Effect of Water Content on the Behavior of Surfactants and Hydrophobic Organic Compounds in the Immobilization Zone for Contaminants Retardation

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Introduction

Formation of an immobilization zone can be a remedial option and it can be constructed by modifying soil materials in the subsurface with surfactants. The retardation of the movement of hydrophobic organic compounds (HOCs) in the subsurface is achieved by enhanced partitioning of HOCs into the modified soil surfaces. Partitioning of HOCs to sorbed surfactants has been investigated in several studies [1-5]. Holsen et al. [1] examined the sorption of several HOCs on sodium dodecyl sulfate (SDS)-coated ferrihydrite and found a linear relationship between the amount of HOCs sorbed and the amount of SDS on the ferrihydrite. This suggests that the sorbed SDS was primarily responsible for sorption of HOCs. Sun and Jaffe [2] investigated the partitioning of phenanthrene to dianionic monomers and micelles and to the same surfactants sorbed on alumina, and found that the sorbed surfactants were generally five to seven times more effective. Nayyar et al. [4] reported partition coefficients for several organic contaminants to SDS sorbed on alumina were higher than the corresponding micellar partition coefficient. Similar experiments were performed by Sun et al. [5] to obtain the partition coefficients of HOCs to a silt soil with a sorbed nonionic surfactant (Triton X-100). They observed that the sorbed surfactant increased partitioning of HOCs relative to the untreated soil.

In many cases, organic contaminants are present in unsaturated conditions, and the immobilization technology proposed in this research is to be applied to vadose zones to prevent contaminants migration into saturation zones. However, the research on the immobilization of organic contaminants has mainly simulated sorption behavior in saturated conditions. Unsaturated region of soil is composed of three parts, i.e., soil grains, pore water, and air, whereas, saturated region of soil is made up of two parts, i.e., pore water and soil. Thus it is important how water content could affect transport of organic contaminants in the immobilization zone.

In this research, column experiments were conducted to simulate transport of organic contaminants in unsaturated zones in the field. Surfactants with different molecular structure - MADS (monoalkylated disulfonated diphenyl oxide), DADS (dialkylated disulfonated diphenyl oxide) - were tested and naphthalene was used as a representative organic contaminant. The objectives of this research were (1) to study the effect of water content on the sorption characteristics and transport behavior of the two surfactants in columns containing an aluminum oxide as a sorbent ; (2) to examine the effect of water content on the partitioning of the model HOC (naphthalene) into the surfactants sorbed on the aluminum oxide and on its transport behavior in the column experiments; (3) to evaluate transport of the surfactants and naphthalene in saturated and unsaturated conditions by using a transport model.

Experimental Methods

The aluminum oxide was obtained from Aldrich. The two surfactants with different structures were tested and their performances were compared. MADS has one hydrophobic alkylchain, whereas DADS has two hydrophobic alkylchains. One-dimensional column transport experiments were performed in a glass column with a length of 15cm and an inner diameter of 1cm, packed with the aluminum oxide. The aluminum oxide was placed by a wet packing method and the pore volume of the packed column was determined by the weights difference. Influent solutions of surfactants were injected into the column at flow rates of 3 and 6 ml/min,

respectively. The injection flow rate of naphthalene was 0.8 ml/min. The effluent was collected in a 10ml test tube and was analyzed for the two surfactants with an ultraviolet spectrophotometer and for naphthalene with a liquid chromatograph. Three different unsaturated conditions (25, 50, 75% of the saturated condition) were obtained by draining appropriate aliquots of the pore water in the column.

Mathematical Modeling

One dimensional advection-dispersion equation based on linear equilibrium sorption and on steady state is described by:

$$\left[1+\frac{r}{q}\mathrm{K}\right]\frac{\partial C}{\partial t}=D\frac{\partial^2 C}{\partial x^2}-v\frac{\partial C}{\partial x} \tag{1}$$

$$R=1+\frac{r}{q}\mathrm{K} \tag{2}$$

where, ρ is soil bulk density (M/L^3), K is linear partition coefficient (L^3/M), θ is volumetric water content (L^3/L^3), , C is solute concentration (M/L^3), t is time (T), D is hydrodynamic dispersion coefficient (L^2/T), ν is average Darcy velocity (L/T), and x is distance (L). CXTFIT 2.1 model was used to describe behavior of the surfactants and the contaminant based on the above equations [6]. The nonequilibrium transport module of the model was used.

Results and Discussion

1. Transport and sorption behavior of the surfactants

In the column experiments conducted at a flow rate of 3 ml/min, the amounts of MADS and DADS sorbed on the aluminum oxide at the saturated condition were 26.99 mg/g and 46.87 mg/g, respectively. More sorption of DADS onto the sorbent than MADS is probably due to a higher hydrophobicity of DADS that has two hydrophobic tails. As the flow rate was increased from 3 ml/min to 6 ml/min, the amounts of the surfactants sorbed decreased in both cases of MADS and DADS. However, the decrements in the amount sorbed were not so extensive (~10%), suggesting that surfactant injection rate may not seriously affect the process of the solid phase modification in the immobilization zone.

The transport and sorption behavior of two surfactants were similar under the conditions with different water contents (25%, 50%, 75%, 100%). In the case of the experiments with DADS at the flow rate of 3 ml/min (Fig. 1), the amounts of the surfactant sorbed on the aluminum oxide in the 25%, 50%, 75%, and 100% H_2O experiments were 45.7 mg/g, 46.2 mg/g, 49.0 mg/g, and 46.9 mg/g, respectively. Retardation factors estimated by CXTFIT 2.1 model were 13.3, 13.2, 14.7, and 11.4 in the order of increasing water content. These observations appear to be due to high pore velocities in the column experiments, which were 4.95 ml/min and 10.5 ml/min on the average in the cases of 3 ml/min and 6 ml/min experiments, respectively. When the pore velocity is high, the access of a solute to active sorption sites would be limited regardless of the water content due to the presence of a preferential solution path.

2. Transport and sorption behavior of naphthalene

Behavior of organic contaminants in an immobilization zone was simulated by injecting naphthalene into the columns containing the aluminum oxide modified with DADS. Four different porewater contents (25%, 50%, 75%, 100%) were tested and the injection rate was 0.8 ml/min. As shown in Figure 2, the movement of naphthalene was retarded as the water content decreased. CXTFIT 2.1 model also predicted that retardation factor for naphthalene would increase as the water content decreased. The retardation factors obtained were 112, 122, 166, and 187 in the order of decreasing water content.

As described in equation (2), retardation factor is dependent on partition coefficient (K) and water content (θ). Partition coefficient as well as water content is believed to have affected changes in retardation factors. Partition coefficients that are obtained from traditional sorption isotherm experiments or column experiments at saturated conditions cannot be directly applied to unsaturated conditions. For example, in trichloroethylene (TCE) sorption experiments on an aluminum oxide coated with humic acid [7], partition coefficients obtained were two to three orders of magnitude higher in unsaturated conditions than in saturated conditions. The amounts of naphthalene sorbed in this study were 19.3 mg/g, 23.1 mg/g, 31.9 mg/g, and 35.0 mg/g in the order of decreasing water content. The hydrophobicity of naphthalene may have progressively hindered its access to active sorption sites as the porewater content is increased. These results show that immobilization of hydrophobic organic contaminants would be more effective in unsaturated zones modified with surfactants than in saturated zones.

References

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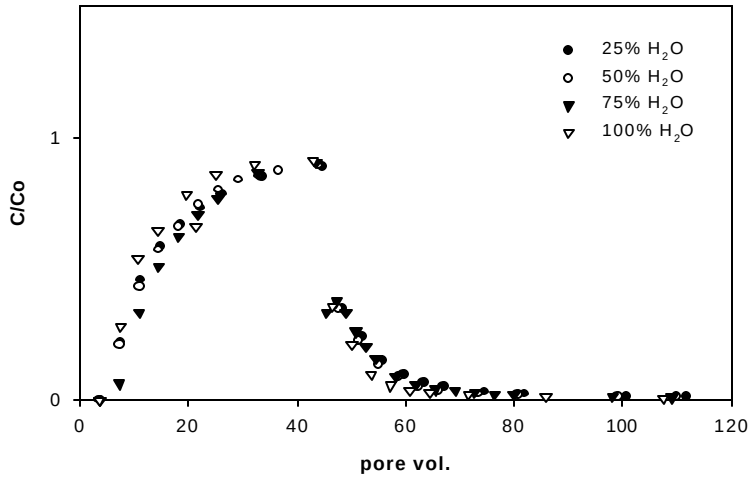

Figure 1. The Breakthrough Curve of DADS at a Flow Rate of 3 ml/min.

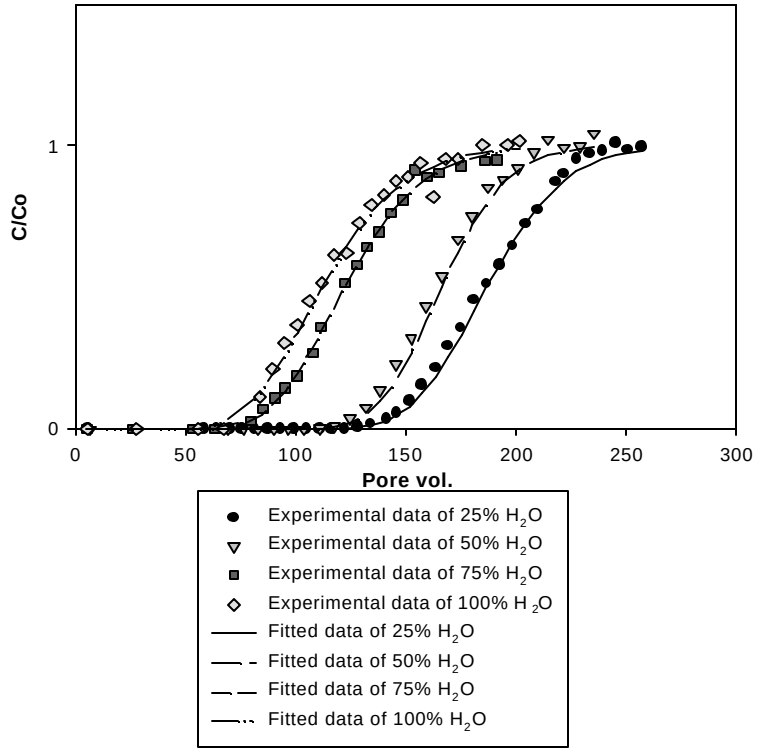

Figure 2. The Breakthrough Curve of Naphthalene from the Columns Containing an Aluminum Oxide Modified with DADS. The lines represent data fitting with a model CXTFIT 2.1.