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Inadequacy of carbamazepine-spiked model wastewaters for testing photocatalysis efficiency

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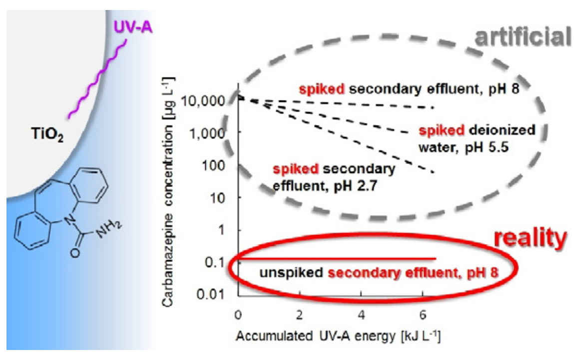
HIGHLIGHTS

- Efficient photocatalytic removal of carbamazepine from spiked deionized water
- Efficiency is reduced in spiked secondary effluent at pH ≥ 8.
- Efficiency is enhanced in spiked secondary effluent at pH 2.7.
- No photocatalytic carbamazepine removal from unspiked secondary effluent at pH 7.3
- Evaluating process efficiency with model wastewaters is misleading.

GRAPHICAL ABSTRACT



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ABSTRACT

The study was performed in order to clarify whether carbamazepine-spiked solutions used as model wastewaters are suitable for the assessment of carbamazepine removal from real secondary municipal effluents by photocatalytic oxidation in the presence and absence of activated carbon. Therefore, carbamazepine (10 mg L^{-1}) was dissolved in deionized water or in secondary municipal effluent. Photocatalytic oxidation of these model wastewaters was carried out with TiO_2 "P25" (100 mg L^{-1}) and UV-A lamps in the absence and in the presence of 20 mg L^{-1} powdered activated carbon (PAC). Carbamazepine was analyzed photometrically. In deionized water at pH 5.5, carbamazepine was nearly completely removed with a UV dose of 6.48 kJ L^{-1}. A similar efficiency of photocatalytic oxidation of carbamazepine added to secondary effluent was observed when the suspension pH was 2.7, while at pH 8 and 10.6, carbamazepine removal from spiked secondary effluent with the same UV dose was only 40 and 60%, respectively. Although PAC addition resulted in an initial adsorptive carbamazepine reduction of 20 to 35% from the model wastewaters, it did not lead to markedly enhanced carbamazepine removal in the subsequent photocatalysis phase. During photocatalytic oxidation of unspiked secondary effluent (initial carbamazepine concentration: 133 ng L^{-1}) at pH 7.3 with and without PAC, carbamazepine concentrations were analyzed by HPLC/MS/MS. While PAC addition resulted in the adsorption of about 90% of the initial carbamazepine, photocatalysis did not lead to any carbamazepine removal at all. This indicates that the experiments with spiked model wastewaters – even in a secondary effluent matrix – are absolutely inadequate for predicting photocatalytic carbamazepine removal under real conditions.

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1. Introduction

The antiepileptic carbamazepine which is also prescribed as an antidepressant was found to be a recalcitrant pharmaceutical discharged to surface waters with secondary effluents. Maximum carbamazepine concentrations found in secondary effluents were 250 ng L^{-1} (Miao et al., 2005, Gros et al., 2010), 1000 ng L^{-1} (Joss et al., 2005) and even 6300 ng L^{-1} (Ternes, 1998). Accordingly, the antiepileptic is frequently detected in water bodies like rivers and lakes (Metcalfe et al., 2003, Stamatelatou et al., 2003, Ternes, 1998) and also in groundwater as a consequence of wastewater infiltration to aquifers (Godfrey et al., 2007, Kreuzinger et al., 2004, Ternes et al., 2007). There is concern about carbamazepine in surface waters because it showed chronic toxicity toward rainbow trout and carp with respect to ultrastructural alterations of kidney and gill tissue (Triebskorn et al., 2007). The lowest observed effect concentration (LOEC) was 1 μg L^{-1}, while carbamazepine concentrations in rivers were observed to be up to 1.1 μg L^{-1} (Ternes, 1998). Another problem with carbamazepine in secondary effluents is the following: Facing expected reduced rainfall during dry seasons in some regions of the world due to climatic change, reuse of secondary municipal effluents for agricultural irrigation is increasingly looked at as a realistic option also in non-arid countries such as Germany (Meyer et al., 2014). However, carbamazepine is also recalcitrant toward biodegradation in irrigated soils and was shown to be taken up by plants (Winker et al., 2010). This restricts utilization of secondary municipal effluents for agricultural irrigation.

From these reasons, oxidative processes such as ozonation (Andreozzi et al., 2002, 2004, Ternes et al., 2003) or advanced oxidation processes (AOPs) (Vogna et al., 2004) are considered to be implemented as tertiary treatment in municipal wastewater treatment. Heterogeneous photocatalytic oxidation (PCO), i.e. the UV irradiation of photosemiconductor particles suspended in wastewater resulting in the formation of negative and positive charge carriers as well as hydroxyl radicals on the surface of the semiconductor particles (Gulyas, 2014), is a promising AOP, because it can be powered by the sun, and was optimistically evaluated by many authors, e.g. Dalrymple et al. (2007) and Doll and Frimmel (2004). Due to its recalcitrance and environmental impacts, carbamazepine has frequently been investigated for its susceptibility to be degraded by heterogeneous photocatalytic oxidation. A great deal of the investigations were carried out with carbamazepine solutions in pure demineralized water (Appavoo et al., 2014, Avisar et al., 2013, Czech and Buda, 2015, Dai et al., 2012, Doll and Frimmel, 2004, 2005a,b, Gao et al., 2015, Georgaki et al., 2014, Haroune et al., 2014, Im et al., 2012, Jelic et al., 2013, Martínez et al., 2011, Miranda-García et al., 2010, Shirazi et al., 2013, Ziegmann and Frimmel, 2010). Tested carbamazepine concentrations in the studies varied between 0.1 and 18.9 mg L^{-1}. In one study (Georgaki et al., 2014), even carbamazepine concentrations of up to 80 mg L^{-1} were investigated.

More relevantly, several studies were executed with carbamazepine-spiked secondary effluents (Chong and Jin, 2012, Chong et al., 2011, Mohapatra et al., 2014, Murgolo et al., 2015, Rizzo et al., 2009) and also with secondary effluent that was not spiked with carbamazepine (Sousa et al., 2012). In these studies, carbamazepine concentrations were between 295 ng L^{-1} and 5 mg L^{-1}. Contrasting to investigations of carbamazepine solutions in pure water, these studies consider the effects of the matrix such as inorganic salts and "natural organic matter" (NOM, comprising humic substances and polysaccharides formed during biodegradation of organics). Unfortunately, the comparison of different studies on carbamazepine photocatalysis in secondary effluent and in demineralized water does not allow for conclusions on the impact of secondary effluent matrix, because different UV sources (with different power outputs and emission spectra), different irradiated liquid volumes and different types and concentrations of photocatalysts were utilized.

Therefore, experiments in both demineralized water and real waters and wastewaters such as secondary municipal effluent spiked with carbamazepine are of special merits. The matrix impact was clearly shown by Avisar et al. (2013) who found carbamazepine removal efficiency by photocatalysis with nitrogen-doped TiO_2 under sun simulation conditions with a xenon arc lamp at pH 7 to decrease in the following order: demineralized water > surface water > groundwater > tertiary effluent > secondary effluent (initial carbamazepine concentration: 1 mg L^{-1}). Accordingly, results of Shirazi et al. (2013) clearly showed that carbamazepine (initial concentration 5 mg L^{-1}) removal by heterogeneous photocatalysis (photocatalyst: TiO_2 P25, UV sources: 250 W and 400 W medium pressure mercury lamps) is more efficient from distilled water than from groundwater. Also Jelic et al. (2013) demonstrated that efficiency of carbamazepine photocatalysis was decreasing with respect to matrices as follows: demineralized water > groundwater > tertiary municipal effluent. Murgolo et al. (2015) accordingly found that carbamazepine removal by heterogeneous photocatalysis with graphene/TiO_2 nanocomposites was less efficient in secondary municipal effluents than in demineralized water.

From these and other studies (Choi et al., 2014, Doll and Frimmel, 2005a), it can be clearly concluded that pure demineralized water is not at all a proper matrix to test the photocatalytic removal of organic target compounds such as carbamazepine because the results obtained in pure water are too optimistic. Also adding humic acid to demineralized water will not reflect real conditions.

Another question is whether spiking of secondary effluent with high concentrations of carbamazepine in the 1–10 mg L^{-1} range is a suitable model for representing real conditions. This cannot be answered as so far no investigation was conducted which compared photocatalytic oxidation for carbamazepine removal from secondary municipal effluents spiked with unrealistically high carbamazepine concentrations and from unspiked secondary effluent with realistic carbamazepine concentrations of some hundred ng L^{-1}.

Addition of activated carbon has been claimed to increase PCO rate constants. This was concluded from studies with phenol (Matos et al., 1998, Gulyas et al., 2013a,b), while the photocatalysis of some other organics was not affected by hybridization with activated carbon (Gulyas et al., 2013a,b). The type of the activated carbon had an impact on the efficiency of the hybrid process as well. Several studies on the impact of different carbon materials on carbamazepine removal by PCO showed conflicting results (Appavoo et al., 2014, Czech and Buda, 2015, Khraisheh et al., 2013, Martínez et al., 2011, Murgolo et al., 2015, Ziegmann and Frimmel, 2010).

This study was performed in order to compare photocatalytic carbamazepine removal from spiked demineralized water, from spiked secondary municipal effluent and from unspiked secondary municipal effluent. Deionized water and secondary municipal effluent were spiked with 10 mg L^{-1} carbamazepine and subjected to TiO_2-based photocatalysis with UV-A light. Concentrations of carbamazepine during the process were determined spectrophotometrically. Carbamazepine concentrations during photocatalytic treatment of the unspiked municipal effluent were analyzed by HPLC/MS/MS. As some activated carbon types were reported to be beneficially hybridized with photocatalytic oxidation, also the impact of different powdered activated carbon (PAC) types on carbamazepine photocatalysis was investigated in this study.

2. Materials and methods

2.1. Wastewater, photocatalyst and activated carbon

Secondary effluent was sampled from a small municipality's wastewater treatment plant (18,600 population equivalents) consisting of screen, grit removal, primary clarifier and a sequential batch reactor (SBR) activated sludge process with phosphate precipitation by Fe^{3+}. Samples of the SBR supernatant were allowed to flow directly into methanol-rinsed and dried 20-L-Duran glass bottles from a sampling valve at the end of the sludge sedimentation cycle. The secondary effluent samples showed the following characteristics: (10 ± 1.2) mg L^{-1}