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Removal of antibiotics in a parallel-plate thin-film-photocatalytic reactor: Process modeling and evolution of transformation by-products and toxicity

Can Burak Özkal[1,*], *Zacharias Frontistis*[2,*], *Maria Antonopoulou*[3], *Ioannis Konstantinou*[4], *Dionissios Mantzavinos*[2], *Süreyya Meriç*[1]

1. *Environmental Engineering, Namık Kemal University, Faculty of Engineering, Tekirdag, Turkey*
2. *Department of Chemical Engineering, University of Patras, GR-26504 Patras, Greece*
3. *Department of Environmental & Natural Resources Management, University of Patras, GR-30100 Agrinio, Greece*
4. *Department of Chemistry, University of Ioannina, GR-45110 Ioannina, Greece*

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ABSTRACT

Photocatalytic degradation of sulfamethoxazole (SMX) antibiotic has been studied under recycling batch and homogeneous flow conditions in a thin-film coated immobilized system namely parallel-plate (PPL) reactor. Experimentally designed, statistically evaluated with a factorial design (FD) approach with intent to provide a mathematical model takes into account the parameters influencing process performance. Initial antibiotic concentration, UV energy level, irradiated surface area, water matrix (ultrapure and secondary treated wastewater) and time, were defined as model parameters. A full of 2^5 experimental design was consisted of 32 random experiments. PPL reactor test experiments were carried out in order to set boundary levels for hydraulic, volumetric and defined defined process parameters. TTIP based thin-film with polyethylene glycol + TiO_2 additives were fabricated according to pre-described methodology. Antibiotic degradation was monitored by High Performance Liquid Chromatography analysis while the degradation products were specified by LC–TOF-MS analysis. Acute toxicity of untreated and treated SMX solutions was tested by standard *Daphnia magna* method. Based on the obtained mathematical model, the response of the immobilized PC system is described with a polynomial equation. The statistically significant positive effects are initial SMX concentration, process time and the combined effect of both, while combined effect of water matrix and irradiated surface area displays an adverse effect on the rate of antibiotic degradation by photocatalytic oxidation. Process efficiency and the validity of the acquired mathematical model was also verified for levofloxacin and cefaclor antibiotics. Immobilized PC degradation in PPL reactor configuration was found capable of providing reduced effluent toxicity by simultaneous degradation of SMX parent compound and TBPs.

* *Corresponding authors.*
E-mail addresses: cbozkal@nku.edu.tr (Can Burak Özkal), zfrontistis@chemeng.upatras.gr (Zacharias Frontistis).

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Introduction

Among the emerging class of micropollutants, pharmaceuticals are mainly arising from point sources like production effluent, wastewater disposal as well as diffuse sources like runoff from fields and anthropogenic effluents. Development of optimal removal technologies for their removal from urban wastewater flows and surface and drinking water sources is one of the main focused research lines within scope of water treatment (Kümmerer, 2009).

Photocatalysis process has been known to provide substantial levels of degradation and mineralization of emerging pollutants under both artificial and solar irradiation conditions. Studies mainly focused on building or developing more cost and energy efficient systems that have enhanced ability to run under solar irradiation or simulated ultraviolet energy (Carbajo et al., 2016; Malato et al., 2015; Visan et al., 2014). It has been emphasized in the recent literature reviews that the lack of optimal design and comparable experimental conditions are major drawbacks for the development of photocatalytic (PC) reactors (Imoberdorf et al., 2007; Leblebici et al., 2015b). Most of the optimization and intensification studies are categorized under overcoming mass transfer limitations, increasing catalyst surface, optimizing photon transfer limitations, scaling up, and catalyst separation purposes (Charles et al., 2011; Vezzoli et al., 2011; Visan et al., 2014).

The majority of modeling work on PC processes has been carried out either in the field of air purification or for slurry system water purification (Castrillón et al., 2006; Taghipour and Mohseni, 2005). Modeling studies mainly focused on readily oxidized pollutants, while in real cases most of the target molecules are within the scope of contaminants of emerging concern for aquatic environment (Vezzoli et al., 2011). Kinetic models regarding immobilized systems do not generally include the influence of light flux and amount of catalyst on the degradation rate, which give rise to limited representation of the model for different reactors (Yue and Legrini, 1992). Since the mechanism of heterogeneous reactions involves diffusion of species to the active catalyst sites, mass transport has to be addressed and considered accordingly (Dijkstra et al., 2002). The classical approach is to use a differential reactor which consists of a reaction chamber and a mixing tank, where the reaction volume is much smaller than the total volume. The lower ratio of conversion per each pass enables the system to converge to a batch reactor condition, that would enable possible elimination of external mass transfer (Duran et al., 2010; Marugán et al., 2008; Pozzo et al., 2010; Satuf et al., 2007).

This paper is the first attempt to develop a factorial design based model that considers the effect of parameters known to influence PC degradation of a complex molecule (rather than a readily oxidized pollutant), sulfamethoxazole (SMX) antibiotic in an immobilized photocatalyst system configuration. Experimental studies were performed in a parallel-plate (PPL) reactor under plug-flow conditions with no re-circulation or dead-zones along the flow direction within the reaction area. PPL(s) provide very high surface area-to-volume values just like the micro-reactor configurations that are used to address mass transfer limitations in immobilized catalyst reactors (Leblebici et al., 2015b).

Longevity and stability of PC activity were addressed as indispensable properties to provide replicable experimental conditions. The degraded amount of SMX by PC oxidation was specified as the response factor of the factorial experimental design. The system was operated *versus* time under different conditions of UV energy, initial antibiotic concentration, irradiated surface area (ISA), and water matrix (WM) properties. Furthermore, the applicability of thin-film (TF) photocatalysis was evaluated for cefaclor (CFL) and levofloxacin (LVX) antibiotics known with their common usage and activity against gram (–) and (+) bacteria. Usage patterns (sulphonamide and fluoroquinolone are one of the most widely used antibiotics in most European countries), frequency of detection in water bodies (high detection of cephalosporins and fluoroquinolones in hospital effluents), and exact location of detection in the environment (detection in manure, soil, water *etc.*), were taken as indicative of selecting macrolide (SMX), cephalosporin (CFL) and fluoroquinolone (LVX) group of antibiotics (Christian et al., 2003; Kümmerer, 2009; Rodriguez-Mozaz et al., 2015; Tong et al., 2014).

Besides, PPL reactor effluent was subjected to an acute toxicity evaluation based on *Daphnia magna* immobility, taking into account a plausible PC degradation pathway of SMX and intermediate products formed along the process duration (Trovó et al., 2009; Gómez-Ramos et al., 2011).

1. Materials and methods

1.1. Chemicals and WM

LVX (CAS# 100986-85-4) and CFL (CAS# 53994-73-3) were purchased from Santa Cruz Biotech (USA) and SMX (CAS number: 723-46-6), was purchased from Sigma-Aldrich (Germany), all at analytical grade. Titanium tetra-isopropoxide solution (CAS# 546-68-9), titanium dioxide (TiO_2) (CAS# 1317-70-0), nitric acid (64-19-7, 70% reagent grade), isopropanol (67-63-0, 99.7% grade), and PEG-600 (polyethylene glycol 600–CAS# 25322-68-3) were purchased from Sigma-Aldrich (Germany).

The STWW (secondary treated urban wastewater) effluent sample was collected from the wastewater treatment plant of the University of Patras, Greece. Ultrapure water was taken from a water purification system (EASY pure RF-Barnstead/Thermolyne, USA). Characterization of both STWW sample is presented in Table 1. Ultrapure water pH: 6.5, resistivity: 18.2 MΩ/cm and conductivity: μS/cm.

1.2. TF preparation

The methodology of TF preparation is selected based on previous findings of comparative study among three different sol–gel methodologies that were reported elsewhere. TTIP (titanium tetra isopropoxide) based sol–gel prepared with acetic acid and PEG + TiO_2 addition was used for TF coated glass substrates preparation through dip-coating procedure followed by a final calcination step as described in a recent study of ours (Özkal et al., 2016).