Photocatalytic degradation of antifungal agents fluconazole and voriconazole by TiO_2 particles: Effect of operational parameters and transformation products

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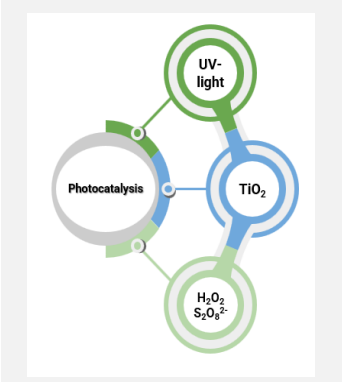
D.A. Lambropoulou[1,2]*., P. Parthenidis*[1]*, A. Faka, E.N. Evgenidou*[1,2]
(1) Department of Chemistry, Aristotle University of Thessaloniki, GR- 541 24 Thessaloniki, Greece,
2) Centre for Interdisciplinary Research and Innovation Balkan Center, GR 57001, Thessaloniki, Greece



The aim of this research study was to investigate the photocatalytic degradation of two antifungal agents, fluconazole and voriconazole, by TiO_2 photocatalyst. In this context, effects of operational parameters, like the catalyst's concentration and the utilization of oxidants, were examined. The results clearly demonstrated that high removal efficiencies can be achieved within a short span of time. The investigation revealed that photocatalytic performance was enhanced by increasing the catalyst's concentration due to the increase in the active sites. Additionally, the obtained findings showed that the utilization of oxidants, namely hydrogen peroxide and persulfate ions, can have a positive impact on the photodegradation as a consequence of the synergistic effects between the catalyst and the promoter. The TPs generated via hydroxylation, dehalogenation and dealkylation were identified employing LC-HRMS.

Introduction

Antifungal agents hold a pivotal position in environmental research area, as is evident from the existing literature [1]. This scientific interest can perhaps be attributed to the detection of these compounds in aqueous matrices and to their well-documented impact for human health and living organisms. Although there are many pathways through which antifungals can reach the environment, the ongoing research efforts have shown that wastewater treatment plants are the main reason behind their pervasiveness. Given their negative effects, efficient water treatment processes must be developed and applied. In this regard, heterogeneous photocatalysis has proven to be a particularly useful tool in the field of environmental remediation. Photocatalysis can be described as photo-assisted reactions that take place on the surface of semiconductor materials. Perhaps the most popular semiconductor is titanium dioxide (TiO_2) because of its exceptional advantages like the high photocatalytic performance, the stability and non-toxicity [2]. The aim of this study was to investigate the photocatalytic activity of TiO_2 for the degradation of two well-known antifungals, fluconazole and voriconazole.

Material and Methods

- All the photocatalytic tests were performed in a magnetically stirred batch reactor, which was covered with aluminum foil so as to enhance the effect of UV irradiation. The light source was a mercury lamp (125 W)
- In order to evaluate the performance of the processes, an Ultimate 3000 ultra-high-performance liquid chromatography system (UHPLC) and a UV–Visible diode array detector (DAD) were used.The detection of fluconazole and voriconazole occurred at 210 and 257 nm
- With the aim of investigating the reaction pathways, an Ultimate 3000 ultra-high-performance liquid chromatography system (UHPLC) and a Q Exactive™ Focus Orbitrap (Thermo Fisher Scientific) were utilized

Results and Discussion

The amount of the photocatalyst is one of the most important parameters that can affect the photocatalytic oxidation rate of the organic compounds. In order to examine its impact on the photodegradation rate of the selected antifungal agents, a series of experiments were conducted, employing different concentrations of titanium dioxide (50-300 mg/L). The initial concentration of both compounds was set at 5 ppm. As expected, degradation of the antimycotics increased with increasing TiO_2 concentration in the range of 50-200 mg/L (**Fig 1A** and **B**). These results could be attributed to the greater surface area and to the active sites available for the oxidation. However, the photocatalytic efficiency of the process was greatly reduced when using higher concentration (300 mg/L). The phenomenon is quite common in TiO_2 applications and can be the result of many causes such as the shielding effects that prevent the illumination of the photocatalyst and the high aggregation tendencies [3].

Apart from the amount of the catalyst, the impact of the utilization of oxidants, like hydrogen peroxide and persulfate ions, was also evaluated. According to the scientific literature, the synergy between titanium dioxide and these oxidants can lead to a positive

effect on the photo-degradation of the target pollutants, as it can cause an enhanced formation of ROS [4]. With the aim of investigating this research topic, experiments were performed using different concentrations of the two oxidants (50-300 mg/L) and keeping the other parameters constant ([TiO_2] = 100 mg/L). **Fig. 2A** and **B** demonstrate the photocatalytic degradation of fluconazole and voriconazole at different concentrations of the oxidants. As it is apparent in these figures, the photodegradation rates affirmed the theoretical expectations, since higher removal rates were accomplished compared to that of UV/TiO_2 applications.

The arising transformation products (TPs) were identified with LC-HRMS analysis. The results revealed that the photocatalytic degradation of the target compounds proceeded through three main transformation routes such as like hydroxylation, cleavage and dehalogenation.

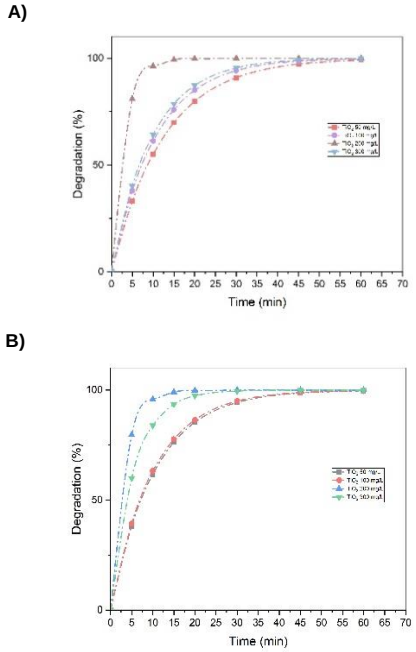


Fig. 1: Photocatalytic degradation of fluconazole (A) and voriconazole (B) by UV/TiO_2 process. Experimental conditions: [Flu] = 5 mg/L. [Vor] = 5 mg/L, matrix = pure water, treatment time = 60 min

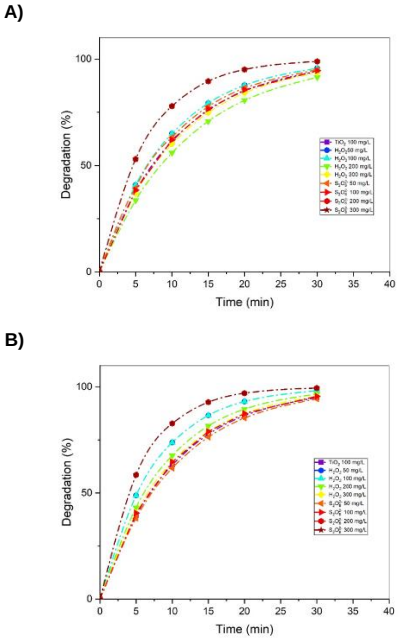


Fig. 2: Photocatalytic degradation of fluconazole (A) and voriconazole (B) by UV/TiO_2/H_2O_2 and UV/TiO_2/$S_2O_8^{2-}$ processes. Experimental conditions: [Flu] = 5 mg/L. [Vor] = 5 mg/L, [TiO_2] = 100 mg/L, matrix = pure water, treatment time = 60 min

Conclusions

This research study examined the photocatalytic degradation of two well-known antifungal pharmaceuticals, fluconazole and voriconazole, by TiO_2-based advanced oxidation processes. The article showed that all the UV/TiO_2 applications demonstrated exceptional efficiencies in reducing the concentration of the two compounds. However, the findings also evinced that an increased dosage of the catalyst and/or oxidants can lead to decreased yields as consequence of shielding effects and scavenging phenomena. Finally, the encouraging findings were reinforced by the identification of the degradation products, which were generated from various reactions like hydroxylation, cleavage and dehalogenation

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