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THE PHOTOCATALYTIC DEGRADATION OF CEFTRIAXONE IN WASTEWATER USING HYBRID ZnS-ZnO PHOTOCATALYST

BY

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Abstract. The elimination of organic pollutants from water poses a considerable challenge in environmental remediation in this study, the potential of ZnS-ZnO semiconductors as efficient photocatalysts for degrading aqueous solutions of ceftriaxone (CEF) was investigated in a mini-UV reactor. The ZnS-ZnO heterostructures were synthesized via the hydrothermal method and characterized using analytical techniques (SEM, FTIR), demonstrating considerable photocatalytic activity (UV-Vis monitoring), with degradation of CEF occurring within a relatively short period of time.

Keywords: ceftriaxone, degradation, photocatalysis, ZnS - ZnO.

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1. Introduction

The quality of human life directly depends on water resources, in terms of water availability and quality. The presence of potentially toxic substances in water intended for human consumption is responsible for a number of serious diseases. Antibiotics have become indispensable in combating bacterial infections, but their extensive use has led to an unintended consequence—their persistent presence in wastewater. When humans and animals ingest these pharmaceuticals, a significant portion remains unmetabolized and is excreted into the sewage systems. Antibiotics in wastewater come from various sources, including pharmaceutical manufacturing, hospital effluent, agricultural runoff, and insufficiently treated urban sewage (Danner *et al*., 2019; Yang *et al*., 2022). These contaminants create a selective pressure on the microbial communities, nudging them towards resistance. The presence of non-metabolized antibiotics in wastewater is particularly concerning because these compounds enter aquatic ecosystems with their biological activity intact, posing a significant risk to environmental and public health. Non-metabolized antibiotics are those that pass-through organism, either human or animal, without being substantially altered by metabolic processes. As a result, they maintain their antimicrobial properties and, when discharged into water systems, can affect non-target organisms and contribute to the spread of antibiotic resistance. The environmental persistence of non-metabolized antibiotics can lead to prolonged exposure of aquatic organisms to low levels of these compounds. This exposure creates selective pressure that favours the survival of microbes with resistance genes, which can spread across different bacterial populations through horizontal gene transfer. Consequently, there is a critical need to address the issue of non-metabolized antibiotics in wastewater streams to prevent long-term ecological disturbances and preserve the efficacy of antibiotics against pathogenic bacteria. The wastewater treatment plants often are not equipped to fully remove these compounds, leading to the dissemination of antibiotics into aquatic environments.

Eliminating unmetabolized antibiotics or other organic pollutants is not a simple task and requires sophisticated and expensive removal processes, which often leads to the impossibility of treatment. The detection of antibiotics in both wastewater and drinking water, albeit in trace amounts, raises significant concerns regarding environmental safety (Dan *et al*., 2020; Wang *et al*., 2021). Unmetabolized antibiotics and their metabolites can be removed from wastewater by using several technologies and treatment methods as biological treatments, adsorption on different types of adsorbents, filtration, advanced oxidation processes (AOP): involves the use of a combination of strong oxidants and UV radiation to disintegrate organic substances (Danner *et al*., 2019; Hosny and Hargreaves, 2024; Liu *et al*., 2023; Nordin *et al*., 2023; Rizkallah *et al*., 2023; Yang *et al*., 2022).

In general, the method or combination of methods used to remove antibiotics from wastewater depends on the type of antibiotic present, the concentration and volume of wastewater, costs and other specific factors. In this context, heterogeneous photocatalysis has gained ground as a technology that allows the removal or at least transformation of these elements into less toxic forms, contributing to the improvement of water quality.

It consists of using a photocatalyst, usually a semiconductor, which, when exposed to light radiation, is able to promote oxidation / reduction reactions that can be used to remove pollutants. It is a relatively simple process in its operational requirements, which due to its heterogeneous nature allows the recovery and reuse of the photocatalyst, reducing costs.

In addition, this method has the advantage of being a more environmentally friendly and efficient alternative to conventional wastewater treatment methods such as biological treatment or chlorine treatment (Tran *et al*., 2023, Guo *et al*., 2023, Zhang *et al*., 2023, Zhang *et al*, 2021; Malato *et al*., 2016; Inamuddin *et al*., 2021; Murugesan *et al*., 2019).

Among the various treatment methods, the advent of hybrid semiconductor photocatalysts, has shown promising potential in degrading antibiotics and mitigating the risk they pose to both the environment and public health. ZnO and ZnS are two semiconductor materials that have been extensively studied for their photocatalytic activities due to their favourable bandgaps, which enable the absorption of a broad range of the ultraviolet and visible light spectrum, making them highly effective for photocatalytic degradation. When combined, the hybrid ZnO-ZnS structure benefits from a type-II heterojunction photocatalytic system. The unique band alignment between ZnO and ZnS facilitates the efficient separation of photo-generated charge carriers–electrons and holes–which is paramount in the acceleration of photocatalytic reactions. The physical and chemical properties of ZnO-ZnS photocatalysts can be fine-tuned by controlling the compositional ratios and synthesis methods, such as sol-gel, hydrothermal, and co-precipitation approaches, among others. Tailoring the morphology and surface characteristics of these nanocomposites extends their range of practical applications, including the degradation of numerous antibiotics commonly found in wastewater (Batterjee *et al*. 2022; Khan *et al*., 2022; Mohamed *et al*., 2023; Siwinska-Ciesielczyk *et al*., 2021). Insights into the reactivity of ZnO-ZnS photocatalysts reveal that they can degrade a broad spectrum of antibiotics, from tetracyclines to fluoroquinolones, through various oxidative processes (Chankhanittha *et al*., 2023).

2. Experimental

Materials

Thiourea ($(NH_4)_2CS$), Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$), Ceftriaxone disodium salt hemi(heptahydrate) ($C_{18}H_{16}N_8Na_2O_7S_3{\cdot}3.5H_2O$) and

Poly(vinyl alcohol) were purchased from Sigma-Aldrich and used without further purification. For all experiments bidistilled water was used.

ZnO nanoparticles synthesis

For the synthesis of ZnO, we used a simple way, starting from zinc acetate dihydrate, which was grinded for 20 minutes in an agate mojar, then it was calcined in air, at 450°C, for 3 hours. (Rosman *et al*., 2018), as is shown in Eq. (1).

$$(\mathrm{CH_3COO})_2\mathrm{Zn}\cdot 2\mathrm{H_2O} \xrightarrow{450℃} \mathrm{ZnO} + 2\mathrm{CH_3COOH} + \mathrm{H_2O} \qquad (1)$$

ZnS nanoparticles synthesis

In this method ZnS NPs were prepared by a hydrothermal reaction between $Zn(CH_3COO)_2·2H_2O$ as Zn^{2+} source, $(NH_4)_2CS$ as S^{2-} source and PVA as capping surfactant and dispersing agent. Typically, 0.05 mole of $Zn(CH_3COO)_2$ $2H_2O$ was dissolved in 50 mL distilled water and 0.5 mL of PVA (5% wt) was added to that. Then, the stoichiometric $(NH_4)_2CS$ (10^{-3}Mol/L) was added, drop by drop, under continuous stirring, at 90°C till the colour changes from transparent to fluorescent white-yellow.

ZnO-ZnS hybrid photocatalyst

ZnO nanoparticles, previously synthesized, are added to above prepared suspension. The obtained precipitate was centrifuged at 6000 rpm for 10 min, and the collected particles were washed three times with bi-distilled water, in order to remove the unreacted metals traces and finally, dried at 110°C, for 10 h. The discharged S^{2-} and Zn^{2+} will react together to form ZnS which growth in presence of the PVA as capping agent, resulted in the ZnS-ZnO NPs formation (Eq. (2), (3)).

$$(\mathrm{CH_3COO})_2\mathrm{Zn}\cdot 2\mathrm{H_2O} \rightarrow \mathrm{Zn^{2+}} + 2(\mathrm{CH_3COO})^- + 2\mathrm{H_2O} \qquad (2)$$

$$(\mathrm{NH_2})_2\mathrm{CS} + \mathrm{Zn^{2+}} + 2(\mathrm{CH_3COO})^- + \mathrm{H_2O} \rightarrow \mathrm{ZnS} + 2\mathrm{CH_3COOH} + (\mathrm{NH_2})_2\mathrm{CO} \quad (3)$$

Acetic acid and urea are water soluble products and have been eliminated by repeated washing with bi-distilled water. The schematic illustration of hydrothermal ZnS-ZnO heterojunction hydrothermal synthesis is indicated in Fig. 1.

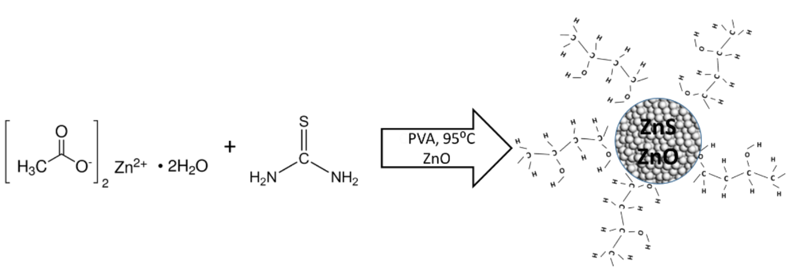


Fig. 1 – Schematic illustration of ZnS-ZnO heterojunction hydrothermal synthesis.

Experimental procedure

The setup employed for the photocatalytic experiments comprises a Phillips 18W UV radiation source situated at the upper section of a sealed dark chamber, with reaction vessels positioned atop magnetic stirrers, as illustrated in the diagram below (Fig. 2). The UV lamp is positioned 2 cm away from the solutions being irradiated. The intensity of UV radiation was assessed using a Hamamatsu C9536-01 meter equipped with an H9958 detector designed for wavelengths ranging from 310 to 380 nm. The measurement scale spans from 1µW/cm² to 100 mW/cm², yielding a recorded intensity of 2.1 W/m².

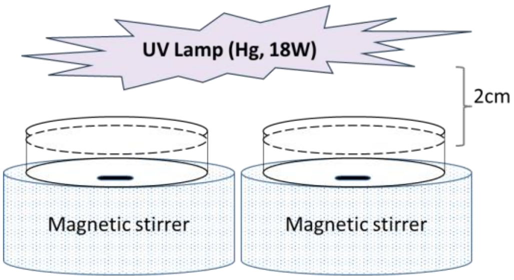
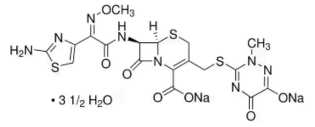


Fig. 2 – Experimental photocatalysis set-up.

Variable amounts of photocatalytic ZnS-ZnO were introduced into 50 mL aqueous antibiotic solutions (different concentrations). The reaction systems thus prepared were stirred magnetically for 30 minutes in the dark to establish the adsorption-desorption balance between the pollutant dye and the photocatalyst surface. Before starting the stirring and after the 30 minutes of stirring, the absorbance of the antibiotic was measured by the spectrophotometric method, at the specific wavelengths specified in Table 1.

Table 1

Characteristics of organic compounds subject to degradation

Antibiotic	***The chemical structure***	***Molecular formula***	λ_{max} nm	***Molar mass*** g/mol
Ceftriaxone CEF		$C_{18}H_{16}N_8Na_2O_7S_3 \cdot 3.5H_2O$	234, 275	661.60

The degradation rate was determined spectrophotometrically based on the residual concentration. Similar experiments were conducted by adjusting the catalyst quantity (0.25-0.75g/L) for initial concentration of antibiotic 10 mg/L.

The percentage of photodegraded CEF was calculated with the following formula (Eq. (4)).

$$\% D = 100x(A_0 - A_t)/A_0 \tag{4}$$

Where A_0 is the initial absorbance and A_t is the absorbance at some time t (for λ=275nm).

3. Results and discussion

The SEM analysis revealed the characteristics of the synthesized ZnO, with the results presented in Fig. 3. The sample exhibited polydispersity, characterized by agglomerations measuring roughly 0.1 x 0.2 x 0.4 µm. Additionally, each prismatic agglomeration comprised nanometer-sized particles.

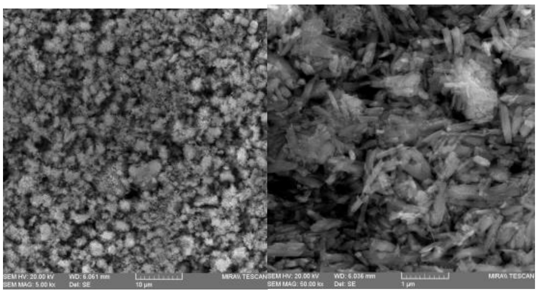


Fig. 3 − SEM microscopy images of ZnO nanoparticles.

FTIR characteristic of ZnS particles

Many inorganic compounds containing simple anions (oxides, sulphides) are transparent in the IR domain and cannot be analysed by this technique. FTIR analysis was performed due to the use of PVA as a structure directing agent. The surface chemistry of the synthesized ZnS nanoparticles were analysed using Fourier- Transform Infrared Spectroscopy in the range of 4000–400 cm^{-1} (Fig. 4).

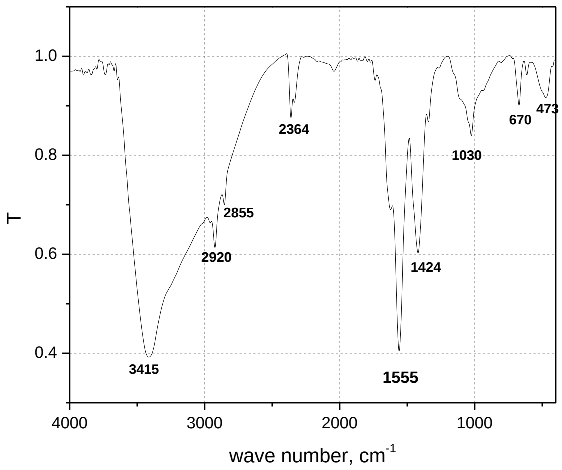


Fig. 4 – FTIR spectra of ZnS sample.

The peaks observed at 473 and 670 cm^{-1} are the characteristic of the ZnS symmetric bending vibration (Tadesse *et al.*, 2023; Yun *et al.*, 2018). The organic phase (PVA) is responsible from 1030 cm^{-1} (secondary OH), 1424 cm^{-1} (vinyl CH in plane blend, δ_{CH2}), 2855 cm^{-1} ν_{sCH2}, 2920 cm^{-1} ν_{aCH3} asymmetric /symmetric stretch (Nakamoto, 1997), the band at around 1600 cm^{-1} is due the C-O stretching from PVA molecule (Mansur *et al.*, 2008) and the broad band at 3415 cm^{-1} is attributed to the polymeric OH stretch (ν_{OH}) from the intermolecular and intramolecular hydrogen bonds.

Photocatalytic test

Figure 5 shows the evolution of (CEF UV-Vis +UV+0.5 g/L ZnS-ZnO) system absorption spectra in time. The results showed that the intensity of the representative peaks for CEF decreases after irradiation begins.

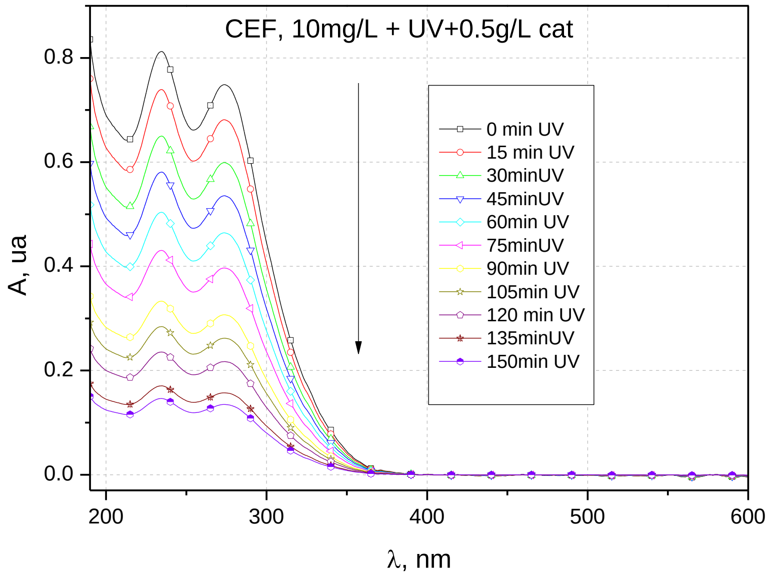


Fig. 5 – The evolution of CEF (10 mg/L) UV-Vis absorption spectra in time.

The effect of photocatalyst dosage was studied for concentrations of 0.25, 0.5 and 0.75 g/L, using a solution containing 10 mg/L CEF for time exposure of 180 min. The results are shown in Fig. 6. Analysing the values of the absorbance (λ_{max} = 275 nm) for the studied systems, it is observed that its decrease is insignificant for the cases where the CEF is irradiated only with UV or is only in the presence of the photocatalyst. But the combined ZnS-ZnO-UV system led to appreciable decreases in absorbance, the best values being for the high dose of photocatalyst (0.75 g/L).

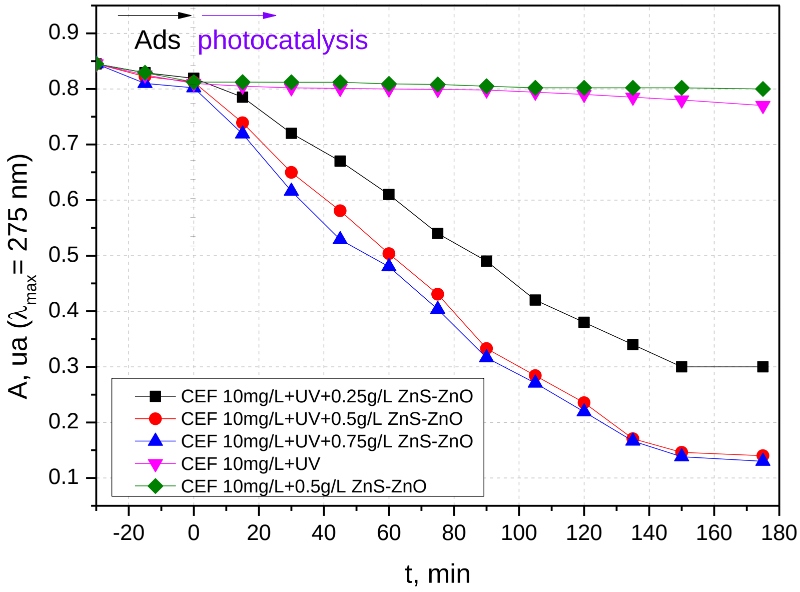


Fig. 6 – Plots showing CEF photodegradation versus time by ZnS-ZnO (different photocatalyst concentration).

The photo-degradation process exhibits a consistent rise with increasing photocatalyst concentration, as is shown in Fig. 7.

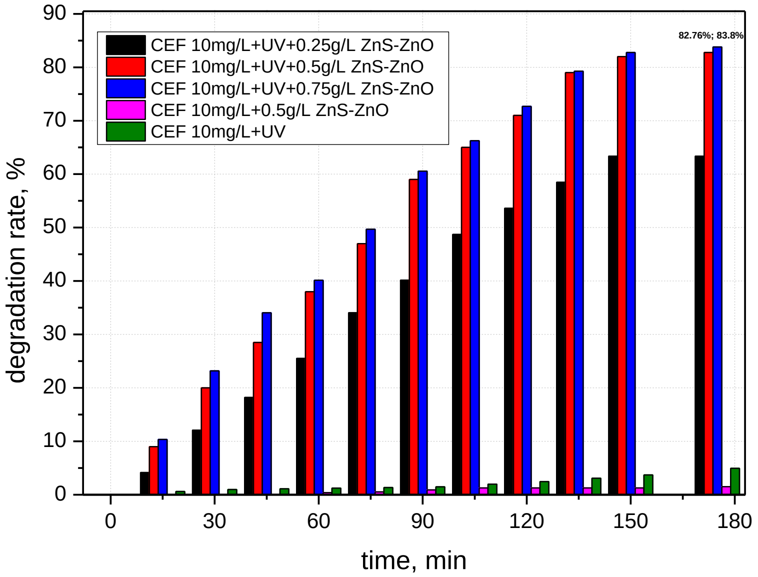


Fig. 7 – A histogram showing the comparison of CEF photodegradation efficiencies

There are subtle disparities in the photocatalytic performance of ZnS-ZnO depending on the dosage employed. For instance, at a concentration of 0.25 g/L ZnS-ZnO, the degradation efficiency reaches 63.36%, increasing to 82.46% for 0.5 g/L, and 83.79% for 0.75 g/L ZnS-ZnO. Although the degradation efficiency values show a slight uptick with higher ZnS-ZnO doses, a concentration of 0.25 g ZnS-ZnO/L solution, was selected. This decision is grounded on economic and environmental considerations, as the addition of larger quantities of ZnS-ZnO is not justified.

4. Conclusions

A successful hydrothermal synthesis method was utilized to produce the ZnS-ZnO photocatalyst, employing PVA as a templating agent. The FTIR spectrum exhibited characteristic vibrational modes indicative of ZnS and ZnO composites. The ZnS-ZnO photocatalyst demonstrated a maximum photodegradation efficiency of 83.8%, underscoring its potential as an effective material for photocatalytic degradation. These findings suggest that the developed ZnS-ZnO composites could find utility across diverse applications, notably in the removal of detrimental organic compounds from wastewater.

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ELIMINAREA FOTOCATALITICĂ A CEFTRIAXONEI DIN APELE UZATE FOLOSIND MATERIALE FOTOCATALITICE HIBRIDE ZnS-ZnO

(Rezumat)

Eliminarea poluanților organici din apă este o provocare semnificativă în remedierea mediului. În acest studiu, potențialul semiconductorilor ZnS-ZnO ca fotocatalizatori eficienți pentru degradarea soluțiilor apoase de ceftriaxonă (CEF) a fost investigat într-un mini-reactor UV. Heterostructurile ZnS-ZnO au fost sintetizate prin metoda hidrotermală și caracterizate prin tehnici analitice (SEM, FTIR), demonstrând o activitate fotocatalitică considerabilă (monitorizată UV-Vis), degradarea CEF realizându-se într-o perioadă de timp relativ scurtă.