Applied Catalysis B: Environmental 101 (2011) 540–547

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

UV-A and UV-C induced photolytic and photocatalytic degradation of aqueous ciprofloxacin and moxifloxacin: Reaction kinetics and role of adsorption

Xander Van Doorslaer, Kristof Demeestere, Philippe M. Heynderickx, Herman Van Langenhove, Jo Dewulf*

Research Group EnVOC, Department of Sustainable Organic Chemistry and Technology, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, B-9000 Ghent, Belgium

ARTICLE INFO

Article history:
Received 31 August 2010
Received in revised form 20 October 2010
Accepted 21 October 2010
Available online 10 November 2010

Keywords:
Heterogeneous photocatalysis
Photolysis
Adsorption
Moxifloxacin
Ciprofloxacin

ABSTRACT

UV-A (485 μW cm^{-2}) and UV-C (389 μW cm^{-2}) induced photolysis and TiO_2-P25 mediated heterogeneous photocatalysis are investigated as advanced oxidation technologies for the removal of fluoroquinolone (FQ) antibiotics ciprofloxacin (CIP) and moxifloxacin (MOX) in aqueous solution. Experiments performed in a thermostated (298 K) lab scale batch reactor show that pH is of main importance for FQ degradation kinetics with both processes. Whereas apparent first-order kinetics of UV-A photolysis were slow for both FQs in the entire investigated pH range ($k_{1,CIP} \leq 0.015$ min^{-1}; $k_{1,MOX} \leq 0.006$ min^{-1} at $3 \leq pH \leq 10$), UV-C photolysis was faster with maximum k-values obtained at pH 7 and pH 10 for CIP ($k_{1,CIP} = 0.072$ min^{-1}) and MOX ($k_{1,MOX} = 0.058$ min^{-1}), respectively. The highest removal rates, however, are obtained at pH 7 in the presence of TiO_2 (0.5 g L^{-1}) as a photocatalyst ($k_{1,CIP,UV\text{-}A} = 0.137$ min^{-1}, $k_{1,CIP,UV\text{-}C} = 0.163$ min^{-1}; $k_{1,MOX,UV\text{-}A} = 0.227$ min^{-1}; $k_{1,MOX,UV\text{-}C} = 0.236$ min^{-1}). Both the difference in reaction kinetics between photolysis and heterogeneous photocatalysis and the observed pH dependency indicate that surface reactions are of main importance during TiO_2/UV photocatalysis. A positive relationship is noticed between the photocatalytic FQ degradation rate and the fraction of FQ adsorbed onto the catalyst surface, with the latter being strongly pH dependent. Adsorption experiments reveal that FQ adsorption is favoured at neutral pH. Explanations are proposed based on the amphoteric nature of the FQ molecules and the pH dependent catalyst surface charge. Based on reported pK_a values and experimental adsorption data, partition ratios are calculated for the different FQ species. These indicate that mainly the single positively charged and zwitter FQ ion participate in the adsorption process, explaining the highest photocatalytic degradation at pH 7.

1. Introduction

Fluoroquinolones (FQ) are a family of synthetic, broad-spectrum antibacterial compounds, used in a variety of human and veterinary applications. They have gained substantial popularity since their introduction in the 1980s. Within Europe, the most widely prescribed quinolone antibiotic is ciprofloxacin (CIP), see Fig. 1A, a second generation FQ. CIP is used for complicated urinary tract infections, sexually transmitted diseases and skin infections. The search for newer quinolones resulted in a third generation FQs. The use of this newer generation FQs, e.g., moxifloxacin (MOX) see Fig. 1B, is increasing due to an expanded antibacterial spectrum which makes them useful in a broader range of applications, e.g. acute sinusitis and community-acquired pneumonia in the case of MOX [1]. In Europe, the average defined daily dose (DDD)/1000 inhabitants/day of outpatient and hospital MOX use increased from 0.05 to 0.14 and 0.001 to 0.015, respectively, over a time span 2001–2007 [2].

Most of the FQs are not fully metabolized in the body and are partially excreted in its pharmaceutically active form (>50%) and in a lesser extent as Phase I (addition of reactive functional groups through oxidation, reduction or hydrolysis) or Phase II metabolites (covalent conjugation to polar molecules, e.g., glucuronic acid, sulfate, acetic acid or amino acid) [3,4]. Due to the limited biodegradability and widespread use of these antibiotics, an incomplete removal is attained in conventional wastewater treatment plants and relative large quantities are released into the environment. As a result, numerous antibiotics can be found in surface waters causing adverse effects on aquatic organisms [5,6]. The

Abbreviations: AOP, advanced oxidation process; CIP, ciprofloxacin; CB, conduction band; DDD, defined daily dose; ESAC, European Surveillance of Antimicrobial Consumption; HPLC, high pressure liquid chromatography; ISC, inter system crossing; FQ, fluoroquinolone; MOX, moxifloxacin; ODR, orthogonal distance regression; PDA, photodiode array detector; PZC, point of zero charge; ROS, reactive oxygen species; RSSQ, residual sum of squares; VB, valence band; VDW, van der Waals.

* Corresponding author. Tel.: +32 9 264 59 49; fax: +32 9 264 62 43.
E-mail address: Jo.Dewulf@UGent.be (J. Dewulf).

0926-3373/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcatb.2010.10.027

Nomenclature

Roman symbols

A	component A
C	concentration (mol L^{-1} or m kg_{cat}^{-1})
C_0	initial concentration (mol L^{-1})
K	partition ratio (L kg_{cat}^{-1})
K'	partition ratio (mol mol^{-1})
k_1	apparent first-order degradation rate constant (min^{-1})
L_l	left hand side Eq. (6) and (S-33)
m_{cat}	catalyst mass (kg_{cat})
n	number of observations
n_{rep}	number of repetitions
n_{resp}	number of responses
R_l	right hand side of Eq. (6) and (S-33)
S	adsorbed fraction (mol mol^{-1})
S^*	objective function
V	liquid reactor volume (L)
w_l	weight factor for experiment l

Greek symbols

$\gamma_{i,j}$	$10^{pH_i - pK_{aj}}$
φ	index in Eq. (4)
$\rho_{i,j}$	correlation between parameter i and j

Subscripts

ad	adsorbed
aq	aqueous
i	pH level i
j	index number of pK_a values
l	index in Eq. (7) and (S-34)
q	index in Eq. (4)

Superscripts

+	positively charged
−	negatively charged
z	zwitter ion
0	zwitter/non-charged molecule

concern is not as much the acute effects of these FQs but rather the long-term chronic effects of low concentrations in surface waters. The presence of these concentrations may induce selective pressure in microbial populations leading to quinolone resistant pathogens [7,8] and/or chronic toxicity on aquatic organisms, although experimental data on this latter phenomenon are still lacking [9].

To prevent these adverse effects, physical chemical technologies are needed for degradation prior to discharge in the environment. Recently, the degradation of CIP has been investigated using advanced oxidation processes (AOPs) like ozonation, sonification, photolysis and heterogeneous photocatalysis [10–14]. Especially the interest in the degradation pathays of FQs has increased over the last few years [15,16]. To the author's knowledge, however, there is no data available on the AOP based degradation of the third generation fluoroquinolone MOX.

In this paper, the effect of pH and irradiation conditions on the photolytic and TiO_2 mediated photocatalytic removal kinetics of both CIP and MOX in aqueous solutions are studied. The degradation of CIP is used as a benchmark for the results obtained with MOX. In heterogeneous photocatalysis, adsorption is a key step in the degradation mechanism, but quantitative data on the adsorption process and partition ratios are lacking for CIP and MOX. Therefore, the relationship between adsorption on the catalyst surface and the degradation rate is investigated in more detail by quantifying partition ratios for the different CIP and MOX species.

Table 1
Experimental conditions during the photolytic and photocatalytic experiments.

Process variable	Unit	Value
Component	–	MOX or CIP
Initial concentration	μM	37.4 or 45.3
Temperature	K	298
pH	–	3, 7 or 10
Total reaction solution volume	mL	200
Catalyst concentration	g L^{-1}	0.5
Oxygen flow	mL min^{-1}	60
Buffer concentration	mM	10
Light intensity UV-C at 3 cm[a]	μW cm^{-2}	389
Light intensity UV-A at 3 cm[a]	μW cm^{-2}	485

[a] Distance measured from light source.

2. Procedures

2.1. Photolytic and photocatalytic degradation

2.1.1. Chemicals and set-up

Ciprofloxacin·HCl (99.5%) is purchased from MP Biomedicals Inc. and moxifloxacin·HCl (BAY12-80369) is provided by the Bayer corporation (Berlin). KH_2PO_4 (Sigma–Aldrich, 99%), K_3PO_4 (Sigma–Aldrich,≥98%), NaOH (Acros), K_2HPO_4 (Acros,≥98%) and concentrated H_3PO_4 (Merck, 85%) are used for pH adjustment. All stock and buffer solutions are prepared with deionized water. As a photocatalyst, commercial Aeroxide TiO_2-P25 (BET specific surface area = 50 ± 15 m^2 g^{-1}, 80% anatase, 20% rutile, average primary particle size = 21 nm) is used.

Photolytic and photocatalytic experiments are performed in a lab scale batch reactor (Fig. 2). An overview of the experimental conditions is listed in Table 1. A glass reactor is kept at a constant reaction temperature of 298 ± 1 K by immersing the reactor in a thermostated water bath. UV-A (485 μW cm^{-2}, 300–440 nm with main peak at 365 nm) and UV-C (389 μW cm^{-2}, main peak at 254 nm and four minor peaks around 400 nm) pen rays are used as a light source in the photolytic and photocatalytic experiments. The first is provided by UVP (United Kingdom), the latter by Ningbo Sunfine UV Lighting Co. (China). Reaction solutions are prepared by

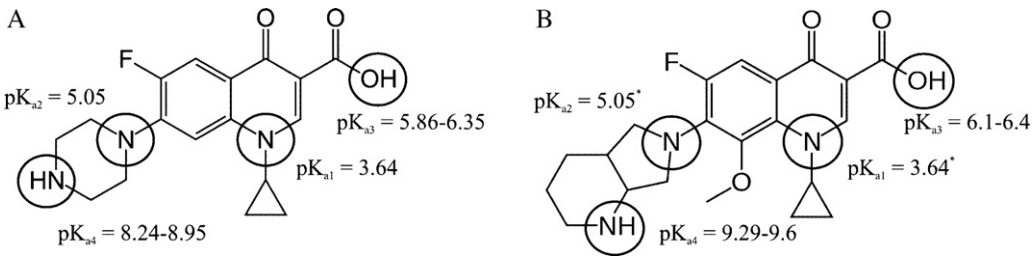

Fig. 1. Molecular structure of (A) CIP and (B) MOX with range of pK_a values [25,28,47–50]. The pK_a values marked with '*' are not yet mentioned in literature, but are assumed to be equal to CIP pK_a values due to a similar structure.