New evidence of accelerated elimination of an emergent water pollutant by TiO₂ assisted photo-oxidation

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Abstract
This study focuses on the photocatalytic degradation of a pharmaceutical compound essentially employed for the treatment of hypertension using TiO₂ as catalyst and UV-A irradiation. An efficient elimination yield of 99% was obtained after 10 minutes of irradiation at initial pollutant concentration of 5 mg/L and 1.2 g/L of catalyst. A higher mineralization yield of 87% was reached in 2h of reaction. Results showed that under all studied process conditions the target molecule was degraded according to a pseudo first order kinetics. Obtained data clearly demonstrate the potential application of the investigated process for the remediation of polluted water.

Keywords: emergent water pollutant, photocatalysis, water treatment, removal, mineralization

1. Introduction
Sartans, are group of antihypertensives pharmaceuticals frequently detected in the aquatic system due to the rapidly growth of pharmaceutical industry and their increased consumption world wide (Pereira et al., 2016). To date, they are considered as emerging pollutants because they are not regulated yet. Next to that, some of the pharmaceuticals are not completely eliminated by the conventional wastewater treatment plants (WWTPs) and are continuously released into the receiving waters affecting the development of aquatic and wildlife. Thus, to prevent the environmental pollution, complementary efficient technologies are required prior to their discharge into the aquatic system. Several studies showed that advanced oxidation processes (AOPs), and more especially heterogeneous photocatalysis were successfully applied for the removal of organic pollutants from water. Other works pointed out the interest of TiO₂ photocatalysis. Indeed, it is considered as an attractive option for the elimination of such kind of molecules due to its ability to mineralize organic compounds, to operate without pH adjustment, in mild conditions of pressure and temperature, and its saving treatment costs (Rizzo et al., 2009). In this context, this study deals with the photodegradation of a drug of the sartans family by using a commercial titanium dioxide as catalyst. The target molecule considered in this work is the antihypertensive losartan (LS) which was recently detected in many WWTPs around the world. The effect of different key operating parameters such as catalyst load, initial pollutant concentration, light intensity and solution pH were systematically investigated in order to enhance the elimination efficiency. To the best of our knowledge, this is the first study reporting on the photocatalytic elimination of this molecule. In addition, the contribution of reactive oxygen species was studied to have a better understanding of mechanism involved in the photodegradation of this emergent organic pollutant. The degradation kinetics were also evaluated in different water matrices to evaluate the practical application of the considered process.

2. Materials and Methods
Losartan potassium (99% of purity) was provided by Sigma Aldrich (France). The working solutions were prepared with ultrapure water and all the reagents employed in this work were used without any purification. Three commercial TiO₂ catalysts were investigated in this work: AEROXIDE® P25, KRONOS® uvlp 7500 and PC500. Photodegradation experiments were carried out at room temperature, at laboratory scale in a batch reactor, magnetically stirred and with a working volume of 1L. A UV-A mercury vapor lamp (Philips PL-S 9W/10/4P, emitting at 365 nm) positioned axially in the center of photoreactor was used as light source. Solution was stirred in the dark for 2h to attain the adsorption/desorption equilibrium. Samples were taken at different reaction times and filtered (0.45 µm PTFE Millipore syringe filter). The progress of the photocatalytic degradation and the mineralization rate of LS were evaluated in terms of its residual concentration by HPLC analysis and of dissolved organic carbon (DOC) by using a Shimadzu TOC-5050 analyser, respectively.
3. Results

Different commercially available TiO\textsubscript{2} catalysts were evaluated for their photocatalytic activity for elimination of the target molecule and it was observed that TiO\textsubscript{2} AEROXIDE® P25 was more active than the other considered TiO\textsubscript{2} samples (Figure 1). Preliminary tests were designed in the presence and in the absence of the selected catalyst to determine its contribution on the degradation of the target molecule. Maximal removal of LS was achieved in the presence of TiO\textsubscript{2} P25 after 40 min. of irradiation while only 17% of elimination was observed by direct photolysis. Adsorption experiments, carried out to determine the adsorption of LS on the catalyst surface, showed that the equilibrium is reached after a contact time of 80 min. and less than 5% of LS was adsorbed. In addition, the different photodegradation experiments carried out in this work clearly demonstrated that the LS removal and its mineralization rate depends on some key operating factors including the catalyst amount, the initial pollutant concentration and irradiation flux. It was observed that the LS elimination and mineralization were enhanced by increasing the catalyst concentration and light intensity. A significant removal yield (99%) was found after 10 min. of reaction when the initial pollutant amount was decreased from 60 mg/L to 5 mg/L. Under these conditions, a high mineralization rate of 87% was obtained. However, the measured removal rate was higher than the percentage of elimination of DOC, which can be due to the formation of organic intermediates. To determine the effect of water matrix on the degradation kinetics of LS, different natural water samples were spiked with 10 mg/L with the target compound. It was clearly observed that the degradation extent of LS decreases in the natural water samples, which can be attributed to dissolved organic matter which is presented naturally in the real water samples. This is probably due to the competitive absorption of short wavelength photons, conducting to the light attenuation inside the reactor so, to a decrease of the elimination rate of the target molecule.

Figure 1. Pseudo-first order kinetics for the degradation of the target molecule with different catalysts.

4. Conclusions

Results reported in this study clearly demonstrated that UV-A/TiO\textsubscript{2} photocatalysis is very efficient for the degradation and mineralization of this drug of the satins family which was recently detected in many WWTPs. It was also found that the removal and mineralization efficiencies depend on the considered operating conditions such as catalyst type and its concentration, initial pollutant concentration, solution pH and light intensity. A high mineralization yield of about 87% was achieved after an irradiation time of 2h. The next step of this study is to identify the by-products which are generated during this oxidation process.

References
