



# Comprehensive study on effects of water matrices on removal of pharmaceuticals by three different kinds of advanced oxidation processes



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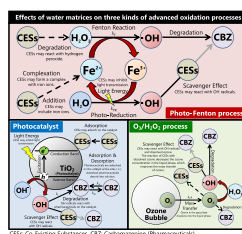
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## HIGHLIGHTS

- Effect of water matrices on drug removal by advanced oxidation processes was studied.
- Higher initial concentrations of pharmaceuticals gave higher inhibition ratios (IR).
- Water matrices and properties of CBZ and DCF affected IR of AOPs in different ways.
- The simple individual models could aid understanding of the effects of water matrices.
- Combined ozone and hydrogen peroxide process was most affected by CESSs.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 14 January 2016

Received in revised form

2 June 2016

Accepted 5 June 2016

Available online 15 June 2016

Handling Editor: Shane Snyder

### Keywords:

advanced oxidation processes

Ozonation

Photocatalyst

Photo-Fenton process

## ABSTRACT

Simple semi-theoretical models were developed to estimate the performance of three different kinds of advanced oxidation processes (AOPs) in the degradation of pharmaceuticals. The AOPs included the photo-Fenton process as an example of a liquid-liquid reaction, the TiO<sub>2</sub> photocatalytic oxidation process as a solid-liquid reaction, and the combined ozone and hydrogen peroxide oxidation process as a gas-liquid reaction; the effects of the aqueous matrices (CESSs: co-existing substances) of actual wastewater on the removal of pharmaceuticals (carbamazepine and diclofenac) was taken into account. By comparing the characteristic parameters of the models, obtained from the experiments using pure water and actual wastewater, the effects of CESSs on the respective removal mechanisms could be separately and quantitatively evaluated. As a general tendency, the AOPs proceeded less effectively (were inhibited) in the matrices containing CESSs, as observed with the use of a lower initial concentration of pharmaceuticals. The inhibition mechanisms differed for the three types of AOPs. In the photo-Fenton process, the Fenton reaction was improved by the incorporation of CESSs, while the photo-reduction reaction was significantly inhibited. In the TiO<sub>2</sub> photocatalytic oxidation process, competition between the pharmaceuticals and CESSs for adsorption on the catalyst surface was a less significant inhibitory factor than the

**Abbreviations:** AOPs, Advanced oxidation processes; CESSs, co-existing substances; CBZ, carbamazepine; DCF, diclofenac; NOM, natural organic matter; NSAIDs, non-steroidal anti-inflammatory drugs.

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## 1. Introduction

Pharmaceuticals administered to humans are excreted and are discharged into the sewage system. Conventional sewage treatment plants are not specifically designed for the efficient and complete removal of pharmaceuticals (Ribeiro et al., 2015). These residual pharmaceuticals are eventually discharged into the aquatic environment (Miege et al., 2009; Lester et al., 2014). In fact, pharmaceuticals have been found in sewage effluent, surface water, rivers, etc., at  $\mu\text{g/L}$  to  $\text{ng/L}$  levels (Mompelat et al., 2009; Zorita et al., 2009; Sim et al., 2010). Even at low concentrations, pharmaceuticals are suspected to pose a threat to the aquatic environment due to their high bioactivities (Neamțu et al., 2014). As a result, aquatic pollution with pharmaceutical residues has been recognized as an environmental concern (Schwarzenbach et al., 2006). Given the importance of pharmaceuticals in modern society, not all pharmaceuticals can be regulated, and it is therefore necessary to develop more efficient processes for wastewater treatment to prevent pharmaceuticals from entering the aquatic environment.

To deal with this problem, advanced oxidation processes (AOPs) have recently gained recognition as a promising approach (Ahmed et al., 2014; Klavarioti et al., 2009; Lee et al., 2014; Meenatchisundaram et al., 2014; Ribeiro et al., 2015; Wols and Hofman-Caris, 2012). The degradation of recalcitrant pollutants by AOPs is based on highly-reactive hydroxyl radicals (OH radicals) that have the capability for total mineralization of a variety of organic compounds with high reaction rate constants, generally around  $10^9$  L/mol/s (Moradi and Ghanbari, 2014; Ribeiro et al., 2015). These properties allow for removal of a large number of chemically different micropollutants on much shorter time-scales. A much faster degradation rate is preferred in terms of practical sewage treatment plant operation, in which a large amount of sewage has to be treated. Thus far, a number of AOPs have been applied to mitigate micropollutant problems (Klavarioti et al., 2009; Ribeiro et al., 2015; Schwarzenbach et al., 2006).

Although AOPs are recognized as effective for removal of pharmaceuticals, the complete mineralization of pharmaceuticals by AOPs is generally a costly process (Van Doorslaer et al., 2015). The pathway for degradation of organic pollutants by OH radicals generates intermediates having electron-lucent structures (e.g., organic acids). Since OH radicals act as electrophilic agents, they are not suitable for the degradation of such intermediates (Tokumura et al., 2013). This leads to increased chemical dosages and operating cost. A process combining AOPs and a conventional biological process has therefore been investigated to reduce the operation costs (Meenatchisundaram et al., 2014; Oller et al., 2011). If AOPs are used as a pretreatment, since most sewage naturally contains co-existing substances (CESs) (e.g., natural organic matter (NOM), organic acids, and inorganic ions) that have the potential to significantly affect the efficiency of removal of the target pollutants, the water matrices must be taken into account to select the optimum AOPs and determine the operating conditions for practical use. Neamțu et al. (2014) reported that the degradation of eight micropollutants (atenolol, benzotriazole, clarithromycin, gabapentin, methylbenzotriazole, metformin, metoprolol, and primidone) in lake water and wastewater effluent by the photo-Fenton process and the combined UV light irradiation (254 nm)

and hydrogen peroxide ( $\text{UV}_{254}/\text{H}_2\text{O}_2$ ) process was inhibited. The photo-Fenton process and the combination process ( $\text{UV}_{254}/\text{H}_2\text{O}_2$ ) were affected by CESs contained in the lake water and the wastewater effluent to the same extent. In ultrapure water, the mean removal efficiency for the eight micropollutants by both processes was around 70% at 60 min. However, in lake water, the removal efficiency declined to around 55% with a corresponding value of around 30% in the wastewater effluent. Doll and Frimmel (2005) reported that the presence of NOM and other organic substances retarded the degradation of micropollutants (clofibrac acid, carbamazepine, iomeprol, and iopromide) subjected to the  $\text{TiO}_2$  photocatalytic oxidation process via several complicated phenomena. Although there are countless studies on AOPs, most studies did not include the effects of water matrices. Additionally, available studies on the effects of water matrices have focused on the individual AOPs. Therefore, little is known about the effects of water matrices on AOPs, and more comprehensive research is thus required.

In this study, to evaluate the actual performance of three different kinds of AOPs, namely, the photo-Fenton process ( $\text{Fe}/\text{H}_2\text{O}_2/\text{UV}$ ) (as an example of a liquid-liquid reaction), the  $\text{TiO}_2$  photocatalytic oxidation process ( $\text{TiO}_2/\text{UV}$ ) (a solid-liquid reaction), and the combined ozone and hydrogen peroxide ( $\text{O}_3/\text{H}_2\text{O}_2$ ) oxidation process (a gas-liquid reaction), for the removal of pharmaceuticals, respective simple semi-theoretical models that take into account the effects of the aqueous matrices of actual wastewater were developed. To obtain the characteristic parameters for the models, the degradation of pharmaceuticals by the three different kinds of AOPs was evaluated in pure water and actual wastewater (sewage). The effects of the initial pharmaceutical concentration on the processes were also investigated. Furthermore, to evaluate the effects of the physico-chemical properties of the pharmaceuticals on the processes, two pharmaceuticals, carbamazepine (CBZ) and diclofenac (DCF) were used as model pharmaceuticals (see Table S1 in the Supporting Information). CBZ and DCF are respectively anti-epileptic and non-steroidal anti-inflammatory drugs (NSAIDs). Due to their persistent properties, they are resistant to biological treatment in sewage treatment plants, thus they are frequently detected in sewage treatment plant effluent and surface water in  $\mu\text{g/L}$  levels (Bae et al., 2013; Clara et al., 2004; Ghauch et al., 2011; Ternes, 1998). These pharmaceuticals reportedly exert adverse effects on the aquatic environment (Martínez et al., 2011; Schwaiger et al., 2004). To the best of our knowledge, this is the first comprehensive and comparative study on the effects of water matrices on AOPs.

## 2. Experimental methods

### 2.1. Materials

CBZ and DCF were purchased from Sigma-Aldrich (USA) and Wako Pure Chemical Industries (Japan), respectively. Stable isotope-labeled CBZ-d10 and DCF-d4 were obtained from CDN isotopes (Canada). Methanol (Wako Pure Chemical Industries, Japan) was used to dissolve the pharmaceuticals (Klammerth et al., 2010). High performance liquid chromatography (HPLC) grade acetonitrile and acetic acid (glacial) were supplied by Wako Pure Chemical Industries (Japan). Reagent grade hydrogen peroxide

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