Successful use of UV light driven photocatalytic oxidation for the removal of an emergent water contaminant

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Abstract
The degradation of a new anti-epileptic drug, named levetiracetam in aqueous solution has been investigated by heterogeneous photocatalysis, under UV light irradiation. For the photocatalytic assays, the photocatalytic activity of two different commercial catalysts (TiO_2 Aeroxide® P25 and TiO_2 Kronos uvlp 7500) was compared. The influence of some operating conditions (catalyst dosage, UV light irradiation, initial pollutant concentration, pH and water matrix was studied) and the main kinetic parameters were determined. For optimal degradation conditions an elimination yield of 99% was achieved. Kinetic studies have shown that the degradation of target molecule can be described by the Langmuir-Hinshelwood model. Toxicity tests were also carried out to evaluate the potential of detoxification of the considered oxidation process.
Keywords: photocatalytic degradation, antiepileptic drug, toxicity

1. Introduction

An emerging environmental problem, nowadays, is represented by water contamination with pharmaceutical compounds, because of their potential risk for aquatic organisms. Several studies have found that such molecules are not efficiently removed during the wastewater treatment or not bio-degraded in the environment. Other works reported that their elimination level depends on their physicochemical properties and on the nature of the considered treatment process (Belgiorno, 2007). Thus, many pharmaceutical compounds have been detected in surface waters in concentrations levels ranging from ng/L to μg/L. Thus, the need in finding alternative technologies for their elimination in water is increasing. In this context, heterogeneous photocatalysis is to date considered as a sustainable solution regarding water purification (Favier et al., 2016). This involves the generation of hydroxyl radicals by semiconductor irradiation which promotes the degradation of pollutants in water, mineralizing them into harmless compounds such as H_2O and CO_2 (Deletze et al., 2015). One of the most widely used photocatalyst is TiO_2, because chemical stablility, low cost and its high photocatalytic activity.

There are few published studies on the photocatalytic elimination of antiepileptic drugs but none of this investigated the levetiracetam (LEV). This molecule is a new antiepileptic drug licensed for the treatment of partial seizure in adults.

In this framework, the present study investigates the photocatalytic degradation efficiency of LEV in aqueous solutions in the presence of commercial TiO_2 as catalyst. It provides information about the influence of some key process parameters including catalyst type and its loading, initial pollutant concentration, light intensity and solution pH on the elimination of the target molecule and dissolved organic carbon reduction. The oxidation of the selected drug was also studied in two water systems in order to evaluate the treatment efficiency under more realistic conditions. Moreover, the toxicity of LEV prior and after the photocatalytic treatment was assessed in order to estimate the potential of detoxification of the considered advanced oxidation process.

2. Materials and Methods

Levetiracetam (≥98%), TiO_2 Aeroxide® P25 (P25) and TiO_2 Kronos uvlp 7500 (K7500) were purchased from Sigma Aldrich Co. and used without further purification. Photocatalytic experiments were performed at room temperature in a batch reactor, mechanically stirred, and with external irradiation provided by two Philips PL-S 9W/10/2P lamps (UVA emitting, 365 nm). The working solutions were obtained by dissolving a well-known amount of LEV in ultrapure water. The aqueous solution, containing the catalyst, was firstly stirred in the dark for 30 min. in order to obtain adsorption-desorption equilibrium of the substrate on catalyst surface. The tests were carried out for 140 min and samples were taken at specific times, filtered to separate the catalyst and measured. LEV residual concentration was determined by HPLC and the extent of mineralization was determined using a Shimadzu TOC-5050 analyzer. In addition some tests were designed in tap water and well water in order to investigate the effect of water matrix on the pollutant removal efficiency.

3. Result and discussion

The results obtained in this work showed that the TiO_2 Aeroxide® P25 is more active for the removal of LEV than the other considered commercial catalyst which can be due to P25's slow electron/hole recombination rate. It was clearly observed that the photocatalytic efficiency increases with increasing the catalyst load and the optimal amount of catalyst was found 1g/L. The tests run in the absence of the catalyst and in the absence of light showed that the removal of LEV is principally due to the photo activity of the catalyst. Further, it was observed that higher light intensity improves the photocatalytic process. Indeed, the degradation yield reached 80% after 140 min. of reaction for the maximal irradiation flux while only 31.8% were observed when the light intensity was minimum.

The initial concentration of LEV had also a major impact on photocatalytic degradation efficiency. Thus, at an initial pollutant concentration of 29 µM the pollutant was completely removed from the aqueous solution, after an irradiation time of 140 min (Figure 1).

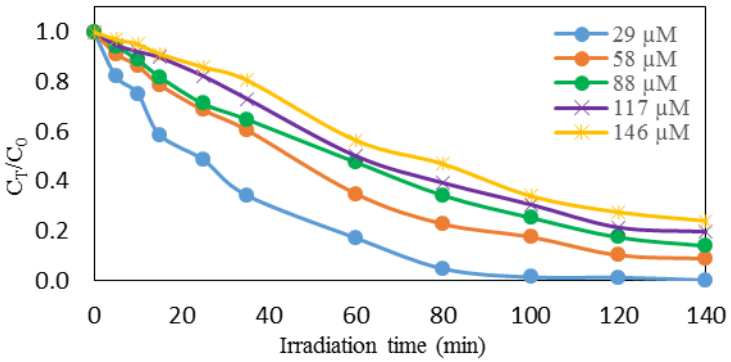

Figure 1. Influence of the initial pollutant concentration on its elimination

Furthermore, it was observed that the degradation of LEV follows the Langmuir-Hinshelwood kinetic model. In addition, it was also found that the extent of degradation decreases (about 12%) in real water samples because of the presence of the natural organic matter which can compete with the pollutant.

Toxicity assays performed in this work indicated that effluent toxicity is higher than the one of treated solution.

4. Conclusion

New data and insights related to the elimination of the antiepileptic drug, levetiracetam are reported in this work. The results obtained in this study clearly showed that this emergent water pollutant can be successfully eliminated by the TiO_2/UV photocatalysis with an elimination yield of 99%. It was also found that the treatment efficiency depends on the operating conditions. The reaction intermediates generated during the process seems to be less toxic than the parent compound. Moreover, studies on the determination of reactions intermediates are currently in progress to confirm the results obtained during the toxicity studies and to propose a degradation mechanism of this molecule.

References

Belgiorno V., Rizzo L., Fatta D., Della Rocca C., Lofrano G., Nikolaou A. and Meric, S. (2007). Review on endocrine disrupting-emerging compounds in urban wastewater: occurrence and removal by photocatalysis and ultrasonic irradiation for wastewater reuse. *Desalination*, **215**, 166-176.

Deletze E., Antoniadis A., Kitsiou V., Kostopoulou E., Lutic D., Cretescu I. and Poulios, I. (2016), Photocatalytic treatment of colored wastewater from medical laboratories: photodegradation of Nuclear Fast Red, *Desalination and Water Treatment*, **57**, 18897-18905.

Favier L., Harja M., Simion A.I., Rusu L., Kadmi Y., Pacala M.L., Bouzaza A., (2016), Advanced Oxidation Process for the Removal of Chlorinated Phenols in Aqueous Suspensions, *Journal of Environmental Protection and Ecology*, **17**, 1132-1141.

Gurke R., Roessler M., Marx C., Diamond S., Schubert S., Oertel R. and Fauler J. (2015). Occurrence and removal of frequently prescribed pharmaceuticals and corresponding metabolites in wastewater of a sewage treatment plant. *Science of the Total Environment*, **532**, 762-770.