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PHOTOCATALYTIC REMOVAL OF CEFOTAXIME USING Mn–ZnO MATERIALS

BY

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Abstract. Cefotaxime residues in environments can contribute to the selection and dissemination of antimicrobial resistance, which motivates advanced treatment processes. In this study, undoped ZnO and Mn-doped ZnO samples containing 2 and 5 wt.% Mn were synthesized via a citrate-assisted sol–gel route and subsequently calcined at 500°C for 3 h. The materials were examined by FTIR spectroscopy, while their photocatalytic activity was evaluated using 25 mg·L⁻¹ cefotaxime solutions at pH 5.59 and a catalyst dose of 0.05 g·L⁻¹. Under UV irradiation at an incident flux of 0.21 mW·cm⁻², 2%Mn-ZnO achieved 96.2% removal after 90 min, compared with 91.5% for 5%Mn-ZnO and 81.4% for ZnO. The apparent first-order constant reached 0.0421 min⁻¹. Only 4.2% removal was obtained under visible light. The results identify 2% Mn as the most effective composition under the investigated conditions and show that excessive doping reduces the photocatalytic benefit.

Keywords: β-lactam antibiotic, advanced oxidation, semiconductor, pseudo-first-order kinetics, water treatment.

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1. Introduction

Antibiotics are continuously introduced into urban and hospital wastewater through patient excretion, direct disposal, veterinary use and manufacturing activities. Because conventional treatment systems were not designed specifically for pharmaceutical micropollutants, removal can be incomplete and variable. Even when individual compounds occur at low concentrations, their continuous discharge and biological activity may favour the selection and dissemination of antimicrobial resistance in receiving environments (Ribeiro *et al.*, 2018; Yang *et al.*, 2022). Consequently, treatment technologies capable of transforming residual antibiotics before effluent discharge remain an important objective in environmental engineering.

Cefotaxime (CFX) is a third-generation β -lactam cephalosporin used in the treatment of severe bacterial infections. Renal elimination of the parent drug and microbiologically active metabolites creates a direct pathway from clinical use to wastewater. The β -lactam structure is susceptible to transformation, but partial conversion does not necessarily eliminate biological activity or the environmental relevance of the resulting products. Studies using TiO_2 , ZnO, ZnO-ZnS, ZnO-CeO₂, α -Fe₂O₃ and electrochemical advanced oxidation systems have therefore examined CFX as a model pharmaceutical contaminant (Apostolescu *et al.*, 2023, Apostolescu *et al.*, 2024; León *et al.*, 2017; Lei *et al.*, 2020; Al-Gariaa *et al.*, 2023).

Heterogeneous photocatalysis is based on the photoexcitation of a semiconductor and the subsequent generation of electrons and holes capable of initiating reduction and oxidation reactions at the solid-liquid interface. ZnO is attractive because of its relatively low cost, chemical accessibility and strong absorption in the ultraviolet region. Its practical efficiency is nevertheless limited by electron-hole recombination, particle agglomeration and a weak response to visible radiation. Modification with transition-metal ions is one strategy used to alter defect chemistry, charge-carrier trapping and surface morphology. For Mn-doped ZnO, these effects depend strongly on dopant content and preparation conditions; moderate loading can improve charge separation, whereas excessive Mn may create recombination centres or unfavourable agglomeration (Das *et al.*, 2020; Aadnan *et al.*, 2022).

Previous studies have reported improved degradation of organic compounds and antibiotics using Mn-containing ZnO materials. Turkyilmaz *et al.* (2017) demonstrated that the effect of a metallic dopant can be either synergistic or antagonistic, depending on its chemical identity and concentration. Al-Gariaa *et al.* (2023) reported efficient CFX photodegradation with Mn-doped ZnO nanospheres, while the recent results of Chang *et al.* (2025) confirm the relevance of Mn-ZnO for other antibiotic classes. These observations indicate that the nominal presence of Mn is not sufficient to predict performance; the dopant level and irradiation spectrum must be assessed experimentally.

The present study compares undoped ZnO with materials containing nominal Mn contents of 2 and 5%, prepared by a citrate-assisted sol–gel route. The samples were characterized by Fourier-transform infrared spectroscopy (FTIR) and their performance was evaluated for the removal of CFX from water under UV irradiation. The activity of the most efficient composition was also examined under visible light. The objective was to establish the relationship between nominal Mn content, morphology and apparent photodegradation kinetics under identical reaction conditions. The novelty of this study lies in the comparative evaluation of sol–gel-derived ZnO materials containing two nominal Mn levels (2 and 5%) at a low catalyst loading (0.05 g L^{-1}), revealing a non-monotonic influence of Mn content on cefotaxime removal and apparent pseudo-first-order kinetics under UV-B irradiation.

2. Experimental

2.1. Materials

Zinc acetate dihydrate, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, manganese(II) acetate tetrahydrate $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich), citric acid monohydrate, $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (ACS reagent), ethanol (96%, Chimreactiv S.R.L.) and cefotaxime sodium salt, $\text{C}_{16}\text{H}_{16}\text{N}_5\text{NaO}_7\text{S}_2$ molar mass $477.45 \text{ g} \cdot \text{mol}^{-1}$, (Sigma-Aldrich) were used as received. Bidistilled water was used for synthesis and photocatalytic experiments.

2.2. Photocatalyst preparation

Undoped and Mn-modified ZnO powders were prepared by a citrate-assisted sol–gel procedure. Zinc acetate dihydrate (0.01 mol) was dissolved in ethanol and maintained at $40\text{--}45^\circ\text{C}$ under stirring. For the doped samples, manganese acetate was added in the amount required to obtain nominal Mn contents of 2 and 5% (wt) relative to the zinc precursor. Citric acid (0.02 mol) was introduced as a complexing and gel-forming agent. The resulting sol was aged (3h) until a white-brown gel was obtained. After drying at 102°C for 12 h, the gel was heated in air to 500°C at a rate of $10^\circ\text{C} \cdot \text{min}^{-1}$ and maintained at this temperature for 3 h to remove the organic fraction and obtain the oxide powder. The samples are denoted ZnO, 2%Mn-ZnO and 5%Mn-ZnO.

FTIR spectra (Agilent Cary 630 instrument, with 32 scans per sample at a spectral resolution of 4 cm^{-1} , $4000\text{--}400 \text{ cm}^{-1}$ range) were recorded to evaluate the elimination of citrate and acetate residues after calcination and to identify surface hydroxyl species.

2.3. Photocatalytic experiments

Photocatalytic tests were carried out in a 0.10 L working volume using an initial CFX concentration of 25 mg·L⁻¹. The natural pH of the antibiotic solution was 5.59 and the temperature was maintained at 22 ± 2°C. Catalyst doses between 0.05 and 0.50 g·L⁻¹ were considered during preliminary testing; the comparative data presented in this paper correspond to 0.05 g·L⁻¹. A catalyst loading of 0.05 g·L⁻¹ was selected for the comparative series to minimize light-scattering and screening effects while optimizing the economic viability and active surface area exposure during photocatalytic degradation. Before irradiation, the suspensions were magnetically stirred in the dark for 30 min to approach adsorption–desorption equilibrium.

UV irradiation was provided by an 18 W mercury UV-B lamp positioned 2 cm above the surface of the photocatalytic suspensions. The lamp-to-sample distance was maintained constant throughout all experiments to ensure comparable irradiation conditions. The suspensions were irradiated under an incident UV flux of 0.21 mW·cm⁻². Aliquots were withdrawn at selected time intervals up to 90 min and immediately passed through 0.45 μm PTFE syringe filters to separate the catalyst. Residual CFX was monitored by UV–Vis spectrophotometry (Jasco V-550 device) at 234 nm. A visible-light experiment was performed with 2%Mn-ZnO, and a CFX solution without catalyst was monitored under visible irradiation as a blank.

2.5. Data processing

Because the Beer–Lambert response at 234 nm was used to follow the parent compound, the removal efficiency was calculated from absorbance values according to Eq. (1):

$$R(\%) = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where A_0 is the absorbance after the dark-equilibration stage and A_t is the absorbance at irradiation time t . Apparent kinetic constants were obtained using the linearized pseudo-first-order expression:

$$\ln\left(\frac{A_0}{A_t}\right) = k_{app} \cdot t \quad (2)$$

where k_{app} is the apparent rate constant, expressed in min⁻¹. This treatment provides a convenient comparison under identical conditions.

3. Results and discussion

3.1. FTIR analysis

The FTIR spectra of ZnO and 2%Mn-ZnO are presented in Fig. 1. The intense increase in absorption below approximately 600 cm^{-1} is consistent with metal–oxygen lattice vibrations.

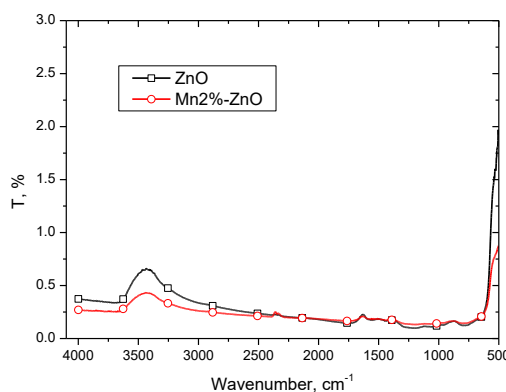


Fig. 1 – FTIR spectra of undoped ZnO and 2%Mn-ZnO after calcination at 500°C .

The broad feature in the $3500\text{--}3300\text{ cm}^{-1}$ region is assigned to O–H stretching from surface hydroxyl groups and adsorbed water, while the contribution near 1620 cm^{-1} is more appropriately attributed to the H–O–H bending vibration of molecular water. The low intensity of bands associated with acetate or citrate groups supports substantial removal of organic precursors during calcination.

3.2. UV–Vis monitoring of cefotaxime removal

The CFX spectrum contains a characteristic absorption maximum at 234 nm . During irradiation in the presence of 2%Mn-ZnO, this band decreased progressively and approached the baseline after 70–90 min (Fig. 2). The absence of an evident bathochromic shift in the recorded spectral window indicates that no strongly absorbing intermediate accumulated at a concentration comparable with that of the parent compound. Nevertheless, UV–Vis monitoring at one analytical wavelength primarily quantifies disappearance of the initial chromophore.

The time profiles in Fig. 3 show only limited absorbance change during the 30 min dark stage, indicating that adsorption was not the dominant removal pathway. Under UV irradiation, all catalyst-containing systems exhibited a marked decrease in CFX absorbance. The slope was highest for 2%Mn-ZnO,

followed by 5%Mn-ZnO and undoped ZnO. In contrast, the visible-light blank remained almost constant, and 2%Mn-ZnO produced only a small change under visible irradiation. These results show that the tested Mn modification improved UV-driven activity but did not provide a practically significant visible-light response under the selected conditions. Each experiment was carried out three independent times to ensure reproducibility.

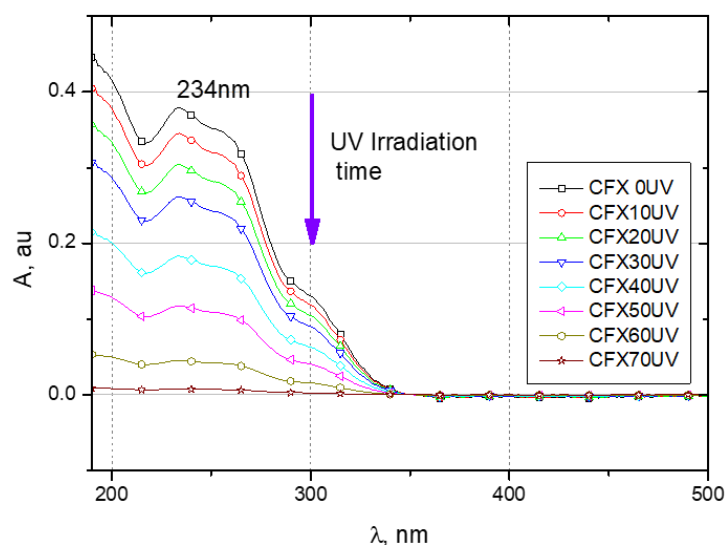


Fig. 2 – Evolution of the CFX UV–Vis spectra in the presence of 2%Mn-ZnO under UV irradiation.

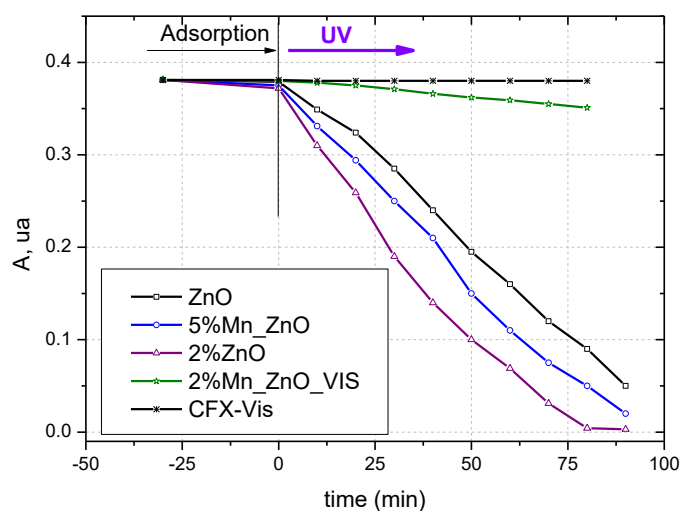


Fig. 3 – Absorbance profiles during dark equilibration and irradiation, conditions: CFX $25 \text{ mg} \cdot \text{L}^{-1}$, catalyst $0.05 \text{ g} \cdot \text{L}^{-1}$, pH 5.59 and $22 \pm 2^\circ\text{C}$.

3.3. Effect of manganese content and irradiation spectrum

After 90 min of UV irradiation, ZnO removed 81.4% of CFX, while the efficiencies of 5%Mn-ZnO and 2%Mn-ZnO reached 91.5 and 96.2%, respectively. Relative to undoped ZnO, the absolute improvement was 10.1 percentage points for the 5% sample and 14.8 percentage points for the 2% sample. The non-monotonic dependence on dopant concentration is important: increasing the nominal Mn content from 2 to 5% did not produce an additional benefit. Instead, the larger aggregates observed for 5%Mn-ZnO may reduce accessible surface area and light penetration. At the electronic level, a moderate concentration of Mn-related states may facilitate temporary carrier trapping, whereas an excessive concentration may favour non-radiative recombination. These interpretations are consistent with the broader Mn-ZnO literature (Turkyilmaz *et al.*, 2017; Aadnan *et al.*, 2022).

Under visible irradiation, 2%Mn-ZnO produced only 4.2% CFX removal after 90 min. This result is substantially lower than the corresponding UV value and indicates that the material remains predominantly UV responsive.

3.4. Apparent kinetic behaviour

Linearization according to Eq. (2) yielded apparent rate constants between 0.0173 and 0.0421 min⁻¹ for the UV-irradiated systems (Table 1 and Fig. 4). The 2%Mn-ZnO value was approximately 2.43 times that of undoped ZnO and 1.72 times that of 5%Mn-ZnO. The ranking of the kinetic constants therefore agrees with the 90 min removal efficiencies. This internal consistency supports the selection of 2%Mn-ZnO as the most active material under the investigated conditions.

The coefficients of determination for the UV experiments ranged from 0.9106 to 0.9499.

Table 1

Photocatalytic efficiency and apparent kinetic parameters for cefotaxime removal

Sample	Light	R ₉₀ , %	k _{app} , min ⁻¹	R ²
ZnO	UV	81.4	0.0173	0.9499
5%Mn-ZnO	UV	91.5	0.0245	0.9427
2%Mn-ZnO	UV	96.2	0.0421	0.9106
2%Mn-ZnO	Visible	4.2	0.0010	0.9954

The obtained results indicate that the pseudo-first-order model is useful despite deviations from ideal linearity. They can arise from changes in catalyst surface coverage, intermediate formation, light-screening effects or the use of absorbance rather than chromatographically determined concentration. The high R² obtained for the visible-light experiment is not evidence of high activity

because the fitted slope is only 0.0010 min^{-1} and the total change is close to the experimental uncertainty expected for a weakly varying signal.

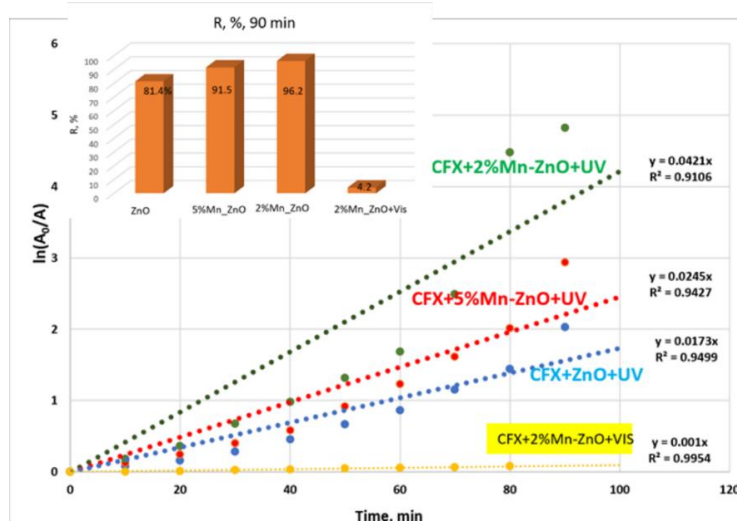
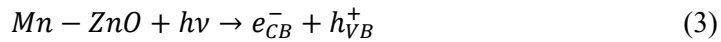


Fig. 4 – Pseudo-first-order linearization and CFX removal efficiency after 90 min (inset) for ZnO and Mn-modified ZnO.

3.5. Proposed photocatalytic mechanism

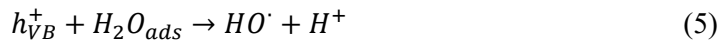
Under UV irradiation with photon energy equal to or greater than the ZnO band gap, electrons are promoted from the valence band (VB) to the conduction band (CB), leaving positively charged holes in the VB (Fig 5). The reactions presented in Eqs. (3)-(15) represent a literature-supported mechanistic hypothesis (Aadnan *et al.*, 2022; León *et al.*, 2017; Zhao *et al.*, 2022):



The photogenerated charge carriers can migrate toward the catalyst surface, where they participate in interfacial redox reactions. Conduction-band electrons reduce dissolved or adsorbed oxygen, producing superoxide radicals:



Simultaneously, valence-band holes can oxidize adsorbed water molecules or surface hydroxyl groups, leading to the formation of hydroxyl radicals:



Superoxide radicals may undergo protonation and subsequent reactions that generate additional oxidizing species:



Hydrogen peroxide may also undergo UV photolysis:



Cefotaxime adsorbed on or located near the photocatalyst surface can be transformed through direct oxidation by valence-band holes or through reactions with the generated reactive oxygen species:

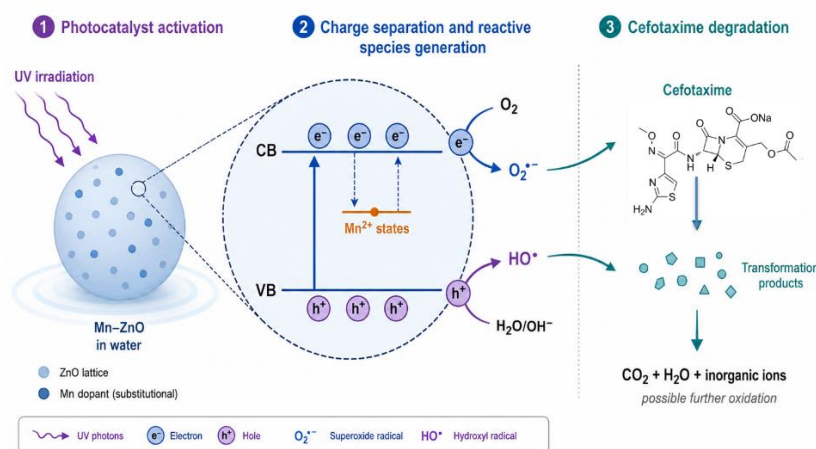
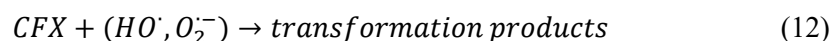
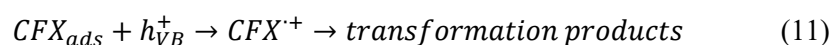
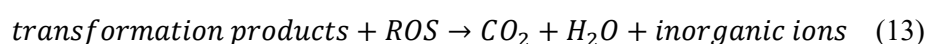


Fig. 5 – Proposed schematic representation of Mn–ZnO photoactivation, charge-carrier separation, reactive oxygen species generation and cefotaxime transformation under UV irradiation.

These reactions may involve hydroxylation, cleavage of the β -lactam ring, oxidation of the thioether-containing nucleus and fragmentation of the side chains (Lei *et al.*, 2020, Samal *et al.*, 2026). Continued oxidation could ultimately produce CO₂, H₂O and inorganic ions:



The substitution of Zn^{2+} by Mn^{2+} can introduce localized Mn 3d states capable of temporarily trapping photogenerated charge carriers. A possible formal hole-trapping and regeneration cycle can be represented as:



At an appropriate Mn concentration, temporary carrier trapping may delay direct electron–hole recombination and increase the probability of interfacial reactions with O_2 , water and adsorbed CFX. Conversely, an excessive concentration of Mn-related states may promote trap-assisted recombination and reduce photocatalytic activity.

Mn-related states can modify carrier lifetimes and surface reactivity. The maximum observed at 2% nominal Mn is compatible with an optimum between beneficial trapping and detrimental recombination or aggregation.

4. Conclusions

Undoped ZnO and Mn-modified ZnO photocatalysts were obtained by a citrate-assisted sol–gel route and calcined at 500°C . FTIR analysis indicated substantial removal of the organic precursors. Under UV irradiation, Mn addition enhanced cefotaxime removal, but the response was not proportional to dopant concentration. The 2%Mn-ZnO sample reached 96.2% removal after 90 min and an apparent rate constant of 0.0421 min^{-1} , compared with 81.4% and 0.0173 min^{-1} for undoped ZnO. Increasing the nominal Mn content to 5% reduced the kinetic benefit, which can be associated provisionally with stronger aggregation and an excessive concentration of defect states.

The 2%Mn-ZnO material removed only 4.2% of CFX under visible light, demonstrating that its activity remained predominantly UV driven. The results identify 2% nominal Mn as the most favorable composition within the investigated series, but further structural characterization, UV photolysis controls, mineralization measurements, transformation-product analysis and reuse tests are required before the material can be proposed for water-treatment applications.

REFERENCES

- Aadnan I., Zegaoui O., El Mragui A., Daou I., Moussout H., Esteves da Silva J.C.G., *Structural, Optical and Photocatalytic Properties of Mn Doped ZnO Nanoparticles Used as Photocatalysts for Azo-Dye Degradation under Visible Light*, *Catalysts*, **12**, 11, 1382, <https://doi.org/10.3390/catal12111382> (2022).

- Al-Gariaa A.M., Elsalala G.S., Ismail E.H., Khalil M.M.H., El-Sewify I.M., *Photodegradation of Antibacterial Cefotaxime Using Mn Doped ZnO Nanosphere*, Inorganic Chemistry Communications, **158**, 111434, <https://doi.org/10.1016/j.inoche.2023.111434> (2023).
- Apostolescu G.A., Vizitiu M.A., Luchian I.C., Dubăsari V., Zaharia I.I., Bobeș Ș.A., Balan C.D., Tătaru-Fărnuș R.E., Apostolescu N., *The Photocatalytic Degradation of Ceftriaxone in Wastewater Using Hybrid ZnS-ZnO Photocatalyst*, Bul. Inst. Polit. Iași, **70** (74), **1**, 89-100, <https://doi.org/10.5281/zenodo.11145904> (2024).
- Apostolescu N., Tataru Farmus R.E., Harja M., Vizitiu M.A., Cernatescu C., Cobzaru C., Apostolescu G.A., *Photocatalytic Removal of Antibiotics from Wastewater Using the CeO₂/ZnO Heterojunction*, Materials, **16**, 850, <https://doi.org/10.3390/ma16020850> (2023).
- Chang Z., Huang L., Wang J., Shu Y., Zhang L., Shen F., Lu C., *Photocatalytic Degradation of Levofloxacin and Vancomycins by Mn-Doped ZnO Nanoparticles*, Catalysis Letters, **155**, **7**, 252, <https://doi.org/10.1007/s10562-025-05068-8> (2025).
- Das A., Wary R.R., Nair R.G., *Mn-Doped ZnO: Role of Morphological Evolution on Enhanced Photocatalytic Performance*, Energy Reports, **6**, 737-741, <https://doi.org/10.1016/j.egy.2019.11.148> (2020).
- Lei J., Duan P., Liu W., Sun Z., Hu X., *Degradation of Aqueous Cefotaxime in Electro-Oxidation-Electro-Fenton-Persulfate System with Ti/CNT/SnO₂-Sb-Er Anode and Ni@NCNT Cathode*, Chemosphere, **250**, 126163, <https://doi.org/10.1016/j.chemosphere.2020.126163> (2020).
- León D.E., Zúñiga-Benítez H., Peñuela G.A., Mansilla H.D., *Photocatalytic Removal of the Antibiotic Cefotaxime on TiO₂ and ZnO Suspensions under Simulated Sunlight Radiation*, Water, Air, & Soil Pollution, **228**, 361, <https://doi.org/10.1007/s11270-017-3557-4> (2017).
- Ribeiro A.R., Sures B., Schmidt T.C., *Cephalosporin Antibiotics in the Aquatic Environment: A Critical Review of Occurrence, Fate, Ecotoxicity and Removal Technologies*, Environmental Pollution, **241**, 1153-1166, <https://doi.org/10.1016/j.envpol.2018.06.040> (2018).
- Samal M., Sharma D. S., Rath D., Raju Acharya P.G., Nanda B., *Nanostructured ZIF-67/LaFeO₃ p-n heterojunction interface for amplified cefotaxime sensing & intensified photo-Fenton degradation*, Nanoscale Advances, **8**, 2690, DOI: 10.1039/d6na00081a (2026).
- Turkyilmaz S.S., Guy N., Özacar M., *Photocatalytic Efficiencies of Ni, Mn, Fe and Ag Doped ZnO Nanostructures Synthesized by Hydrothermal Method: The Synergistic/Antagonistic Effect between ZnO and Metals*, Journal of Photochemistry and Photobiology A: Chemistry, **341**, 39-50, <https://doi.org/10.1016/j.jphotochem.2017.03.027> (2017).
- Yang Y., Ji Y., Gao Y., Lin Z., Lin Y., Lu Y., Zhang L., *Antibiotics and Antimycotics in Wastewater Treatment Plants: Concentrations, Removal Efficiency, Spatial and Temporal Variations, Prediction, and Ecological Risk Assessment*, Environmental Research, **215**, 114135, <https://doi.org/10.1016/j.envres.2022.114135> (2022).

Zhao L., Yu T., Yang B., Guo H., Liu L., Zhang J., Gao C., Yang T., Wang M., Zhang Y., *Wastewater Purification and All-Solid Z-Scheme Heterojunction ZnO-C/MnO₂ Preparation: Properties and Mechanism*, Catalysts, **12**(10), 1250, <https://doi.org/10.3390/catal12101250> (2022).

DEGRADAREA FOTOCATALITICĂ A CEFOTAXIMEI PE MATERIALE Mn-ZnO

(Rezumat)

Prezența reziduurilor de antibiotice în mediile acvatice impune dezvoltarea unor procese avansate de tratare. În acest studiu, ZnO nedopat și ZnO cu un conținut nominal de 2 și 5% Mn au fost obținute printr-o metodă sol-gel asistată de acid citric și calcinate la 500°C timp de 3 h. Materialele au fost analizate prin spectroscopie FTIR, iar activitatea fotocatalitică a fost evaluată pentru soluții de cefotaximă cu concentrația de 25 mg·L⁻¹, la pH 5,59 și o doză de catalizator de 0,05 g·L⁻¹. Sub iradiere UV, proba 2%Mn-ZnO a realizat o îndepărtare de 96,2% după 90 min, comparativ cu 91,5% pentru 5%Mn-ZnO și 81,4% pentru ZnO. Constanta aparentă de viteză a atins 0,0421 min⁻¹. Sub lumină vizibilă, îndepărtarea a fost de numai 4,2%, ceea ce indică menținerea caracterului predominant UV-activ al materialului.