

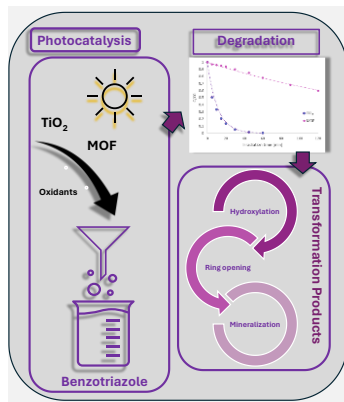
Heterogenous Photocatalytic Degradation of Benzotriazole using TiO₂-based and MOF-based photocatalytic processes.

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In this study the photocatalytic degradation of benzotriazole, an emerging pollutant widely detected in the aquatic environmental matrices, has been explored using two commercial catalysts TiO₂ and a Fe-based MOF (metal organic framework). Degradation of the target compound in the presence only of the suspended catalyst revealed the excellent performance of TiO₂ while the MOF catalyst exhibited poor efficiency. Oxidant-assisted photocatalytic processes with H₂O₂ and persulfate were also evaluated exhibiting even higher degradation efficiencies, especially for the MOF catalyst due to ability of the oxidants to prevent recombination of the produced electron-hole pairs. Several affecting factors were also investigated such as the concentration of the catalyst or the concentration of the oxidant. The arising transformation products of benzotriazole were identified with LC-HRMS analysis while TOC measurements showed that complete mineralization requires more prolonged irradiation times in order to be achieved.

Introduction

Benzotriazole is a widely used chemical which has been regarded as a typical emerging contaminant and is broadly utilized to protect products from yellowing and photochemical degradation. Benzotriazole is also used as an anticorrosive additive and as a flame retardant. Its high water solubility and high polarity endorse its occurrence in the aquatic environment becoming a ubiquitous contaminant with serious adverse effects in aquatic organisms. Furthermore, owing to its persistence, bioaccumulation and toxic properties, only partial amounts of benzotriazole can be removed by conventional wastewater treatment processes [1]. Consequently, alternative degradation processes are compelled to be applied. Advanced oxidation processes are an attractive way-out for the elimination of recalcitrant organic pollutants. Heterogenous photocatalysis is one of the most applied AOP based on the photo-activation of semiconductor catalysts. Among the various semiconductors used, TiO₂ occupies a prominent position due to its high efficiency, low cost and non-toxicity [2]. However, other photocatalysts like the light responsive metal organic frameworks (MOFs) have also proved effective in photocatalytic removal of pollutants and they are endowed with extremely tunable photocatalysts for efficient utilization of solar light [3].

Under this light, the main scope of this study was to apply heterogenous photocatalysis for the degradation of benzotriazole using and comparing two commercial catalysts TiO₂ and a Fe-based MOF. The objectives were i) to examine the efficiency of both catalysts and evaluate the obtained degradation kinetics ii) to examine the effect of the concentration of the catalyst, iii) to examine the effect of the addition of two oxidants (hydrogen peroxide (HP) and persulfate (PS)), iv) to investigate the effect

of the concentration of the oxidants and v) to identify the arising transformation products.

Material and Methods

Benzotriazole (>99%) was supplied by Sigma Aldrich (Germany). TiO₂ P25 was supplied by Evonik while Basolite® F300 (Fe-BTC, Iron 1,3,5-benzenetricarboxylate; produced by BASF) was purchased from Sigma Aldrich/ Merck (Germany). Sodium persulfate (Na₂S₂O₈, 99+%) was supplied from Chem-LabNV (Zedelgem, Belgium). Hydrogen peroxide (H₂O₂, 30% w/v) was purchased from Panreac (Barcelona, Spain). All photocatalytic experiments were conducted in a pyrex UV-reactor equipped with a high-pressure mercury lamp and a water-cooled pyrex filter restricting the transmission of irradiation with wavelengths below 290nm. Working solutions of benzotriazole (5ppm) in ultra-pure water were prepared daily and were put in the reactor with the appropriate amount of catalyst and oxidant. Aliquots were withdrawn from the reactor at specific time intervals and proceeded to analysis. The determination of the concentration of the remaining benzotriazole in the treated solution along with the identification of the arising transformation products was conducted employing liquid chromatography coupled with an orbitrap high resolution mass spectrometer (LC-HRMS).

Results and Discussion

Preliminary photocatalytic experiments, without the addition of a catalyst showed that the target compound is not degraded without the addition of a catalyst while dark experiments in the presence of the catalysts revealed negligible adsorption of benzotriazole on the catalysts' surface. However, photocatalytic treatment leads to complete degradation of the target compound within 60 min of irradiation in the presence of TiO₂. On the other

hand, MOF catalyst demonstrates low efficiency achieving only 40% reduction of benzotriazole within 120 min (Figure 1).

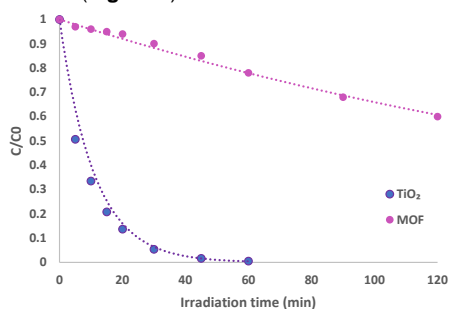


Figure 1. Photocatalytic degradation of benzotriazole in the presence of TiO₂ or MOF catalyst.

Using larger amounts of catalyst lead to an increase of the reaction rate for both photocatalytic systems, however the enhancement of the degradation was less intense in the MOF photocatalytic system.

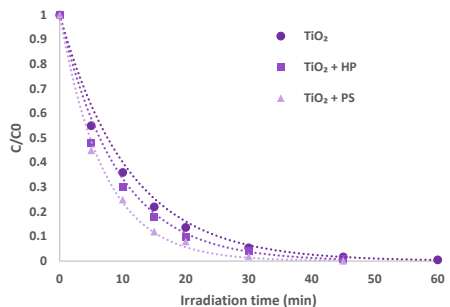


Figure 2. Effect of the addition of oxidants on the photocatalytic degradation of benzotriazole in the presence of TiO₂.

Conclusions

In this study the photocatalytic degradation of benzotriazole, using two commercial catalysts TiO₂ and a Fe-based MOF have been explored. Complete degradation of the target compound in the presence only of the suspended TiO₂ proceeded within 60 min while the MOF catalyst showed poorer efficiency achieving less than 50 % reduction within 2h of treatment. Addition of oxidants such as H₂O₂ and persulfate were exhibited higher degradation efficiencies, especially for the MOF catalyst due to ability of the oxidants to prevent recombination of the produced electron-hole pairs. The concentration of the catalyst or the concentration of the oxidant appear to affect also the degradation process. The arising transformation products of benzotriazole identified with LC-HRMS analysis showed that degradation of the target compound proceeds through hydroxylation and ring opening as main transformation routes while complete mineralization requires more prolonged irradiation times in order to be achieved.

References

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- [2] E. Evgenidou, K.Vasilopoulou, L-A. Koronaiou et al. Molecules, 28 (2023) 1866.
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In order to examine the effect of the addition of oxidant two different oxidants were tested H₂O₂ (HP) and persulfate (PS) in both photocatalytic systems. As it can be observed in Figure 2 and Figure 3 both HP and PS can enhance the photocatalytic process especially in the presence of MOF were the reaction rate constant showed an almost 10-fold increase due to the prevention of the recombination of the generated electron-hole pairs and the additional production of sulfate and hydroxyl radicals.

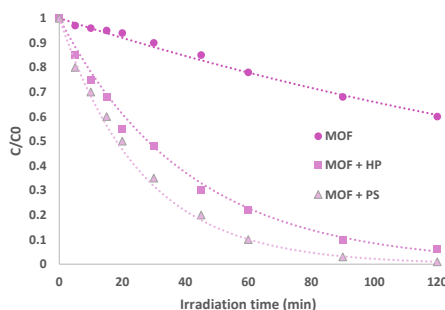


Figure 3. Effect of the addition of oxidants on the photocatalytic degradation of benzotriazole in the presence of MOF.

TOC measurements showed that complete mineralization requires more prolonged irradiation time in order to be achieved while TiO₂ appears to be more effective in the mineralization of benzotriazole while the addition of oxidants had small effect in the overall procedure. Finally, identification of the arising TPs revealed that degradation of benzotriazole through photocatalysis proceeds via i) hydroxylation and ii) ring opening while the benzene ring appears to be the main site of reaction.