



Effects of organic matter–goethite interactions on reactive transport of nalidixic acid: Column study and modeling

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1. Introduction

Quinolone antibiotics are broad-spectra antimicrobial agents that are widely used in medicine and the impacts of their overuse on the environment are becoming of big concern, it is necessary to investigate the transport and mobility of quinolones in order to accurately assess their ecological impacts. Adsorption to immobile soil/sediment minerals is one of the key processes governing the fate and mobility of quinolones in environment and this process can be strongly influenced by Natural Organic Matter (NOM).¹ Currently available studies on the subject were limited to batch experiments,^{2,3} and little is known about the influence of NOM on binding and transport of antibiotics under flow-through conditions. To address these concerns, the sorption and transport of a widely used quinolone antibiotic, Nalidixic acid (NA), were investigated in goethite-coated sand (GCS) columns over a wide concentration range (5–50 mg/L) of Leonardite humic acid (LHA), a representative NOM.

2. Materials and Methods

Breakthrough column experiments were conducted at constant flow rate and under water-saturated conditions. Briefly, 15 g of dry goethite coated sand was packed into a glass chromatographic column and the column was wetted upward with a 0.01 M NaCl solution at pH 5 and 0.5 mL/min. Then impacts of LHA on NA transport was investigated in two scenarios: (i) NOM initially present in contaminated water and then interact with co-occurring compound to mineral surfaces, where 10 μ M NA and different concentrations of LHA (0, 5, 10, 50 mg/L) were equilibrated in 0.01 M NaCl at pH 5 and then injected simultaneously into column at 0.5 mL/min; (ii) NOM found as organic coatings on the mineral surface as in natural sedimentary materials, where a LHA solution (5, 10 or 50 mg/L) in 0.01 M NaCl at pH 5 was injected into the column at 0.5 mL/min. After the complete breakthrough of LHA, 10 μ M NA with the corresponding LHA (5, 10, 50 mg/L) in 0.01 M NaCl at pH 5 was injected in the same column. Desorption was initiated by injecting 0.01 M NaCl at pH 5 into column at 0.5 mL/min. In both cases, molecular fractionation of LHA and NA breakthrough were monitored HPLC, UV–Vis spectrophotometry and TOC analyses of column effluents. Hydrus-1D program was used to obtain the model parameters for the two-site nonequilibrium model.

3. Results and Discussion

3.1 Sorption of NA in LHA preloaded columns

Overall, the preliminary loading of column with LHA considerably facilitated the transport of NA, with a very similar breakthrough behavior over the concentration range of LHA (5–50 mg/L). Under these conditions, NA retention was mainly driven by weak van der Waals-type hydrophobic interactions, and/or through π – π electron coupling interactions with LHA-covered goethite surfaces. These interactions could govern the transport behavior in preloaded columns, independently on the LHA preloading concentration. This hypothesis was further confirmed in the simulation results using a two-site nonequilibrium model of the breakthrough curves of NA in LHA-preloaded columns. Similar adsorption parameters (K_d , α and β) described the breakthrough curve of NA for the three preloading LHA concentration (Fig. 1a, Table 1).

3.2 Mutual effects of NA sorption and LHA molecular fractionation

Simultaneous injection of NA and LHA in goethite-coated sand column alters NA mobility. At low LHA loadings (5 or 10 mg/L), both NA and LHA compounds bind to surface sites of goethite and the breakthrough of NA was only altered in the adsorption front (Fig. 1b). In contrast, at higher LHA loading (50 mg/L), NA breakthrough was altered both in the initial breakthrough point and adsorption front. This rapid breakthrough of NA is likely ascribed to strong competitive adsorption of LHA compounds to goethite, as well as intermolecular interactions between NA and unbound LHA that decreased NA retention. The model adequately predicted NA adsorption ($r^2 \geq 0.9823$, Table 1) using a lower K_d but a higher α at high LHA concentrations, thus suggesting the modification of sorption mechanisms.

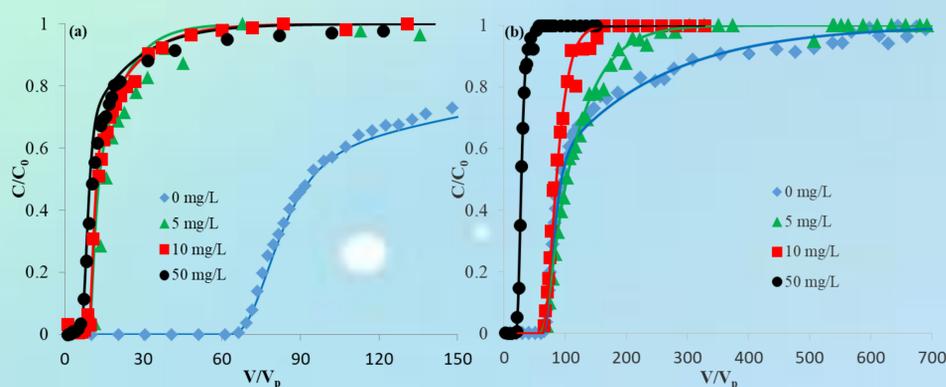


Fig.1 Breakthrough curves of NA (a) onto different concentrations of LHA preloaded column, (b) with the presence of different concentrations of LHA. 10 μ M NA with the corresponding LHA and 0.01 M NaCl at pH 5 was injected. Lines are modeling results.

4. Conclusion

We notably demonstrated that LHA facilitated NA transport in columns but this effect depends on how organic matter is contacted to mineral surfaces. When LHA was present as a mineral coating, van der Waals-type hydrophobic interactions governed NA transport. However, when both LHA and NA were initially present in the influent solution, the breakthrough was characterized first by a primary step involving competitive adsorption of NA and carboxylic/aromatics compounds, and a second step involving nonspecific adsorption of NA to LHA-covered goethite. This two-step process controls both NA retention and LHA molecular fractionation in column. NOM fractionation alters sorption mechanisms and kinetics of quinolone antibiotics, which in turn affect their fractionation. Furthermore, the low and incomplete desorption of LHA compounds from mineral surfaces also alters the desorption and mobility of NA under flow through conditions.

5. References

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Table 1. Fitted parameters of two-site nonequilibrium sorption model

Experiment	K_d	β	α	R^2
NA	39.77	0.89	0.00095	0.9961
Preloaded 5 mg/L LHA	5.65	0.86	0.00766	0.9928
Preloaded 10 mg/L LHA	4.39	0.90	0.01063	0.9960
Preloaded 50 mg/L LHA	3.72	1.15	0.00968	0.9982
NA-5mg/L LHA	34.55	0.76	0.00313	0.9978
NA-10mg/L LHA	24.63	0.76	0.01859	0.9893
NA-50mg/L LHA	7.60	0.74	0.05800	0.9995