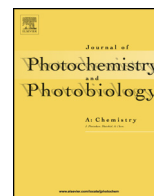




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## Sunlight photodegradation of marbofloxacin and enrofloxacin adsorbed on clay minerals



Michela Sturini<sup>a,\*</sup>, Andrea Speltini<sup>a</sup>, Federica Maraschi<sup>a</sup>, Elisa Rivagli<sup>a</sup>, Luca Pretali<sup>b</sup>, Lorenzo Malvasi<sup>a</sup>, Antonella Profumo<sup>a</sup>, Elisa Fasani<sup>a</sup>, Angelo Albini<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Pavia, via Taramelli 12, Pavia 27100, Italy

<sup>b</sup> Parco Tecnologico Padano, via Albert Einstein, Lodi 26900, Italy

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### ABSTRACT

Fluoroquinolone antibiotics (FQs) are important “emerging” micropollutants, and their environmental diffusion is an issue of great concern. In this study, the photochemical degradation of marbofloxacin (MAR) and enrofloxacin (ENR) adsorbed on montmorillonite (MMT) and kaolinite (KAO) clays was investigated. Being FQs photosensitive molecules, the sunlight-induced degradation of clay-adsorbed FQs and of their photoproducts was monitored as function of irradiation time. The photoproducts were identified by high performance liquid chromatography electrospray tandem mass spectrometry (HPLC-ESI-MS/MS) and the photochemical pathways have been elucidated. X-ray diffraction (XRD) has been employed to deeply study the solid-state photodegradation process of MAR and ENR on MMT. Interestingly, the XRD results clearly evidenced a significative variation of the interlayer spacing of MMT not only as function of FQs adsorbed amounts, but also in relationship with their photodegradation, not investigated by means of XRD as yet. The results confirmed that FQs adsorption is a bulk phenomenon that occurs in the interlayer spacing of the MMT structure; moreover, it was proved that sunlight largely degraded the adsorbed FQs, both on the external surface and in the interlayer spacing.

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### 1. Introduction

The widespread of pharmaceuticals in the environment and their fate, effects and threats associated to their occurrence are matter of great concern. Among these drugs, fluoroquinolones (FQs) are an important class of “emerging” micropollutants [1–5].

In view of their broad activity spectrum against Gram bacteria and their good oral intake, FQs are the fourth largest class of human antibiotics and they are widely administrated also to animals for therapeutic purposes, and as feed additives to support growth in livestock [6]. Once administrated, FQs are metabolized to a minor extent and a large part of the unmodified initial dose reaches urban sewage treatment plants (STPs) that are not able to quantitatively remove such complex molecules [7,8]. This causes a continuous release of FQs in surface water overcoming their transformation and removal rates. These drugs rapidly move from water bodies to the soil compartment. Additionally, veterinary antibacterials can directly reach soil and groundwater through the common practice of recycling manure from animal husbandry and/or sewage sludge

from STPs as fertilizers. Indeed FQs have been detected up to few micrograms per kilogram also in soil and sediment [9] due to their strong binding to natural organic matter and minerals, with the high distribution coefficients observed in loamy matrices [10]. Recent studies have attributed to FQs ecotoxicity and genotoxicity against *Vibrio Fischeri*, *Daphnia Magna* and *Pseudomonas Putida* [11–13]. Furthermore, FQ residuals are able to induce environmental bacterial resistance [14,15].

Although photochemistry represents a natural removal pathway for these antimicrobials from the environment [1–3,5], on the other hand the photochemical processes involve the release of significant amounts of photoproducts that contribute to the overall environmental impact of the parent compounds [16,17]. Indeed, it was proved that FQ photoproducts maintain significant antibiotic activity [4].

Montmorillonite (MMT) and kaolinite (KAO) clays are natural constituents of soils and, due to their high surface area, have been recently proposed for adsorption of 4-chlorophenol and 2,4,6-trichloroaniline [18], tetracycline antibiotics [19], diphenhydramine [20], polychlorinated biphenyl and other organic pollutants [21,22]. With regard to FQs, recent studies have investigated the mechanistic interactions of ciprofloxacin onto MMT [23] and KAO [24], and those of ENR on smectite clays [25].

\* Corresponding author. Tel.: +39 0382 987347; fax: +39 0382 528544.

E-mail address: [michela.sturini@unipv.it](mailto:michela.sturini@unipv.it) (M. Sturini).

In this paper we report the solid-state photochemical degradation of two largely employed FQs, marbofloxacin (MAR) and enrofloxacin (ENR), adsorbed on MMT and KAO clays. MAR and ENR were chosen as probe molecules because largely used in cattle and swine farms in the South Lombardy plain (Italy) and as a result directly released in ditches and rivers by farms wastewaters [26]. Moreover, they present different photochemical behavior both in water and soil [2,3]. Batch sorption experiments were carried out in water at the milligrams per litre levels, and the adsorption capacities were calculated by sorption isotherms, described by the Langmuir model. Then clay samples were fortified with the two drugs and irradiated under natural sunlight. The decay profiles over irradiation time were traced and the main photodegradation pathways were proposed on the basis of the FQs photoproducts identified by HPLC-ESI-MS/MS. The solar light-induced degradation of MMT-adsorbed FQs was also studied by X-ray diffraction (XRD). The variation of the MMT interlayer spacing was investigated before and after irradiation.

## 2. Experimental

### 2.1. Reagents and materials

Ca-MMT STx-1 was acquired from the Clay Mineral Society and KAO was distributed as an international standard by the Ceramic Society of Slovakia (Zettlitz). These materials were used as received, with no further purification, so their physical-chemical properties are the ones reported in literature [27–29].

All the chemicals employed were reagent grade or higher in quality. MAR and ENR, in the injectable form, were purchased from Bayer (Baytril 25 mg mL<sup>-1</sup>) and Vétoquinol (Marbocyl 20 mg mL<sup>-1</sup>), respectively. HPLC gradient grade acetonitrile (ACN) was from VWR. H<sub>3</sub>PO<sub>4</sub> (85%, w/w) and NH<sub>3</sub> solution (30%, w/w) were purchased from Carlo Erba Reagents; HCOOH (98–100%, w/w) was from Merck. Hexahydrate Mg(NO<sub>3</sub>)<sub>2</sub> (97%, w/w) was from Sigma-Aldrich.

Ultra-pure water (resistivity 18.2 MΩ cm<sup>-1</sup> at 25 °C) was produced by a Millipore (Milan, Italy) Milli-Q system. FQs stock solutions were prepared and stored in the dark at 4 °C for a maximum of three months. Working solutions were renewed weekly.

### 2.2. Adsorption experiments

FQs adsorption experiments, performed in triplicate by a batch equilibration method [30], were carried out in distilled water with initial FQs concentrations ranging from 25 to 2000 mg L<sup>-1</sup>.

### 2.3. Sample preparation

For irradiation experiments, 0.5 g of clays were fortified with MAR and ENR at concentrations in the range 15–77 mg g<sup>-1</sup> of each drug, according to the batch procedure described in Ref. [30]. After equilibration and filtration, the remaining pastes were dried at 50 °C and homogeneously dispersed on glass Petri capsulae (Ø 8.5 cm, depth 2 cm) to obtain a monolayer (thickness below 1–2 mm). Afterwards, samples were exposed to natural sunlight (9.00 am–5.00 pm) during the summer (June–September), at temperatures ranging from 25 to 35 °C. The solar power ranged from 170 to 470 W m<sup>-2</sup> (in the visible range) and from 8 to 30 W m<sup>-2</sup> (in the UV), respectively. The flux was measured by means of a HD 9221 (Delta OHM) (450–950 nm) and of Multimater (CO.FO.ME.GRA) (295–400 nm) radiometers. At regular intervals, each one of the irradiated samples was extracted by microwave-assisted extraction (MAE) according to a green method [31] selective for FQs. All experiments were performed in triplicate. The

extracts were analyzed by HPLC–UV for tracing degradation decays, and by HPLC–ESI–MS/MS for photoproducts identification.

For XRD analyses, MMT samples (0.3 g) were enriched at different concentrations of MAR and ENR ranging from 15 to 100% of their maximum adsorption capacity (see Table S1). After 24 h equilibration, the suspensions were filtered and the remaining pastes were dried at 50 °C. All the samples were measured by means of high-resolution XRD, before and after irradiation.

### 2.4. Analytical determinations

The HPLC-ESI-MS/MS analyses were performed by using an Agilent 1100 HPLC with a Luna C18 (150 × 4.6 mm, 5 μm) column, maintained at 30 °C. The mobile phase was HCOOH 0.5% v/v in ultrapure water-ACN (85:15). The flow rate was 1.2 mL min<sup>-1</sup> and the injection volume was 5 μL. The MS/MS-system consisted of a linear trap Thermo LXQ. ESI experiments were carried out in positive-ion mode under the following constant instrumental conditions: source voltage 4.5 kV, capillary voltage 20 V, capillary temperature 275 °C and normalized-collision energy 35.

The HPLC–UV system consisted of a PU-1580 pump (JASCO) equipped with a programmable UV-1575 UV-vis detector (JASCO). The detection wavelength was 275 nm. 20 μL of each sample were injected into a 150 × 4.6 mm, 5 μm Symmetry Column (Waters) coupled with a similar guard-column. The mobile phase was water (pH adjusted to 2.5 with 37% HCl)-ACN (90:10), at a flow rate of 1.2 mL min<sup>-1</sup>.

## 3. Results and discussion

### 3.1. Adsorption experiments

The adsorption isotherms were determined both to confirm the adsorption capacity of the two clays and to better evaluate FQs concentrations to be considered for the irradiation experiments.

The adsorption profiles of MAR and ENR on MMT and KAO are reported in Fig. 1. It can be seen that MAR and ENR adsorption curves show a similar trend, but the FQs observed adsorption capacities on MMT are higher than those found on KAO, due to the higher surface area of the former (84 m<sup>2</sup> g<sup>-1</sup> for MMT and 10 m<sup>2</sup> g<sup>-1</sup> for KAO) and due to its interlayer spacing. These results are reported in Table S1 and are comparable with those found in a previous investigation [30].

Langmuir and Freundlich models were used to fit experimental data, according to the Eqs. (1) and (2), respectively:

$$q_e = \left[ \frac{K_L C_e}{1 + K_L C_e} \right] q_m \quad (1)$$

$$q_e = K_f C_e^n \quad (2)$$

$q_e$  is the amount of the adsorbed antibiotic at the equilibrium and  $C_e$  is the equilibrium antibiotic concentration.  $K_L$  is the Langmuir constant and  $q_m$  represents the total number of sorption sites (Eq. (1));  $K_f$  is the Freundlich adsorption constant and  $n$  is the Freundlich exponent (Eq. (2)).

The isotherm parameters were obtained by a dedicated software (Origin<sup>®</sup>). The calculated Langmuir and Freundlich adsorption constants are listed in Table S1.

The correlation coefficients ( $R^2$ ) and chi-square ( $\chi^2$ ) showed that the Langmuir model (Eq. (1)) better fitted the experimental points than the Freundlich model (Eq. (2)) in all cases. The higher values of correlation coefficient ( $R^2$ ), as well as the lower standard deviations of Langmuir parameters compared to those obtained for the Freundlich model, indicated that the adsorption of the two drugs occurs through a monolayer coverage [30,32].

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