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Graphene oxide-facilitated transport of levofloxacin and ciprofloxacin in saturated and unsaturated porous media

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ABSTRACT

In this work, effects of graphene oxide (GO) on the co-transport of the two typical Fluoroquinolones (FQs) - levofloxacin (LEV) and ciprofloxacin (CIP) in saturated and unsaturated quartz sand media were studied. The adsorption isotherms showed that GO had much larger sorption capacities to LEV and CIP than sand with the largest Langmuir adsorption capacity of 409 mg g^{-1} (CIP-GO); while the sorption affinity of the two FQs onto the two adsorbents might follow the order of CIP-sand > LEV-sand > LEV-GO > CIP-GO. GO promoted the mobility of the two FQs in both saturated and unsaturated porous media due to its strong mobility and sorption capacity. The GO-bound LEV/CIP was responsible for the LEV/CIP transport in the porous media, and transport of GO-bound FQs increased with the increasing of initial GO concentration. Under unsaturated conditions, moisture showed little effect on the transport of GO-bound CIP; however, the mobility of GO-bound LEV reduced with the decreasing of moisture content, suggesting the transport of adsorbed LEV from GO to air-water interface. GO sorption reduced the antibacterial ability of the two FQs, but they were still effective in inhibiting *E. coli* growth.

1. Introduction

As a class of wide spectrum antibacterial, fluoroquinolone antibiotics (FQs) play a key role in human therapy and animal husbandry for diseases treatments [1]. They are the third largest group of antibiotics accounting for 17% of the global market share with a sale of 7.1 billion US dollars in 2009 [2]. With their widespread of manufacture and application, some of FQs have been released into environment and frequently detected in various environmental matrices, including groundwater [3–5]. Due to the slow degradation [6,7] and continuous discharge of FQs, these pseudo-persistent compounds would exert a threat to activity and composition of microbial communities [8,9], may even create a significant source of resistance genes in the environment [10]. Due to extensive occurrence and potential toxicological effects of FQs, in-depth research needs to be carried out to evaluate their fate and transport in the environment, especially in groundwater that is one of the major sources of drinking water [11].

The fate and transport of FQs in the subsurface environment significantly depend on their interactions with surrounding porous media such as soils and aquifer solids. Only few studies have attempted to examine the retention and transport behaviors of FQs in porous media [12–17], although these processes play critical roles in controlling the fate of FQs in subsurface environment systems. And these studies showed that FQs are more prone to be retained in soils and aquifer materials due to its strong sorption onto solid surfaces, comparing with other groups of antibiotics. Chen [12] investigated the effects of solution pH and ionic strength (IS) on ciprofloxacin (CIP) retention and transport in saturated porous media, and demonstrated that CIP has a much lower mobility than sulfamethoxazole. Dong [17] found that, comparing with that of sulfacetamide, the transport of levofloxacin (LEV) in porous media is limited under various physicochemical conditions. Similarly, Ostermann [16] studied leaching of three groups of antibiotics in calcareous Chinese croplands, and observed the mobility decreases in the order of FQs < tetracycline < sulfonamides.

In general, colloids in the subsurface can act as carriers for contaminants due to the mobility and large sorption capacity. This process is often referred to as “colloid-facilitated contaminant transport” and is especially important for the movement of contaminants that have low solubility or strong affinity for solid surfaces [18–21]. Natural colloids have been reported as effective carriers to enhance the mobility of FQs

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[15,22]. Chen [15] demonstrated that montmorillonite can mobilize CIP presorbed onto sand media and increase its mobility in sand media. Xing [22] report that the presence of soil colloids promotes the breakthrough of CIP from 4% to 30–40%. Although natural colloid-facilitated contaminant transport has been studied previously, only few studies have focused on the enhanced transport of antibiotics by engineering nanoparticles in porous media [23,24].

As an emerging engineering nanomaterial, graphene oxide (GO) has shown great promises in many fields, such as biotechnology, polymer composites, chemical sensor, and energy storage [25]. Because of the rapid growth in manufacture and extensive utilization of GO, it is inevitable that, during production, utilization, and treatment, GO nanoparticles will likely release into the environment including soil and groundwater [26]. With negative surface charges that benefiting from containing large numbers of hydrophilic oxygen-containing surface functional groups [27,28], GO nanoparticles can disperse in aquatic environment easily [29–31], then may form stable colloids under certain conditions to enhance their mobility in soils and groundwater [26,32]. In addition, GO nanoparticles have excellent sorption ability to antibiotics due to the attractive electrostatic and π-π interactions arising from their charged functional groups and aromatic structures, including FQs [14,33]. Several previous studies have shown that GO nanoparticles can act as a carrier to enhance the transport of copper, 1-naphthol and phenanthrene in porous media [34,35]. Although FQs show limit transport ability in soils and groundwater, their strong associations with dispersed GO nanoparticles may greatly enhance their mobility in porous media, which may in turn increase the risk of FQs. Therefore, the co-transport information is crucial for understanding environmental risks of both GO and the FQs being carried. Nevertheless, none of the previous studies have examined how the presence of GO can affect the transport behaviors of FQs in porous media, especially in unsaturated porous media. Furthermore, how the interactions between GO and FQs affect their antibacterial properties has also not been studied previously.

The overarching objective of this work was to fill the knowledge gaps to determine the effect of GO on the transport behaviors as well as the antibacterial properties of two typical FQs, LEV and CIP in porous media. Both LEV and CIP are among the most commonly used antibiotics that have been often detected in the soil and water systems [1,3–5]. The specific objectives were as follows: 1) determine the graphene oxide-facilitated transport of LEV and CIP in saturated porous media; 2) determine the graphene oxide-facilitated of the two FQs in unsaturated porous media; and 3) determine the effect of GO sorption on the antibacterial ability of the two FQs.

2. Materials and methods

2.1. Materials

Levofloxacin (CAS 177325-13-2, > 98.5%) and ciprofloxacin (CAS 86393-32-0, > 99%) were purchased from Meilun Biology Technology (China). Chemical structure and properties of the two FQs are listed in Table S1 and Fig. S1 (Supporting Information). Stock solutions were separately prepared by adding 25 mg of LEV or CIP into 250 mL deionized (DI) water to get the concentration of 100 mg L^{-1}. The stock solutions were stored at 4 °C in darkness prior to use.

Single-layer GO was purchased from ACS Material (Medford, MA). GO stock solution with concentration of 500 mg L^{-1} was prepared by adding 125 mg pristine GO into 250 mL DI water, and the mixture was then sonicated for 2 h to ensure thorough dispersion. Prior to each experiment, the stock solutions were diluted to desired concentrations with corresponding experimental working solutions. Quartz sand (Unimim-Le Sueur, MN, USA) was used as the porous media in this study. The sand sieved into 0.35–0.45 mm, then sequentially washed by tap water, 10% nitric acid (v: v) and DI water to remove the metal oxides and other impurities [36]. The zeta potential of GO particles and sands under this experimental conditions were determined using a Zetasizer Nano ZSE (Malvern Instruments corporation, England).

2.2. Batch experiments

The adsorption kinetics and the adsorption isotherms of LEV and CIP onto GO and sand were conducted in Teflon centrifuge tubes at 30 ± 1 °C (detailed in S1), and all batch experiments were performed in triplicate.

In order to determine whether FQs on GO would be transferred to sand, competitive adsorption experiments were conducted. Briefly, 5 mL of the antibiotics (1 mg L^{-1}) were first mixed with 5 mL of the GO suspension (20 mg L^{-1}) in the centrifuge tubes and shaken for 24 h at 30 °C to reach equilibrium, and the batch experiments were performed in six. Three of the samples were then taken to determine aqueous antibiotic concentrations used the procedures described above. For the rest of the three samples, 25 g sand were added into the tubes and the mixtures were shaken for 36 h. After the sand was settled in the tubes, 1 mL of suspensions were filtered through 0.22 μm polytetrafluoroethylene membrane (Jinteng, China) immediately to determine antibiotic concentrations in the aqueous phase (see S3 for detailed procedures). At the same time, 3 mL of suspensions were withdrawn to determine the total concentrations of the antibiotics (the aqueous and GO phases) in suspensions (see S3 for detailed procedures). The amounts of the antibiotics on sand were determined through mass balance calculations.

2.3. Column experiments

All column experiments were performed in duplicate. Quartz sand was wet-packed as saturated porous media into acrylic columns (diameter: 2.5 cm, length: 16.8 cm) with 30 μm stainless-steel screens on both ends. Porosity of the packed column was 0.36–0.38 and bulk density of the sand was 1.84–1.87. The peristaltic pump (BT100-1F, Longer Pump, Hebei, China) was used to control the flow at a constant flow rate of 1.0 mL min^{-1}. And to prepare an unsaturated column, two peristaltic pumps were used to drain the column following the method developed by Liu et al. [32] (detailed in S4).

Each of these sand-packed columns was flushed with DI water for about 10 pore volumes (PV) to remove impurities, followed by flushing with background solutions to equilibrate the pore water IS and pH (~10 PV). Then for the co-transport experiments, 0.5 mg L^{-1} antibiotics (LEV or CIP) were premixed with 0, 5, 8 and 10 mg L^{-1} GO 8 h to reach equilibrium according to the adsorption kinetics results and the mixtures were applied to column inlets as a 130-min pulse (> 4 PV). The columns were then flushed with background solution for another 70 min (> 2 PV). For the remobilization experiments, the columns were firstly injected with 800 min 0.5 mg L^{-1} CIP/LEV solution (A, > 26 PV), followed by injected 64 min background solution (B, ~2 PV), then 130 min GO suspension (C, > 4 PV), and finally 190 min background solution (D, > 6 PV). The pH of all the background solutions and working solutions were adjusted to about 7.0 ± 0.1 and IS was 0.5 mM, respectively. The detailed experimental conditions of the columns are summarized in Table 3. Effluent samples were collected with a fraction collector (BS–100A, Puyang Scientific Instrument Research Institute, China) to analyze antibiotic and GO concentrations. The concentration of GONPs suspensions in this study was measured with UV–vis Spectrophotometer (UNICO Instrument Co., Ltd. China) at a wavelength of 230 nm. After measuring the GO concentrations, the samples were divided into two parts for the measure the total (GO-adsorbed and dissolved) and dissolved antibiotic concentration with the HPLC (see S1 for detailed procedures). The GO-adsorbed antibiotic concentrations were calculated by the total concentrations and the dissolved concentrations.

To determine the retention profiles of antibiotics, each column was separated into 8 layers at the end of the transport experiments. The

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