Chemical Engineering Journal 351 (2018) 967–975

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Model-based evaluation of tetracycline hydrochloride removal and mineralization in an intimately coupled photocatalysis and biodegradation reactor

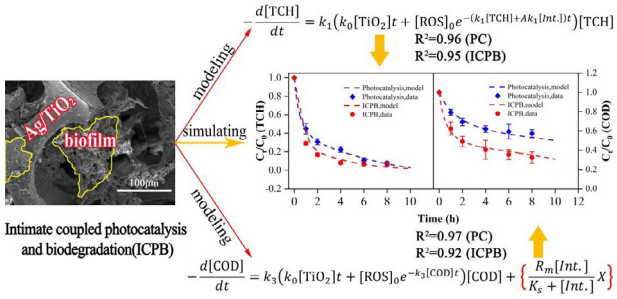
Yue Ma[a], Houfeng Xiong[b], Zhiquan Zhao[c], Yang Yu[c,d], Dandan Zhou[c,d,*], Shuangshi Dong[a,*]

[a] Key Laboratory of Groundwater Resources and Environment, Ministry of Education, Jilin University, Changchun 130021, China
[b] School of Chemistry and Environmental Engineering, Jiujiang University, Jiujiang 332005, China
[c] State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China
[d] Jilin Engineering Lab for Water Pollution Control and Resources Recovery, Northeast Normal University, Changchun 130117, China

HIGHLIGHTS

- Kinetic models of intimately coupled photo-biological reaction (ICPB) were developed.
- Tetracycline (TCH) removal kinetics by ICPB were successfully validated.
- The root square errors between experimental results and model simulations were at max 2.1%.
- Biodegradation in ICPB played a crucial role in modeling TCH removal and mineralization.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Intimately coupled photocatalysis and biodegradation (ICPB)
Modeling
Refractory pollutants
Kinetics
Mechanisms

ABSTRACT

Intimately coupled photocatalysis and biodegradation (ICPB) shows great potential for treatment of refractory pollutants; however, no kinetics for modeling ICPB performance has been developed and the major challenge is to determine the relationship between photocatalysis and biodegradation. In this work, we developed a simplified kinetic model to predict removal and mineralization of a target pollutant (tetracycline hydrochloride; TCH) by hypothesizing that all of the biodegradable photocatalysis products are immediately bio-utilized. Combined with a second-order photocatalytic kinetic model and Monod-type biodegradation model, we observed the interactions between photocatalysis and biodegradation in ICPB. Parameters in the kinetic equations were estimated using the First Optimization software to fit the experimental data to the proposed model with nonlinear regression. Our experimental results showed that TCH and chemical oxygen demand (COD) removal were as high as 94% and 70% within 8 h, respectively. TCH was transformed to non-toxic intermediates in only 4 h. Significantly, the kinetic models could satisfactorily predict the TCH and COD removal, and agreed well with the experimental data with an $R^2 > 0.92$. The models confirmed that biodegradation in ICPB played a major role in accelerating TCH and its intermediates removal and mineralization, as the kinetic coefficient k_1 of ICPB was 10% greater than that of photocatalysis alone. The developed models accurately predicted the ICPB efficiencies, and revealed the mechanisms of ICPB operation.

* Corresponding authors at: School of Environment, Northeast Normal University, Changchun 130117, China (D. Zhou).
E-mail addresses: zhoudandan415@163.com (D. Zhou), dongshuangshi@gmail.com (S. Dong).

https://doi.org/10.1016/j.cej.2018.06.167
Received 11 February 2018; Received in revised form 16 May 2018; Accepted 25 June 2018
Available online 28 June 2018
1385-8947/

Nomenclature

[TCH]	TCH concentration (mg L^{-1})
[COD_T]	total bulk chemical oxygen demand (mg L^{-1})
[COD_{TCH}]	theoretical COD of the remaining TCH (mg L^{-1})
[COD_{INT}]	amount of intermediates (= [COD_T] – [COD_{TCH}], mg L^{-1})
k_0	production rate constant of RS (h^{-1})
k_1	second-order rate constant for degradation of TCH (L h^{-1} mol^{-1})
k_2	second-order rate constant for degradation of Int. (L h^{-1} mol^{-1})
k_3	second-order rate constant for degradation of COD (L h^{-1} mol^{-1})
R_m	maximum specific cell growth rate (h^{-1}) TCH phenol
K_s	half-saturation constant (mg L^{-1})
X	biomass concentration at stable state (mg L^{-1})
RS	reactive species (mol L^{-1})
[TiO_2]	TiO_2 concentration (mg L^{-1})
C_{mod}	value of model calculated results (mg L^{-1})
C_{exp}	value of experimental results (mg L^{-1})
P	protocol of photolysis alone
AD	protocol of adsorption alone
B	protocol of biodegradation alone
PC	visible-light-induced photocatalysis alone
ICPB	intimately coupled photocatalysis and biodegradation

1. Introduction

Intimately coupled photocatalysis and biodegradation (ICPB) technology shows great potential for enhancing the removal and mineralization of refractory pollutants [1–3]. In a typical ICPB system, millimeter-sized macro-porous carriers support a photocatalyst on their outer surface and a biofilm within their pores [3]. The concept is that bacteria in the carrier pores are protected from photocatalytic oxidation. This arrangement enables bacteria away from free radical damage but is close enough to rapid degradation of the biodegradable photocatalytic products. ICPB in treatment of bio-refractory pollutants overcomes the weaknesses of incomplete mineralization by photocatalysis alone or inhibition of toxic compounds by bioreactor alone [3–5]. Currently, ICPB has been successfully applied for the treatment of many refractory pollutants, such as phenols [1–3], dinitrotoluene [4] and dyes [5]. Recently, Xiong et al. [6] has used a visible-light-driven ICPB reactor to enhance TCH degradation and mineralization, with which the TCH and COD removal improved by 11% and 20% respectively by ICPB, compared to the photocatalysis alone. This was the first report of treatment of an antibiotic by ICPB. Notably, it was found that biofilm benefitted TCH degradation by reducing interaction of reactive species (RS) and TCH intermediates.

Mathematical modeling serves as a both useful and reliable tool to probe into emerging technologies, while significantly reducing the workload related to process evaluation or optimization [7]. In particular, a kinetic model can be used to: (1) identify the key factors of degradation [8–10], (2) provide improved understanding of the complicated reaction mechanisms [11–13], (3) help to scale up relevant processes, and (4) predict the treatment duration and therefore running cost [14]. However, only the biodegrading kinetics of an ICPB reactor has previously been quantified, using an Aiba self-inhibition model [15]. This model lacks the structure of the real ICPB manifestation, i.e., mutually promotion between the photocatalysis and biodegradation [3–5]. The main challenge to determining an ICPB model is to integrate both photocatalytic and biological degradation, where the immediate consumption of photocatalytic intermediates by biodegradation has to be considered.

To the best our knowledge, no mathematical model with the above-mentioned real ICPB manifestation structure has been developed to date, consequently, the modeling evaluation of pollutants degradation in an ICPB remained unknown. In this work, we approached the mathematic model of ICPB for the first time, employing a strategy of hypothesizing that all the biodegradable photocatalysis products were immediately bio-utilized. This in fact constitutes an ideal ICPB reaction [6]. Modeling photocatalysis alone was achieved based on a second-order kinetic model [6,16–18] and the biodegradation alone was simulated using the well-known Monod model [19]. Then, we developed the ICPB kinetic model by fully considering the transfer of the predicated photocatalytic products into the biodegradation models, under determination of the final removal and mineralization of pollutants. TCH was employed as model pollutant and the experimental data for TCH removal and mineralization were directly compared with the simulated results. This study is important for predicting removal and mineralization of refractory pollutants by ICPB technology, and achieving a direct scale-up and operation of ICPB reactors.

2. Material and methods

2.1. Carriers, photocatalysts and biofilms

We used a sol–gel method to prepare Ag/TiO_2 nanoparticles, which are visible-light responsive photocatalysts. Briefly, Ag/TiO_2 was prepared with titanium tetraisopropoxide [$Ti(OCH(CH_3)_2)_4$] (Sigma-Aldrich Co. LLC., USA) and silver nitrate (Sigma-Aldrich Co. LLC., USA). Silver reduction and doping were conducted in sodium citrate tribasic dihydrate (Beijing Chemical Works, China) according to a previous report [20].This Ag/TiO_2 sol was used for the following coating procedure.

Polyurethane sponge carriers (2 mm × 2 mm × 2 mm) with a porosity of 87% and wet density of 0.89 g/mL (Hayi-diverse, Yixing, China) were coated with Ag/TiO_2 by using the method of evaporation-induced self-assembly (EISA) [21]. Basically, Ag/TiO_2 sol (50 mL) was ultrasonically dispersed in ethanol (150 mL) for 5 min and then the carriers (4 g) were added to the suspension. The carriers in the Ag/TiO_2 sol mixture were further ultrasonically dispersed for another 5–10 min before drying in an oven at 80 °C by stirring with a glass rod every 30 min. After rinsing with deionized water in ultrasonic three times to remove the loosely attached Ag/TiO_2 nanoparticles, porous carriers coated with photocatalysts were ready to use. The Ag/TiO_2 coating amount was 0.39 g-catalyst/g-carrier, with a coating ratio of 28.3% (wt %).

The coated carriers were immersed in an activated sludge (South WWTP, Changchun, China) for the initial attachment of microbes and the biofilm was developed at room temperature (~20 °C) with a synthetic wastewater containing sodium acetate (330 mg/L), NH_4Cl (29 mg/L), $Na_2HPO_4{\cdot}2H_2O$ (8 mg/L), and NaH_2PO_4 (4 mg/L) in an internal loop airlift-driven reactor, which was described in our previous report [22]. When COD of the effluent was stabilized, the biofilm was considered to be mature.

2.2. Reactors and protocols

Photolytic circulating-bed bioreactors of a working volume of 540 mL were used to simulate TCH degradation and mineralization in ICPB reactors with biofilm developed on the Ag/TiO_2 coated sponge carriers, which was described in our previous publications [3], and schematically drawn in Fig. S1. Synthetic wastewater and biofilm carriers were circulated by bubbling air from the bottom of the reactor, supplied by a 35 W aeration pump (SOBO, Weifang, China) and controlled by a flow meter (superficial velocity in the draft tube was