Effect of *Pseudomonas aeruginosa* Biofilm on the Transport of PFOS in Saturated Quartz Sand

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Abstract. Soil and groundwater are important sites for the storage and transport of perfluorooctane sulfonic acid (PFOS), as well as areas for the presence and movement of bacteria. Bacteria are usually present as biofilms on the surface of media. It is reported that bacteria can also adsorb PFOS, so the direct contact between bacteria/biofilms and PFOS may affect the transport of PFOS. To investigate the effect of biofilm on PFOS transport, Gram-negative *Pseudomonas aeruginosa* was selected as the representative strain to construct indoor column experiments to investigate the effect of biofilm on PFOS transport in saturated quartz sand under different background solutions. The results showed that the presence of biofilm can enhance the retardation of PFOS transport in quartz sand. When the background solution was $CaCl_2$, the retardation of PFOS was more significant than that of NaCl with the same ionic strength. This study is helpful to better understand the effect of biofilm on the transport of PFOS, and provides a new idea for evaluating the transport characteristics of PFOS in underground environment.

Keywords: PFOS; biofilm; groundwater; transport.

1 Introduction

Perfluorooctane sulfonic acid (PFOS) is a persistent organic pollutant consisting of hydrophilic sulfonic acid functional groups and hydrophobic fluorinated carbon chains. This special structure makes it have good chemical properties and is widely used in a variety of products, including carpets, food packaging materials and semiconductor industry [1].

PFOS can transport long distances in the environment and has been widely detected in atmosphere, surface water, groundwater and soil [2, 3]. Numerous studies have been reported on the sorption of PFOS by media such as soil, sediment and metal oxides, and the effect of different solution chemistry on sorption [4, 5]. The adsorption of PFOS by biofilms and the subsequent influence on PFOS transport has re-

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ceived comparatively little research. Bacteria have been reported to have a strong ability to adsorb PFOS, and biofilms are also expected to influence the transport process of PFOS [6, 7]. Therefore, in this study, Gram-negative Pseudomonas aeruginosa was selected as the representative strain, and indoor column experiments were conducted to explore the transport behavior of PFOS in Pseudomonas aeruginosa biofilm coated sand under different background solution conditions.

2 Materials and methods

2.1 Chemicals and bacteria

PFOS (CAS # 1763-23-1, 40% in water) was obtained from Sigma-Aldrich. Pentafluorobenzoic acid (PFBA, CAS # 602-94-8, 98 % pure) was used as the nonreactive tracer (NRT) and obtained from Macklin Inc. (China). As a background solution, 0.01 M NaCl was used in all solutions.

The porous medium used was 40–50 mesh quartz sand. The quartz sand was pretreated by the method described by Li et al [8].

Gram-negative *Pseudomonas aeruginosa* CCTCC 91095 (PA) was purchased from the China Center for Type Culture Collection.

2.2 Experimental setup

Figure 1 shows the column experimental setup, which consists of four parts: the aqueous solution to be passed, the precision HPLC pump, the acrylic column, and the automatic fraction collector.

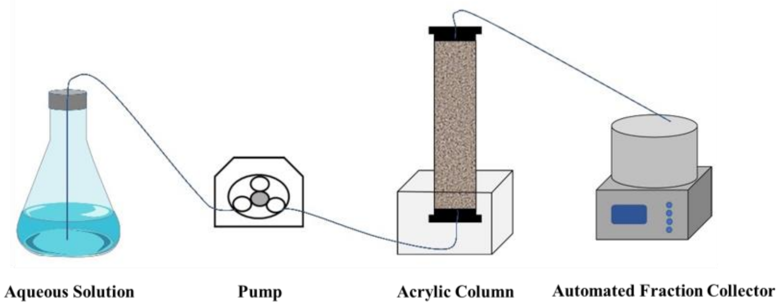

Fig. 1. Schematic diagram of column experiment setup.

2.3 Miscible-displacement column experiments

Sterilized quartz sand was premixed with Pseudomonas aeruginosa bacterial suspension (OD 600=0.04), and the suspension was then wet filled in an acrylic column with an inner diameter of 2.5 cm and a length of 15 cm. After packed, the column was filled with sterilized Luria-Bertani (Luria-Bertani) broth (2 g/L) at a flow rate of 1 mL/min for 3 days, changing the flow direction every 12 h. Finally, approximately 15 well volumes (PV) of background solution (0.01 M NaCl or 0.003 M $CaCl_2$) were passed through the column in an upward flow direction of 1 mL/min. Two parallel sets of experiments were set up for each group. Clean quartz sand was also wet filled into the columns as a control experiment. Miscible-displacement experiments were first performed with the NRT before the transport experiments of PFOS (input concentration of 1 mg/L). The measured retardation factors (R) were determined for the transport experiments by calculating the first moment [9].

2.4 Analytical Methods

NRT samples were measured by ultraviolet−visible (UV−vis) spectrophotometry and PFOS samples are measured by Thermo UltiMate 3000 HPLC coupled with an AB-Sciex QTRAP 4500 mass spectrometer.

At the end of the miscible-displacement experiment, the inlet to outlet of each column was divided into five layers, and the content of EPS (extracellular polymeric substance) in the sand column was determined by formaldehyde-NaOH method.

3 Results and discussion

3.1 Determination of EPS

It can be seen from figure 2 that the spatial distribution of EPS along the column is relatively uniform, indicating the existence of biofilm in the column and the column filling method used in this study is reasonable. When the background solution was $CaCl_2$, the EPS produced by PA was higher than that of EPS when the background solution was NaCl. This may be due to the fact that compared with monovalent Na^+, the existence of divalent Ca^{2+} helps to maintain the stability of EPS [10].

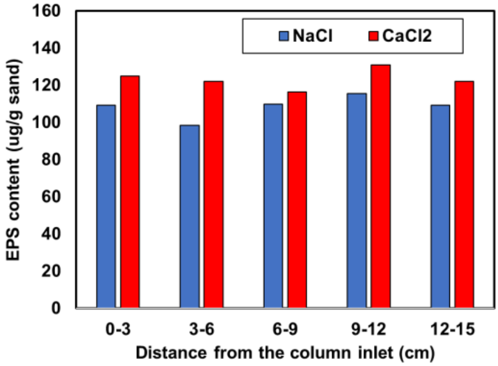

Fig. 2. Spatial distribution of EPS within the columns.

3.2 NRT transport experiment

As can be seen in figure 3, the arrival front of the breakthrough curves (BTCs) for NRT transport in different background solutions in sand with and without PA biofilm coated are sharp and symmetric. The analysis yielded a measured retardation factor of 1, indicating that the column packing was homogeneous and that ideal hydrodynamic conditions existed within the columns.

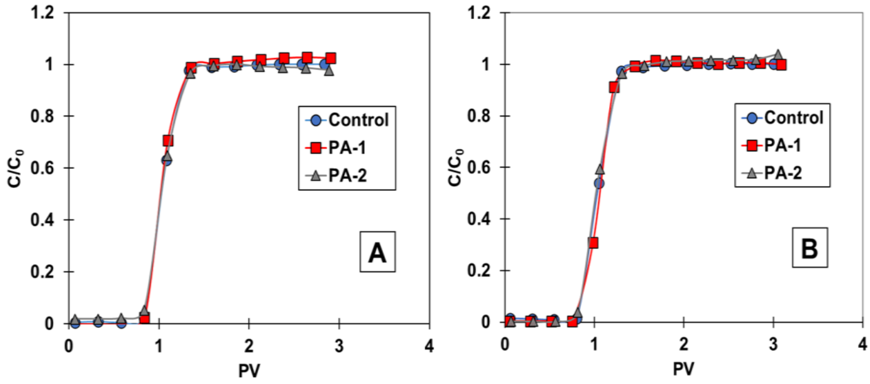

Fig. 3. Arrival fronts for the nonreactive tracer (NRT) in sand with and without PA biofilm coated (A: background solution is 0.01M NaCl, B: background solution is 0.003M $CaCl_2$).

3.3 PFOS transport experiment

The BTCs of PFOS transport for all experiments are shown in figure 4, and the relevant parameters are shown in table 1. The BTCs of PFOS transport in sand without biofilm at different background solutions are asymmetric and the concentration tails. The retardation factor measured with the background solution of NaCl was 1.65 and the K_d was 0.20 L/kg. And the retardation factor measured with the background solution of $CaCl_2$ was 1.93 and the K_d was 0.28 L/kg. Ca^{2+} can promote the adsorption of PFOS on the quartz sand surface more than the same ionic strength of Na^+ and caused the transport of PFOS to exhibited greater retardation. This is because Ca^{2+} playing the role of cation bridging between PFOS and quartz sand, which promotes the adsorption of PFOS.

Compared with the experiment without biofilm, the BTCs of PFOS in quartz sand with biofilm exhibit greater magnitudes of retardation, and the R and K_d values increased significantly, indicating that the presence of biofilm could promote the adsorption of PFOS, thus hindering the transport of PFOS. When the background solution is NaCl, the K_d value of the experiment with biofilm is about 2 times that of the control experiment. When the background solution is $CaCl_2$ with the same ionic strength, the K_d value of the experiment with biofilm is about 2.5 times that of the control experiment. This indicates that the existence of Ca^{2+} may have an additional effect on the biofilm and PFOS, resulting in greater adsorption of PFOS. Some studies have shown that divalent cations can bridge the negatively charged PFAS and activated sludge, thus promoting the adsorption of PFAS on the sludge [11]. Therefore, the existence of Ca^{2+} may also play the role of cation bridging between biofilm and PFOS, thus promoting the adsorption of PFOS.

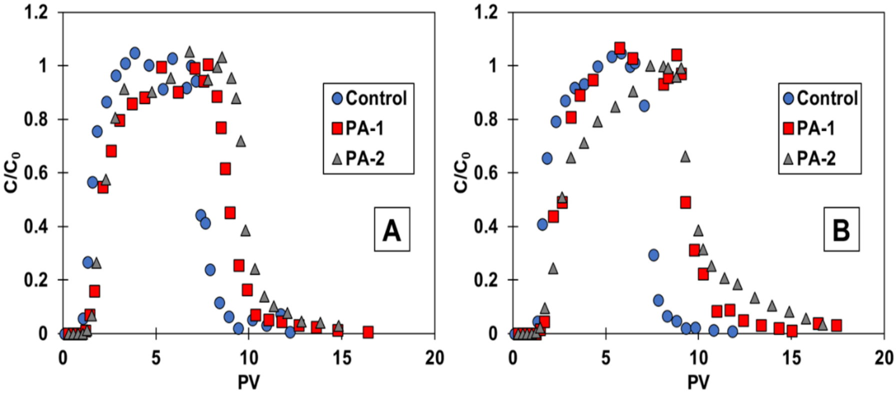

Fig. 4. Breakthrough curves for transport of PFOS in sand with and without BA biofilm coated (A: background solution is 0.01M NaCl, B: background solution is 0.003M $CaCl_2$).

Table 1. R and K_d values of transport experiments.

Experiment	Background solution	R	K_d (cm^3/g)
Control	0.01M NaCl	1.65	0.20
Control	0.003M $CaCl_2$	1.93	0.28
PA-1	0.01M NaCl	2.19	0.37
PA-2	0.01M NaCl	2.55	0.50
PA-1	0.003M $CaCl_2$	3.38	0.77
PA-2	0.003M $CaCl_2$	3.20	0.71

4 Conclusion

Our results suggest that biofilm plays an important role in the transport of PFOS in porous media. The transport of PFOS showed more retardation when biofilm was present. PFOS transport in the sand with a $CaCl_2$ background solution exhibits larger magnitudes of retardation than PFOS transport in the sand with a NaCl background solution, which may be due to Ca^{2+} playing the role of cation bridging between PFOS and quartz sand, or/and biofilm, thus promoting the adsorption of PFOS.

Acknowledgments

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