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Engineering Surface Functional Groups on Silica Aerogel for Enhanced Cleanup of Organics from Produced Water

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Abstract: Engineering the surface functional groups of silica aerogels has resulted in greatly enhanced separation capabilities. This approach is used to design a material that is effective at reducing the dissolved organic components of produced water. This study reports the initial results of removing dissolved hydrophobic organics using a hydrophobic ($CH_2CH_2CF_3$) surface group on the silica aerogel. The 30% by weight formulation CF_3-aerogel was able to adsorb dissolved organic species with log $K_{ow} > 2.0$, with adsorption affinity increasing with increasing log K_{ow}. Seawater salinities did not have a large effect on the adsorption of aromatic compounds. Most dissolved aromatics and organic acids with the same log K_{ow} that were tested had differing affinities for the CF_3-aerogel, with the aromatics affinity being greater. These results show the utility of modifying the aerogel surface hydrophobicity for absorbing hydrophobic dissolved organic compounds.

INTRODUCTION

Offshore oil exploration and production generates far more liquid waste than crude oil recovered. Environmental concerns and government regulations

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related to the disposal of produced water often limit its ability to be directly discharged into the surrounding environment. As a result, dealing with produced water is costly, as the water must be fully treated on the drilling platform for local discharge, reinjected into the reservoir, or shipped to the mainland for treatment and/or disposal (1, 2).

Produced waters are complex mixtures of free oil with dissolved organics and inorganics that have the potential to impact the local environment. Current on-site treatment methods are able to remove much of the free oil but are insufficient in most cases for the removal of dissolved organics in order for drilling platforms to discharge locally. Thus, new treatment approaches that can economically address both free and dissolved organic phases both in practical time and space requirements would result in significant cost savings and easier waste disposal over current handling and treatment options (2).

Free oil is conventionally removed from produced water using skimmer vessels, plate separators, gas flotation systems, and static hydrocyclones; but these systems have limited effectiveness for dissolved species. A new generation of technologies is able to provide a more complete waste treatment through gas strippers, biotreatment, adsorption, wet air oxidation, and membrane separation. These systems each vary in cost, rate of waste treatment, space required, and ease of use. From these new approaches, membrane technology and adsorption appear to be most feasible and adaptable to full-scale application. Current systems for dissolved organics removal via adsorption employ activated charcoal because of its widely utilized adsorption capability and capacity. Still, given the limited variety of surface functional groups, activated charcoal alone is unable to adsorb all of the targeted dissolved organics from produced water. As an alternative, new materials are being developed that are engineered with surface functional groups that target specific organics or compound classes and thus improve overall treatment efficiency (3).

This paper reports the first attempts at modifying the surface functional groups of silica aerogels to remove dissolved organics from production water. Silica aerogels are generally derived from sol–gels and have open foam-like structures yielding nanostructured materials with high surface areas and high porosities. As an initial attempt to remove dissolved organics, the surface functional groups have been altered to have hydrophobic $-CH_2CH_2CF_3$ end members. Previous work (4) has demonstrated these functional groups have high affinity for the free-oil phase of produced water and are readily recyclable following extraction of adsorbed organics. In this study, the ability of $-CH_2CH_2CF_3$ surface functional groups to remove dissolved organics found in produced water has been characterized. Silica aerogels can be engineered with numerous types of functional groups, so as to ultimately remove different classes of dissolved organics. As a result, this material can be synthesized to have greater porosity and surface area than activated charcoal with surface functional groups engineered to remove a greater variety of the targeted dissolved organics.

Composition of Produced Waters

The chemical composition of production water varies greatly from field to field. As a result, an average composition is difficult to define. There is typically a wide variability in the concentration of organics in production water at different locations, as it is affected by variables such as crude oil contact, temperature, and salinity. In addition, production additives, that are usually complex proprietary formulations, are added to aid in the exploration and production process. Thus, the major dissolved organic constituents can generally be separated into a few components: (a) aromatics, (b) organic acids, (c) corrosion and scale inhibitors, (d) demulsifiers and defoamers, and (e) biocides. The major aromatics found in produced water are benzene, toluene, ethylbenzene, xylenes, napthalenes, and phenols; and typical concentrations reported from oil fields from various locations are shown in Table 1. Fatty acids that have been reported in produced water range from C_1 to C_9, and reported concentrations are also shown in Table 1. Although there are methods for measuring production additives (8–11), little data are available about specific compounds and concentrations of corrosion and scale inhibitors, demulsifiers and defoamers, and biocides in produced water. Thus, engineering treatment

Table 1. Aromatic and organic acid compounds in produced water [from Somerville (1987) (5), Stephenson (1992) (1), Hansen and Davies (1994) (6), and Utvik (1999)(7)]

Compound	Typical mean (mg/L)	Reported Range (mg/L)	Log K_{ow}
Benzene	1	0.002–9	2.1
Toluene	2	0.1–5	2.7
Ethylbenzene	0.4	0.3–0.6	3.2
Xylenes	0.4	0.2–0.7	3.2
Naphthalenes	1	0–4	3.3
Phenols	7	0.5–12	1.5
Formic acid	300	30–600	−0.54
Acetic acid	700	—	−0.17
Propanoic acid	60	40–100	0.33
Butanoic acid	20	0–50	0.79
Pentanoic acid	10	0–30	1.4
Hexanoic acid	5	—	1.9
Heptanoic acid	3	—	2.4
Octanoic acid	3	—	3.1
Nonanoic acid	1	—	3.4

methods to remove these components can only be done in collaboration with industrial partners. Although not investigated here, ultimately these additives may be the most important component of produced water to remove, as the toxicity of these compounds is generally poorly characterized.

MATERIALS AND METHODS

Materials

For aerogel synthesis, 3,3,3-trifluoropropyl-trimethoxysilane and tetramethoxysilane were purchased from Gelest Inc. Methanol and ammonium hydroxide were purchased from Aldrich Chemicals.

Benzene (>99%), propanoic acid (99%), pentanoic acid (99%), and heptanoic acid (99%) were purchased from Sigma Chemical Co. Phenol (99+%), hexanoic acid (99.5+%), octanoic acid (99.5+%), and nonanoic acid (96%) were purchased from Aldrich Chemicals. Xylene (99%) was purchased from Baker Scientific. Toluene (99.8%) was purchased from Fisher Scientific. Naphthalene was purchased from Eastman Kodak. Glacial acetic acid (99.7%) was purchased from EM Scientific. Salt water (3%) for simulating seawater salinity was made with NaCl (100.0%) from Mallinkrodt Baker Inc. and Milli-Q water.

Methods

The synthesis of the 30% by weight CF_3-hydrophobic silica aerogel has been described previously (12, 13). In general, the hydrophobic aerogels were made by sol–gel processing a fluoropropyl containing alkoxide, $CF_3CH_2CH_2$-$Si(OCH_3)_3$, with tetramethoxysilane, $(CH_3O)_4Si$. Methanol, water, and ammonium hydroxide are added and poured into molds. After gelation, the gels are exchanged and dried under CO_2 or supercritical methanol in an autoclave at 13°C/5.5 MPa and 300°C/12.2 MPa pressure, respectively.

In order to determine the affinity of the hydrophobic aerogel for the dissolved organics, batch adsorption experiments were performed in silanized 5 mL glass vials with gas-tight septa seal caps. Initially, hydrophobic aerogel was weighted and transferred into the glass vial. Milli-Q water was added to the final volume desired less the volume to be added during addition of the compound of interest. Volatile compounds were transferred into the sealed vial through a septa cap using gas-tight syringes to prevent compound loss, whereas organic acids were added directly into the vial before sealing. Vials were mixed for 2 min using a vortex mixer. Concentrations of dissolved compounds were varied for constant aerogel mass, as well as varying aerogel mass for constant dissolved organics concentration.

The affinity of the hydrophobic aerogel for each aromatic compound was done individually, quantifying the change in dissolved concentration using a HP 8453 UV-Vis spectrophotometer at 200–220 nm calibrated to known standards for each compound. The affinity of the hydrophobic aerogel for the organic acids was performed as a mix of acids and quantified using 1 μL aqueous injections of filtered solutions into a HP 5890 GC-FID with a Nukol, 15 m × 0.53 mm ID, 0.50 μm film column (Supelco). The oven isothermal was ramped from 100°C to 200°C at 10°C/min with 1 min isothermal holds at the beginning and end of the run such that the total run time was 12 min, and the helium flow was ~15 mL/min.

RESULTS

The CF_3-aerogel used in this study has been characterized and discussed in detail previously (12–14). Spectroscopic and elemental analyses verify the $CH_2CH_2CF_3$ group is somehow incorporated into the silica framework. The formulation used here was also found to absorb only 2.5 wt % water (in a water-saturated atmosphere) over a period of 2+ months indicating the aerogel is highly hydrophobic (15).

The efficiency of hydrophobic aerogels with $-CH_2CH_2CF_3$ functional groups to remove dissolved organics can be determined by measuring the adsorption affinity. Figure 1 shows the adsorption affinity of the CF_3-hydrophobic aerogel toward dissolved aromatic compounds. The isotherms are fairly linear for each of the aromatic compounds. Xylene and naphthalene have the greatest affinity for the hydrophobic aerogel; toluene and benzene have an intermediate affinity; phenol has virtually no affinity. The relative affinities follow the octanol-water partitioning coefficients for each of the compounds (Table 1), with the compounds with the greatest log K_{ow} also having the highest affinity for the hydrophobic aerogel. This indicates that the removal of dissolved organics is purely due to the hydrophobic affinity of the dissolved organics to the aerogel.

Figure 2 compares the absorption isotherms measured for toluene and xylene measured in simulated seawater (3 wt % NaCl) to the absorption isotherms in deionized H_2O. The NaCl may cause a slight reduction for xylene absorption but none for the toluene absorption.

The affinity of the organic acids for the hydrophobic aerogel is shown in Fig. 3. The isotherms have more scatter than with the aromatic compounds but still exhibit isotherms that are generally linear at the concentration range investigated. As with the aromatic compounds, the organic acids with the greatest log K_{ow} (Table 1) also had the highest affinity for the hydrophobic aerogel. In addition, compounds with log $K_{ow} < 2.0$ demonstrated no affinity for hydrophobic aerogel, which is also similar to the results from the aromatic compounds.

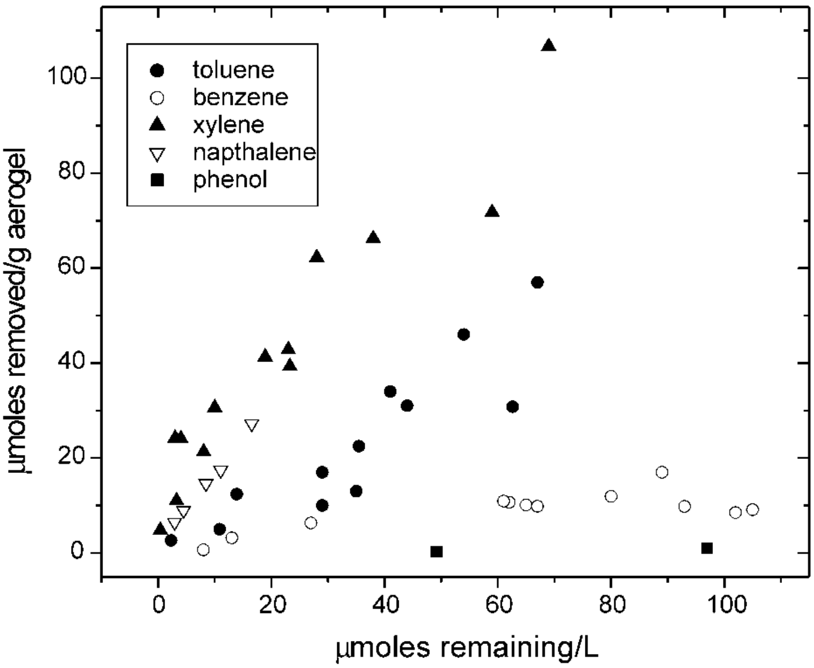

Figure 1. Adsorption of dissolved aromatic compounds found in produced water to silica aerogel with 30% (by weight) $-CH_2CH_2CF_3$ functional groups.

The hydrophobicity of the CF_3-aerogel appears to control the removal of some of the dissolved organics. Figure 4 plots the K_{ow} vs. the adsorption affinity (slope of the adsorption isotherm). For compounds with log $K_{ow} > 2.0$, the affinity for the aromatic compounds appears greater than for the organic acids, with the difference in affinity becoming more pronounced at higher log K_{ow} values. This may be a result of overriding complex surface interactions (discussed next). Nonetheless, this relationship between partitioning coefficient and removal efficiency provides some ability to predict the removal efficiency for dissolved organic components similar to those measured.

DISCUSSION

Although $-CH_2CH_2CF_3$ is a hydrophobic functional group, its current formulation has demonstrated a limited ability to remove hydrophobic compounds. Compounds with log $K_{ow} > 1$ and <2 would be expected to have some affinity for a hydrophobic surface site, but none were removed. In order to increase the hydrophobicity of the aerogel, the number of $-CH_2CH_2CF_3$ sites can be increased or a more hydrophobic surface functional group may

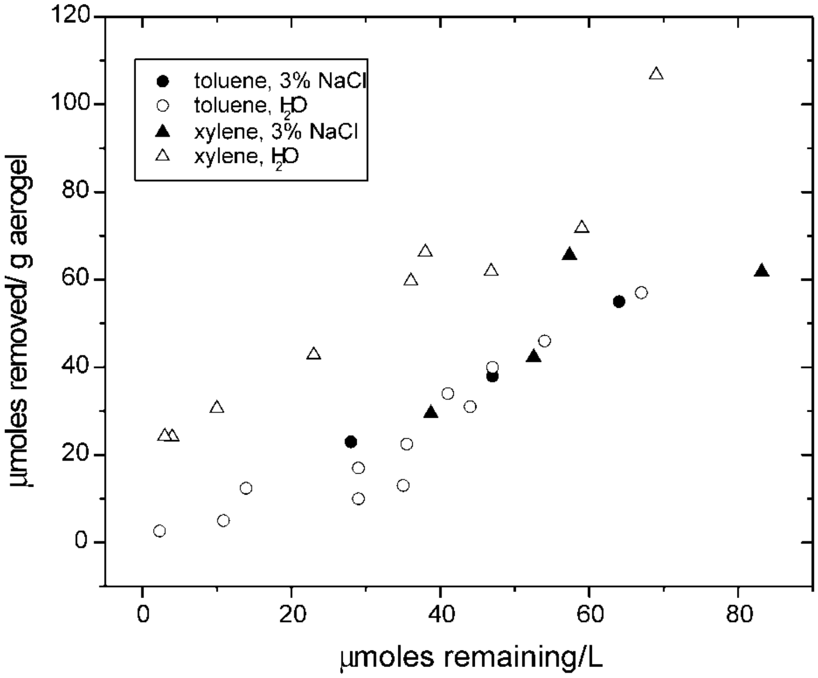

Figure 2. Adsorption in deionized water and simulated seawater of toluene and xylene to silica aerogel with 30% (by weight) $-CH_2CH_2CF_3$ functional groups.

be used. Future work intends to investigate these methods of increasing the hydrophobicity of the silica aerogel and, thus, enhance the removal of highly hydrophobic compounds already removed and enable the removal of moderately hydrophobic compounds currently left untreated.

In the formulation for the hydrophobic aerogel used in these experiments, the molar ratio of the CF_3 to silica backbone is 0.35 (by formulation). This indicates, if all the $CH_2CH_2CF_3$ group are incorporated, that one in every four Si sites are being utilized for hydrophobic absorption. Depending on how the aerogel is prepared, the remaining sites may be capped with a variety of groups, such as hydroxyl or methoxy. In this preparation, the other sites are probably Si–OH with associated water, resulting in some partial hydrophilic character, as well as hydrophobic character to the surface. This may enhance organic acid over aromatic absorption. Because the absorption affinity is higher toward the aromatics suggests other factors, such as steric effects may have an important role in the adsorption process.

In some preliminary experiments to be reported elsewhere, three different formulations of CF_3-aerogels, where the non-CF_3 surface groups were hydroxyl, methoxy, or $CH_2CH_2NH_2$, were used to adsorb xylenes. In all three cases,

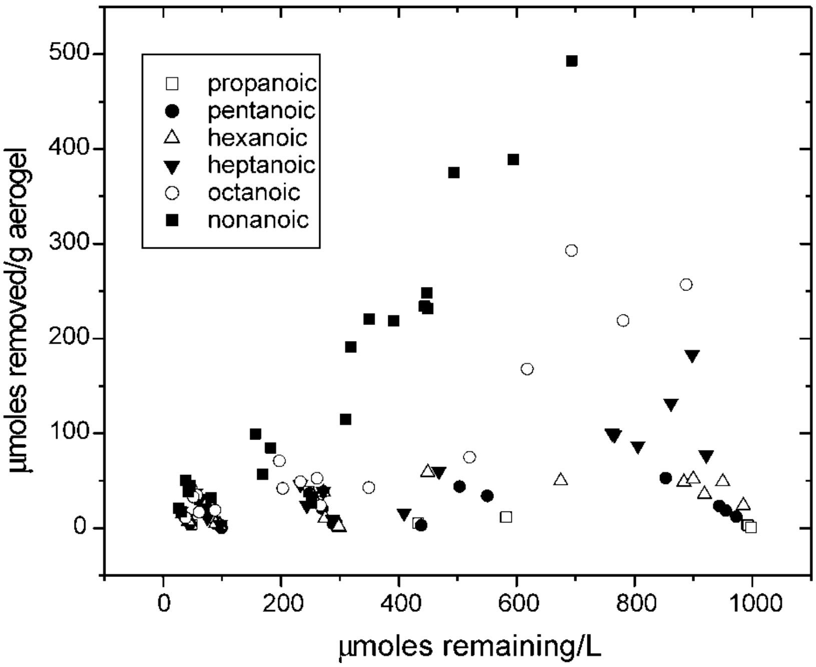

Figure 3. Adsorption of dissolved organic acids found in produced water to silica aerogel with 30% (by weight) $-CH_2CH_2CF_3$ functional groups.

similar absorption isotherms were observed as seen in Fig. 1. Thus, the functionality of these nonhydrophobic sites does not appear to interfere with the affinity of dissolved hydrophobic compounds for hydrophobic CF_3 surface functional groups. As a result, additional sites for surface adsorption can be engineered with functional groups that remove dissolved organics not removed using hydrophobic interactions. Future work intends to investigate the use of polar surface functional groups in combination with hydrophobic surface functional groups to remove dissolved organics that are either hydrophobic or hydrophilic.

In addition to having a high affinity for dissolved organics, regeneration of the hydrophobic aerogels for repeated use is critical to the feasibility of this material in production water cleanup applications. Reynolds et al. (4) demonstrated that 100% of free oil adsorbed to the CF_3-aerogel could be extracted using methylene chloride/methanol mixture and that the extraction did not affect the affinity in subsequent adsorptions. Thus, similar extractability is expected for dissolved organics; and future work will verify the extractability of dissolved organics, the affinity of the hydrophobic aerogel after extraction, and the number of times an aerogel can be extracted and remain practical for dissolved organics removal.

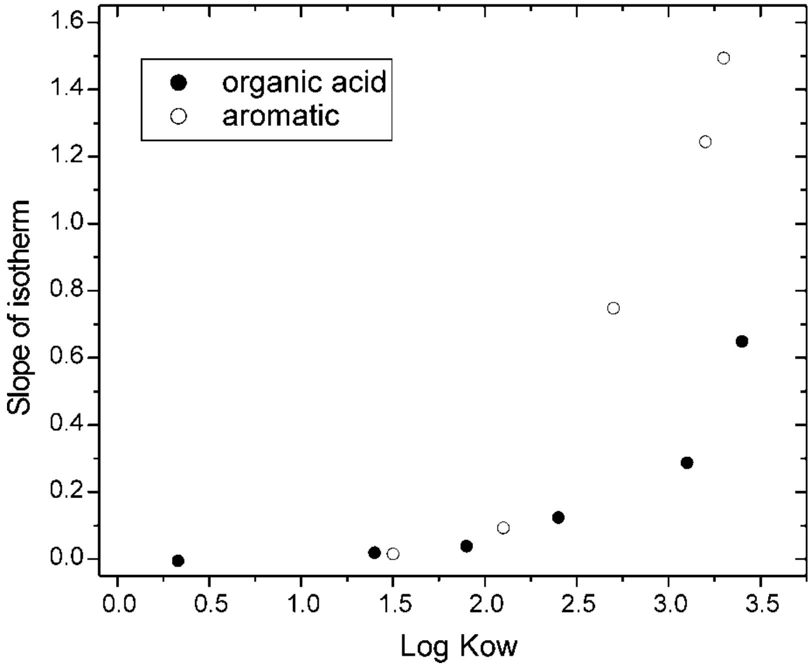

Figure 4. Affinity of dissolved organic acids and aromatic compounds to the CF_3-hydrophobic silica aerogel (slope of the linear adsorption isotherm) related to the hydrophobicity of the compounds (log K_{ow}).

SUMMARY

The role of hydrophobic aerogels specifically engineered for the treatment of produced water may result in a completely new approach in waste treatment. The configuration and costs of such a treatment process have not yet been determined. This new material has the potential to be used as the only adsorption required, or it may be more efficient to use such materials as a waste-polishing step after conventional methods. The ability to engineer functional groups on this material results in an enormous array of potential applications for efficient and targeted separations.

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