Novel hydroxyapatite-TiO_2 composite material for photocatalytic degradation of diclofenac

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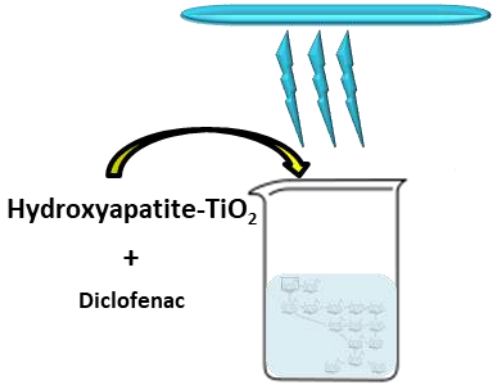

Diclofenac (DCF) is one of the most widely prescribed non-steroidal anti-inflammatory drugs. Since conventional wastewater treatment does not achieve its complete removal, it has been detected in environment. Advanced oxidation processes such as photocatalysis received increasing attention as effective technologies for environmental remediation. In this study, degradation of DCF was investigated by photocatalysis using a new synthetized photocatalyst based on hydroxyapatite obtained from cod fish bones and TiO_2. Degradation of 95% of the target compound was achieved in 24h. Investigation of photo-transformation products was performed by means of UPLC-QTOF/MS/MS their chemical structure was proposed. The toxicity evaluation of final solution was performed using different assays. Overall, the toxicity of the water samples obtained from the photocatalytic experiment decreases, showing the potential applicability of this catalyst for the removal of DCF and detoxification of water matrices.

Introduction

Pharmaceuticals have emerged as environmental contaminants for which concern is increasing. Conventional wastewater treatment plants (WWTPs) have a limited capability to remove these compounds, resulting in their release into the environment. Diclofenac (DCF) is a widely prescribed nonsteroidal anti-inflammatory drug. Nowadays, this drug is ubiquitously present in the aquatic environment [1] due to its continuous release from WWTPs, being considered a pseudo-persistent pollutant [2]. DCF is one of the substances on the watch list for European Union-wide monitoring in the Decision 2015/495/EU.

Advanced oxidation processes (AOPs) such as photocatalysis has being pointed out as effective technologies for pollutants degradation. In this context, materials showing photocatalytic activity have been widely investigated, specially heterogeneous photocatalysts composed of titanium dioxide (TiO_2) [3]. The combination with hydroxyapatite ($Ca_{10}(PO_4)(OH)_2$, HAp), which also possess photocatalytic activity, seems very promising. Previous work demonstrates the possibility to produce high-value Hap-based materials from cod fish bones by-products and its photocatalytic activity [4,5]. A multiphasic material constituted of HAp and TiO_2 (HApTi) showed to be effective for degradation of pharmaceuticals. The objective of this work was the use of this novel synthesized HApTi material to photodegrade DCF; investigate the formation of phototransformation products, and to assess the toxicity of the photocatalysis treatment samples in comparison with the parent compound and photolysis without catalyst.

Material and Methods

A detailed description of the photocatalytic material preparation and characterization was previously published [5]. Briefly, washed and dried cod fish bones were treated in titanium sulphate and then calcinated at 800 ºC. Photocatalysis experiments were performed as previously described [6]. Briefly, DCF solution (5 mg/L) in distilled water was placed with 0.2 g of HApTi (4 g/L) and irradiated from the top with a XX-15 BLB UV lamp (λ 365 nm; 1.80 mW/cm^2). Controls without HApTi were performed to evaluate DCF degradation by photolysis. DCF concentration was determined by HPLC [7]. The investigation of intermediates was performed by UPLC/ESI-QTOF-MS-MS [8]. Evaluation of the toxicity of photodegradation samples was performed by: *Daphnia magna* acute toxicity test, Toxi-ChromoTest and *Lactuca sativa* germination inhibition test.

Results

Results of photodegradation of DCF showed that in the photolysis treatment without catalyst, it was observed about 60% of DCF degradation, while in the photocatalytic experiment with HApTi, it was achieved 95% degradation of the compound in 24h [9]. The DCF photodegradation rate constants were well fitted to the pseudo-first order kinetics (the value of R^2 = 0.97). According to the obtained results, the presence of the catalyst resulted in higher reaction rate and, consequently, half-life times revealed an inverse trend (Table 1). These results indicate that the HApTi is an effective catalyst for the degradation of DCF.

Table 1. Pseudo-first order rate constant (k) and half-life ($t_{1/2}$) for photodegradation of DCF

Treatment	k (h^{-1})	$t_{1/2}$ (h)
UV light	0.034	20.39
UV light + HApTi	0.122	5.68

In previous experiments, TOC measurements showed that not all DCF removed was completely mineralised [6]. In this perspective, samples collected at different times during photodegradation experiments were analysed for phototransformation products (TPs) and toxicity evaluation. Major TPs were identified by UPLC/ESI-QTOF-MS-MS. For each potential TP, the elucidation of the structure was assessed based on the accurate mass of the MS/MS fragments and considering all the reaction mechanisms likely to occur. A pathway of DCF degradation in presence of HApTi was proposed. The time-profiles of TPs revealed that higher concentrations were detected at 4h or 6h and then decreased at the end of the experiment, being the extent of reduction much higher in the samples from photocatalysis with HApTi [9].

At the beginning of the experiments, original DCF solutions (5 mg/L) exhibit high toxicity on *D. magna* (total inhibition)

while the toxicity for the other tested organisms was absent (mutant bacteria) or very low (*L. sativa*). The toxicity of the DCF samples for *D. magna* drastically decreased after 4h of photocatalytic experiment with HApTi and completely disappeared at the end of the experiment. While in the case of the photolysis without catalyst, the toxicity did not vary significantly. *D. magna* was the most sensitive testing organisms for DCF but other tests revealed the same trend - reduced toxicity of the samples resulted from the photocatalytic experiment in relation to the photolysis. Is important to notice that for other organisms the toxicity of the samples increased with the treatments, especially in the case of photolysis without catalyst, probably due to the accumulation of TPs more toxic for these organisms that the parent compound [9].

Conclusions

The present study demonstrated the effectiveness of the novel synthesized multiphasic HAp-TiO_2 material, the former obtained from codfish bones, for the photocatalytic degradation of a pollutant of major concern - DCF. Major transformation products were detected and the chemical structure elucidated. Despite the mineralization not being complete, a reduced toxicity was observed in the samples treated with the photocatalytic experiment in comparison to the photolysis without catalyst and in comparison to the original DCF sample. HApTi photocatalyst was effective for the detoxification of samples containing DCF and DCF transformation products and represents an interesting and eco-safe technology for DCF degradation. It is important to notice that HApTi has a size mesh much higher than conventional TiO_2 catalyst, which facilitates its removal at the end of the wastewater treatment. These results confirm that the valorisation of food by-products such as fish bones could lead to the development of high added value products, which can be used for environmental remediation.

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