoperazone is higher. Consequently, using all three irradiation types, cefoperazone's photocatalytic degradation is higher with adding $H_2O_2$.

The photocatalytic degradation kinetics of cefoperazone in the presence of ZnO and $H_2O_2$ fit the Langmuir–Hinshelwood model (eq. 1):

$$-\frac{dc}{dt}=\frac{kKc}{1+Kc} \tag{1}$$

where $k$ is the intrinsic reaction rate constant (mmol/(dm$^3$ min)), $K$ is the Langmuir–Hinshelwood adsorption constant (dm$^3$/mol), and $c$ is the concentration of the substance. In cases of very low substance concentrations, the value of $Kc$ becomes significantly smaller than 1. As a result, Eq. (1) can be simplified to a pseudo-first-order kinetic equation (eq. 2):

$$-\frac{dc}{dt}=k_1c \tag{2}$$

where $k_1$ is the pseudo-first-order rate constant which can be calculated from the linear dependence

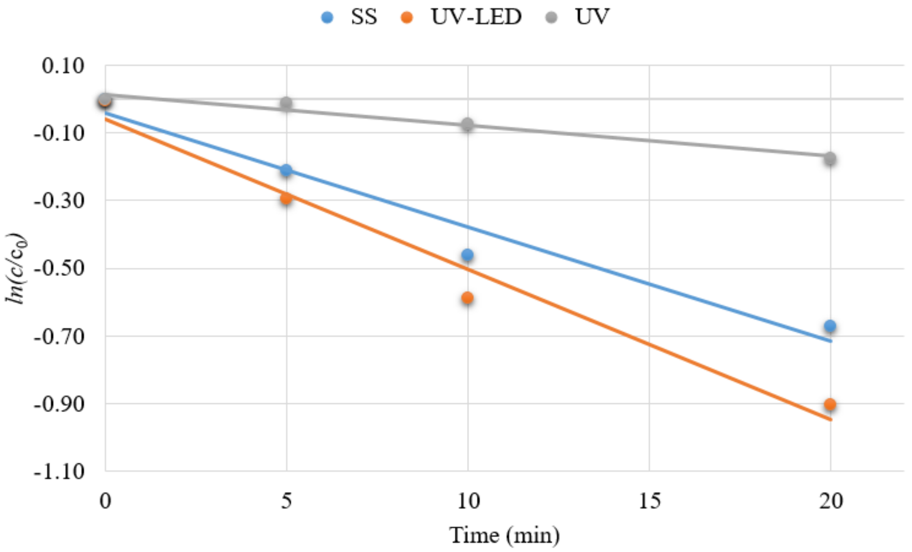

***Figure 2.*** *The reaction rate constant of cefoperazone in the presence of ZnO/$H_2O_2$ under different irradiation sources*

of ln($c/c_o$) vs. irradiation time. The reaction rate constants for photocatalytic degradation of cefoperazone with ZnO under SS, UV-LED, and UV irradiation were calculated as $33.6 \cdot 10^{-3}$ 1/min, $44.0 \cdot 10^{-3}$ 1/min and $9.2 \cdot 10^{-3}$ 1/min with the linearity correlation coefficients of 0.939, 0.958 and 0.947, respectively, for the first 20 min of degradation (Figure 2).

Considering all statements so far, it is certain that ZnO is an effective photocatalyst for the degradation of cefoperazone. However, adding $H_2O_2$ to this system increases degradation efficiency under all irradiation types compared to photocatalysis with ZnO.

## 4. CONCLUSION

Antibiotics have been employed for numerous years to address human and animal health bacterial infections. Nonetheless, their utilization has led to detrimental impacts on the environment. Antibiotics could be deemed among the most hazardous forms of pollutants due to having toxicologic properties causing microorganism resistance in the environment. Because of their limited biodegradability, standard treatment methods prove inadequate in effectively eliminating these substances. As a result, they contribute to contamination within the surrounding environment through processes like bioaccumulation. Nevertheless, AOPs offer a promising solution to this predicament. Namely, heterogeneous photocatalysis garnered significant interest due to its capability to mineralize persistent pollutants by utilizing highly reactive $^\bullet$OH radicals.

The subject of this paper is the determination of the efficiency of photocatalytic degradation of cefoperazone under different irradiation types (SS, UV-LED, and UV irradiation) with ZnO and $H_2O_2$. HPLC–PDA technique was used to monitor the degradation kinetics. First, the direct photolysis of cefoperazone under SS, UV-LED, and UV radiation was investigated and shown to be inefficient, wherein 1.9%, 7.5%, and 29.5% of cefoperazone was degraded, respectively, after 60 min of irradiation. Further, the kinetics of photocatalytic degradation using ZnO under SS, UV-LED, and UV irradiation was monitored. The results showed that ZnO is more efficient in the photodegradation of cefoperazone under UV irradiation, where complete removal of cefoperazone occurs after 20 min of irradiation. Adding $H_2O_2$ led to higher effectiveness in degrading cefoperazone under all irradiation types. The most substantial enhancement in process efficiency is particularly evident when employing UV-LED irradiation, wherein 90.0% of cefoperazone was degraded after 60 min of irradiation. Under all irradiation types, photocatalytic degradation of cefoperazone by ZnO and $H_2O_2$ followed the pseudo-first-order.

The obtained results can be considered as initial studies of the stability of the selected pharmacologically active compound, after which the efficiency and economy of the process can be improved by the development of new biopolymer materials that have advanced photocatalytic properties and the potential for the successful removal of dangerous and polluting substances in natural waters.

## 5. ACKNOWLEDGEMENT

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## 6. REFERENCES

[1] J. Singh, P. Yadav, A.K. Pal, V. Mishra, *Water Pollutants: Origin and Status*, in: D. Pooja, P. Kumar, P. Singh, S. Patil (Eds.), Sens. Water Pollut. Monit. Role Mater., Springer, Singapore, (2020) 5–20. https://doi.org/10.1007/978-981-15-0671-0_2.

[2] L. Huang, X. Huang, J. Yan, Y. Liu, H. Jiang, H. Zhang, J. Tang, Q. Liu, *Research progresses on the application of perovskite in adsorption and photocatalytic removal of water pollutants*, J. Hazard. Mater. 442 (2023) 130024. https://doi.org/10.1016/j.jhazmat.2022.130024.

[3] A.O. Oluwole, E.O. Omotola, O.S. Olatunji, *Pharmaceuticals and personal care products in water and wastewater: a review of treatment processes and use of photocatalyst immobilized on functionalized carbon in AOP degradation*, BMC Chem. 14 (2020) 62. https://doi.org/10.1186/s13065-020-00714-1.

[4] M. Qin, Y. Shi, D. Lu, J. Deng, G. Shi, T. Zhou, *High-performance Hf/Ti-doped defective Zr-MOFs for cefoperazone adsorption:*

*Behavior and mechanisms*, Appl. Surf. Sci. 595 (2022) 153494. https://doi.org/10.1016/j.apsusc.2022.153494.

[5] A. Wang, Y. Zhang, S. Han, C. Guo, Z. Wen, X. Tian, J. Li, *Electro-Fenton oxidation of a β-lactam antibiotic cefoperazone: Mineralization, biodegradability and degradation mechanism*, Chemosphere. 270 (2021) 129486. https://doi.org/10.1016/j.chemosphere.2020.129486.

[6] S.B. Svendsen, H. El-taliawy, P.N. Carvalho, K. Bester, *Concentration dependent degradation of pharmaceuticals in WWTP effluent by biofilm reactors*, Water Res. 186 (2020) 116389. https://doi.org/10.1016/j.watres.2020.116389.

[7] R. Kumar, M. Qureshi, D.K. Vishwakarma, N. Al-Ansari, A. Kuriqi, A. Elbeltagi, A. Saraswat, *A review on emerging water contaminants and the application of sustainable removal technologies*, Case Stud. Chem. Environ. Eng. 6 (2022) 100219. https://doi.org/10.1016/j.cscee.2022.100219.

[8] K.M. Lee, C.W. Lai, K.S. Ngai, J.C. Juan, *Recent developments of zinc oxide based photocatalyst in water treatment technology: A review*, Water Res. 88 (2016) 428–448. https://doi.org/10.1016/j.watres.2015.09.045.

[9] X. Chen, Z. Wu, D. Liu, Z. Gao, *Preparation of ZnO Photocatalyst for the Efficient and Rapid Photocatalytic Degradation of Azo Dyes*, Nanoscale Res. Lett. 12 (2017) 143. https://doi.org/10.1186/s11671-017-1904-4.

[10] A. Bilić, M.M. Savanović, S. Armaković, D.D. Četojević-Simin, B. Srđenović Čonić, N. Kladar, S.J. Armaković, *Exploring the influence of free radicals on photolytic removal of nadolol from water: Mechanism of degradation and toxicity of intermediates*, Front. Environ. Sci. 11 (2023) 1119944. https://doi.org/10.3389/fenvs.2023.1119944.

# УНАПРЕЂЕЊЕ ЕКОЛОШКЕ ОДРЖИВОСТИ: ПОБОЉШАНА ФОТОКАТАЛИТИЧКА РАЗГРАДЊА ЦЕФОПЕРАЗОНА У ПРИСУСТВУ ZnO И $H_2O_2$ ПОД РАЗЛИЧИТИМ ИЗВОРИМА ЗРАЧЕЊА

**Сажетак:** Цефоперазон је широко коришћен антибиотик из групе цефалоспорина, који се користи за лечење бактеријских инфекција. Ипак, због широке употребе као β-лактамског антибиотика, откривено је да се акумулира у воденим срединама, што доводи до значајних штетних ефеката на флору и фауну. Сходно томе, јавља се потреба за његовим уклањањем из животне средине. Циљ овог рада био је да се испита ефикасност фотокаталитичке разградње цефоперазона применом ZnO и $H_2O_2$ у присуству различитих извора зрачења (симулираног сунчевог (СС), УВ-ЛЕД и УВ). Примењени наноматеријал у присуству $H_2O_2$ показао је значајну ефикасност у уклањању цефоперазона у поређењу са директном фотолизом. У првих 20 мин озрачивања, 49,0% и 59,4% цефоперазона је разграђено у присуству СС, односно УВ-ЛЕД зрачења, док је применом УВ зрачења цефоперазон потпуно уклоњен. Константа брзине реакције указује на то да се разградња цефоперазона одвија по псеудо-првом реду.

**Кључне речи:** антибиотици, фотокатализа, заштита животне средине.

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