



# Sorption of nalidixic acid onto sediments under batch and dynamic flow conditions

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## ABSTRACT

The sorption of nalidixic acid (NA) onto artificial sediments composed of Fe-oxides, Al-oxides, clay and quartz sand was studied under both static batch and dynamic flow conditions. Kinetic and equilibrium sorption experiments showed that the presence of clay increased the sorption capacity of synthetic sediment and that bentonite had the highest sorption coefficient compared to kaolinite. Solute reactive transport experiments showed that the breakthrough point and steepness of the breakthrough curve (BTC) were dependent on both clay type and water velocity. Agreement between batch and column results in terms of sorbed amount and retardation factor was poor regardless of the sediment tested. The presence of even a small amount of clay (3%) can decrease the permeability of the mixed bed and lead to the formation of preferential flow paths in the column system. Different sets of column experiments at various flow rates gave rise to different sorbed amounts at complete breakthrough, leading to chemical nonequilibrium in the flow system. However, this kinetic limitation cannot completely explain the breakthrough behavior of NA in the bentonite column, suggesting that other factors are responsible for this disparity. The presence of immobile water regions was unlikely in the column since more than 90% of the pore water was mobile according to the tracer tests. The inaccessibility of reactive sites and limited physical diffusion in the clay-packed column may play a significant role under flow-through conditions. The reactive transport behavior of NA is therefore strongly dependent on the mineralogy of the clay present in sediments.

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## 1. Introduction

Pharmaceutical compounds (PCs) have been introduced into the environment for many years without being given much attention (Löffler et al., 2005; Chefetz et al., 2008). Many of them are not completely metabolized in humans or animals and are eventually discharged into the environment, where they may persist in aquatic systems (Heberer, 2002; Scheytt et al., 2004). Classes of PCs commonly detected in the environment include antibiotics, endocrine disrupters and other non prescriptive analgesic drugs (Lorphensri et al., 2007). Concern has mostly focused on antibiotics and steroids which may cause resistance in natural bacterial populations (Hernando et al., 2006). Although, environmental concentrations generally occur at trace levels (ng/L to low µg/L) in the environment, they can be sufficient to induce toxic effects. However, little information exists on the fate and transport of PCs in groundwater systems (Lorphensri et al., 2006).

Under certain circumstances some pharmaceutical compounds may even percolate into the groundwater (Scheytt et al., 1998, 2005). Besides flow conditions and persistence, sorption is one of the key factors controlling the input, transport, and transformation of these substances in the aquatic environment and in the subsurface (Scheytt et al., 2005). It is strongly influenced by media properties such as organic content, surface reactivity and specific surface area (Bailey and White, 1970). For soils and sediments containing significant amounts of organic matter, the sorption of organic chemicals is often controlled by the organic carbon content of the medium due to the hydrophobicity of organic matter (Stevenson, 1976; Chiou et al., 1979). However, in aquifer sediments (i.e., sand and clay) the level of organic carbon content is typically low, and adsorption on mineral surfaces can be significant (Schwarzenbach and Westall, 1981; Schwarzenbach et al., 2003; Thiele-Bruhn et al., 2004). Clays and iron- and aluminum-oxides are the most reactive mineral constituents in soils and sediments, where they play a major role in the fate and transport of contaminants. However, little is known about the extent and the mechanisms involved in the sorption of pharmaceutical products on sediment mineral constituents. Therefore, it is important to consider the potential mobilization risks of

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water pollution associated with the PCs, and investigate their interaction with these constituents.

Nalidixic acid (NA) is a common human and animal antibiotic that is representative of many PCs in that it is ionizable, polar, and contains an aromatic ring (Robberson et al., 2006). PCs including NA are not completely removed by wastewater treatment and can be found at relatively high concentrations in surface waters (between 10 ng/L and 2 µg/L) (Kolpin et al., 2002; Schäfer et al., 2003; Carballa et al., 2004). This study is devoted to investigating the effect of clay on the sorption of NA under batch vs flow-through conditions. Batch sorption experiments are standard methods for deriving kinetic and equilibrium sorption constants, while column transport experiments are used to study interactions at solid/water interfaces under experimental conditions close to natural conditions. In contrast to batch studies, continuous flow experiments allow studying the impact of nonequilibrium sorption and hydrodynamic parameters on the breakthrough of solutes. In addition, column tests can provide more accurate field estimations by giving an appropriate solid/liquid ratio. Previous studies have reported that disparity in terms of sorbed amount or sorption constant occurs between batch and column dynamic experiments, even when carried out with identical compounds and solid samples (Maraqa et al., 1998; Altfelder et al., 2001; Hanna et al., 2010). Although many factors have been reported to cause discrepancies between the results of the two methods, the main reasons are not clear and remain open to speculation.

In this work, the sorption of NA was investigated for three synthetic sediments prepared with goethite, gibbsite and sand as the basic porous media, and containing the following: (i) 0% clay for SD (sediment basic media composed of Fe-oxide, Al-oxide and quartz sand), (ii) 3% kaolinite for SD-k (sediment basic media + kaolinite), and (iii) 3% bentonite for SD-b (sediment basic media + bentonite). These compositions allowed us to test the effect of clay type on the sorption and reactive transport of NA. Metal oxides generally do not occur as homogeneous assemblages or individual phases in subsurface soils and sediments. Metal oxides are frequently present as coatings on less soluble soil particles such as silica sand and silicate clay (Poulton and Raiswell, 2005). In addition, coating on silica sand allows performing column transport experiments with a hydraulically conductive porous medium, without clogging the columns (Hari et al., 2005; Hanna et al., 2010).

Batch tests were first conducted to determine the kinetic rate and sorption capacity at neutral pH with a constant liquid/solid ratio and at fixed ionic strength. The breakthrough curve (BTC) of NA were then determined at near neutral pH. The hydrodynamic properties of porous materials containing different sediment constituents were determined using bromide as a non-reactive tracer. Also, the retardation factors derived from batch and column data were determined and compared. Column series tests were carried out under different water velocities (0.018–0.188 cm/min) to evaluate the potential of

nonequilibrium sorption. To quantify the influence of chemical sorption kinetics on the breakthrough of NA in the bentonite sediment (SD-b), a macroscopic sorption model was used and test calculations were performed using HYDRUS-1D software. The effects of aggregation structures in the clay-packed column and physical diffusion limitations on the disparity batch vs column are also discussed.

## 2. Materials and methods

### 2.1. Chemicals

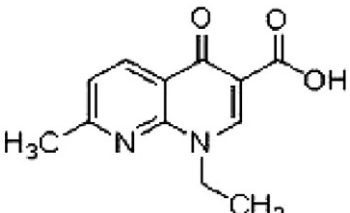
NA is a quinolone antibiotic purchased from Aldrich Chemical Co. The molecular structure and chemical properties of NA are shown in Table 1. An aqueous solution of NA was prepared in the background electrolyte (NaCl 10<sup>-2</sup> M), without any purification. Hydrochloric acid and sodium hydroxide were used for pH adjustment.

### 2.2. Sediment samples and characterization

Five pure materials were used to prepare the synthetic sediments: goethite, gibbsite, quartz sand Fontainebleau (France), Georgia kaolinite (KGa-1) and bentonite (Na-montmorillonite). Goethite and gibbsite were synthesized in the laboratory. Goethite was prepared by neutralizing 500 mL of 0.5 M ferric nitrate solution (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) with 400 mL of 2.5 M sodium hydroxide solution. This method was based on the protocol described by Villalobos and Leckie (2000), in which the sodium hydroxide solution is added quickly. The solid was washed to remove soluble Fe and electrolytes and stored in an anaerobic N<sub>2</sub> (g) chamber at ambient temperature. This goethite was characterized in a previous study (Gaboriaud and Ehrhardt, 2003). Gibbsite synthesis has been described in detail elsewhere (Jodin et al., 2005). Briefly, gibbsite particles were obtained by aging a supersaturated solution of sodium aluminate (Bayer liquor) prepared by oxidizing metallic aluminum in a concentrated sodium hydroxide solution. The solid particles were separated from the solution after 7 to 10 days of aging. Solid particles were separated from the solution by centrifugation at 5000 G for 5 min. They were then washed several times with a nitric acid solution at pH 4.0 (to decrease the pH of the supernatant to within 4.5–5) and then once with Milli-Q water. The sample was then filtered and freeze dried.

Quartz sand from Fontainebleau (France) was used as a model material. As this sand occurs in a wide range of grain sizes, only the fraction sieved in the 100–150 µm fraction was used for this study. The sand was washed with HCl, H<sub>2</sub>O<sub>2</sub> and then with pure water several times to remove impurities and fines. X-ray diffraction (XRD) and Raman spectroscopy confirmed this material was composed exclusively of quartz. It should be noted that the XRD

**Table 1**  
Physical and chemical characteristics of NA.

Molecular structure	Formula	Molecular weight (g/mol)	Water solubility (mg/L)	log Kow	pKa
	C <sub>12</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub>	232.24	328 <sup>a</sup> (pH 7)	0.37 <sup>a</sup> (pH 7)	5.95 <sup>a</sup>

<sup>a</sup> Lorphensri et al. (2006, 2007).

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