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Clay minerals for adsorption of veterinary FQs: Behavior and modeling☆

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ABSTRACT

The adsorption of two veterinary fluoroquinolones, Enrofloxacin (ENR) and, for the first time, Marbofloxacin (MAR), was investigated on kaolinite and montmorillonite clays with the aim of evaluating the efficiency of these adsorbents in removing pharmaceuticals from soils and waters. Experiments were carried out at two different pHs in tap water and aqueous salt solution. Adsorption isotherms show that these drugs were adsorbed in remarkable amounts by the three materials examined (STx-1, SWy-1, kaolinite) with different mechanisms, as confirmed by XRD (X-ray diffraction) analysis. Different thermodynamic models have been applied and the best fit was obtained by means of Langmuir interactions models. In order to remove FQs from contaminated wastewaters, the three clays were contacted with water samples collected from ditches near cattle and swine farms obtaining a quantitative removal. The results proved that such minerals are suitable for the remediation of environmental matrices.

Introduction

Marbofloxacin (MAR) and Enrofloxacin (ENR) are two synthetic antibiotics largely employed in cattle and swine farms near Pavia, in northern Italy. They belong to the class of fluoroquinolones (FQs), which are among the most important antibacterial agents used both in human and in veterinary medicine. After intake, they are not completely metabolized [1] and, moreover, they are only partially removed by wastewater/sewage treatment plants (WWTPs) [2,3], therefore they are found in surface waters. The common practice of recycling manure from animal husbandries and sewage sludge from WWTPs as fertilizers favors the accumulation of these antimicrobials in soils where FQs can be present at concentrations in the range of micrograms per kilogram and in some cases up to about 10 mg kg^{-1} [4,5], mainly adsorbed on clay minerals and humic substances [6]. The presence of FQs in the environment may pose serious threats to the ecosystem and human health. Indeed, a matter of concern is their ability to stimulate bacterial resistance [7], which makes natural-contaminated soils a terrain of resistant bacteria potentially transferable to other bacteria living in groundwater, drinking water or plants and finally to humans [7–9]. In addition, the formation of pharmacologically active photoproducts is another issue of great concern in the context of the overall environmental impact [9,10], although photodegradation represents the major natural FQs depollution pathway both in water and soil systems [5,11]. Developing more efficient methods to remove such recalcitrant pollutants from contaminated waters is thus an urgent task and new proposals must be sustainable and cost-effective. Advanced Oxidation Processes (AOPs) have been proposed for removing pharmaceuticals, including FQs and their photoproducts from wastewaters, though little information is available regarding their effectiveness and at any rate result to be expensive and not fully environmental friendly [12–18]. Adsorption processes employing metal and metal oxide nanomaterials, dendrimers, carbon nanomaterials and polymer nanocomposites have been considered as well for the environmental remediation of various organic pollutants, not for FQs [19]. In this work veterinary FQs remediation through clay minerals was explored because of the low cost, high surface area, high porosity and abundance of these adsorbents.

FQs, consisting of a quinolonic nucleous bearing a carboxyl and a piperazinyl amine group, can exist as cationic, zwitterionic, and anionic species depending on pH conditions [20,21]. Such chemical properties make them prone to be strongly adsorbed on sediments

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and soils, mainly due to cation bridging, electrostatic and hydrogen bond interactions with clay minerals, with enlarged adsorption coefficients ($K_{d,\ solid}$) by increasing the cation exchange capacity (CEC) of the matrix [22].

In the last years several papers focusing on the mechanistic aspects of the adsorption on clay minerals of the most employed FQ in human medicine ciprofloxacin [6,23–30], norfloxacin [31] and ENR [6,32,33] have been published. Although the adsorption behavior is expected to show a general trend for the different FQs, due to their similar structure [22], intermolecular interactions with the clay minerals sites would be influenced by substituent groups present on the peculiar FQ ring and matrix composition.

In this work, the adsorption behavior of MAR and ENR was studied on the two most common clay minerals present in soil and sediment, kaolinite and montmorillonite, at two different pH conditions, both in tap water and 0.01 M $CaCl_2$.

A thermodynamic modeling of the interactions between FQs and clay minerals, covering the whole range of concentrations tested, was carried out by using different thermodynamic models, such as Freundlich, Langmuir, sigmoidal and combined models (Dual Langmuir and Dual Mode Model).

To elucidate the intermolecular interaction between the FQ molecule and clay minerals, XRD analysis were performed on montmorillonite where contrary to kaolinite [6,29], intercalation or ion exchange in the interlayer space is expected after adsorption of the selected antibiotics.

Finally, the application of these minerals in removing traces FQs from wastewater was tested on samples collected from ditches near cattle and swine farms.

Experimental

Materials and reagents

Ca-montmorillonite STx-1, Na-montmorillonite SWy-1 were acquired from the Clay Mineral Society, and kaolinite was distributed as an international standard by the Ceramic Society of Slovakia (Zettlitz). These materials were used as received, without further purification, so the physical–chemical properties of these samples are the ones reported in literature [34–36].

All the chemicals employed were reagent grade or higher in quality and were used without any further purification. $CaCl_2$ (93%, w/w) was supplied by Fluka (Sigma–Aldrich, Milan, Italy); MAR and ENR, in the injectable form, were purchased from Bayer (Baytril 25 mg mL^{-1}) and Vétoquinol (Marbocyl 20 mg mL^{-1}), respectively. The dissociation constants pK_{a1} and pK_{a2} [37] and the molecular dimensions, calculated by Gaussian and optimized with the semi-empirical method PM3, are listed in Table 1. Ultra-pure water (resistivity 18.2 $M\Omega\ cm^{-1}$ at 25 °C) was produced in laboratory by means of 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.

Batch experiments

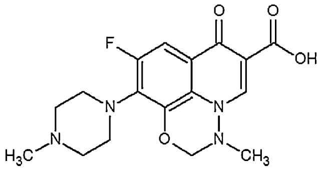
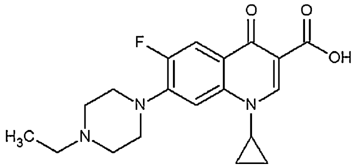
FQ adsorption on clay minerals was studied using a batch equilibration method. Batch adsorption experiments were performed in tap water and in the presence of 0.01 M $CaCl_2$ as suggested by OECD Test Guideline [38]. All the laboratory operations were conducted under red light.

Series of MAR and ENR solutions were prepared with initial concentrations (C_0) ranging from 10 to 1600 mg L^{-1} and from 10 to 1500 mg L^{-1}, respectively.

50 mg clay minerals were weighed into 50 mL polypropylene centrifuge tubes, mixed with 10 mL of FQ solutions, pH values were adjusted to 2 and 7.5 with 1 M HCl or 1 M NaOH and monitored every 2 h until stabilized at the desired value. From the adsorption kinetics of the diluted antibiotic solutions, calculated by determining the concentrations of the solution at different contact times, it can be seen that equilibrium was reached after 10 min (data not shown). Nevertheless, when the batch adsorption experiments were performed, a contact time of 24 h, longer than the equilibration time, was employed in order to guarantee that system reaches the equilibrium state. Therefore, the tubes, wrapped with aluminum foils to prevent FQ light-induced decomposition, were shaken at 150 rpm for 24 h at room temperature (20 ± 1 °C).

The suspensions were filtered through a 0.22 μm membrane filter for analysis. The equilibrium MAR and ENR concentrations (C_w) in the filtered solutions were measured by a UVmini-1240 UV-vis spectrophotometer (Shimadzu Corporation) at the wavelengths of 290 and 270 nm, respectively. Calibrations with four standards at concentrations between 0 and 11 mg L^{-1} yielded optimal linearity ($R^2 > 0.99$). The detection and quantification limits for MAR were 0.1 and 0.37 mg L^{-1}, while for ENR were 0.2 and 0.47 mg L^{-1}. The MAR and ENR adsorbed amounts (C_s) were calculated from the difference between C_0 and C_w. All experiments were performed in triplicate with good reproducibility (RSD < 10%). Control experiments, consisting of each FQ solution without clay minerals, were also performed. No changes in FQ concentrations were detected in the control samples.

Table 1
MAR and ENR dissociation constants and molecular dimensions.

Antibiotic	Lenght (Å)	Height (Å)	pK_{a1}	pK_{a2}
Marbofloxacin  	13.36	7.61	5.51–5.69	8.02–8.38
Enrofloxacin  	14.1	7.58	6.27	8.3