IOP Conference Series:
Earth and
Environmental Science

PAPER • **OPEN ACCESS**

Photocatalytic treatment of metronidazole-containing wastewater

To cite this article: Perizat Abdirova *et al* 2022 *IOP Conf. Ser.: Earth Environ. Sci.* **1123** 012078

Photocatalytic treatment of metronidazole-containing wastewater

Perizat Abdirova[1], Yerkanat N. Kanafin[2,*], and Stavros G. Poulopoulos[2]

[1]Chemistry Department, School of Sciences and Humanities, Environmental Science and Technology Group (ESTg), The Environment and Resource Efficiency Cluster (EREC), Nazarbayev University, 010000, Nur-Sultan, Kazakhstan
[2]Chemical and Materials Engineering Department, School of Engineering and Digital Sciences, Environmental Science and Technology Group (ESTg), The Environment and Resource Efficiency Cluster (EREC), Nazarbayev University, 010000, Nur-Sultan, Kazakhstan
*Corresponding author, Email: yerkanat.kanafin@nu.edu.kz

Abstract. The presence of antibiotics in wastewater is risky for the environment as the conventional wastewater treatment plants are not always capable of removing them completely. Therefore, antibiotics may enter the water bodies and affect the health of aquatic living organisms. In this work, the effluent after the continuous flow activated sludge process was collected and analyzed. The average total organic carbon (TOC) and metronidazole (MNZ) concentrations were 43 ± 13.1 mg/L and 5.3 ± 0.2 mg/L, respectively. The catalytic activities of TiO, TiO_2, Bi_2O_3, and WO_3 were tested under the visible light (VIS, 500 nm) and near-visible ultraviolet light (UV, 365 nm) irradiations. The structure and properties of the catalysts have been verified using SEM-EDX and Mastersizer 3000. 25% of MNZ have been degraded under VIS only after 150 min. Even though all four catalysts were able to degrade MNZ to some extent (28-33%) after 150 min of VIS irradiation, they were not able to mineralize the organic compounds of the wastewater. On the other hand, the application of UV alone and with the catalysts resulted in the complete degradation of MNZ. Moreover, UV/TiO_2 achieved 52% TOC removal after 150 min of the experiment.

1. Introduction

Rapid population growth and climate change are leading to the depletion of water resources worldwide [1]. Currently, the global wastewater generation is estimated to be at 359.4×10^9 m^3 per year [2]. One of the ways of tackling water scarcity is an implementation of adequate wastewater treatment practice and re-use of the treated wastewater for agricultural and industrial purposes. Nowadays, 52% of the generated wastewater is treated and 40.7×10^9 m^3 of wastewater is reused annually [2]. The release of untreated wastewater is dangerous for the health of society and aquatic organisms. It may lead to water-borne diseases as the untreated wastewater contains viruses, bacteria, protozoa, fungi, and other microorganisms [3]. To increase the amount of treated wastewater, more wastewater treatment plants (WWTP) need to be constructed, especially in low-income countries with a high population. Moreover, the presence of emerging pollutants (EPs) in wastewater raises huge environmental concerns. EPs are comprised of pharmaceuticals, pesticides, endocrine disrupting chemicals, and other recalcitrant organic compounds [4]. Due to the stable structure of these compounds, some of them escape WWTPs based on the activated sludge process and are released into the aquatic environment [5]. MNZ is a commonly

used water-soluble antibiotic with a stable imidazole ring [5]. According to the previous reports, the activated sludge process is not highly efficient in terms of MNZ removal [5–8]. Therefore, the search for an adequate post-treatment technique for the removal of EPs is important. Advanced oxidation processes (AOPs) could provide interesting solutions to this problem. AOPs are a large class of oxidative techniques that mainly rely on the production of hydroxyl (•OH) and sulfate radicals ($SO_4^{\bullet-}$) [9,10]. Among different AOPs, heterogeneous photocatalysis receives great attention from researchers due to the convenient separation and possible reuse of the photocatalyst [10,11]. Photocatalysts can be activated by light, which results in oxidation of the electron hole in the valence band and reduction of the electron in the conduction band. The generation of •OH radicals using photocatalysts (*Cat*) is shown in equations 1 and 2 [12]:

$$Cat + hv \rightarrow e_{cb}^- + h_{vb}^+ \quad (1)$$

$$h_{vb}^+ + H_2O \rightarrow {}^{\bullet}OH + H^+ \quad (2)$$

In this work, TiO, TiO_2, Bi_2O_3, and WO_3 were used for the photocatalytic treatment of MNZ-containing wastewater under visible (VIS) and ultraviolet (UV) light. The efficiencies of the photocatalysts were compared in terms of TOC and MNZ removal.

2. Materials and Methods

2.1. Wastewater characteristics

The effluent containing MNZ was collected after a laboratory scale continuous flow activated sludge process. The biological treatment results were previously reported [5]. Before the experiments, the effluent was kept in the refrigerator at 4°C. The characteristics of the effluent are shown in Table 1.

Table 1. Characteristics of the effluent

Parameter	Unit	Value
Total carbon (TC)	mg/L	69.5 ± 13.8
Total inorganic carbon (TIC)	mg/L	26.5 ± 3.4
Total organic carbon (TOC)	mg/L	43 ± 13.1
MNZ	mg/L	5.3 ± 0.2
pH		7.8 ± 0.1

2.2. Chemicals

Titanium (IV) oxide, anatase (< 25 nm), titanium (II) oxide (325 mesh), bismuth (III) oxide (90-210 nm), and tungsten (VI) oxide (< 100 nm) were used as catalysts and were purchased from Sigma-Aldrich. All chemicals had an affinity of more than 99%.

2.3. Batch experiments and analysis

Experiments under UV light were conducted using a batch photochemical reactor with a 500 W lamp (365 nm) and visible light experiments were conducted using a 150 W lamp (500 nm). Reactors were equipped with constant agitation, heating, and cooling system. The volume of the solution was 400 mL. Aliquots were taken every 30 minutes and filtered through cellulose membrane filters (0.45 μm). Analytik Jena Multi N/C 3100 equipment was used to determine carbon content. MNZ was detected using high-performance liquid chromatography. The method has been extensively described in the previous work [5].

3. Results and Discussion

3.1. Characterization of the catalysts

The characterization of the catalysts was conducted using Zeiss Crossbeam 540 scanning electron microscope (SEM) and Mastersizer 3000. SEM images of the catalysts were presented in Figure 1.

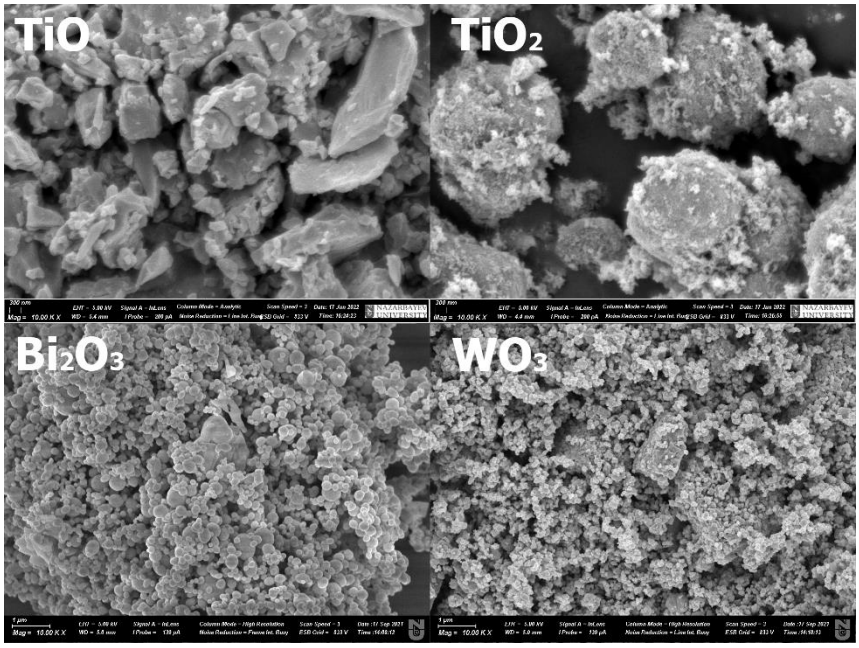

Figure 1. SEM images of the photocatalysts used in this work (magnification: 10,000)

Figure 1 confirms that the particles of all four catalysts are at the nanoscale. However, TiO and TiO_2 particles appeared to form agglomerates. The particle size distributions of the catalysts were measured using Mastersizer 3000 (Figure 2).

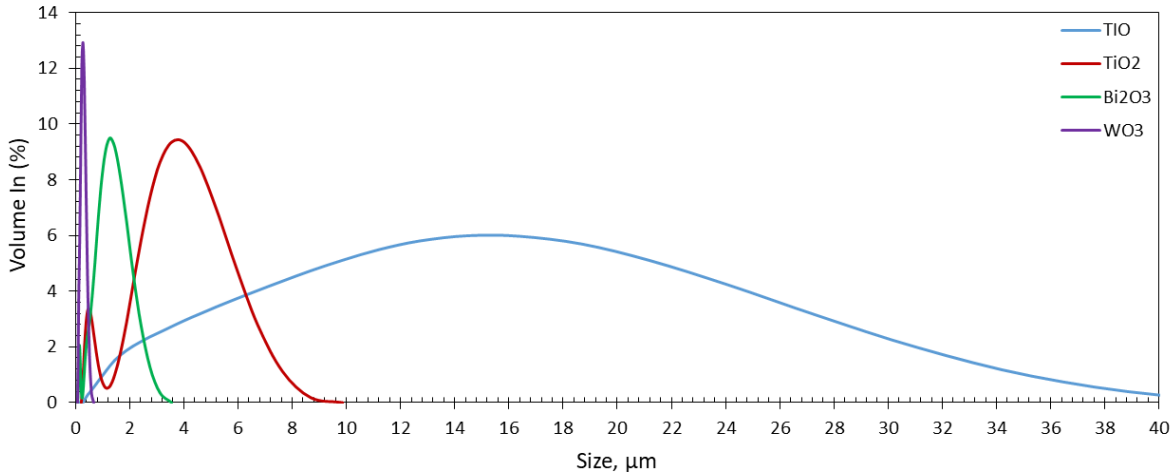

Figure 2. Particle size distribution of the catalysts

The median particle size for TiO, TiO_2, Bi_2O_3, and WO_3 were 9.77, 3.21, 1.15, and 0.269 µm, respectively. The specific surface area for TiO, TiO_2, Bi_2O_3, and WO_3 was 1344, 4178, 9026, and 25090 m^2/kg, respectively.

3.2. Photocatalytic treatment of the effluent

The results of the photocatalytic treatment of the effluent with MNZ are shown in Figures 3 and 4. Unfortunately, the use of visible light alone and with the catalysts did not lead to the mineralization of the organic matter. On the other hand, visible light achieved 25% degradation of MNZ after 150 min. The addition of the catalysts (0.5 g/L) did not lead to a significant increase in MNZ photodegradation.

For example, Vis/Bi_2O_3 and Vis/TiO_2 both had 28% MNZ degradation, while the use of Vis/TiO and Vis/WO_3 processes resulted in 32% and 33% MNZ degradation, respectively.

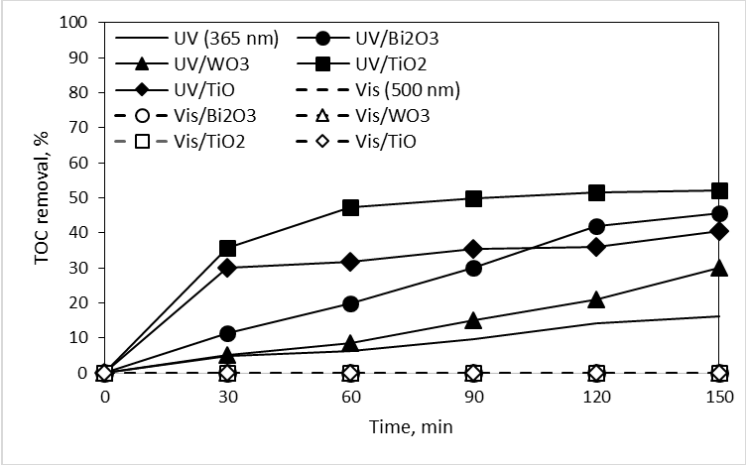

Figure 3. TOC removal during photocatalytic treatment of municipal wastewater (concentration of the catalysts: 0.5 g/L)

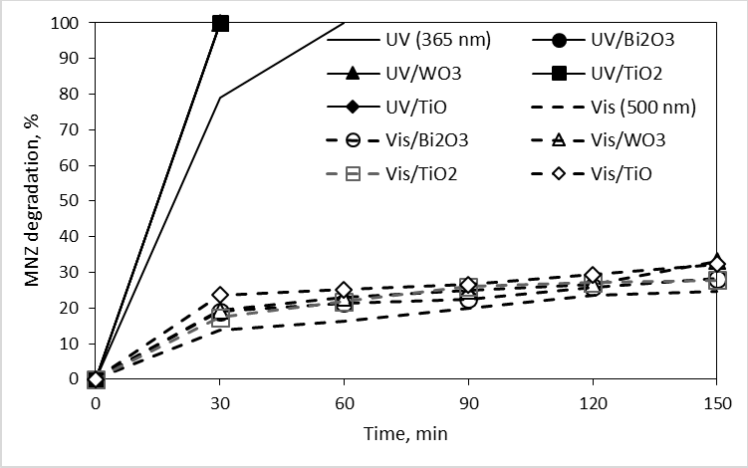

Figure 4. MNZ degradation during photocatalytic treatment of municipal wastewater

UV light was more efficient in mineralization than visible light. 16% removal of TOC was achieved after 150 min of UV irradiation alone. Moreover, the combination of the catalysts with UV light significantly improved the TOC removal efficiency. The highest TOC removal (52%) was achieved using UV/TiO_2, followed by UV/Bi_2O_3 (46 %) and UV/TiO (40 %). UV/WO_3 demonstrated 30 % TOC removal. As it is shown in Figure 4, the application of UV light alone resulted in 79% degradation of MNZ after 30 min, while the combination of the UV with the catalysts resulted in complete degradation of MNZ after 30 min. The efficiency of UV for MNZ degradation was previously described [13,14]. For example, Shemer et al. achieved 12 % degradation of MNZ after 5 min of $UV^{254\ nm}$ light irradiation. In another work, Kanafin et al. reported 31 % MNZ degradation using $UV^{254\ nm}$ light after 30 min. The pH evolution during the photocatalytic experiments is presented in Figure 5.

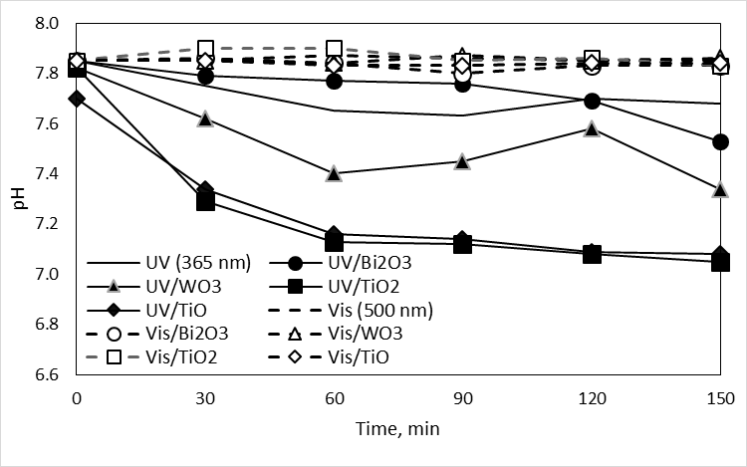

Figure 5. pH evolution during photocatalytic treatment of MNZ-containing effluent

The experiments under visible light did not decrease the pH of the solution. On the other hand, the decrease in pH could be observed for all experiments under UV. For example, the pH of the solution dropped from 7.8 to 7.1 when TiO and TiO_2 were used as a catalyst. The decrease in pH could be explained by the formation of intermediate compounds such as organic and inorganic acids [15].

4. Conclusions

The treatment of the MNZ-containing effluent was studied by visible and UV light photocatalysis. The efficiencies of the processes were evaluated in terms of TOC removal and MNZ degradation. The concentration of the catalysts was 0.5 g/L and the experiments lasted for 150 min. The main results of this work are the following:

(a) No mineralization was achieved when the visible light was used alone and in combination with the catalysts. MNZ photodegradation values after 150 min were 25% and 33% for visible light and Vis/WO_3, respectively.
(b) The use of UV/TiO_2 resulted in the highest TOC removal (52%).
(c) MNZ was fully degraded under UV light after 60 min, while the combination of the UV with the catalysts accelerated the process.

Acknowledgments

This work was supported by the Nazarbayev University project “Cost-Effective Photocatalysts for the Treatment of Wastewaters containing Emerging Pollutants”, Faculty development competitive research grants program for 2020-2022, Grant Number 240919FD3932.

References

[1] Schleich J and Hillenbrand T 2009 *Ecol. Econ.* **68** 1756–1769 (https://doi.org/10.1016/j.ecolecon.2008.11.012)
[2] Jones E R, Van Vliet M T H, Qadir M and Bierkens M F P 2021 *Earth Syst. Sci. Data* **13** 237–(254 https://doi.org/10.5194/essd-13-237-2021)
[3] Peter-Varbanets M, Zurbrügg C, Swartz C and Pronk W 2009 *Water Res.* **43** 245–265 (https://doi.org/10.1016/j.watres.2008.10.030)
[4] Mergenbayeva S, Atabaev T S and Poulopoulos S G 2021 *Catalysts* **11(11)** 1379 (https://doi.org/10.3390/catal11111379)
[5] Kanafin Y N, Kakimov Y, Adamov A, Makhatova A, Yeshmuratov A, Poulopoulos S G, Inglezakis V J and Arkhangelsky E 2021 *J. Chem. Technol. Biotechnol.* **96** 1370–1380 (https://doi.org/10.1002/jctb.6658)
[6] Verlicchi P, Galletti A, Petrovic M, Barceló D, Al Aukidy M and Zambello E 2013 *Sci. Total*

Environ. **454**–**455** 411–425 (https://doi.org/10.1016/j.scitotenv.2013.03.044)
[7] Aboudalle A, Djelal H, Fourcade F, Domergue L, Assadi A A, Lendormi T, Taha S and Amrane A 2018 *J. Hazard. Mater.* **359** 85–95 (https://doi.org/10.1016/j.jhazmat.2018.07.006)
[8] Saidi I, Soutrel I, Floner D, Fourcade F, Bellakhal N, Amrane A and Geneste F 2014 *J. Hazard. Mater.* **278** 172–9 (https://doi.org/10.1016/j.jhazmat.2014.06.003)
[9] Izadifard M, Achari G and Langford C H 2017 *Water Res.* **125** 325–331 (https://doi.org/10.1016/j.watres.2017.07.042)
[10] Mergenbayeva S and Poulopoulos S G 2022 *Processes* **10(1)** 8 (https://doi.org/10.3390/pr10010008)
[11] Nasseh N, Taghavi L, Barikbin B, Nasseri M A and Allahresani A 2019 *Compos. Part B Eng.* **166** 328–40 (https://doi.org/10.1016/j.compositesb.2018.11.112)
[12] Divyapriya G, Nambi I M and Senthilnathan J 2016 *J. Bionanoscience* **10** 356–368 (https://doi.org/10.1166/jbns.2016.1387)
[13] Shemer H, Kunukcu Y K and Linden K G 2006 *Chemosphere* **63** 269–276 (https://doi.org/10.1016/j.chemosphere.2005.07.029)
[14] Kanafin Y N, Satayeva A, Arkhangelsky E and Poulopoulos S G 2021 *Chem. Eng. Trans.* **86** 595–600 (https://doi.org/10.3303/CET2186100)
[15] Schneider J, Matsuoka M, Takeuchi M, Zhang J, Horiuchi Y, Anpo M and Bahnemann D W 2014 *Chem. Rev.* **114** 9919–9986 (https://doi.org/10.1021/cr5001892)