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Partitioning of hydrophobic organic chemicals (HOC) into anionic and cationic surfactant-modified sorbents

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Abstract

Surfactant-modified sorbents have been proposed for the removal of organic compounds from aqueous solution. In the present study, one cationic (HDTMA) and three anionic (DOWFAX-8390, STEOL-CS330, and Aerosol-OT) surfactants were tested for their sorptive behavior onto different sorbents (alumina, zeolite, and Canadian River Alluvium). These surfactant-modified materials were then used to sorb a range of hydrophobic organic chemicals (HOCs) of varying properties (benzene, toluene, ethylbenzene, 1,2-dichlorobenzene, naphthalene, and phenanthrene), and their sorption capacity and affinity (organic-carbon-normalized sorption coefficient, K_{oc}) were quantified. The HDTMA–zeolite system proved to be the most stable surfactant-modified sorbent studied because of the limited surfactant desorption. Both anionic and cationic surfactants resulted in modified sorbents with higher sorption capacity and affinity than the unmodified Canadian River Alluvium containing only natural organic matter. The affinities of the surfactant-modified sorbents (K_{oc}) for most HOCs are lower than octanol/water partition coefficient (K_{ow}) normalized to the organic carbon content (f_{oc}) and the density of octanol (K_{oc} octanol); naphthalene and phenanthrene are the exceptions to this rule.

Keywords: Surfactant-modified sorbent; Cationic surfactants; Anionic surfactants; Zeolite; Alumina; Admicelle; Organic carbon normalized sorption coefficient (K_{oc})

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1. Introduction

Surfactants are known to alter the surface characteristics of soils and create sorbents that immobilize other compounds (e.g., Lee et al., 1989; Burris and Antworth, 1992; Danzer and Grathwohl, 1998). Past research has evaluated several surfactant–sorbent systems in terms of both contaminant retardation and in regard to surfactant remediation efficiency. A wide range of cationic-surfactant-modified soils has been studied for the enhanced retention of hydrophobic organic chemicals (HOCs) (e.g., Lee et al., 1989; Burris and Antworth, 1992). As an alternative to natural soils, cationic-surfactant-modified clays have been evaluated (e.g., Crocker et al., 1995). Cationic surfactants were also used to modify oxide surfaces (e.g., silica: Kibbey and Hayes, 1993; titanium oxide: Esumi et al., 1997).

Cationic-surfactant-modified zeolites were tested and proposed for the retardation of a variety of compounds

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such as HOCs, inorganic cations, anions, and inorganic oxyanions (Haggerty and Bowman, 1994; Bowman et al., 1995, 2000; Li and Bowman, 1998). These systems demonstrated chemical and biological stability (Li et al., 1998) and were pilot tested as a permeable barrier for groundwater remediation (Bowman et al., 2001).

Only a limited number of studies have investigated HOC sorption on anionic-surfactant-modified sorbents. Anionic surfactants have been used to modify alumina surfaces (Park and Jaffé, 1993; Nayyar et al., 1994; Sun and Jaffé, 1996) and kaolinite (Ko et al., 1998). HOC sorption was also studied on nonionic and anionic surfactants sorbed on natural aquifer material during surfactant transport (Danzer, 1999).

The goal of this research is to evaluate the HOC sorption efficiency of both anionic- and cationic-surfactant-modified sorbents and to evaluate factors affecting their relative efficiency. To this end, the present work evaluates sorption and desorption interactions of anionic surfactants with positively charged surfaces and cationic surfactants with negatively charged surfaces and studies the sorption of various HOCs on the different surfactant-modified sorbents. This research evaluates HOCs (i.e. toluene, ethylbenzene, *o*-dichlorobenzene, naphthalene, etc.) originating from oil spills and having differing degrees of hydrophobicity and thus varying transport and fate properties.

The objective of this study is to quantify the surfactant adsorption and the HOC partitioning between the aqueous phase and the adsorbed surfactant pseudophase (admicelles) in batch systems. All partitioning coefficients were converted into organic-carbon-normalized sorption coefficients (K_{oc}) in order to evaluate the similarities and differences among the systems. Surfactant admicelle partition affinities were also compared to K_{ow} values normalized to the organic carbon content (f_{oc}) and the density of octanol (K_{oc} octanol) and K_{oc} values of natural organic matter. Finally, data from the present work and the literature are evaluated to compare micelle and admicelle partition affinities. By evaluating both anionic and cationic surfactants on a range of surfaces, by looking at both surfactant sorption and desorption, and by looking at a range of solutes, this work seeks to provide a broader analysis of surfactant-modified mineral sorbents.

2. Materials

Table 1 presents the surfactants used in the present study along with their properties. Table 2 presents the different sorbents used and their related properties. The surfactants were provided as concentrated aqueous solutions from commercial producers (DOWFAX-8390, 36%; STEOL-CS330, 28%; HDTMA, 50%) or were purchased as pure compounds (Aerosol-OT) from Fisher. All surfactants were analyzed using HPLC methods (Table 1). All analyses utilized a Shimadzu LC 10 AD Liquid Chromatography system including an LC-10AD pump with SIL-10A autoinjector and SCL-10A control system. The column used was Alltech Nucleosil C18 (150×4.6 mm; 5 μm). The mobile phase was 80% HPLC-grade methanol dissolved in HPLC-grade water (~18 MΩ) at a flow rate of 1 ml min^{-1}.

To confirm the surfactant critical micelle concentration (CMC) values provided by the manufacturer or found in the literature, the pinacynal chloride test was used. When pinacynal chloride is added to a surfactant solution, the solution will turn blue if the surfactant is above its CMC, and remains purple if it is below the CMC (Mukerjee and Mysels, 1955; Smith et al., 1996). This is an efficient semi-quantitative process, but is limited by the fact that dye solubilization can slightly alter the CMC.

3. Methods

3.1. Surfactant sorption

Surfactant sorption was studied in batch experiments at different aqueous surfactant concentrations. The sorbent and the solution were shaken for 24 h and then allowed to settle for another 24 h, at room temperature (~25 °C). Danzer (1999) observed equilibrium conditions for surfactant sorption in less than 150 min. At the end of the experiment, the surfactant concentration in the aqueous phase was measured. The sorbed surfactant concentration was calculated based on the difference between the initial concentration and the surfactant concentration in solution after contact with the sorbent. All samples were run in duplicate. Blank samples showed no sorption on the vial or septa. Aliquots were transferred to autosampler vials with a glass Pasteur pipette.

Selected batch samples were also tested for desorption. The solution was decanted once sorption testing was completed and an equal volume of water was added (first wash). The samples were shaken for 24 h and then were allowed to settle for another 24 h. After 48 h of contact, the surfactant concentration in solution was measured and the solution was decanted. This same procedure was repeated once more (second wash). All experiments were performed with synthetic water (deionized water with 44 mg l^{-1} $CaCl_2 \cdot H_2O$, 14 mg l^{-1} $CaSO_4$, and 17 mg l^{-1} $NaHCO_3$ added).

3.2. Surfactant-modified sorbent preparation

In 500-ml laboratory bottles, 50 g of sorbent and 200 ml of aqueous surfactant solution were added. After sorption was completed, the surfactant concentration in