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PHOTOCATALYTIC DEGRADATION OF AMOXICILLIN IN AQUEOUS MEDIA USING $BIVO_4$–MNZO UNDER UV AND VISIBLE LIGHT: EFFICIENCY, MECHANISM, AND BY-PRODUCT ANALYSIS

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ABSTRACT

This article explores photocatalytic degrading that occurs in Amoxicillin (AMX) inside the aqueous medium using a BiVO4 MnZnO heterojunction catalyst in UV and visible. The catalyst, which was prepared by hydrothermal synthesis has shown an impressively higher photocatalytic efficiency in comparison to traditional catalysts. The improvement can be attributed to the synergistic effects that occurs between BiVO4 and MnZnO that allows for efficient charge separation as well as the reactive species, such as radicals hydroxyl. The system has demonstrated significant removal of AMX under both conditions of irradiation and has proven its effectiveness in practical applications in water treatment. Furthermore, (HPLC-MS) revealed the progressive breakdown of AMX into lower-molecular-weight by-products through oxidative degradation pathways. These findings support the use of BiVO4-MnZnO as a promising and sustainable photocatalyst for the remediation of antibiotic-contaminated waters.

KEYWORDS

Antibiotic photodegradation; $BiVO_4$–MnZnO heterojunction; UV–visible photocatalysis; Oxidative degradation pathway; Emerging contaminants in water.

1. INTRODUCTION

Due to the growing populations around the globe and droughts that last for a long time the rising demands and the depletion of water supply has turned into an international concern. (Azdem et al., 2025; El Mouedden et al., 2025; Ghizlane et al., 2022). It is estimated that millions die from water-borne illness every year. (Rahmani et al., 2021). It is crucial that the water's quality is suitable for reuse. (Fattah et al., 2023; Kadhim et al., 2025). In recent times there has been a wide range of organic pollutants have been detected in the water environment, with concentrations ranging from ng/L up to mg/L. (Collier et al., 2021; DeFlorio-Barker et al., 2018). Even though they have a low concentration in the water, a variety of negative effects of organic contaminants on marine life have been documented over the years, such as the long-term and acute toxicity, as well as the disruptions of the endocrine system as well as bioaccumulation. Based on the characteristics of these substances they may reach surface and groundwaters. (Toufik et al., 2025; Zhao et al., 2019). Of the organic pollutants, Enrofloxacin is used as an antibiotic due to its antibacterial properties that is effective against Gram-positive as well as Gram-negative bacteria in sick animals. Its degradation was studied by ionizing radiation(Fattah et al., 2021; Mabrouki et al., 2024). NMR spectroscopy (NMR) as well as Fourier-transform infrared spectroscopy (FTIR) was used to study the metabolic and structural changes caused by enrofloxacin in response to ionizing radiation with 50 kGy. The spectroscopic results show that radiation caused major molecular changes, which are characterized by the disintegration the aromatic rings, as well as the cyclopropyl component, along with the demise of the carboxylic acid group functional. The changes were followed by the development of functionalities that are N-H, as well as the development of chains of aliphatic hydrocarbons that suggest a large radiolytic alteration of the enrofloxacin-containing molecule (Ardestani et al., 2024; Benchrifa et al., 2022). The combined processes of ionizing radiation followed by microbial removal of enrofloxacin seem to be the best solution for the treatment of effluents containing enrofloxacin antibiotics (Azoulay et al., 2023; Pławińska-czarnak et al., 2022). electrochemical oxidation and ionizing UV radiation coupled with biological degradation were also used for the degradation of the organophosphorus insecticide chloropyrifos(Allawi & AL-Mukhtar, 2024; Mohy-Eddine et al., 2023). The chemical oxygen demand (COD) of chloropyrifos sample presented a significant reduction of 64% when electrochemical oxidation was applied (Mabrouki et al., 2022; Pławińska-czarnak et al., 2022). In recent work, black phosphorous quantum dots (BPQDs) anchored onto the nanosheets of Bi_2WO_6 form composite BPQDs/Bi_2WO_6, showed attractive photocatalytic performance in the degradation of various antibiotics as Amoxicillin (AMX), widely used broad-spectrum antibiotic all over the world (Alygizakis et al., 2016)(Fattah et al., 2022).

The conditions of the experiment were optimized in order to increase the efficiency of degradation of AMX as well as its probable degradation mechanism was in light of the discovery of intermediates in the transformation process (Agoud et al., 2025; Hussein et al., 2019). Furthermore, the mechanism of photocatalysis was uncovered through a thorough study of the characterization of the materials. Results indicated the enhanced photocatalytic capacity was due in large part to the distinct hollow and porous structure of Bi2WO6 that facilitated improved luminosity surfaces, surface reactivity, as well as charges transfer processes.(L. Chen et al., 2023; El Ghammad et al., 2025). Amoxicillin Fig. 1. is among the most often found organic pollutants in aquatic ecosystems and wastewater treatment systems specifically in effluents that come from livestock farms, hospitals and various other sources of human anthropogenic origin.(Balarak & Mostafapour, 2019; Wahyuni et al., 2020). AMX is an aminopenicillin of the beta-lactam family, representing one of the most prescribed antibiotics. The molecule contains an azetidin-2-one tetragonal ring, called beta-lactam, which is essential for the activity of this family. Aminopenicillins have an additional amino group to the benzyl penicillin which makes them resistant to gastric acidity and broadens their spectrum towards Gram (Regraguy et al., 2022; Vitiello et al., 2021). Unfortunately, conventional chemical and biological oxidation treatment methods being employed for water and wastewater usually fail to remove most antibiotics (Alnajrani & Alsager, 2020; Azrour et al., 2024). In addition, physical treatment methods of water and wastewater, such as adsorption and membrane filtration, transfer these compounds from one phase to another, rather than removing them (Krzeminski et al., 2020; Wen et al., 2018) (Kankou et al., 2021).

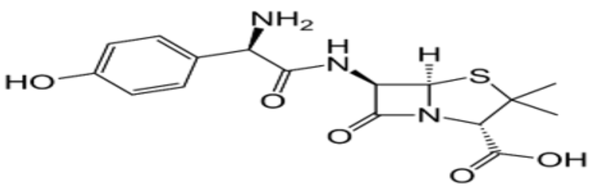

Fig. 1. Amoxicillin structure

The new photocatalysts is attracting enormous importance in photodegradation. Thus, it can be create an efficient technology for the degradation of different contaminants from wastewater (Elgendy et al., 2019; Okhovat et al., 2015; Shokri et al., 2016). Among them, BiVO4 and MnZnO have been found to act as stable photocatalysts for the photochemical decomposition of organic contaminants (Labhane et al., 2018; Mohamed et al., 2019; Naing et al., 2020; Qamar et al., 2021a). In this work we investigate photocatalytic activity of the mixture of $BiVO_4$ and MnZnO to eliminate AMX from water. The intermediate products were also identified and discussed based on the mass spectroscopy (HPLC-MS). Although previous studies have explored the degradation of various antibiotics using Bi_2WO_6-based systems and other nanomaterials(Elouardi et al., 2022; Hussein et al., 2019), many of these approaches remain limited by narrow light absorption ranges, rapid electron–hole recombination, or complex synthesis procedures. For instance, TiO_2-based systems require UV light and often demonstrate low degradation kinetics(Rezvannasab et al., 2025), while Bi_2WO_6-based composites, despite their visible-light responsiveness, face limitations in charge separation and lack comprehensive identification of degradation by-products(Z. Chen et al., 2023). In contrast, the combination of $BiVO_4$ with MnZnO presents a promising alternative. BiVO4 has stable photocatalytic performance under visible light. MnZnO improves charge carrier separation and enhances the creation of hydroxyl radicals, thus increasing the overall reactivity. (Qamar et al., 2021b; Qisse et al., 2022). The current study builds on the earlier research by creating a BiVO4-MnZnO heterojunction, and testing its performance in the degrading of Amoxicillin (AMX) in both visible and UV light. Furthermore, unlike many previous works, this study provides a mechanistic insight into AMX degradation by identifying transformation products through high-performance liquid chromatography–mass spectrometry (HPLC-MS) (Sathya et al., 2023). To better position this research within the context of previous studies, a comparative summary is presented in Table 1, highlighting key differences in photocatalyst design, activation modes, known limitations, and the innovations introduced in this work.

Table 1. Overview of selected photocatalytic studies on antibiotic degradation and comparative insights with the present work.

Study	Photocatalyst	Light Source	Identified Limitation	Improvement Brought by This Study
(Shaykhi & Zinatizadeh, 2014)	TiO_2 (immobilized)	UV only	Requires UV light; limited degradation rate	Effective under both UV and visible light; improved ●OH generation
(Balarak & Mostafapour, 2019)	NiO	UV	No visible-light response; performance limited to UV exposure	Broader light absorption achieved through $BiVO_4$–MnZnO combination
(Hussein et al., 2019)	Bi_2WO_6 composite	Visible	Moderate activity; suffers from charge recombination	MnZnO doping improves charge separation and photocatalytic efficiency
(Z. Chen et al., 2023)	BPQDs/Bi_2WO_6	Visible	Complex synthesis routes; lack of detailed degradation pathway analysis	Simpler synthesis route; transformation products tracked via HPLC-MS
Present Study (This Work)	$BiVO_4$–MnZnO heterojunction	UV–Vis	—	High AMX removal efficiency; enhanced radical formation; mechanistic insight

2. METHODOLOGY

2.1. Amoxicillin Spectrum

In order to determine the absorption maximum of AMX, two solutions, one of 25 mg/L and the other of 100 mg/L, were analyzed by UV spectrophotometer Fig. 2. Two maxima are observed, one at 230 nm and the other at 270 nm. On the spectrum, the zone between 0 and 1 of absorbance is the zone where the precision is the best. Indeed, at an absorbance of 1, 90% of the light comes out of the tank, while at an absorbance of 2 there is only 10% of light left. It is observed, for the 100 $mg.L^{-1}$ solution that at 230 nm the maximum absorbance is between 2 and 3, which is not very precise. For this reason, the wavelength chosen for this study is 270 nm.

2.2. Study of the nature of light

To observe the effectiveness of photocatalysis, it is important to determine the impact of the nature of light on AMX. AMX molecule absorbs photons at a wavelength of 270 nm. AMX will therefore not be degraded by direct photolysis under UV radiation, nor under solar light, which emits at wavelengths > 290 nm. The conclusion is that AMX could be degraded by indirect photolysis under UV–Vis light in the presence of photocatalysts.

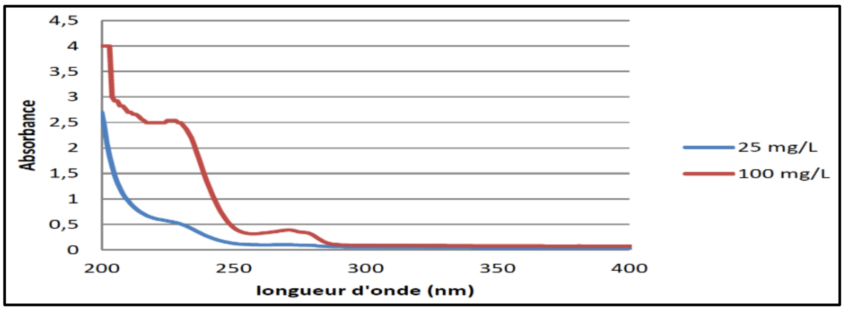

Fig 2. Adsorption spectrum of AMX

2.3. Chemicals and Catalysts preparation

AMX was purchased from SIGMA with high purity (99.9%) The well synthesized and characterized $BiVO_4$ and MnZnO were a gift from Professor, Ozacar, Sarakia University – Turkey. Experiments were conducted at pH = 7.0, buffered with a mixture of K_2HPO_4 3.9×10^{-4} mol/l and KH_2PO_4 6.1×10^{-4} mol/L (1/1; v/v). Photocatalytic activity of the photocatalysts was evaluated by using AMX pharmaceutical as organic pollutant under UV and Visible light irradiation. In the first one (Visible Light), the irradiation experiments were carried out using a high-pressure mercury UV lamp. (Phillips. HPK 125W) equipped with 250 ml cylindrical reactor made of Pyrex in order to simulate sunlight (wavelength > 290 nm). In the second photoreactor (UV Light), the irradiation experiments were carried out using low pressure mercury lamp (Phillips 6W) emitting in UV region with maximum absorption at 254 nm. The initial concentration of AMX in pure water was 50 ppm (250 mL) and a concentration of 200 mg of the photocatalyst was stirred. Before the experiment, the mixed solution (catalyst+ AMX) was magnetically stirred in the dark for 30 min to ensure the establishment of an adsorption-desorption equilibrium between the catalyst and AMX. At specific times, a certain amount of the suspension was removed and then filtered with an adsorbent filter (RC 0.45 um). The amount of AMX in the suspension was measured by measuring the absorbance of approximately 270 nm by using the Cary 300 spectrophotometer(Abed, 2024). Control studies, which included AMX photolysis with UV and visible radiation with no catalysts, were performed in the same conditions that were used in the current research. The mechanism of degradation proposed by photocatalytics is shown in Fig. 3.

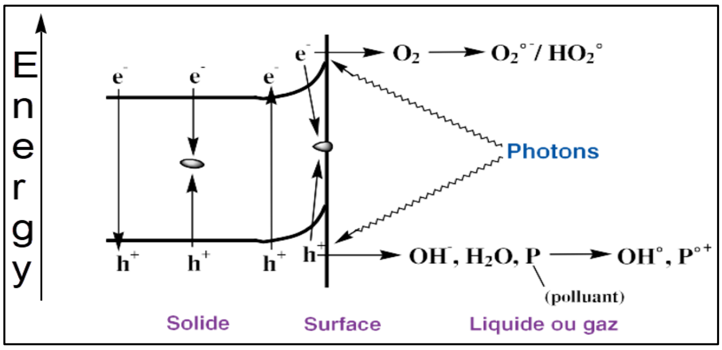

Fig 3. Mechanism of photocatalysis degradation

3. RESULTS AND DISCUSSION

3.1. Temperature profile

Initial tests were performed to determine if AMX was eliminated by 2 photocatalysts $BiVO_4$ and MnZnO in a separate manner in both visible and ultraviolet light. It was observed that in the presence of the photocatalysts $BiVO_4$ and MnZnO no notable reduction in AMX concentration was found under Visible light illumination under our conditions Fig.4 and Fig.5. Therefore, weak photolysis occurs. Also, there was the absence of statistically significant variations in the first AMX concentration was found in dark environments. UV and Visible irradiation over aqueous AMX / $BiVO_4$–MnZnO (5 and 10% of MnZnO) dispersions lead to reduce the absorption intensity of the light Fig. 6. With increasing radiation duration, the absorption band of 270 nm for AMX shrinks gradually as the absorbance for the absorption band around 270nm drops between 1.036 to 0.785 for five percent, or in the range of 1.018 to 0.716 for 10 percent. The observed greater degradation efficiency by 10% MnZnO doping in comparison to 5% doping, could result from the higher amount of surface active sites as well as enhanced charge carrier dynamics. (Biswas et al., 2021). The extra Mn content improves dispersion, and also facilitates charge separation of electron–hole photogenerated by illumination and reduces the rate of recombination. This enhancement promotes the formation of reactive oxygen species, particularly hydroxyl species (●OH), which are primarily responsible for oxidizing the AMX molecules. However, it is important to note that beyond a certain threshold, excessive Mn incorporation could induce the formation of recombination centers. In this study, 10% MnZnO emerged as the most effective loading without such adverse effects. (Shaykhi & Zinatizadeh, 2014; Verma & Haritash, 2020).

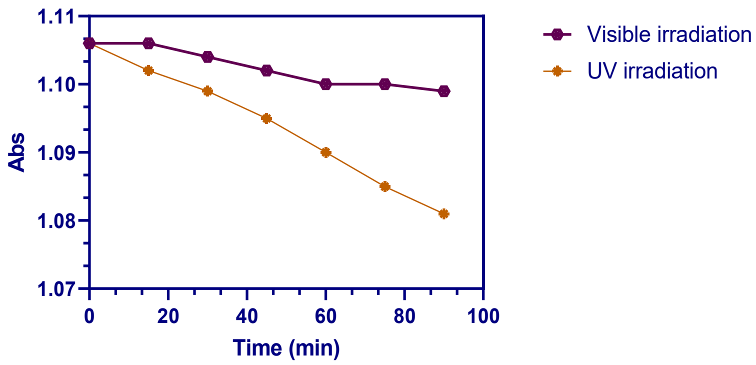

Fig 4. Photochemical degradation of AMX using BiVO4

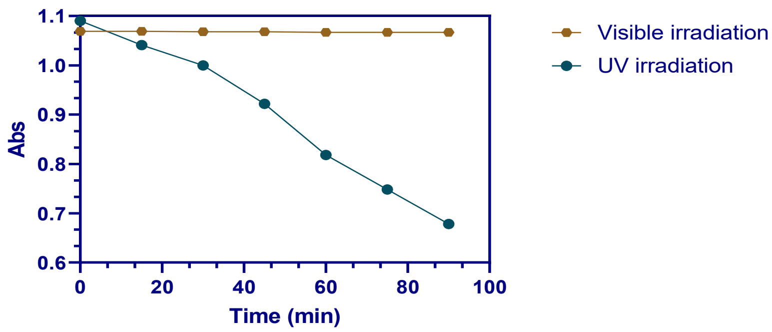

Fig 5. Photochemical degradation of AMX using MnZnO

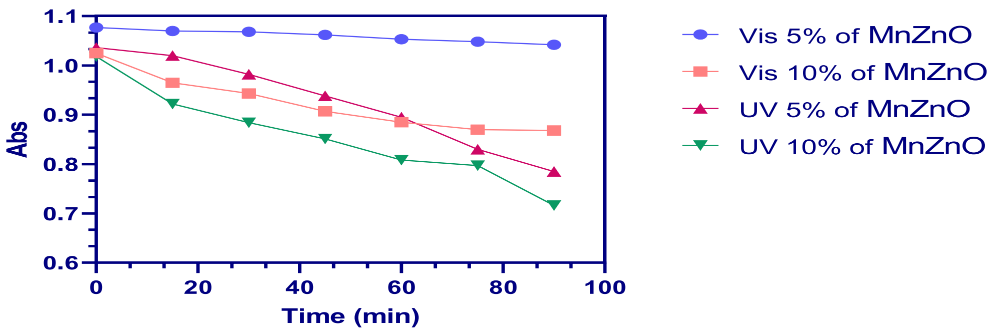

Fig 6. Photochemical degradation of AMX using BiVO4–MnZnO

Compared to similar studies(Roushree & Haimbodi, 2025), the $BiVO_4$–MnZnO system showed higher efficiency under UV-visible light. While NiO- and TiO_2-based photocatalysts reported in previous work required longer durations or UV-only conditions, our composite achieved notable degradation within a short time and under milder conditions. This highlights its potential for practical water treatment.

3.2. Degradation pathway for AMX

Heterogeneous photocatalytic mineralization Fig. 7. The identification and monitoring of AMX degradation by-products from samples taken during the reaction was performed by High performance liquid chromatography-mass spectrometry (HPLC-MS) (Bankole et al., 2022; El

Bakraoui et al., 2022). Hydroxyl radicals $OH^{\bullet}$ are produced as oxidants in the photocatalysis process. According to (Bencheikh et al., 2020; Fawzy et al., 2022), AMX (m/z =366) was decomposed by breaking the β-lactum ring, losing the amine function, and separating the link between the hexagonal and pentagonal cycles in order to generate amoxicillin penicilloic acid (m/z =340) and another fragment (m/z =189). Intermediates with m/z between 160 and 208 were formed because of the oxidation process of the methyl linkage. The further oxidation of these intermediates was then transformed by photochemically produced reactive oxidizing substances into simpler by-products such as carbon dioxide, water Sulfates, amines and simpler organic molecules. As shown in Fig. 8, the photocatalytic degradation of AMX begins with the cleavage of the β-lactam ring, followed by successive oxidation reactions that generate smaller intermediate compounds. These intermediates are further oxidized into low-molecular-weight carboxylic acids, indicating a stepwise mineralization process.

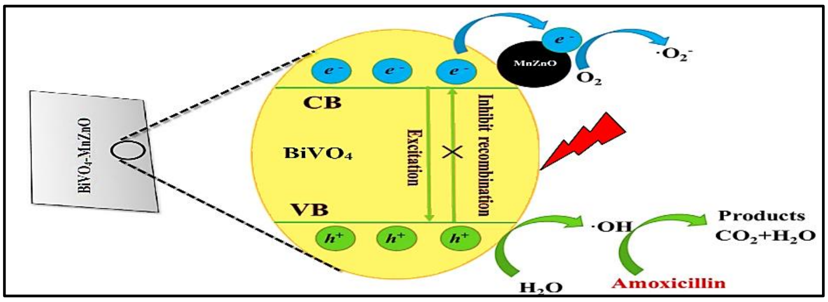

Fig 7. Photocatalytic degradation of AMX by BiVO4–MnZnO

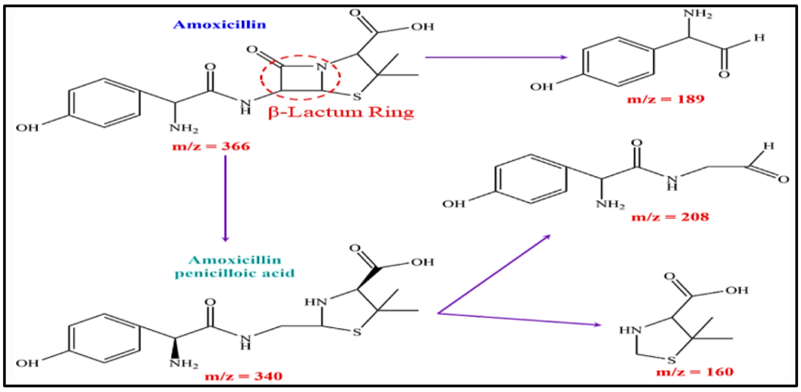

Fig 8. Proposed degradation pathway and identification of AMX by-products

3.3. Mineralization Extent and Limitations

Although the disappearance of the AMX peak and the presence of low-mass intermediates indicate advanced degradation, the complete mineralization of the parent compound cannot be definitively confirmed in the absence of Total Organic Carbon (TOC) or Chemical Oxygen Demand (COD) analysis(Azoulay et al., 2022; Zisti et al., 2024). The detection of small molecular fragments by HPLC-MS strongly suggests partial mineralization; however, quantitative evidence of total carbon removal remains to be established. The future work will incorporate TOC tests to evaluate the amount of mineralization and to confirm that the environment is safe for the effluent treated.

4. CONCLUSIONS

In this study the BiVO4-MnZnO heterojunction was shown to have the greatest photocatalytic efficiency in the reduction of Amoxicillin under visible and ultraviolet light. The improved performance can be due to synergistic interactions among BiVO4 and MnZnO. This leads to a better charge separation and the formation reactions, specifically radical’s hydroxyl. The detection of transformants by HPLC-MS offered an understanding of the process of degradation in a stepwise manner and confirmed the gradual disintegration of AMX into intermediates with low molecular weight. TocBeyond the lab scale, the operation simplicity of the BiVO4 MnZnO system and its efficiency under the conditions of neutral pH as well as visible light, demonstrates its ability to be integrated into small-scale or decentralized wastewater treatment systems. In contrast to conventional Fenton systems, which need acidic environments, the photocatalyst performs effectively at a pH that is environmentally appropriate which makes it an ideal possibility for a real-world wastewater treatment. While TOC tests are required for future studies to verify the mineralization process, the current results offer a promising path to be used in the practical process of removing the residues of antibiotics from water environments. The potential for scaling this method as well as it's compatibility with solar radiation and its low operating requirements make it a feasible option for the development of advanced technology in water purification.

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