Competitive adsorption/desorption of tetracycline, oxytetracycline and chlortetracycline on two acid soils: Stirred flow chamber experiments

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H I G H L I G H T S

- Competitive adsorption of tetracyclines was compared previous non-competitive trials.
- Competitive desorption of the antibiotics was compared previous non-competitive trials.
- Hysteresis has affected adsorption/desorption processes.
- The SFC technique gave new kinetic data for three tetracyclines competing by pairs.
- The technique shed light on rapid kinetics affecting competitive sorption.

A R T I C L E   I N F O

A B S T R A C T

The objective of this work was to study the competitive adsorption/desorption of tetracycline (TC), oxytetracycline (OTC) and chlortetracycline (CTC) on two acid soils. We used the stirred flow chamber technique to obtain experimental data on rapid kinetic processes affecting the retention/release of the antibiotics. Both adsorption and desorption were higher on soil 1 (which showed the highest carbon, clay and Al and Fe oxides content) than on soil 2. Moreover, hysteresis affected the adsorption/desorption processes. Experimental data were fitted to a pseudo-first order equation, resulting q_{amax} (adsorption maximum) values that were higher for soil 1 than for soil 2, and indicating that CTC competed with TC more intensely than OTC in soil 1. Regarding soil 2, the values corresponding to the adsorption kinetics constants (k_a) and desorption kinetics constants for fast sites (k_{d1}), followed a trend inverse to q_{amax} and q_{dmax} respectively. In conclusion, competition affected adsorption/desorption kinetics for the three antibiotics assayed, and thus retention/release and subsequent transport processes in soil and water environments.

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1. Introduction

Soil and water pollution due to antibiotic residues is a matter of growing concern (Giger et al., 2003). Specifically, the veterinary use of antibiotics, as well as sewage sludge recycling, have caused subsequent soil and water pollution due to the spreading of excreta-derived products on farmland soils (Kumar et al., 2005).

Tetracyclines are antibiotics broadly used (Torre et al., 2012), and some previous works have studied their retention/release on soils or other solid media by means of batch-type experiments (Hamscher et al., 2002; Sassman and Lee, 2005; Figueroa-Diva et al., 2010; Ji et al., 2011; Zhang et al., 2011; Kong et al., 2012; Teixidó et al., 2012; Huang et al., 2013). Recently we have studied non-competitive adsorption/desorption of the antibiotics tetracycline (TC), oxytetracycline (OTC) and chlortetracycline (CTC) on acid soils (Fernández-Calviño et al., 2014), using the stirred flow chamber (SFC) technique. This technique has higher potential than batch-type experiments to elucidate details characterizing processes with rapid kinetics (Aharoni and Sparks, 1991).

Few studies have focused on competitive adsorption/desorption of tetracyclines. Some previous works studied interactions (potential competition) of tetracyclines with cations such as Cd^{2+} (Bao et al., 2013), Cd^{2+}, Cu^{2+} and Pb^{2+} (Zhao et al., 2013), with herbicides (Zhang et al., 2013), or with other antibiotics (Ji et al., 2011). However, no previous work has studied competitive

adsorption/desorption of tetracyclines (or any other antibiotics), using the SFC procedure. Furthermore, no previous study has focused on competitive adsorption/desorption of TC, OTC and CTC, even using the more classical batch-type approach.

In view of that, in this work we have carried out binary competitive adsorption/desorption experiments for the antibiotics TC, OTC and CTC on two acid soils, using the SFC technique to shed light on retention/release process governed by rapid kinetics, which is of environmental relevance.

2. Materials and methods

2.1. Soil samples

The soils used have been previously studied by Fernández-Calviño et al. (2014) to investigate non-competitive adsorption/desorption of the antibiotics TC, OTC and CTC. The soil characteristics and the standard analytical methods employed were previously described by Bermúdez-Couso et al. (2012). Briefly, soil pH was 4.5 for soil 1, and 4.4 for soil 2, with main differences affecting to texture, which was clay for soil 1 and clay loam for soil 2, and to soil organic carbon (22.7% and 2.7% for soil 1 and soil 2); the Fe oxides concentrations were 4.5 and 1.3 mg g^{-1} for soil 1 and soil 2, while the NaOH-extracted Al concentrations were 5.4 and 1.5 mg g^{-1} for soils 1 and 2; the effective cation exchange capacities (eCEC) were 8.63 cmol(+) kg^{-1} for soil 1, and 8.15 cmol(+) kg^{-1} for soil 2.

2.2. Antibiotics and high performance liquid chromatography (HPLC) chemicals

We used three different tetracyclines of HPLC-grade purity supplied by Sigma–Aldrich: (a) TC, 95% tetracycline hydrochloride ($C_{22}H_{24}N_2O_8$ HCl, CAS number: 0 000 064 755); (b) OTC, 95% oxytetracycline hydrochloride ($C_{22}H_{24}N_2O_9$ HCl, CAS number: 0 002 058 460); and (c) CTC, 76% chlortetracycline hydrochloride ($C_{22}H_{23}ClN_2O_8$ HCl, CAS number: 0 000 064 722). Chemical characteristics of the three antibiotics were presented in Fernández-Calviño et al. (2014).

All chemical reagents used for HPLC were of high purity analytical grade, supplied by Sigma–Aldrich (Spain). All solutions were prepared with ultrapure water obtained with Milli-Q® equipment (Millipore, Spain).

2.3. Quantification of the antibiotics

TC, OTC and CTC were quantified following a procedure indicated in Fernández-Calviño et al. (2014), which was similar to that used by López-Peñalver et al. (2010). Briefly: gradient HPLC was used, by means of a high performance liquid chromatographer with a UV–Visible detector (Dionex Corporation, USA), further equipped with a P680 quaternary pump, an ASI-100 auto-sampler, a TCC-10 thermo-stated column compartment and a UVD170U detector. Chromatographic separations were performed with a Symmetry C18 column, particle size 5 μm and 4.6 × 150 mm inner diameter (Waters, Milford, MA, USA). The mobile phase (flow = 1.5 mL min^{-1}) consisted of 0.02 M acetonitrile (phase A) and oxalic acid/0.01 M triethylamine (pH = 2) (phase B). The linear gradient elution program was run from 5% to 32% of phase A (and 95% to 68% of phase B) within 10.5 min. The initial conditions were re-established in 2 min and held for 5 min. The examined TCs were monitored at 360 nm; run time was 15 min, and injection volume was 50 μL. The retention time obtained for each tetracycline was 6.2 min, 6.8 min, and 9.0 min for OTC, TC,

and CTC, respectively. The detection limits were 0.27, 0.14 and 0.24 mg L^{-1} for TC, OTC and CTC, respectively.

2.4. Stirred flow chamber (SFC) tests

The reactor used was the same previously employed and described by Fernández-Calviño et al. (2014).

For the adsorption phase, an amount of 0.2 g of soil (<2 mm) was placed inside the micro-reactor with a magnetic stirring bar, then a solution containing one of the three binary combinations of antibiotics (TC-OTC, TC–CTC, or OTC–CTC) (10 + 10 = 20 μM) was passed through. These solutions contained 0.005 M CaCl$_2$ as background electrolyte and had pH ∼5 before being passed through the chamber. In total, for each of the three binary combinations of antibiotics, 80 subsamples of 5.0 mL were collected in different vials (all filled in 5 min each, thus 5 min being the sampling interval). Once collected the samples, the antibiotic solution was replaced by another solution of 0.005 M CaCl$_2$ to carry out the desorption experiment, collecting the same number of samples in the same time. The determination of the antibiotics was performed in all samples by triplicate.

2.5. Modeling of the adsorption–desorption process

As in Fernández-Calviño et al. (2014), we used a *pseudo* first-order equation (Eq. (1)) (Aharoni and Sparks, 1991) to describe antibiotics adsorption and desorption kinetics. The formulation of the equation for a process taking place at two different types of sites is:

$$
\begin{aligned}
dq_x/dt &= k_{x1}(Fq_{x\max} - q_x) \quad \text{for } q_x < q_F \\
dq_x/dt &= k_{x2}[(1 - F)q_{x\max} - q_x)] \quad \text{for } q_x \geq q_F
\end{aligned}
\tag{1}
$$

where dq_x/dt (mmol kg^{-1} min^{-1}) is the antibiotic adsorption or desorption rate, k_{x1} is the adsorption or desorption rate constant for fast sites (min^{-1}), k_{x2} that for slow sites (min^{-1}), F the fraction of fast sites, $q_{x\max}$ (mmol kg^{-1}) the maximum adsorption or desorption capacity of the soil under the experimental conditions used, q_x the amount of antibiotic adsorbed or desorbed by the soil, and q_F the amount of antibiotic retained or released in the transition from fast to slow sites. F was determined by using an iterative method involving successive approximations to the solution. If only one site is present, $F = 1$, and hence the model coincided with the *pseudo* first-order equation for one site. In the equation, x is a in the adsorption experiments and d in the desorption experiments.

The statistical package SPSS 19 (IBM, USA) was used to perform modeling and statistical treatment.

3. Results and discussions

3.1. Adsorption results

As shown in Fig. 1, adsorption was higher on soil 1 than on soil 2. In the previous non-competitive study with the same two soils, the same three antibiotics, and the same total molar concentrations of antibiotics (20 μM in the non-competitive, and 10 + 10 = 20 μM in the competitive experiment), Fernández-Calviño et al. (2014) found that, at the end of their experiment (400 min), adsorption was higher for TC, OTC and CTC in soil 1 (with values in the range 20–25 mmol kg^{-1}) than in soil 2 (adsorption between 11 and 15 mmol kg^{-1}). In view of that, in competitive experiments adsorption results remained lower for soil 2 (the one with the lowest carbon, clay and Al and Fe oxides contents), as in the previous non-competitive trials. Cumulated adsorption has diminished in competitive trials (mainly in soil 2), comparing each antibiotic individually, but it remained equivalent comparing the