



Enhanced photocatalytic degradation of sulfamethoxazole by zinc oxide photocatalyst in the presence of fluoride ions: Optimization of parameters and toxicological evaluation

Amir Mirzaei ^a, Laleh Yerushalmi ^a, Zhi Chen ^{a, *}, Fariborz Haghghat ^a, Jianbo Guo ^b

^a Department of Building, Civil and Environmental Engineering (BCEE), Faculty of Engineering & Computer Sciences, Concordia University, Montreal, Quebec, Canada

^b Tianjin Chengjian University, 26 Jinjing Road, Xiqing District, Tianjin, 300384, China

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ABSTRACT

The presence of antibiotics in water bodies has received increasing attention since they are continuously introduced and detected in the environment and may cause unpredictable environmental hazards and risks. The photocatalytic degradation of sulfamethoxazole (SMX) by ZnO in the presence of fluoride ions (F-ZnO) was evaluated. The effects of operating parameters on the efficiency of SMX removal were investigated by using response surface methodology (RSM). Under the optimum condition, i.e. photocatalyst dosage = 1.48 g/L, pH 4.7, airflow rate = 2.5 L/min and the concentration of fluoride ions = 2.505 mM, about 97% SMX removal was achieved by F-ZnO after 30 min of reaction. The mechanism of reactions, COD removal efficiency and reaction kinetics were also investigated under optimum operating conditions. In addition, about 85% COD reduction was obtained after 90 min photocatalytic reaction. The pseudo-first-order kinetics rate constants for the photodegradation of SMX were found to be 0.099, 0.058 and 0.048 min⁻¹ by F-ZnO, ZnO and TiO₂ (P25), respectively. The figure-of-merit electrical energy per order (E_{EO}) was used for estimating the electrical energy efficiency, which was shown to be considerably lower than the energy consumption for the reported research on removal of SMX by photocatalytic degradation under UV irradiation. Toxicity assays were conducted by measuring the inhibition percentage (PI) towards *E. coli* bacteria strain and by agar well diffusion method. The results showed that after 30 min of reaction, the toxicity of the treated solutions by all photocatalysts fell within the non-toxic range; however, the reduction in toxicity by F-ZnO was faster than those by ZnO and P25. Despite the positive effects of surface fluorination of ZnO on the SMX and COD removal and reaction kinetics, its lower stability compared to ZnO and P25 in the repeated experiments gave rise to some doubts about its performance from a practical point of view.

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1. Introduction

Widespread detection of emerging contaminants (ECs), including many synthetic antimicrobial agents, in water bodies is raising public health concerns even at sub-therapeutic concentration levels (Beltran et al., 2008; Ryan et al., 2011). Although there is an ongoing debate about the risks posed by chronic exposure to trace concentrations of antimicrobials compounds, recent studies have demonstrated adverse health effects caused by mixtures of ECs in the environment, even at trace levels, and enhancement of

antibiotic resistance (Beltran et al., 2008). Sulfonamide antibacterial compounds such as sulfamethoxazole (SMX) are the oldest group of antibiotics and they are widely prescribed to treat infectious and respiratory diseases in human and veterinary medicine (Długosz et al., 2015; Li et al., 2017). Sulfonamide antibiotics show high excretion rates in the feces and urine, either as parent compound or metabolites (Yang et al., 2015). It is reported that conventional biological treatment processes are ineffective and/or too slow to eliminate sulfonamides in water (Abellán et al., 2007). Thus, it is not surprising that research has recently focused on utilizing advanced oxidation processes (AOPs) for the degradation of antibiotics in water.

Photocatalytic oxidation (PCO) is a promising AOPs for the

* Corresponding author.

E-mail address: zhi.chen@concordia.ca (Z. Chen).

removal of recalcitrant and/or toxic compounds from water (Abellán et al., 2007; Kim and Kan, 2016; Liu et al., 2016). However, most photocatalytic processes are complicated and difficult to use in water treatment operations because of high preparation and operating costs and relatively low photocatalytic efficiency (Li et al., 2017). Photocatalysts such as ZnO, when illuminated by photons having an energy level that exceeds their band gap, produce reactive species such as e^- , h^+ , OH^\bullet , and O_2^\bullet which can participate in the elimination reactions of organic contaminants. A list of complete reactions which may contribute to the photocatalytic process by ZnO can be found elsewhere (Mirzaei et al., 2016).

Unfortunately, the low quantum efficiency caused by the high recombination rate of the photo-induced electron/hole pairs leads to high energy consumption during the operation and greatly restricts the applications of photocatalytic removal processes (Liu et al., 2012; Shayegan et al., 2018). So far, numerous modifying strategies have been proposed for promoting the efficiency of photocatalysts (Li et al., 2016). However, most efforts have been focused on narrowing the band gap of photocatalyst by introducing dopant(s) into the structure of semiconductor in order to reduce the recombination rate and harvest visible instead of UV light. From the thermodynamic viewpoint, narrowing the band gap of semiconductor will lead to reducing the oxidation and reduction potential (Li et al., 2016). Therefore, the incomplete degradation of ECs due to low redox potential may enhance the probability of toxic by-products formation during the treatment by narrow band gap photocatalysts (Catalá et al., 2015). Improving the efficiency of wide band gap photocatalysts by alternative methods such as surface modification will not only promote the removal efficiencies without band gap engineering, but may also improve the disinfection process by UVC ($\lambda_{max} = 254$ nm) and further reduce operating cost by process intensification (Cruz-Ortiz et al., 2017).

The photocatalytic activities of semiconductors are strongly related to their surface characteristics, charge transfer/recombination rate, contaminant-surface interactions and the type and amount of reactive oxygen species (ROS) (Ryu et al., 2017). Surface modification of photocatalyst can alter the surface characteristics, including polarity, surface charge, acidity, adsorption capacities, etc. (Liu et al., 2012). Most current methods of surface modification use long-chain fluorinated and polyfluorinated compounds (PFCs) (Mirzaei et al., 2013; Xing et al., 2012). The use of PFCs is restricted because of their acute toxicity, high bioaccumulative potential in biota and high cost (Bai et al., 2016; Mirzaei et al., 2017a; Xing et al., 2012). As an alternative, surface fluorination by fluoride anions has become a popular method because this technique is simple to implement, highly effective, inexpensive and less bioaccumulative (Mirzaei et al., 2017a; Ryu et al., 2017). The enhancement of photocatalytic degradation efficiency of organic contaminants such as methylene blue (Kim et al., 2010), *N*-nitrosodimethylamine (Lee et al., 2005), phenol (Park and Choi, 2004; Wang et al., 2007), acid orange 7 (Park and Choi, 2004), acid red 1 (Mrowetz and Selli, 2005), benzoic acid (Mrowetz and Selli, 2006), and cyanuric acid (Oh and Jenks, 2004) in the presence of F^- ions in aqueous TiO_2 suspensions has been reported. Although, the higher removal efficiency of ZnO compared to TiO_2 under certain operating conditions is demonstrated in several studies (Elmolla and Chaudhuri, 2010; Kansal et al., 2007; Mirzaei et al., 2016), the surface fluorination of ZnO has not been reported. The higher photocatalytic activity of fluorinated photocatalysts is related to the substantial changes in their surface characteristics such as surface charge, polarity, acidity and adsorption capacity (Liu et al., 2012). On the other hand, it is proven that the photostability of photocatalyst is heavily dependent on its surface properties (Chu et al., 2009). However, the effects of surface fluorination on the stability and

reusability of photocatalysts has been rarely reported in the literature.

In this study, response surface methodology (RSM) was used to optimize four process parameters, namely, catalyst loading, fluoride ions concentration, solution pH and airflow rate for maximum SMX degradation. Possible mechanisms of photocatalytic degradation of SMX as well as COD removal and reaction kinetics are investigated under the optimum operating conditions. The effect of surface fluorination on photocorrosion of ZnO and reusability of F-ZnO in consecutive experiments is also investigated. In addition, the figure-of-merit *electrical energy per order* (E_{EO}) for photocatalysis process at the optimum operating condition is calculated and compared to the reported results of SMX removal by PCO under UV light irradiation. Since oxidation treatment processes may cause the formation of toxic by-products, the final stage of this research was devoted to the assessment of solution toxicity before and after the treatment.

2. Experimental section

2.1. Chemicals

Zinc oxide, ammonium fluoride, potassium iodide and *tert*-butanol (TBA) were purchased from Fisher Scientific (ON, Canada). Commercial TiO_2 Degussa P25 was used to compare its photocatalytic efficiency with bare and fluorinated ZnO (F-ZnO). Sulfamethoxazole (SMX) was purchased from MP Biomedicals (ON, Canada). All chemicals were reagent grade and were used as received without any further purification. Deionized Milli-Q water ($18 \mu S cm^{-1}$) was used to prepare the different solutions in this study.

2.2. Analytical procedures

The concentration of zinc ion in the solution was measured by an atomic absorption spectrophotometer (PinAAcle 900F, PerkinElmer, USA). The variations of SMX concentration were evaluated by the method reported by Liu et al. (2016) by using a UV-Vis spectrophotometer (Evolution 201, Thermo Scientific, USA). Ultra-low range COD (0.7–40 mg/L) digestion vials, ToxTrak™ toxicity assay kit and H_2O_2 titration kit were purchased (all from HACH Co.) and used according to the manufacturer's methods. The degree of removal for SMX and COD was determined based on Eq. (1) and Eq. (2), respectively:

$$R = \left(1 - \frac{C_t}{C_0}\right) \times 100 \quad (1)$$

$$Y = \left(1 - \frac{COD_t}{COD_0}\right) \times 100 \quad (2)$$

where R and Y are the degree of SMX and COD removal (%) respectively. C_t (mM) is the concentration SMX at time t and C_0 (mM) is the initial concentration of SMX.

2.3. Photocatalytic experiments

The photocatalytic degradation experiments were conducted in a 700 mL tubular stainless steel photoreactor working in slurry mode. The light source was provided by a UVC lamp (10 W, Trojan Technologies, On, Canada), the intensity of UVC radiation was $3.5 mJ cm^{-2}$, measured by a radiometer (Trojan Technologies, On, Canada). In all cases, air was continuously bubbled into the solution mixture through a sparger located at the bottom of reactor to

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