



## Heterogeneous photocatalysis of moxifloxacin in hospital effluent: Effect of selected matrix constituents



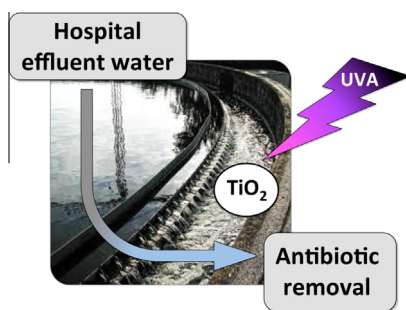
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### HIGHLIGHTS

- MOX photocatalysis is 2 times slower in hospital effluent than in demineralized water.
- The effect of selected inorganic and organic matrix constituents is investigated.
- Inorganics inhibit MOX adsorption and to a lesser extent its degradation rate.
- Organics enhance moxifloxacin adsorption but inhibit its photocatalytic degradation.
- (In)organics at effluent levels explain 70% of the drop in effluent degradation rate.

### GRAPHICAL ABSTRACT



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### ABSTRACT

TiO<sub>2</sub> mediated photocatalysis of the fluoroquinolone antibiotic moxifloxacin in hospital effluent water is found to be two times slower than in demineralized water. Since little knowledge exists regarding how different types of effluent matrix components affect heterogeneous photocatalytic processes, this paper investigates in a systematic and quantitative way the effect of suspended particulate matter and selected inorganic and organic matrix constituents on both the adsorption–desorption equilibrium and initial photocatalytic degradation rate of moxifloxacin in water. Regarding adsorption, the most pronounced effect is observed when inorganics, i.e. chloride anions and inorganic carbon, are added into demineralized water (reference matrix), hereby decreasing moxifloxacin adsorption by a factor of three at 600 mg Cl<sup>-</sup> L<sup>-1</sup>. Organic constituents like humic and fulvic acid and bovine serum albumin favor moxifloxacin adsorption (by a factor of 1.6 at 15 mg C L<sup>-1</sup> TOC), which might be explained by the formation of TiO<sub>2</sub>–organic matter complexes. Despite this opposite effect in adsorption, both inorganics and organics cause a drop in photocatalytic degradation rate, with the highest effect observed for humic and fulvic acid (factor of 1.3–1.4; TOC = 15 mg C L<sup>-1</sup>). This is most probably because of scavenging of, or limited accessibility to reactive species and/or light shielding. Overall, at relevant concentrations, a mixture of the investigated matrix constituents can explain about 70% of the inhibitory effect that hospital effluent causes on the moxifloxacin degradation, showing their high relevance for photocatalytic treatment of real water matrices.

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**Abbreviations:** AOP, advanced oxidation process; AOX, adsorbable organohalogen; BSA, bovine serum albumin; COD, chemical oxygen demand; DOM, dissolved organic matter; F, filtered; FA, fulvic acid; FQ, fluoroquinolone; HA, humic acid; HPLC, high performance liquid chromatography; IC, inorganic carbon; K<sub>d</sub>, adsorption coefficient; kDa, kiloDalton; MOX, moxifloxacin; NF, not filtered; NOM, natural organic matter; PDA, photo diode array; SPM, suspended particulate matter; SRNOM, Suwannee river NOM; TOC, total organic carbon; WWTP, wastewater treatment plant.

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## 1. Introduction

Antibiotics are an important group of pharmaceuticals and are frequently detected in wastewater treatment plant (WWTP) and hospital effluent waters around the world, with concentrations ranging from  $\text{ng L}^{-1}$  up to  $\mu\text{g L}^{-1}$  [1,2]. An important subgroup of the antibiotics are the fluoroquinolones (FQ). They are a synthetic group of broad-spectrum antimicrobial agents with an increasing consumption rate, especially for the third generation FQs such as moxifloxacin (MOX) [3]. Low removal efficiencies (50–80%) by conventional WWTPs result in a continuous discharge of these compounds into the natural environment. As a result, fluoroquinolone antibiotics have been detected in European, American and Asian surface waters [4]. To degrade these micropollutants, physico-chemical treatment techniques like advanced oxidation processes (AOPs) are needed [5–7]. AOPs are by definition processes that generate reactive hydroxyl radicals at ambient conditions and are studied as an application to degrade organic micropollutants in wastewater [8,9]. Full mineralization is not the aim of an AOP treatment since it is not cost-effective [10]. The focus is more on the partial degradation of recalcitrant pollutants to deactivate their biological activity, decrease toxicity or increase the biodegradability [11,12]. Commonly used AOPs for antibiotic removal from wastewater are ozonation, sonolysis, (photo)-Fenton and heterogeneous photocatalysis, among others [9,13–16].

Current research on photocatalytic water treatment for antibiotic removal is mostly performed in demineralized water matrices and focuses mainly on reactor optimization, reaction kinetics and degradation product identification [9]. To evaluate the applicability of a photocatalytic treatment technique, research in real effluent matrices is necessary. A transition from synthetic matrices towards applications in effluent waters is ongoing [9,17–21]. Still, it is difficult, however, to fully understand and quantify the effect of an effluent matrix on a photocatalytic process, since little studies so far investigated photocatalytic antibiotic removal in both effluent and demineralized water in the same experimental setup. Next to that, no specific research is performed to clarify how and to what extent different types of effluent matrix components affect the different steps of a heterogeneous photocatalysis process.

Therefore, in this manuscript, the effect of selected inorganic and organic effluent water constituents on both the adsorption and photocatalytic degradation of MOX is investigated in a systematic approach. Focus is put on suspended particulate matter, chloride anions and inorganic carbon (IC), and different types of dissolved organic matter (DOM). Adsorption–desorption equilibria and initial degradation rates in (un)filtered hospital effluent waters and in demineralized water enriched with different amounts of the selected matrix compounds are determined. In a last part, it is estimated to what extent the combined effect of the studied matrix constituents can explain the observed difference between photocatalytic removal in demineralized and hospital effluent water.

## 2. Materials and methods

### 2.1. Chemicals

Moxifloxacin (MOX, moxifloxacin-HCl, BAY12-80369) is provided by Bayer, Berlin. A phosphate buffer is prepared using  $\text{KH}_2\text{PO}_4$  (Sigma Aldrich, 99%) and  $\text{K}_2\text{HPO}_4$  (Acros,  $\geq 98\%$ ). NaOH (Acros, extra pure) and HCl (Fiers, 37%) are used for pH adjustment of the reaction solutions. All stock and buffer solutions are prepared with demineralized water and reagents are used as received without any purification.

As a photocatalyst, commercial Degussa P25  $\text{TiO}_2$  is used with a BET specific surface area of  $48.3 \pm 0.7 \text{ m}^2 \text{ g}^{-1}$  (TRISTAR

Micromeritics),  $86.7 \pm 0.6\%$  of anatase, and primary anatase and rutile particle sizes of  $18.7 \pm 0.1 \text{ nm}$  and  $23.3 \pm 1.2 \text{ nm}$ , respectively (Siemens D5000 scintillation counter,  $\theta = 0.02^\circ$ ) [22].

Chloride and bicarbonate anions are added to the reaction solution using NaCl (Sigma Aldrich,  $> 99.5\%$ ) and  $\text{NaHCO}_3$  (Chem-Lab, 99–100.5%). Humic acid sodium salt (HA), bovine serum albumin (BSA), alginic acid sodium salt, Suwannee River Fulvic Acid Standard I (FA) and Suwannee River NOM (SRNOM) are provided by Sigma Aldrich and International Humic substances Society, USA.

Hospital effluent water has been sampled at the settling tank effluent side of the WWTP of the Maria Middelaes hospital (Ghent, Belgium). Grab samples were collected in amber glass bottles and stored in the dark at  $4^\circ\text{C}$  for maximum 48 h without acidification. The Maria Middelaes hospital uses a biologic wastewater treatment plant consisting of two activated sludge reservoirs of  $201 \text{ m}^3$  with a total effluent flow of  $250 \text{ m}^3$  per day. Effluent characteristics and company specific discharge levels are presented in Table S-1.

### 2.2. Photocatalytic degradation experiments setup

The photocatalytic degradation of MOX is performed in a batch reactor of 300 mL (Fig. S-1). The reactor is kept at a constant temperature of  $298 \pm 1 \text{ K}$  using a thermostated water bath. A UVA ( $4.0 \text{ mW cm}^{-2}$ , 300–440 nm with main peak at 365 nm) pen ray is used as a light source and positioned axially in the reactor (UVP, United Kingdom). A more detailed description on the reactor setup and experimental procedure is given in previous published work [23].

Each photocatalytic degradation experiment consisted of two phases: (i) dark adsorption of MOX and/or matrix constituents on the catalyst surface, and (ii) photocatalytic degradation after switching on the UV light. The amount of MOX adsorption is expressed by an adsorption coefficient  $K_d$  ( $\text{L kg}^{-1}$ ) by measuring the liquid phase MOX concentration initially added in the reactor solution and that after adsorption–desorption equilibrium. The photocatalytic degradation is expressed as the initial degradation rate,  $r_0$  ( $\mu\text{mol}_{\text{MOX}} \text{ L}^{-1} \text{ min}^{-1}$ ), calculated according to previous published work [24].

Reaction solutions are spiked to an initial MOX concentration ( $C_{0,\text{MOX}}$ ) of  $37.4 \mu\text{M}$  before catalyst addition and buffered using a phosphate buffer (10 mM). Effluent water is not buffered due to the formation of precipitates, but is brought to pH 7 using NaOH or HCl. The catalyst is added ( $C_{\text{cat}}: 1.0 \text{ g L}^{-1}$ ) and the solution is stirred (13.2 rps) under complete darkness for 30 min during experiments in demineralized water; for four hours when demineralized water spiked with in/organic constituents is used; and for eight hours in the experiments performed with (un)filtered hospital effluent, to attain adsorption–desorption equilibrium.

During irradiation, the solution is continuously stirred and sparged with dry air at a flow of  $60 \text{ ml min}^{-1}$  ( $20 \pm 1\% \text{ O}_2$ , Air Liquide, Belgium). Aliquots of 2 mL are collected with a spinal needle syringe at time intervals of 2 min and filtered over a Whatman  $0.2 \mu\text{m}$  Spartan mini disk filter to remove the residual  $\text{TiO}_2$  before analysis. Extra pH adjustments to pH 7 were performed in the hospital effluent during sampling.

Preliminary photolytic MOX experiments in both demineralized and effluent water showed no significant ( $p > 0.05$ ) degradation in the time interval (0–14 min) during which photocatalytic degradation is performed in this study.

### 2.3. Analytical methods

MOX is analyzed using high performance liquid chromatography (HPLC) coupled to a photodiode array detector (PDA, Surveyor, Thermo Scientific, USA). A Luna C18(2) column

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