



# Montmorillonite enhanced ciprofloxacin transport in saturated porous media with sorbed ciprofloxacin showing antibiotic activity



Hao Chen<sup>a</sup>, Bin Gao<sup>b</sup>, Liu-Yan Yang<sup>c</sup>, Lena Q. Ma<sup>c,a,\*</sup>

<sup>a</sup> Department of Soil and Water Science, University of Florida, Gainesville, FL 32611, United States

<sup>b</sup> Department of Agricultural and Biological Engineering, University of Florida, Gainesville, FL 32611, United States

<sup>c</sup> State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Jiangsu 210046, China

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## ABSTRACT

Antibiotic ciprofloxacin (CIP) is immobile in the subsurface but it has been frequently detected in the aquatic system. Therefore it is important to investigate the factors impacting CIP's mobilization in aquifer. Laboratory columns packed with sand were used to test colloid-facilitated CIP transport by 1) using kaolinite or montmorillonite to mobilize presorbed-CIP in a column or 2) co-transporting with CIP by pre-mixing them before transport. The Langmuir model showed that CIP sorption by montmorillonite ( $23 \text{ g kg}^{-1}$ ) was 100 times more effective than sand or kaolinite. Even with strong CIP complexation ability to Fe/Al coating on sand surface, montmorillonite promoted CIP transport, but not kaolinite. All presorbed-CIP by sand was mobilized by montmorillonite after 3 pore volumes through co-transporting of CIP with montmorillonite. The majority of CIP was fixed onto the montmorillonite interlayer but still showed inhibition of bacteria growth. Our results suggested that montmorillonite with high CIP sorption ability can act as a carrier to enhance CIP's mobility in aquifer.

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## 1. Introduction

Antibiotics are widely used in the treatment or prevention of human and animal diseases (Thiele-Bruhn, 2003). They can reach the environment from different sources including land application of biosolids, wastewater irrigation, and disposal of expired pharmaceutical prescriptions (Golet et al., 2002; Zorita et al., 2009). As antibiotics have been detected in various environmental samples and they are persistent and effective at low doses, concerns have been raised about their potential effects on human health (Jones et al., 2001; Thiele-Bruhn, 2003).

Ciprofloxacin (CIP) is one of the most widely prescribed fluoroquinolone antibiotics. CIP is not readily biodegradable and has high sorption affinity onto aquifer materials (Nowara et al., 1997; Vasudevan et al., 2009), so high concentration of CIP could accumulate in aquifer materials. Previous studies showed that CIP can bond with aquifer materials (e.g., Fe/Al hydrous oxides and clays) through columbic attraction (cation exchange and cation bridging) and surface complexation (Gu and Karthikeyan, 2005; Otker and Akmeahmet-Balcloglu, 2005; Trivedi and Vasudevan, 2007). However, sorption by aquifer materials does not eliminate the antibiotic effects of CIP (Girardi et al., 2011), making CIP contamination in the aquatic system of increasing concern. Hence it is important to study the factors impacting its mobility in aquifer.

With high surface area and cation exchange ability, colloids (1 nm to 10  $\mu\text{m}$ ) are known for their reactivity and mobility in aquifer, which may help transport immobile contaminants such as CIP in the aquatic system (Roy and Dzombak, 1997).

\* Corresponding author at: State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Jiangsu 210046, China.

E-mail address: [lqma@ufl.edu](mailto:lqma@ufl.edu) (L.Q. Ma).

Contaminants with high affinity to immobile aquifer materials can be attracted to mobile colloids and move with colloids. Although it is known that mobile colloids have the potential to enhance the mobility of immobile contaminants (Grolmund and Borkovec, 2005), few studies have focused on colloid-enhanced transport of antibiotics in porous media (Kanti Sen and Khilar, 2006).

Kaolinite and montmorillonite are common soil colloids. They are detected in groundwater down gradient from the disposal sites, indicating that they are highly mobile in the subsurface (Baumann et al., 2006; Hennebert et al., 2013). Previous studies showed that both montmorillonite and kaolinite have high affinity for CIP (Wu et al., 2013a), making them effective in transporting CIP in the subsurface. The ability of colloids in transporting CIP is determined by the interaction among CIP, colloids and aquifer materials (Roy and Dzombak, 1997) including the following factors: (a) the interaction between CIP and immobile aquifer materials; (b) the nature of the interaction between CIP and colloids; (c) the property and concentration of colloids; and (d) the colloid mobility in the environment. These factors may alter the dynamic behavior of CIP, making it difficult to understand the fate and transport of CIP in the subsurface.

Little information is available regarding the dynamic association between colloids and emerging organic contaminants such as CIP. It is therefore important to examine colloid-enhanced CIP mobilization in the subsurface. The goal of this study was to provide insights into the ability of common colloids in facilitating CIP mobilization in saturated porous media. Clay colloids (kaolinite and montmorillonite) and CIP were used in column experiments. Our objectives were to: 1) compare the transport of kaolinite, montmorillonite and CIP in saturated porous media; 2) examine the ability of kaolinite and montmorillonite in mobilizing presorbed-CIP from saturated porous media; 3) investigate colloid-facilitated CIP transport in saturated porous media; and 4) measure the antibiotic activity of CIP sorbed by montmorillonite.

## 2. Materials and methods

### 2.1. Materials

Ciprofloxacin (ACS 85721-33-1) was purchased from Applichem (Darmstadt, Germany). All other chemicals were of analytical grades from Fisher Scientific (Pittsburgh, PA). CIP stock solution was prepared in deionized (DI) water at a concentration of  $40 \text{ mg L}^{-1}$ , which was stored at  $4 \text{ }^\circ\text{C}$  in darkness. All solutions were prepared in DI water at pH 7 and glassware was acid-washed before use.

Quartz sand from Standard Sand & Silica Co. (Davenport, FL) was sieved to 0.5–0.6 mm. The point of zero charge (PZC) at 5.1 was determined by potentiometry titration method (Chen et al., 2013). Sand was washed by 5%  $\text{HNO}_3$  and DI water to remove soluble impurity before use. The elemental composition of the sand was determined by ICP-MS after digesting with  $\text{HNO}_3/\text{H}_2\text{O}_2$  hot-block digestion procedure (USEPA, 1986).

Kaolinite (EM Science, Gibbstown, N.J.) and montmorillonite (Southern Clay Products Inc., Gonzales, TX) powders were used to make colloidal suspension according to Gao et al. (2004). The mean colloid size, as determined by photon

correlation spectroscopy, was  $0.80 \text{ }\mu\text{m}$  for kaolinite and  $0.65 \text{ }\mu\text{m}$  for montmorillonite and did not vary significantly during the experiments. The cation exchange capacity of sand, kaolinite and montmorillonite was determined by the ammonium acetate method (Borden and Giese, 2001).

### 2.2. CIP sorption by kaolinite and montmorillonite

CIP sorption by kaolinite and montmorillonite was conducted using 50 mL polytetrafluoroethylene centrifuge tubes. Each vessel was filled with a predetermined amount of sorbent of  $\sim 1000 \text{ mg L}^{-1}$  kaolinite or  $100 \text{ mg L}^{-1}$  montmorillonite and 30 mL solutions containing 0, 0.5, 1, 1.5, 2.5, or  $5 \text{ mg L}^{-1}$  CIP. The vessels were shaken for 24 h (predetermined) to reach apparent equilibrium, and the suspension was then centrifuged at  $10,000 \text{ g}$  for 30 min. Aliquots of supernatant were withdrawn to determine CIP concentrations in liquid phase using HPLC (Waters 2695, Milford, MA) equipped with a fluorescence detector (Waters 2475, Milford, MA).

To better understand the interactions between CIP, sand and kaolinite/montmorillonite, two sets of batch experiments were conducted: 1) 15 mL of  $200 \text{ }\mu\text{g L}^{-1}$  CIP was first mixed with 15 mL of  $200 \text{ mg L}^{-1}$  montmorillonite,  $400 \text{ mg L}^{-1}$  kaolinite, or DI water and shaken for 24 h, then 3 g of sand was added to the mixture and shaken for another 24 h; and 2) 15 mL of  $200 \text{ }\mu\text{g L}^{-1}$  CIP was first mixed with 3 g of sand and shaken for 24 h, then 15 mL of  $200 \text{ mg L}^{-1}$  montmorillonite,  $400 \text{ mg L}^{-1}$  kaolinite, or DI water was added to the mixture and shaken for another 24 h. Due to the effect of CIP fixation in montmorillonite or kaolinite, CIP was extracted by mixing 2 mL suspension containing 1 mL  $\text{H}_3\text{PO}_4$  solution ( $\text{pH} = 2$ ) and 1 mL acetonitrile before HPLC analysis.

X-ray diffraction (XRD) analysis was also carried out to identify montmorillonite interlayer change after CIP sorption using a computer-controlled X-ray diffractometer (Philips Electronic Instruments) equipped with a stepping motor and graphite crystal monochromator. Three treatments of montmorillonite were tested for d-spacing change before and after drying at  $105 \text{ }^\circ\text{C}$  overnight: potassium-saturated montmorillonite and CIP-loaded montmorillonite ( $1 \text{ g kg}^{-1}$ ) before and after being flushed with 500 mM potassium solution.

### 2.3. Colloid-facilitated CIP mobilization in sand media

The sand was wet-packed into an acrylic column with 1.5 cm in diameter and 10 cm in height according to Chen et al. (2011). A small amount of sand was gently poured into 8 mL of DI water standing at the bottom until the sand surface was slightly below the water level. The sand in the column was stirred to remove the air bubbles and ensure uniformity. This procedure was repeated several times until the column was fully packed.  $\sim 32 \text{ g}$  of sand was used to pack one column with a porosity of 0.42. A peristaltic pump (Masterflex L/S, Cole Parmer Instrument) was used to regulate the upward flow at specific discharge of  $0.2 \text{ cm/min}$ . DI water was first pumped through the saturated column for  $\sim 2 \text{ h}$  to remove impurities and then followed by working solutions for column experiment. Bromide was applied to the column as a conservative tracer for the breakthrough studies.

To test co-transport of colloids (kaolinite and montmorillonite) and CIP in sand media, four colloid suspensions

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