



ENHANCED DECOMPOSITION OF METRONIDAZOLE IN WATER: COMPARATIVE ANALYSIS OF TiO₂ AND ZnO HETEROGENEOUS PHOTOCATALYSIS

Sanjay Kumar Patel¹, Farzana Shaheen², Yaseen³, Anirudh Gupta⁴, Dr Haseeb Umar^{5*}, Saba Nosheen⁶, Ali Imran Mallhi⁷, Asaad Babker⁸

¹University of Bridgeport, Connecticut, USA

²Lecturer, Department of Chemistry, Allama Iqbal Open University Islamabad, Pakistan

³Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan

⁴Assistant Professor, Department of Biotechnology, NIMS Institute of Allied Medical Science and Technology, NIMS University Rajasthan, India

^{5*}Department of Forensic Medicine, Alnafees Medical College, Isra University, Islamabad, Pakistan

⁶Department of Chemistry, Riphah International University Islamabad, Pakistan

⁷Assistant Professor, Department of Chemistry, Superior University Faisalabad Campus, Pakistan

⁸Associate Professor, Department of Hematology, College of Medical Laboratory Sciences, University of Science and Technology, Omdurman, Sudan

***Corresponding Author:** Dr Haseeb Umar

*Department of Forensic Medicine, Alnafees Medical College, Isra University, Islamabad, Pakistan,
Email: haseebumarrana517@gmail.com

ABSTRACT:

Background: Concerns about water quality, especially regarding pharmaceuticals and micro pollutants, have escalated due to their resistance to traditional purification methods.

Methods: The efficacy of heterogeneous photocatalysis for decomposing the antibiotic metronidazole (MTZ) in water was examined, employing TiO₂ and ZnO catalysts. Photo reactors maintained at controlled temperatures housed the experiments, utilizing two 6 W U.V. light bulbs for 120 minutes. Metronidazole degradation was investigated across 6 mg L⁻¹ to 24 mg L⁻¹ concentrations using standard solutions. U.V./Visible spectrophotometry was employed to analyze MTZ presence and quantify photo catalytic outcomes.

Results: ZnO demonstrated superior oxidation rates to TiO₂ under identical conditions, indicating its more robust catalytic performance.

Conclusion: Heterogeneous photocatalysis, particularly employing ZnO, presents a promising approach for mitigating metronidazole contamination in water sources, addressing concerns over water quality and micropollutant removal.

KEYWORDS: Antibiotics; Metronidazole; Heterogeneous Photocatalysis; U.V./Visible Spectrophotometry.

INTRODUCTION:

Pharmaceutical compounds have been the subject of extensive research since, according to ARIAS, they represent a relatively new class of aquatic hazards. Both surface water and groundwater have been found to contain these substances. Substances typically created to treat specific human ailments but may also have unstudied effects on other living things are the exact cause of environmental danger

and toxicity.

Even in cases where primary treatments have been administered, these substances may nevertheless contaminate aquatic habitats after consumption and excretion in their natural state of unmetabolized or unaltered molecules (Hayat, Huang, Wang, Ullah, & He, 2024; Shabanian-Boroujeni & Nezamzadeh-Ejhieh, 2024).

Numerous studies have demonstrated that certain pharmaceutical substances are not naturally removed from wastewater treatment systems or biodegraded. In actuality, wastewater treatment facilities and waterways frequently include small amounts of several medicinal chemicals. Inadequate drug disposal and direct emissions from production facilities are additional causes of pollution originating from pharmaceutical chemicals. As a result, before releasing pharmaceutical-containing effluents, it is essential to treat them sufficiently or the water that enters purification plants (Rahman, Suvo, Islam, Yeachin, & Bhuiyan, 2024; Saib et al., 2024).

Metronidazole (MTZ) is a member of the nitroimidazole family and is chemically known as 1-(β -hydroxyethyl)-2-methyl-5-nitroimidazole (Figure 1). It has antimicrobial agents (antibacterial and antiprotozoal) properties and is used to treat anaerobic cocci and gram-negative and gram-positive bacilli. The majority of metronidazole's documented uses are in therapy to combat *Giardia lamblia* and *Trichomonas vaginalis*. This substance, which targets the DNA molecule of microbes, is the primary medication of the nitroimidazole class (Muthukutty et al., 2024; Shuvo, Putul, Hossain, Masum, & Molla, 2024).

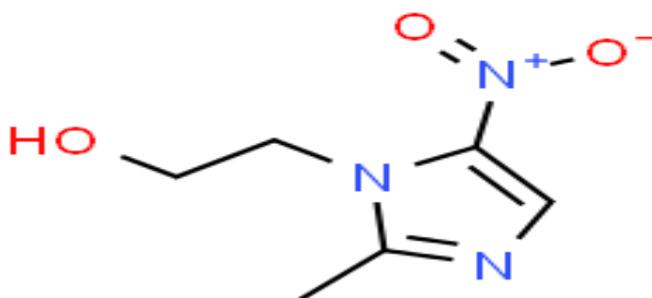


Figure 1: Structural formula of metronidazole

The techniques now employed in wastewater treatment facilities (WTP) and water treatment plants (WTP), such as physical, chemical, and biological processes, must be revised to eliminate these contaminants. BUTH reports that antibiotics, hormones, steroids, and antibacterial agents have been found at $\mu\text{g L}^{-1}$ amounts in treated water from German municipal plants. Due to the absence of municipal wastewater collection systems, complex organic compounds are expected to appear more frequently in natural waters in Brazil and other developing nations (Moslehi et al., 2024; Rani, Choudhary, Shukla, & Shanker, 2024).

The National Health Information System (SNIS) released data for 2015, but only 50.3% of Brazilians have access to wastewater collection. This means that over 100 million people in Brazil use other methods, such as septic tanks or throwing sewage straight into rivers, to eliminate their waste. Advanced oxidative processes (POA) are one of the various approaches with great potential for application in resolving environmental issues stemming from pollution produced by pharmaceutical chemicals (Dali, Benssassi, Harakat, & Sehili, 2024).

These procedures are predicated on producing free radicals, specifically the hydroxyl radical ($\text{OH}\cdot$), with a high potential for oxidation and quick reaction kinetics. This results in a significant mining capacity that allows microcontaminants to be fully mineralized rather than only phase transferred. Heterogeneous photocatalysis might be employed with the assistance of semiconductors to remove

both organic and inorganic chemicals from wastewater, given the potential AOPs (Lushaj et al., 2024; Yaacob, Khasri, Mohd Salleh, & Mohd Jamir, 2024).

The technique has shown promise in the aqueous phase mineralization of pharmaceuticals and their metabolites. ZnO has recently drawn greater attention despite TiO₂ being the most often employed semiconductor in photocatalysis because of its inexpensive cost and intense activity in various photochemical processes. ZnO also exhibits a band gap energy of 3.2 eV, which is close to that of TiO₂. Moreover, research that has been published indicates that ZnO degrades certain pollutants more effectively than TiO₂ (Bouarroudj et al., 2024; Sruthi et al., 2024).

Table 1: Comparative Studies on Pharmaceutical Contaminants in Wastewater Treatment Systems

Study	Findings	References
Moslehi et al. (2024)	Antibiotics, hormones, steroids, and antibacterial agents detected in treated water.	Moslehi et al. (2024)
Rani et al. (2024)	Presence of complex organic compounds in natural waters, especially in developing nations	Rani, Choudhary, Shukla, & Shanker (2024)

Table 2: Advanced Oxidative Processes for Pharmaceutical Chemical Pollution Treatment

Study	Approach	References
Dali et al. (2024)	Utilization of advanced oxidative processes (POA)	Dali, Benssasi, Harakat, & Sehili (2024)
Lushaj et al. (2024)	Application of heterogeneous photocatalysis	Lushaj et al. (2024)
Yaacob et al. (2024)	Use of semiconductors for AOPs	Yaacob, Khasri, Mohd Salleh, & Mohd Jamir (2024)

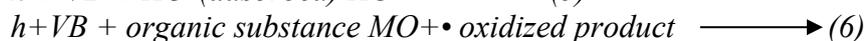
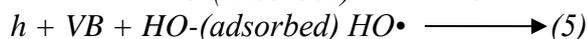
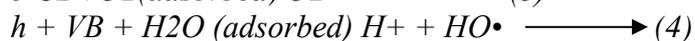
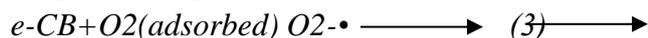
Table 3: Mechanisms of Heterogeneous Photocatalysis

Mechanism	Description	References
Semiconductor + hv and-CB + h+VB	Photon absorption by semiconductor initiates a photocatalytic process.	Kareem, Thenmozhi, Hari, Ponnusamy, & Senthilkumar (2024)
e-CB + h + VB semiconductor + heat	Recombination of electrons with photogenerated vacancies	Kareem, Thenmozhi, Hari, Ponnusamy, & Senthilkumar (2024)
e-CB + O ₂ (adsorbed) O ₂ -•	Electron interaction with adsorbed oxygen molecules produces superoxide anion.	Kareem, Thenmozhi, Hari, Ponnusamy, & Senthilkumar (2024)
h + VB + H ₂ O (adsorbed) H+ + HO•	Valence band vacancies react with adsorbed water molecules to form hydroxyl radicals.	Kareem, Thenmozhi, Hari, Ponnusamy, & Senthilkumar (2024)
h + VB + HO- (adsorbed) HO•	Hydroxide anion reacts with valence band vacancies to produce hydroxyl radicals.	Kareem, Thenmozhi, Hari, Ponnusamy, & Senthilkumar (2024)
h+VB + organic substance MO+• oxidized product	Direct oxidation of adsorbed organic materials by photogenerated holes	Kareem, Thenmozhi, Hari, Ponnusamy, & Senthilkumar (2024)

Whenever a semiconductor consumes photons with activity corresponding to or above its band gap, electrons from the band called the valence band are promoted to the energy level found in the conduction band, starting the photocatalytic process (Eq. (1)). The efficiency of the photocatalytic process can be reduced by electrons in the conduction band (e-CB) recombining with the photogenerated vacancies (holes, h+VB) (Eq. (2)). Conversely, electrons may go to the catalyst

particle's surface where they are captured through the adsorption oxygen molecules, creating the superoxide anion ($O_2^{\bullet-}$) and boosting the process's efficiency (Eq. (3)) (Kareem, Thenmozhi, Hari, Ponnusamy, & Senthilkumar, 2024).

In parallel, the catalyst surface may get stuck with vacancies created in the valence band ($h+VB$), which would encourage the splitting of adsorbed water molecules or the production of radial hydroxyl ($H O$) from the hydroxide anion (Eqs. (4) and (5)). Because of their strong oxidation potential, hydroxyl radicals were thought to be the cause of the oxidation of organic materials. Lastly, oxidized intermediates can be produced by holes directly oxidizing adsorbed organic materials (Eq. (6)) (Hamza et al., 2024).



The primary goal of this work was to assess the degradation of the antibiotic metronidazole resulting from heterogeneous photocatalysis using the UV/visible spectrophotometry approach. Using ZnO and TiO₂ as catalysts, photocatalytic tests were carried out in a continuous complete recirculation system. Based on time, the degradation rates between the two specified MTZ (6 and 24 mg L⁻¹) and catalyst (1.0 and 1.5 g L⁻¹) concentrations were compared and discussed (Arabian et al., 2024).

MATERIALS AND METHODS:

MATERIALS:

A pharmaceutical company offered 100% pure metronidazole. Purchased from Synth, zinc oxide P.A. (minimum purity of 99%) and titanium dioxide (purity of 99.4%, white color, and powder form) were utilized without additional purification. The pH was adjusted using 1 M H₂SO₄ and 1 M NaOH purchased from Merck. Solubilization and various concentrations were created in deionized (DI) water (Yang et al., 2024).

PHOTOCATALYTIC REACTOR:

The photocatalytic studies were conducted in a 200 mL laboratory-scale flow reactor that uses solution sheet irradiation instead of concentrated U.V. irradiation. The target chemical passes through thin glass tubes and silicone tubing. To remove another research variable, namely, to enable the experiment to proceed without interference from temperature and to prevent a decrease in the overall reaction rate, this procedure was carried out inside an incubator to ensure that the process temperature remained at 20° C (Ali et al., 2024; Waghmare, Rathore, Pandey, & Chandra, 2024).

Additionally, it had two U.V. sources with two lamps that produced U.V. light at two different wavelengths: one short wave (254 nm) and the other long wave (365 nm), both with a 6W power output. A thin tube was positioned on either side where the MTZ solution passed (Shee & Kim, 2024).



Figure 2: Diagram of the photocatalytic reactor

The solution was left dark for thirty minutes to achieve adsorption equilibrium. Following the equilibration phase, the stirrer and spotlights were activated. A 10-milliliter sample was drawn and placed in a dark container for further examination every thirty minutes. The reactor solution was continuously stirred and kept at 20°C for up to 120 minutes during the experiments. To get rid of the catalyst, the material was filtered using a 0.2 µm filtering membrane (Gao et al., 2024; Keşir & Bıyıklıoğlu, 2024).

OPERATING PARAMETERS:

The concentration of the MTZ solution was determined using laboratory research to determine the optimal parameters to use request, as well as data from the literature, where the excreted dose of unmodified MTZ is thought to equal 6–18%. The literature data and studies conducted to determine the optimal values for the study were used to specify the concentrations of the ZnO and TiO₂ catalysts. SHEMER and PALOMINOS concluded that the breakdown of antibiotics improves when the catalyst concentration is raised over 0.5 g L⁻¹ (Azmoon, Farhadian, Pendashteh, & Navarchian, 2024).

Thus, 1.0 g L⁻¹ and 1.5 g L⁻¹ were the catalyst concentrations under study for the 6 and 24 mg L⁻¹ metronidazole solution. pH is a significant factor since it affects the semiconductor surface's ability to charge. The pH range of the study was determined to be between 6.5 and 7.0 for both catalysts, considering the wastewater treatment plant situation and data from the literature (Subhiksha et al., 2024).

ANALYTICAL METHOD:

ANALYTICAL APPROACH:

Changing the MTZ content in the medium to gather data on the absorption in the visible region of the MTZ solution was tried to establish a few analytical conditions. Spectrophotometric determinations were performed at room temperature using a spectrophotometer and 10 mm cuvettes. An analytical curve was made, and the equation for the matching straight line was calculated based on the readings of the preset standards and the blank.

The evaluation was conducted to track the degradation of metronidazole by employing the U.V./visible absorption spectrophotometry technique and the Shimadzu UV 1800 spectrophotometer, which has an optical path of 10 mm and scanning wavelengths ranging from 190 to 1100 nm. The analysis was done at 25 C ± 2 Oc (Istiqomah et al., 2024; Salmi et al., 2024).

RESULTS AND DISCUSSIONS:

The MTZ spectrometric behavior results aimed to provide further insight into the analyte's absorption process at various concentrations. Experiments revealed that, as Figure 3 illustrates, the compound's highest absorbance occurs at 320 nm, and its spectrum remains constant across mediums (Liu et al., 2024).

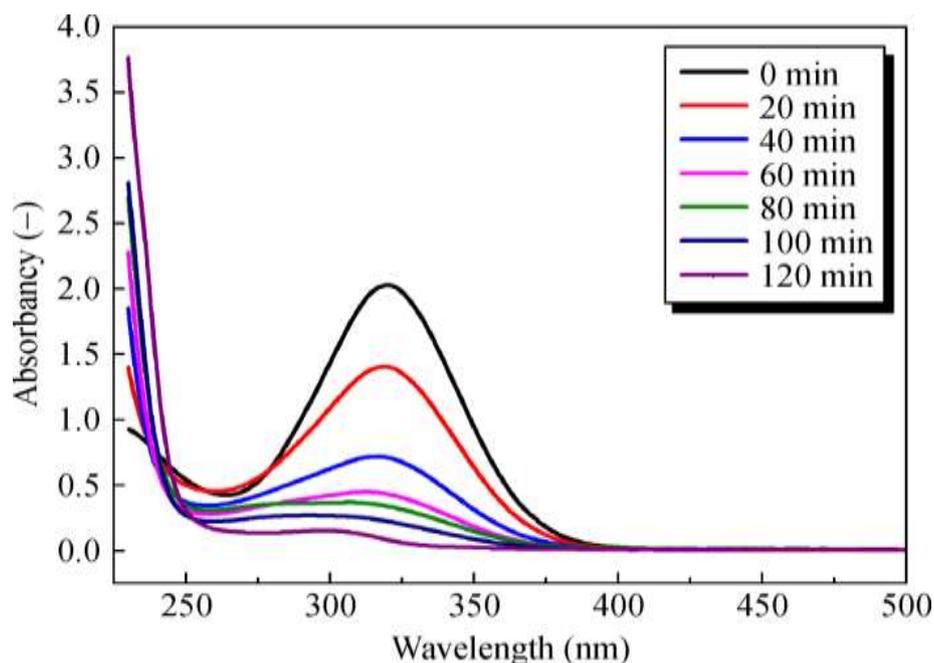


Figure 3: UV-Vis absorption spectra with various MTZ concentrations present

It was feasible to confirm that the spectral profile did not significantly alter and that the chemical experienced increases in absorbance with increasing concentrations. No modifications were found, such as raising the baseline or modifying the maximum lambda (Cojocar et al., 2024).

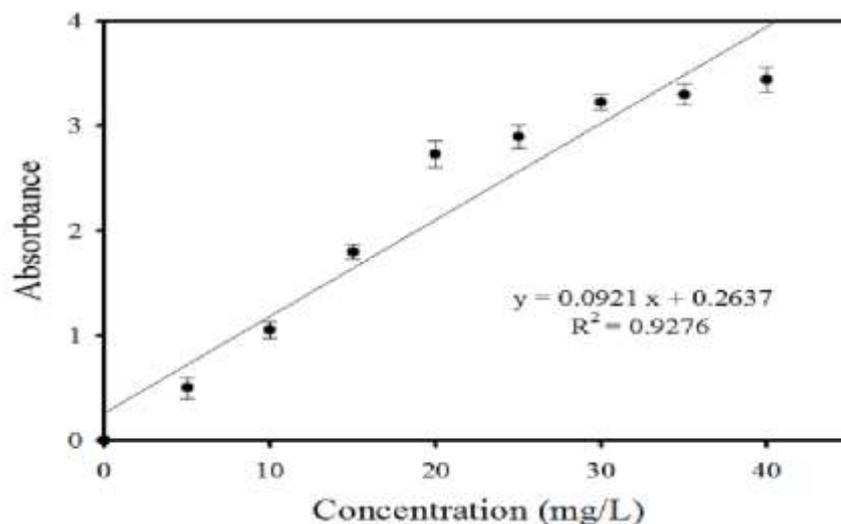


Figure 4: MTZ analytical curve, considering concentrations 6, 12, 18, 24 and 30 mg L⁻¹ ($R^2 = 0.9276$)

The Beer-Lambert law, sometimes known as Beer's law, is the foundational principle of spectrophotometry. The formula for this law is $A = \epsilon c l$, where ϵ is the absorbance and l is the light's travel distance. It links the absorbance (A) to the concentration (c) of the absorbing species. The equation is $A = \epsilon c$ given that $l = 1$ cm. The MTZ absorption can be found by modifying the curve in Figure 4 and calculating the slope ($K=0.0533$) that results from the modification, as seen below (Kharouf et al., 2024).

$$\epsilon = K/l = 0.0533/1 = 0.0533 \text{ L/mg.cm} = 53.3 \text{ L/g.cm} \quad (7)$$

By multiplying the absorption value by the molar mass of MTZ, one can determine the molar

absorption, as demonstrated below:

$$\epsilon = 9114.3 \text{ L/mol.cm} / 53.3 \times 10^{-3} \text{ cm} \quad (8)$$

Verifying if MTZ can absorb U.V. light is crucial since failing could hinder the photocatalyst's ability to function in photocatalytic reactions by making MTZ a rival for the photocatalyst's position in absorbing the radiation. This indicates that MTZ will absorb a significant portion of the U.V. radiation in photocatalysis reactions due to its high molar absorption, which directly suggests the substance's efficacy in absorbing light. Thus, it can be said that the method is appropriate for figuring out how MTZ degrades and that it is simple to find low concentrations of chemicals (Hojamberdiev et al., 2024; Lin, Yang, Fatolahi, Janani, & Sillanpää, 2024).

MTZ SPECTRUM:

MTZ DEGRADATION EVALUATION:

The degradation assessment was conducted by measuring the decrease in absorbance at 320 nm. Before the photocatalysis process began, the sample was taken at time 0 and every 30 minutes until the reaction's 120-minute duration was up. It was feasible to confirm that there was a change in MTZ concentration over time based on the concentration and absorbance results of the ZnO tests. Given that the absorption peak's intensity and the MTZ concentration are directly correlated, it is possible to conclude that the MTZ concentration drops between 0 and 120 minutes, as the absorbance likewise drops during this time (Akhtar et al., 2024; C. Wang et al., 2024).

To assess the relationship between MTZ concentration and absorbance, two analytical curves (Figures 5) and 6) were created for experiments where $[\text{MTZ}] = 24 \text{ mg L}^{-1}$ and 6 mg L^{-1} , respectively. Additionally, the percentage of MTZ degraded over 120 minutes was calculated for the given results (Mohan, Sathya, Vadivel, Seralathan, & Shin, 2024).

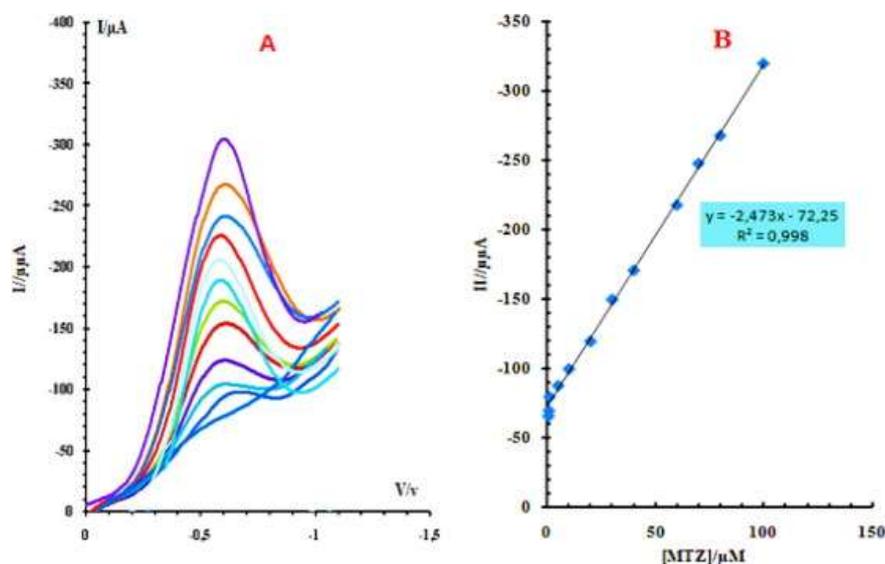


Figure 5: MTZ 24 mg L⁻¹ analytical curve using 1.5 and 1.0 g L⁻¹ of ZnO

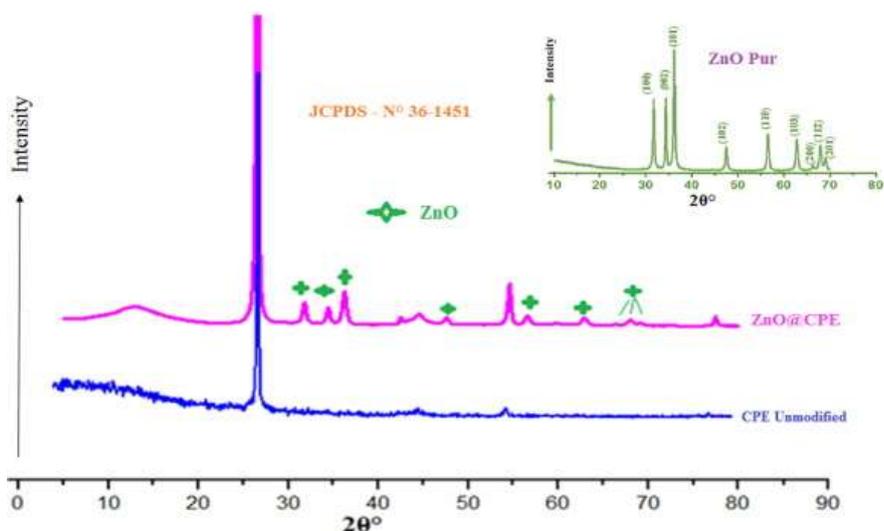


Figure 6: Analytical curve of 6 mg L⁻¹ MTZ with 1.0 g L⁻¹ and 1.5 g L⁻¹ ZnO

It was feasible to confirm that there was no discernible change in the concentration of MTZ over time based on the absorbance and concentration of the TiO₂-based tests.

The presence of TiO₂ in the samples during filtering was the decisive element that prevented an accurate reading of the amounts. Since the spectrophotometer uses this catalyst's absorbance at the same wavelength for readings, the recorded results were higher than the present sample concentrations. Therefore, it was found that even with all of the experimental effort, the samples could not be purified entirely using the laboratory's separation apparatus (Roslan et al., 2024).

Therefore, it was impossible to draw trustworthy conclusions about the studies using TiO₂ in suspension because the experimental data revealed significant differences.

It was possible to create two analytical curves (Figures 7) and 8) for the experiments involving [MTZ] = 24 mg L⁻¹ and [MTZ] = 6 mg L⁻¹, respectively, by taking into account the effect of MTZ concentration versus absorbance. The results also showed the percentage of MTZ degraded throughout the 120 minutes (Iqbal et al., 2024).

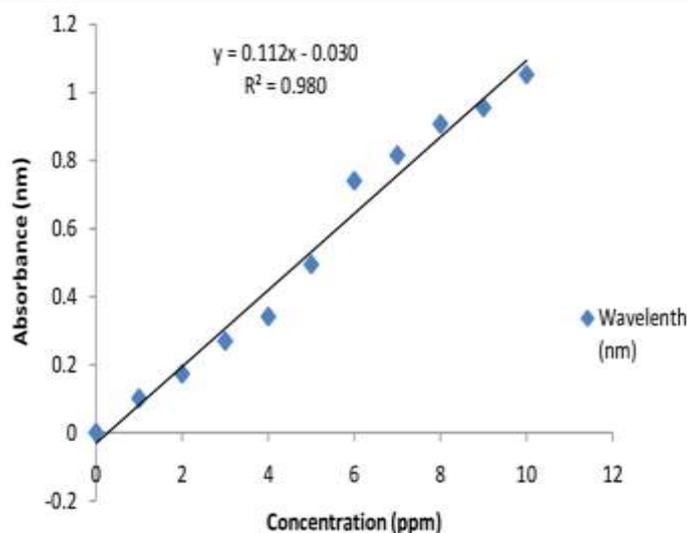


Figure 7: MTZ 24 mg L⁻¹ analytical curve; TiO₂ 1.0 g L⁻¹ and 1.5 g L⁻¹

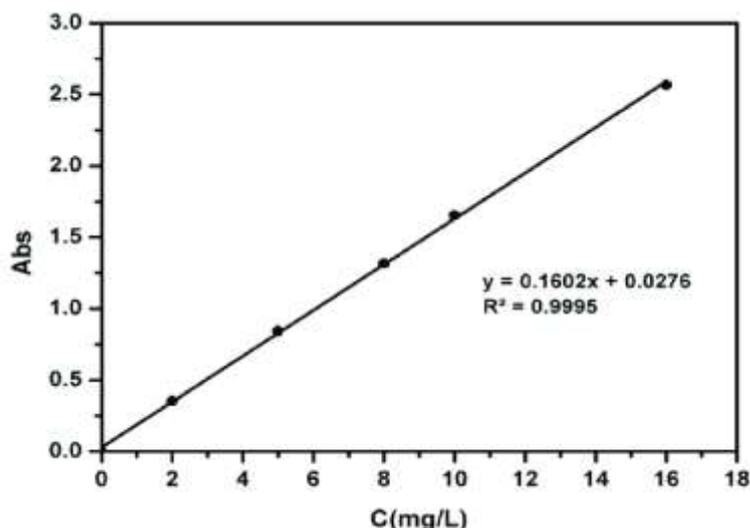


Figure 8: Analytical curve for MTZ 6 mg L⁻¹ with TiO₂ 1.0 g L⁻¹ and 1.5 g L⁻¹

The experiments with ZnO yielded good results; for example, the decrease of MTZ reached nearly 86% in the experiment with [MTZ] = 6 mg L⁻¹ and [ZnO] = 1.0 g L⁻¹. The trial with [MTZ] = 24 mg L⁻¹ and [ZnO] = 1.5 g L⁻¹ had the worst reduction of 22%. TiO₂ reactions did not yield positive results; the reduction was only 6%, and no discernible reduction happened in the case of MTZ 24 mg L⁻¹. Because there was a significant difference in the values obtained, the results of these studies could not be reliably repeated (Chaúque, Jank, Benetti, & Rott, 2024).

The presence of TiO₂ in the samples after filtration was the decisive element that prevented accurate concentration readings. Some measured values were above or very close to the actual sample concentrations since this catalyst also has an absorbance at the wavelength that the spectrophotometer uses to read values. As a result, it was found that, despite all experimental efforts, the materials could only be partially purified utilizing the separation tools in the lab that was used for this investigation (Pascariu, Cojocar, Ciornea, Romanian, & Serban, 2024).

Therefore, making trustworthy conclusions regarding the studies using TiO₂ in suspension was impossible because the experimental data revealed significant differences. Moreover, the results above show that the degradation rate increases with decreasing MTZ starting concentration in the reaction medium. Comparable outcomes have been reported for the deterioration of additional organic substances (Ahmad et al., 2024).

One argument is that the catalyst's surface has a set number of active sites, allowing for higher water molecule absorption on the catalyst's active sites at low pollutant concentrations. This leads to increased production of more hydroxyl radicals, which favor the drug molecules' indirect breakdown pathway and significantly speed up the photocatalytic process. The process's increased starting concentration may have additional effects that lessen the pollutant's ability to degrade by photodegradation (Targhan et al., 2024).

Higher concentrations of excess molecules on the catalyst surface block the catalyst surface significantly, hindering light from reaching the active sites, lowering the rate at which organic compounds are photodegraded, and resulting in a loss of process energy. Because of the organic substance's promotion of blocking, the adsorption may increase above an ideal level to the point where it interferes with the following photocatalytic process by preventing the produced photons from reaching the catalytic surface (Estrada-Vázquez et al., 2024; Z.-Y. Wang et al., 2024).

CONCLUSION:

After taking into account all of the data, it was found that the sample with [MTZ] = 6 mg L⁻¹ and [ZnO] = 1.0 g L⁻¹, which demonstrated an approximate 86% drop in MTZ concentration, had the most excellent results in terms of MTZ photocatalysis. The MTZ concentration did not significantly

decrease in the TiO₂ experiments, indicating a poor outcome in terms of degradation. The catalyst deposition in the narrow glass tubes may have prevented the TiO₂-containing samples from degrading, lowering process efficiency and raising catalyst concentrations after filtration.

The literature indicates that photocatalytic reaction systems that operate with the catalyst in suspension can produce higher rates of drug degradation; however, the catalyst must be separated at the end of the process, which becomes more laborious and is typically not satisfactory because many catalyst particles remain in the final solution. Moreover, the drug's starting concentration in the reaction medium significantly impacts the outcome. The rates attained increased with the decreasing initial MTZ concentration in the solution. The advantage of the indirect photocatalysis mechanism is the primary determinant of this outcome.

As a result, it is essential to assess alternative strategies for preventing interference and to start more thorough investigations that consider all potential interferences. The following methods can be used to conduct these further studies: use thin-tube replacement with quartz tubes, increase the pump flow rate to minimize catalyst loss, lower catalyst concentrations, and use a laminar system. HPLC can be used to assess potential environmental interferences.

REFERENCES:

1. Ahmad, A., Khawar, M. R., Ahmad, I., Javed, M. H., Ahmad, A., Rauf, A., . . . Karami, A. M. (2024). Green synthesis of ZnO nanocubes from *Ceropegia missa* H. Huber extracts for photocatalytic degradation of bisphenol under visible light to mitigate water pollution. *Environmental Research*, 249, 118093.
2. Akhtar, N., Nadeem, N., Yaseen, M., Jilani, A., Mahmood, A., Zubair, U., . . . Zahid, M. (2024). Solar light-driven photocatalytic degradation potential of g-C₃N₄ based binary chalcogenides (AgBiS₂/g-C₃N₄): *Materials Chemistry and Physics*, 316, 129067.
3. Ali, Z. S. N., Okla, M. K., Kokilavani, S., Abdel-Maksoud, M. A., Alatar, A. A., Sivaranjani, P., . . . Khan, S. S. (2024). Unraveling the enhanced rifampicin photocatalytic degradation over green-synthesized SrO₂@ SnIn₄S₈ pn heterojunction: Pathway, toxicity evaluation, and mechanistic insights. *Chemosphere*, 141464.
4. Arabian, S., Gordanshekan, A., Farhadian, M., Nazar, A. R. S., Tangestaninejad, S., & Sabzyan, H. (2024). Adsorption/photocatalytic degradation of cefixime by the green Bi₂WO₆/g-C₃N₄/ZIF-67 dual S-scheme heterojunction: Artificial neural network, genetic algorithm, density functional theory, and toxicity assessments. *Chemical Engineering Journal*, 150686.
5. Azmoon, P., Farhadian, M., Pendashteh, A., & Navarchian, A. H. (2024). Synergistic effect of adsorption and photocatalytic degradation of oilfield-produced water by electrospun photocatalytic Polystyrene/Nanorod-Graphitic carbon nitride fibers. *Journal of Environmental Sciences*, 141, 287-303.
6. Bouarroudj, T., Messai, Y., Aoudjit, L., Zaidi, B., Zioui, D., Bendjama, A., . . . Bachari, K. (2024). Hydrothermal-assisted synthesis of Sr-doped SnS nanoflower catalysts for photodegradation metronidazole antibiotic pollutant in wastewater promoted by natural sunlight irradiation. *Water Science & Technology*, wst2024054.
7. Chaúque, B. J. M., Jank, L., Benetti, A. D., & Rott, M. B. (2024). Preliminary insights on developing a continuous-flow solar system for the photocatalytic degradation of contaminants of emerging concern in water. *Environmental Science and Pollution Research*, 1-13.
8. Cojocar, C., Pascariu, P., Romanitan, C., Sillion, M., Samoila, P., & Serban, A. B. (2024). Intensification of organic pollutant degradation under visible light irradiation using ZnO nanostructured photocatalysts doped with praseodymium. *Applied Surface Science*, 160042.
9. Dali, A., Benssassi, M. E. H., Harakat, D., & Sehili, T. (2024). Enhanced activation of sulfite by the iron-citrate complexes under NUV irradiation for metronidazole degradation: Kinetic, degradation mechanism and efficiency in natural water. *Journal of Water Process Engineering*, 60, 105190.
10. Estrada-Vázquez, R., Vaca-Mier, M., Bustos-Terrones, V., Rangel-Peraza, J. G., Loaiza, J. G.,

- Hermosillo-Nevárez, J. J., & Bustos-Terrones, Y. A. (2024). Degradation of agricultural pollutants by biopolymer-enhanced photocatalysis: application of Taguchi method for optimization. *Reaction Kinetics, Mechanisms and Catalysis*, 137(1), 523-545.
11. Gao, T., Ma, Z., Ren, Y., Wang, Z., Zhang, M., Chen, X., & Wang, J. (2024). Highly sensitive fluorescent sensing and photocatalytic degradation performance of two-dimensional Tb-organic network. *Journal of Rare Earth*, 42(2), 303-313.
 12. Hamza, L., Laouini, S. E., Mohammed, H. A., Meneceur, S., Salmi, C., Alharthi, F., . . . Abdullah, J. A. A. (2024). Biosynthesis of ZnO/Ag nanocomposites heterostructure for efficient photocatalytic degradation of antibiotics and synthetic dyes. *Zeitschrift für Physikalische Chemie*(0).
 13. Hayat, A., Huang, L., Wang, Z., Ullah, R., & He, S. (2024). One-pot in situ synthesis of an NS-ligand co-doped metal-organic framework for the enhanced adsorption-assisted photocatalytic decontamination of metronidazole. *RSC advances*, 14(15), 10229-10243.
 14. Hojamberdiev, M., Vargas, R., Madriz, L., Yubuta, K., Kadirova, Z. C., Shaislamov, U., . . . Teshima, K. (2024). Unveiling the origin of the efficient photocatalytic degradation of nitazoxanide over bismuth (oxy) iodide crystalline phases. *Environmental Science: Nano*, 11(1), 336-350.
 15. Iqbal, Y., Ahmed, S., Aziz, M. H., Alam, M., Asif, M., & Huang, Q. (2024). Greener approach for synthesizing Ag decorated ZnO–CeO₂ nanostructure using *Moringa oleifera* L.E. and its investigation photocatalyst for ciprofloxacin and methylene orange degradation. *Materials Chemistry and Physics*, 129299.
 16. Istiqomah, N. I., Budianti, S. I., Cuana, R., Puspitarum, D. L., Mahardhika, L. J., & Suharyadi, E. (2024). Magnetically separable and reusable Fe₃O₄/chitosan nanocomposites green synthesized utilizing *Moringa oleifera* extract for rapid photocatalytic degradation of methylene blue—*results in Chemistry*, 7, 101245.
 17. Kareem, A., Thenmozhi, K., Hari, S., Ponnusamy, V. K., & Senthilkumar, S. (2024). Metal-free carbon-based anode for electrochemical degradation of tetracycline and metronidazole in wastewater. *Chemosphere*, 351, 141219.
 18. Keşir, M. K., & Bıyıkhoğlu, Z. (2024). Peripherally tetra-substituted zinc (II) phthalocyanine sensitized TiO₂ composite: Monitoring with tandem LC/MS and photocatalytic degradation of amoxicillin—*Journal of Organometallic Chemistry*, 1005, 122969.
 19. Kharouf, M., Zyoud, A., Zyoud, S., Qamhie, N., Hajamohideen, A., & Hilal, H. (2024). Enhanced photocatalytic degradation of phenazopyridine using rutile TiO₂/clay composite: catalyst recovery and environmental implications. *International Journal of Environmental Science and Technology*, 1-18.
 20. Lin, H., Yang, C., Fatollahi, L., Janani, B. J., & Sillanpää, M. (2024). Defect evolution on samarium doped Na₂Ti_nO_{2n+1} activity with different sodium/titanium ratios for photocatalytic degradation of fluoroquinolones drugs, toxicity assessments, and eco-toxicity prediction. *Ceramics International*.
 21. Liu, X., Ghosh, M. K., Wang, J., Zhong, X., Muddassir, M., Zhao, H., & Ghorai, K. (2024). Syntheses and photochemically antibiotic degradation of two Co (II)-based coordination polymers. *Polyhedron*, 116958.
 22. Lushaj, E., Bordin, M., Akbar, K., Liccardo, L., Barroso-Martín, I., Rodríguez-Castellón, E., . . . Polo, F. (2024). Highly Efficient Solar-Light-Driven Photodegradation of Metronidazole by Nickel Hexacyanoferrate Nanocubes Showing Enhanced Catalytic Performances. *Small Methods*, 2301541.
 23. Mohan, H., Sathya, P. M., Vadivel, S., Seralathan, K.-K., & Shin, T. (2024). Photocatalytic degradation of antibiotics and pharma pollutants in water *Advanced Functional Materials and Methods for Photodegradation of Toxic Pollutants* (pp. 255-280): Elsevier.
 24. Moslehi, M. H., Zadeh, M. S., Nateq, K., Shahamat, Y. D., Khan, N. A., & Nasseh, N. (2024). A statistical, computational optimization approach for photocatalytic-ozonation decontamination of

- metronidazole in aqueous media using CuFe₂O₄/SiO₂/ZnO nanocomposite. *Environmental Research*, 242, 117747.
25. Muthukutty, B., Arumugam, B., Ramaraj, S. K., Selvaraj, M., Assiri, M. A., & Lee, D. (2024). Enhancing metronidazole photodegradation by applying dysprosium vanadate/oxidized carbon nanofiber composite. *Journal of Water Process Engineering*, 58, 104806.
 26. Pascariu, P., Cojocaru, C., Ciornea, V., Romanitan, C., & Serban, A. B. (2024). Visible light-responsive Ce-doped ZnO ceramic nanostructures are effective photocatalysts for removing persistent organic pollutants from contaminated waters. *Materials Today Sustainability*, 100719.
 27. Rahman, M. S., Suvo, M. A. H., Islam, M. T., Yeachin, N., & Bhuiyan, M. A. (2024). Fast and efficient removal of metronidazole from aqueous solution using graphene oxide (G.O.) supported nitrogen (N) doped zinc oxide (ZnO) nanoparticles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 133660.
 28. Rani, M., Choudhary, S., Shukla, G., & Shanker, U. (2024). Highly efficient photo-adsorptive degradation of tetracycline and metronidazole antibiotics by green synthesized Ag doped CeO₂@SnO₂ nanocomposites. *Environmental Nanotechnology, Monitoring & Management*, 100935.
 29. Roslan, N. N., Lau, H. L. H., Suhaimi, N. A. A., Shahri, N. N. M., Verinda, S. B., Nur, M., . . . Usman, A. (2024). Recent Advances in Advanced Oxidation Processes for Degrading Pharmaceuticals in Wastewater—A Review. *Catalysts*, 14(3), 189.
 30. Saib, F., Laoui, F., Aoudjit, L., Touahra, F., Rekhila, G., Lerari, D., . . . Trari, M. (2024). Physical and photo-electrochemical characterization of Ca₂Fe₂O₅ for metronidazole antibiotic degradation under sunlight. *Optical Materials*, 148, 114806.
 31. Salmi, C., Souhaila, M., Salah Eddine, L., Mohammed, H. A. M., Hasan, G. G., & Mahboub, M. S. (2024). Biosynthesis of Mn₃O₄/PVP nanocomposite for enhanced photocatalytic degradation of organic dyes under sunlight irradiation. *Journal of Cluster Science*, 35(1), 201-215.
 32. Shabanian-Boroujeni, E., & Nezamzadeh-Ejchieh, A. (2024). The coupled WO₃-AgBr nanocatalyst, part I: Experimental design, kinetics, and mechanism studies of the boosted photocatalytic activity towards metronidazole in an aqueous solution. *Journal of Photochemistry and Photobiology A: Chemistry*, 446, 115148.
 33. Shee, N. K., & Kim, H.-J. (2024). Complementary metalloporphyrin-based nanostructure decorated with silver nanoparticles for photocatalytic degradation of organic dyes. *Inorganic Chemistry Communications*, 112252.
 34. Shuvo, M. S. H., Putul, R. A., Hossain, K. S., Masum, S. M., & Molla, M. A. I. (2024). Photocatalytic Removal of Metronidazole Antibiotics from Water Using Novel Ag-N-SnO₂ Nanohybrid Material. *Toxics*, 12(1), 36.
 35. Sruthi, L., Subhiksha, V., Alahmadi, T. A., Ansari, M. J., Janani, B., & Khan, S. S. (2024). In-situ topotactic transition of LaVO₄/Bi₁₂O₁₇Br₂ NCs by unveiling O defects and pn heterojunction formation for photodegradation of metronidazole: Reactions, pathway, and its by-product toxicity evaluation. *Journal of Alloys and Compounds*, 174019.
 36. Subhiksha, V., Okla, M. K., Sivaranjani, P., Abdel-Maksoud, M. A., Alatar, A. A., Al-Amri, S. S., . . . Khan, S. S. (2024). Interstitial decoration of Ag linking 3D Cu₂O octahedron and 2D CaWO₄ for augmented visible light active photocatalytic degradation of rifampicin and genotoxicity studies. *Journal of Environmental Management*, 354, 120451.
 37. Targhan, H., Rezaei, A., Aliabadi, A., Zheng, H., Cheng, H., & Aminabhavi, T. M. (2024). Adsorptive and photocatalytic degradation of imidacloprid pesticide from wastewater via the fabrication of ZIF-CdS/Tpy quantum dots. *Chemical Engineering Journal*, 482, 148983.
 38. Waghmare, A., Rathore, R., Pandey, A., & Chandra, V. (2024). Highly efficient photocatalytic degradation of methyl orange dye under solar light using Polyaniline@ Iron phosphate nanocomposite. *Materials Science and Engineering: B*, 302, 117253.
 39. Wang, C., Zhan, Z., Liu, H., Li, Y., Wu, J., Sun, P., & Shen, G. (2024). Single-atom iron cocatalyst for highly enhancing TiO₂ photocatalytic degradation of antibiotics and antibiotic-resistant genes. *Chemical Engineering Journal*, 482, 148906.

40. Wang, Z.-Y., Xu, L., Liu, C.-H., Han, S.-J., Fu, M.-L., & Yuan, B. (2024). MXene/CdS photothermal-photocatalytic hydrogel for efficient solar water evaporation and synergistic degradation of VOC. *Journal of Materials Chemistry A*.
41. Yaacob, N. A., Khasri, A., Mohd Salleh, N. H., & Mohd Jamir, M. R. (2024). Optimization of A.C./TiO₂-Cu ternary composite preparation with enhanced U.V. light activity for adsorption–photodegradation of metronidazole via RSM-CCD. *Journal of Dispersion Science and Technology*, 45(2), 249-260.
42. Yang, W., Bu, Q., Zhao, R., Huang, H., Xu, W., Jia, N., . . . Yu, G. (2024). Green batch prepared a novel C/P co-doping urchin-like TiO₂ for enhanced photocatalytic degradation and mineralization of trimethoprim: *emerging Contaminants*, 100329.