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Photocatalytic degradation of carbamazepine and three derivatives using TiO_2 and ZnO: Effect of pH, ionic strength, and natural organic matter

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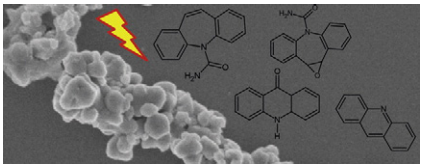
HIGHLIGHTS

- The photodegradation of carbamazepine (CBZ) and three of its metabolites was compared.
- The effect of two catalysts, TiO_2 and ZnO, was tested.
- The effect of environmental parameters, pH, ionic strength and organic matter content was evaluated.
- TiO_2 was the most efficient catalyst for CBZ and its metabolites, with the exception of acridone.
- Environmental parameters have very different effects on the photodegradation of CBZ compared to its metabolites.

GRAPHICAL ABSTRACT



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ABSTRACT

Removal of pharmaceuticals (PhCs) by photocatalysis is a promising avenue in water treatment. The efficiency of these treatments on PhC derivatives compared to their parent molecules remains poorly documented. The present study investigates the efficiency of photodegradation catalyzed by TiO_2 and ZnO nanoparticles on the removal of carbamazepine (CBZ) and three of its derivatives; carbamazepine epoxide (CBZ-E), acridine (AI), and acridone (AO). The effects of environmental parameters such as pH, ionic strength, and natural organic matter content on photodegradation efficiency (transformation after 6 h and kinetics) were tested. We report that the efficiency of the catalysts (TiO_2 and ZnO) can be very different when comparing CBZ and its derivatives (CBZ-E, AI and AO). TiO_2 was more efficient than ZnO at degrading CBZ and CBZ-E. For AI and AO, no significant differences were observed between the two catalysts. We also report that environmental parameters have contrasting effects on the efficiency of the photodegradation of CBZ compared to its derivatives. Changing pH and organic matter content had the most contrasted effects; the photodegradation of CBZ and CBZ-E was significantly affected by pH (especially in presence of TiO_2 NPs) and by the presence of natural organic matter. In contrast, the photodegradation of AI and AO was not affected by pH and organic matter. Only the photodegradation of CBZ was clearly affected by IS and solely at very high IS (1 M). Overall, our results highlight that TiO_2 and ZnO catalysts present contrasted efficiency on the removal of CBZ when compared to its derivatives (CBZ-E, AI and AO). Our results also show that the effect of environmental parameters on the efficiency of the photodegradation of CBZ derivatives cannot be predicted based on the behavior of the parent molecule (CBZ).

1. Introduction

Pharmaceuticals (PhCs) and personal care products (PCPs) have been detected in aquatic systems throughout the world (Kolpin et al., 2002; Richardson et al., 2005; Sacher et al., 2008; Boxall, 2010) while

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their consumption continues to rise (van der Aa et al., 2011). Wastewater treatment plants (WWTPs) have been documented to poorly remove PhCs (Ternes, 1998; Metcalfe et al., 2003; Ternes et al., 2004; Boxall, 2010). As a result wastewater effluents' discharge is the major source of PhCs to the environment (Verlicchi et al., 2012). The effect of PhCs on aquatic organisms is abundantly documented (Oetken et al., 2005; Lawrence et al., 2005, 2012; Boxall, 2010; Nikolaou et al., 2007; Schreiber and Szewzyk, 2008). In recent years, the importance to consider PhC derivatives released by the human body or generated by degradation in the environment has emerged. In comparison to PhCs, studies on the presence and the environmental impacts of PhC derivatives remain limited. It has been reported that derivatives can be more abundant than their parent molecules (Maggs et al., 1997) and may be more harmful to the environment (Pal et al., 2010; Schreiber and Szewzyk, 2008; Bedner and MacCrehan, 2006; Celiz et al., 2009; Zhang et al., 2008; Gros et al., 2006).

To overcome the inefficiency of WWTP to remove PhCs, new avenues of degradation are currently being explored. Photocatalysis is one of the promising approaches (Sousa et al., 2012). It has been proven to efficiently remove various PhCs (e.g. carbamazepine, clorifibric acid, iomeprol, iopromide, levofloxacin, sulfamethoxazole) from wastewaters and natural waters (Doll and Frimmel, 2004, 2005a, 2005b; Lam and Mabury, 2005). Photocatalytic processes have been tested with various catalysts such as TiO_2 and ZnO nanoparticles, and carbon nanotubes. The latter having shown encouraging results (Martinez et al., 2011; Dai et al., 2012). The production of derivatives during wastewater treatments is increasingly considered and documented. For example, the photodegradation of carbamazepine is known to produce various derivatives such as alcohol, phenol, and epoxide derivatives (Doll and Frimmel, 2005b). However, the efficiency of photocatalysis on the removal of these derivatives compared to their parent molecule is currently under-represented in the literature. The effect of environmental parameters, such as pH, ionic strength (IS), and natural organic matter (NOM) on the efficiency of the photocatalytic degradation of PhCs and other contaminants has been addressed in several studies (Doll and Frimmel, 2004, 2005a, 2005b; Carlos et al., 2012). Similar studies on PhC derivatives remain scarce.

The main objectives of this work were (i) to compare the efficiency of photocatalysis in the presence of nanoparticles on the removal of an organic contaminant and its derivatives and (ii) to evaluate the effect of environmental parameters on the efficiency of the photocatalysis. We selected the anticonvulsant and mood-stabilizing drug carbamazepine (CBZ) as model. CBZ is used primarily in the treatment of epilepsy and bipolar disorder, manic depression, as well as trigeminal neuralgia. It is produced in large quantities and is recognized as a particularly persistent molecule in the environment (Ternes et al., 2001; Santos et al., 2007; Gagné et al., 2006; Jelic et al., 2011; Ratola et al., 2012). The photodegradation of CBZ has been and continues to be the subject of intensive research. It is well documented that (i) photocatalysis is an efficient technique for the removal of CBZ, (ii) the presence of TiO_2 significantly improves photocatalysis and (iii) the kinetics of degradation are fast (within hours) and suitable for wastewater treatment (Table 1). Various derivatives of CBZ have been identified in wastewater (Leclercq et al., 2009) and photocatalysis is known to produce several by-products (De Laurentiis et al., 2012; Jelic et al., 2013). While, the fate of this derivative remains poorly documented, some are known to be potentially more toxic than the parent molecule. The efficiency of photocatalysis on CBZ derivatives compared to the parent molecule is poorly documented.

Here, we tested the efficiency of photodegradation on the removal of CBZ and three of its derivatives; carbamazepine epoxide (CBZ-E), acridine (AI) and acridone (AO) (Sup. Info. Scheme S1). The derivatives used in this study were selected with regard to their occurrence in wastewaters and biosolids (Leclercq et al., 2009; Miao et al., 2005) and their potential toxicity (Donner et al., 2013). We specifically evaluated the effect of TiO_2 and ZnO nanoparticles (NPs), two commonly used catalysts, and selected environmental parameters, pH, IS, and NOM content, on the photocatalytic removal of CBZ compared to its derivatives. To the best of our knowledge, this is the first exhaustive comparative study on the photodegradation of CBZ and its derivatives (CBZ-E, AI and AO).

2. Materials and methods

2.1. Materials

TiO_2 and ZnO nanoparticles TiO_2 (99% anatase, 10–30 nm) and ZnO nanoparticles (99.5%, 20 nm) were purchased from Nanostructured and Amorphous materials Inc. (Houston, TX, USA). All chemicals used in this work were of analytical grade. Carbamazepine (CBZ), acridine (AI), acridone (AO), formic acid (FA), humic acid (HA), and tannic acid (TA) were purchased from Sigma-Aldrich (Winston, ON, Canada). Methanol and acetonitrile (Optima® grade for LC/MS) were purchased from Fisher Scientific (Ottawa, ON, Canada). Carbamazepine epoxide (CBZ-E) was synthesized based on a known procedure (Bellucci et al., 1987) (see Supplementary Information for details). It is worth noting that we selected humic acid and tannic acid mostly based on their solubility. Our main objective was to compare the effect of a particulate organic matter (HA) and a soluble organic matter (TA). As for natural organic matter, the exact chemical structure of the organic matter used in this work is poorly defined, especially for the humic acid. For obvious reasons, the impact of photocatalysis on the organic matter was not evaluated.

2.2. Solution preparation

2.2.1. Stock solutions

Nanoparticle suspensions were prepared as follows; 1 g of NPs was pre-wetted in 1 L of milliQ water in a 2 L glass bottle, sonicated for 30 min and then shaken at 130 rpm for 48 h (final concentration = 1 $g \cdot L^{-1}$). Stock solutions of CBZ, CBZ-E, AI, and AO were prepared by weighting 10 mg in 10 mL of methanol in a 20 mL glass vial (final concentration 1 $mg \cdot mL^{-1}$). Stock solutions of TA and HA were

Table 1
Photodegradation kinetics of CBZ in the presence and the absence of TiO_2 reported in the literature.

Condition	Initial [CBZ]	K (kinetic)	$t_{1/2}$	Author
UV/TiO_2	10 $mg \cdot L^{-1}$	0.017 min^{-1}	40 min	Jelic et al. (2013)
UV/TiO_2	417 $ng \cdot L^{-1}$	0.21 h^{-1}	–	Sousa et al. (2012)
UV	5 $mg \cdot L^{-1}$	0.06 h^{-1}	–	Carlos et al. (2012)
UV/TiO_2	4.2 μM	9.99 x 10^{-4} s^{-1}	10.8 min	Dai et al. (2012)
UV/H_2O_2	4.2 μM	6.42 x 10^{-4} s^{-1}	17.6 min	Dai et al. (2012)
UV	10 μM	9.4 x 10^{9} M^{-1} s^{-1}	115 h	Lam and Mabury (2005)
UV/TiO_2	4.3 $mg \cdot L^{-1}$	0.0079 min^{-1}	–	Doll and Frimmel (2004, 2005a)
UV/TiO_2	4.3 $mg \cdot L^{-1}$	0.28 min^{-1}	–	Doll and Frimmel (2004, 2005a)
UV	8.0*10^{-3} $mol \cdot L^{-1}$	5.7 x 10^{-3} h^{-1}	−122 h	Andreozzi et al. (2002)