Effects of ionic strength and cationic type on humic acid facilitated transport of tetracycline in porous media

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HIGHLIGHTS

- Humic acid moderately facilitated the transport of tetracycline in sand column.
- Ionic strength and ionic composition governed the transport.
- HA can act as a carrier on the transport of tetracycline in subsurface.

GRAPHICAL ABSTRACT
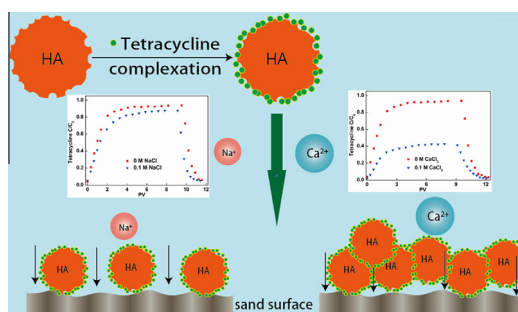
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ABSTRACT

The occurrence of antibiotics in subsurface environments is increasingly reported recently in addition to the widespread distribution in surface waters. However, the mechanisms governing the transport of antibiotics from surface into subsurface are not well understood. In this study, the transport of tetracycline in saturated sand columns were investigated in the presence and absence of humic acid (HA) at different ionic strengths and cationic types. NaCl (0–0.1 M) and CaCl$_2$ (0–0.1 M) were used as representatives of mono- and divalent cations in subsurface. The presence of HA moderately facilitated the transport of tetracycline in sand columns. The presence of Na$^+$ inhibited the transport of tetracycline and HA through increasing the deposition of HA aggregates on the sands. The inhibition increased slightly with the increase in Na$^+$ concentration from 0 to 0.1 M. In contrast, the presence of Ca^{2+} dramatically inhibited the transport of tetracycline and HA even at a low concentration of 0.001 M, which was attributed to the increased aggregation of HA and the greater electrostatic attractive interactions. Results from this study improve our understanding on the penetration of antibiotics from surface into subsurface waters and the transport of antibiotics in saturated aquifers at environmentally relevant conditions.

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1. Introduction

Tetracycline, one of the extensively used antibiotics in the world, has been widely applied to promote animal growth and prevent/treat animal diseases in livestock industry for decades [1,2]. Due to its high solubility (231 mg/L in water, $K_{ow} = -1.37$) [3],

tetracycline was regarded as a hydrophilic compound and has the potential to penetrate into subsurface environments [4]. Adsorption on immobile sediments and mobile colloids is the main process governing the fate and transport of tetracycline in subsurface environments [5–9].

Natural organic matter (NOM) is ubiquitous in soils and groundwater [10]. It generally facilitates the transport of hydrophobic organic contaminants (HOCs) in subsurface environments by serving as a contaminant carrier [11–13]. For example,

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the transport of florfenicol antibiotic in saturated soil columns as well as polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in aqueous medium was enhanced by the presence of NOM [14,15]. With respect to weakly hydrophobic tetracycline, enhanced transport in porous media was also noted in the presence of NOM [9]. However, the transport of HA in porous media is highly determined by solution ionic strength and ionic composition. The transport of HA in the porous media can be inhibited by the presence of Na^+ or Ca^{2+} [16]. The effect of ionic strength on the interaction of colloidal fraction of NOM with solid surface can be typically explained by Derjaguine–Landaue–Verweye–Over beek (DLVO) theory [17,18]. The increase in solution ionic strength tends to compress the double layer thickness decreasing the magnitude of surface charge, thereby facilitating particle deposition on solid surface. In addition, the divalent cation such as Ca^{2+} forms a complex with HA altering the aggregation structure of HA [19]. Both mono- and divalent cations are widespread in soil pore water and groundwater. Although NOM has been shown to facilitate the transport of tetracycline in porous media [9], the facilitated transport impacted by ionic strength and cation is poorly understood, which impedes our understanding of tetracycline penetration into subsurface and transport in subsurface.

In this study, the transport of tetracycline facilitated by the presence of NOM was investigated, with particular attention paid to the influence of ionic strength and cationic type. Humic acid (HA) was used as a representative of NOM. A saturated sand column was used to simulate the transport in porous media. The objective is to reveal the effects of ionic strength and cationic type on tetracycline transport in the presence of NOM.

2. Materials and methods

2.1. Chemicals

Tetracycline was purchased from the Sigma–Aldrich (purity $\geqslant$ 98.0%). HA was provided in the form of sodium salt (Sigma–Aldrich). The stock solution was stored under dark at 4 °C in a refrigerator. All the HA solutions were ultrasonicated for 2 h before use.

The sand consisting of silica with a median grain diameter (d_{50}) of 1–2 mm was used as the model porous media in all experiments. The sand was cleaned thoroughly to remove any metal oxides and clays on the surface according to the following procedure. The sands were immersed in 0.01 M NaOH solution for 24 h, rinsed with DI water, soaked in 0.01 M HCl solution for another 24 h, and finally rinsed with DI water. The sands were dried at 105 °C and stored for usage.

2.2. Transport experiments in columns

Transport experiments were conducted in a borosilicate glass column (2.5-cm inner diameter and 11.0-cm length). About 83.5 g of the sands after pretreatment were packed into the column step by step. An up-flow mode was employed. Prior to the start of experiments, the sand column was flushed with 5 pore volumes (PVs) of the background solution. The influent solution (pH 6) was purged with N_2 for 20 min to remove O_2. During the transport experiments, the effluent was collected at predetermined time intervals. Tetracycline and HA concentrations in the effluent were

Table 1
Parameters and results summarized for the column experiments.

	Solution compositions		Background solution[a] (PVs)	Influent solution[b] (PVs)	Background solution[c] (PVs)	Equilibrium effluent C/C_0 (tetracycline)
C1	20 mg L^{-1} tetracycline, 0.1 M NaCl, different concentrations of HA	0 mg L^{-1} HA	5.00	7.18	3.92	0.77
C2		5 mg L^{-1} HA	5.00	7.18	4.59	0.81
C3		10 mg L^{-1} HA	5.00	7.83	3.59	0.83
C4		20 mg L^{-1} HA	5.00	9.13	3.26	0.85
C5	20 mg L^{-1} tetracycline, 20 mg L^{-1} HA, different concentrations of Na$^+$	0 M NaCl	5.00	8.18	3.41	0.92
C6		0.001 M NaCl	5.00	7.82	3.59	0.89
C7		0.01 M NaCl	5.00	7.82	3.59	0.88
C8		0.1 M NaCl	5.00	7.82	3.59	0.85
C9	20 mg L^{-1} tetracycline, 20 mg L^{-1} HA, different concentrations of Ca^{2+}	0 M CaCl$_2$	5.00	8.18	3.41	0.92
C10		0.001 M CaCl$_2$	5.00	8.13	4.06	0.50
C11		0.01 M CaCl$_2$	5.00	8.13	4.06	0.44
C12		0.1 M CaCl$_2$	5.00	7.82	4.25	0.41
C13	20 mg L^{-1} HA, different concentrations of Na$^+$	0 M NaCl	5.00	8.87	3.41	0.93
C14		0.01 M NaCl	5.00	6.62	3.31	0.81
C15		0.1 M NaCl	5.00	6.62	3.31	0.62
C16		1 M NaCl	5.00	6.62	3.31	0.51
C17	20 mg L^{-1} HA, different concentrations of Ca^{2+}	0 M CaCl$_2$	5.00	8.87	3.41	0.93
C18		0.0005 M CaCl$_2$	5.00	8.13	3.43	0.63
C19		0.001 M CaCl$_2$	5.00	8.13	3.43	0.54
C20		0.01 M CaCl$_2$	5.00	8.13	3.43	0.20

[a] Pre-equilibration with 5 PVs of background solution.
[b] Injection of different PVs of tetracycline and HA suspension.
[c] Injection of different PVs of background solution to flush any unattached tetracycline and HA remaining in the column.