



Short communication

## Sorption and permeability of gasoline hydrocarbons in organobentonite porous media

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### Abstract

We investigate the use of organobentonites as liners for underground gasoline storage tanks to reduce the risk of subsurface contamination. A series of permeability measurements were conducted on two types of organobentonites: benzyltriethylammonium-bentonite (BTEA-bentonite) and hexadecyltrimethylammonium-bentonite (HDTMA-bentonite). Both water and commercial unleaded gasoline were used as the permeant liquids. Results of these measurements indicate that the intrinsic permeability of the organobentonite decreases by one to two orders of magnitude when the permeant liquid is changed from water to gasoline. Results of batch sorption measurements reveal that benzene sorption to both organobentonites from water is greater than benzene sorption to conventional bentonite. The magnitude of benzene sorption is related to the loading of the organic quaternary ammonium cation on the clay. As the HDTMA cation loading increases from 25% of cation exchange capacity (CEC) to 120% of CEC, benzene sorption increases. However, as the BTEA cation loading increases from 40 to 120% of CEC, benzene sorption decreases. Collectively, these results suggest that organobentonites can be used effectively to reduce hydrocarbon migration rates beneath leaking underground gasoline storage tanks, and that the optimal organic cation loading with respect to pollutant sorption may be less than 50% of cation exchange capacity for some organobentonite–solute combinations.

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### 1. Introduction

Ground water contamination from petroleum hydrocarbons can occur from small leaks or large ruptures in underground storage tanks. Small leaks can occur over long periods of

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time and may result in the dissolution of water-soluble organic pollutants such as benzene, toluene, and xylene beneath the tank that can then be transported away in ground water and potentially endanger potable water supplies. Comparatively, large releases from storage tanks can result in a nonaqueous phase liquid (NAPL) product that will migrate through the unsaturated zone and contaminate the underlying ground water. The objective of this research was to evaluate the effectiveness of two organobentonites as relatively inexpensive liner materials for underground gasoline storage tanks.

Organobentonites are organophilic clays synthesized by the ion exchange of quaternary ammonium organic cations (with nonpolar organic functional groups) onto the mineral surfaces of bentonite. Bentonite is primarily composed of  $\text{Na}^+$ -saturated montmorillonite. Previous studies have shown that these organobentonites strongly sorb nonionic organic pollutants relative to conventional bentonite [1–6], and the magnitude and mechanism of sorption is related to the molecular structure of the quaternary ammonium cation [5,7–9]. Unlike conventional bentonite, which swells in the presence of water and desiccates in the presence of nonpolar organic liquids, organobentonites exhibit the reverse behavior. They swell in the presence of nonpolar organic liquids and desiccate in the presence of water [10–13]. Based on these properties, they have been studied for use in earthen liners for waste disposal facilities [14], and their geotechnical engineering properties have been investigated [15,16].

To date, however, only one study has quantitatively measured and compared the permeabilities of organobentonites to water and commercial gasoline [17]. In this work, the authors observed significantly lower intrinsic permeabilities for dicytyldimethylammonium-bentonite when gasoline was the permeant liquid compared to water. Furthermore, only a few studies have quantified how the amount of quaternary ammonium cation exchanged onto the clay corresponds to the magnitude of solute sorption. In a study of organic solute sorption to HDTMA-smectite, it was found that sorption increased with organic-cation loading [1]. Smith and Jaffé [8] reported that the sorption capacity of benzyltriethylammonium-bentonite for tetrachloromethane increased with increasing organic-cation loading. No published studies have reported an inverse relation between organic cation loading and the magnitude of sorption.

We propose that organobentonites can serve as effective and inexpensive liners for underground gasoline storage tanks. In the presence of water, we hypothesize that they will maintain a relatively high permeability and perched water will not easily accumulate on top of the liner. If an underground storage tank leaks significantly, the free product will cause the organobentonite to swell, reducing its permeability and the migration of the non-aqueous phase gasoline. If some of the gasoline is solubilized in the subsurface water, the gasoline hydrocarbons will sorb significantly to the organobentonite to reduce the pollutant migration rate downward.

## 2. Experimental materials and methods

The organoclays used in the permeability measurements were synthesized in the laboratory using Wyoming bentonite obtained from American Colloid Co., Chicago, IL. The grain-size distribution is 3.6% sand, 7.3% silt, and 89.1% clay, its organic-carbon content is

0.1%, and its CEC (as determined by ammonium cation exchange) is 78.5 meq./100 g [5]. Two quaternary ammonium compounds were used to synthesize the organoclays: benzyltriethylammonium (BTEA) chloride and hexadecyltrimethylammonium (HDTMA) bromide. These compounds were obtained from Aldrich. The organobentonite was synthesized by the aqueous system exchange of the dissolved quaternary ammonium compound onto the internal and external mineral surfaces of the Wyoming bentonite [5]. For all permeability measurements, the mass of quaternary ammonium cation exchanged onto the bentonite equaled 75% of the CEC of the bentonite. These sorbents are referred to as 75%BTEA- and 75%HDTMA-bentonite throughout this paper.

For sorption measurements, a Wyoming bentonite sample of slightly different composition was used for organobentonite synthesis. This sample was obtained from Colloid Environmental Technologies Co. The sample has an organic-carbon content of 0.2% and its CEC (as determined by ammonium cation exchange) is 69.1 meq./100 g. For each organic cation, four organobentonites were synthesized, with each sorbent characterized by a different loading of the organic cation onto the bentonite. For BTEA, the mass of cation exchanged onto the bentonite corresponds to 40, 70, 100, and 120% of CEC. These four sorbents will be referred to as 40%BTEA-bentonite, 70%BTEA-bentonite, etc. throughout this paper. For HDTMA, the mass of cation exchanged onto the bentonite corresponds to 25, 80, 100, and 120% of CEC. These four sorbents will be referred to as 25%HDTMA-bentonite, 80%HDTMA-bentonite, etc. throughout this paper.

Measurements of the intrinsic permeability of specimens composed entirely of 75% BTEA-bentonite or 75%HDTMA-bentonite were performed in triplicate using a changing-head flexible-wall permeameter according to ASTM method D5084 along with modifications to this method described by Li et al. [13]. Four lifts of the sample were compacted in a 5 cm diameter compaction mold with Standard Proctor compaction effort. The optimum compaction moisture contents of the 75%BTEA- and 75%HDTMA-bentonites were 20 and 16%, respectively. The compaction moisture contents for the 75% BTEA- and 75%HDTMA-bentonites were chosen to be 2% wet of optimum, or 18 and 22%, respectively. Following compaction, the specimens were placed in flexible-wall permeameters and back-pressure saturated with the permeant liquid at 43 psi (296 kPa) for 24 h. The confining (cell) pressure was 45 psi (310 kPa). The pressure at one end of the specimen was reduced to initiate fluid flow. The lowest practical hydraulic gradient was used for each measurement to allow completion of the test within 4–8 weeks. In all cases, hydraulic gradients were less than 75. Permeability measurements were concluded when three criteria were met: (1) results of three consecutive permeability determinations fell within  $\pm 25\%$  of their mean, (2) the ratio of the inflow rate to the outflow rate for the specimen was between 0.75 and 1.25, and (3) a plot of intrinsic permeability as a function of time showed no distinct increasing or decreasing slope. The mean of the final three intrinsic permeability values was reported as the permeability of the soil specimen. The permeant liquids used were a 0.005N  $\text{CaSO}_4$  aqueous solution and 87-octane unleaded commercial gasoline.

Sorption isotherms were generated with a batch sorption procedure at 20 °C using  $^{14}\text{C}$ -benzene and a Packard 1900CA scintillation analyzer to quantify the concentration of benzene in the aqueous phase at equilibrium. Sorbed concentrations were calculated by difference. Additional details of this experimental procedure are given elsewhere [18].

### 3. Results and discussion

The results of the permeability measurements for the two types of specimens and for both permeant liquids are shown in Table 1. The permeability values for both types of organobentonites increase as the permeant liquid is changed from gasoline to water. Because the intrinsic permeability is not a function of the fluid properties, this result indicates that the physical structure of the porous medium changes with different permeant liquids. These observations support the hypothesis that organobentonites effectively intercalate gasoline hydrocarbons into the interlamellar space, and that these hydrocarbons wet external mineral surfaces more effectively than water, presumably because of the organophilic nature of the organic-cation-exchanged mineral surfaces. It should also be noted that all of these permeabilities are significantly higher than the permeabilities of a compacted earthen liner composed of 8% or more untreated Wyoming bentonite when water is the permeant liquid. For example, [13] reported permeabilities on the order of  $10^{-14}$  cm<sup>2</sup> for compacted earthen liner specimens composed of 92% fine sand and 8% Wyoming bentonite. The permeabilities of water to the organobentonites reported here are on the order of water permeabilities for fine sand; the permeabilities of gasoline to these organobentonites is comparable to permeabilities reported for uncompacted silt or silty-clays with water as the permeant liquid.

Isotherms depicting benzene sorption to each of the four BTEA-bentonites are shown in Fig. 1. Sorption is strong and nonlinear (Fig. 1) compared to benzene sorption to untreated bentonite reported previously [18]. For this system, benzene sorption occurs primarily by a physical adsorption process driven by London forces between the nonpolar solute and the relatively rigid, nonpolar surface formed by the BTEA cations on the clay mineral surface [5,8]. The most interesting result depicted by these data is the observation that the magnitude of benzene sorption decreases as the organic-cation loading onto the bentonite (as measured in terms of percent of cation exchange capacity) increases from 40 to 120%. One possible reason for this behavior is that surface area is reduced at higher organic-cation concentrations, thereby reducing sorption. This result has great practical significance, as it indicates that commercial organobentonites may actually function more effectively at lower, less costly, organic cation loadings.

The sorption isotherm data for the BTEA-bentonites were fit to the linearized form of the Langmuir isotherm model:

$$\frac{C_e}{C_s} = \frac{1}{ab} + \frac{C_e}{a} \quad (1)$$

Table 1  
Mean values of intrinsic permeabilities and associated standard errors for organobentonite soil specimens

| Organobentonite    | Permeant liquid | Mean intrinsic permeability (cm <sup>2</sup> ) | Standard error        |
|--------------------|-----------------|--|-----------------------|
| 75%BTEA-bentonite  | Water           | $2.4 \times 10^{-9}$                           | $1.6 \times 10^{-9}$  |
| 75%BTEA-bentonite  | Gasoline        | $3.4 \times 10^{-11}$                          | $5.3 \times 10^{-12}$ |
| 75%HDTMA-bentonite | Water           | $1.0 \times 10^{-10}$                          | $4.7 \times 10^{-11}$ |
| 75%HDTMA-bentonite | Gasoline        | $8.0 \times 10^{-12}$                          | $1.1 \times 10^{-12}$ |

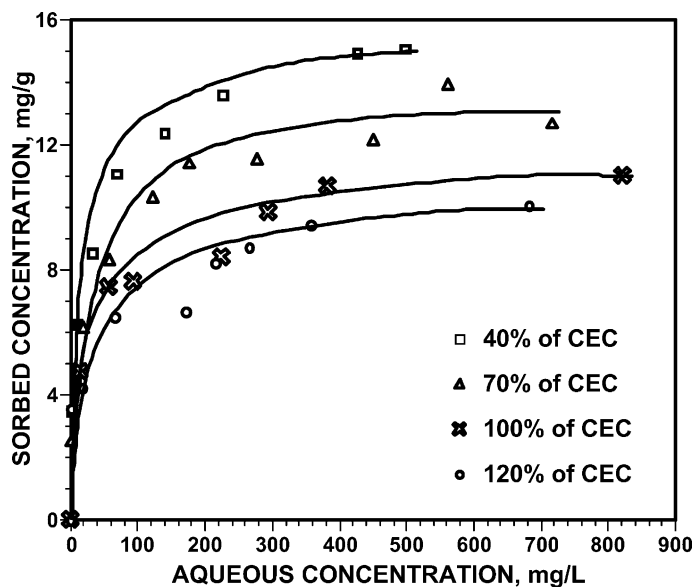


Fig. 1. Equilibrium isotherms for benzene sorption to four benzyltriethylammonium-bentonites from water. Different symbols identify sorbents exchanged with different amounts of organic cations expressed in terms of the bentonite's cation exchange capacity (CEC).

where  $C_e$  and  $C_s$  are the equilibrium aqueous (mg/l) and sorbed (mg/kg) benzene concentrations, respectively, and  $a$  and  $b$  are constants determined by linear regression. We do not assume that the theoretical Langmuir assumptions apply to this system. As such, we use Eq. (1) only as a curve-fitting tool for the isotherm data. These isotherm parameters are reported in Table 2 along with their associated regression coefficients of determination ( $R^2$ ).

For benzene sorption to each of the four HDTMA-bentonites (Fig. 2), the isotherms are approximately linear. This result is also consistent with previous observations, and indicates that sorption is caused by benzene partition between water and the organic-matter phase formed by conglomeration of the alkyl chains of the HDTMA cations [1,18]. As the organic-cation loading increases from 25 to 100% of CEC, the magnitude of sorption increases. However, as the cation loading onto the bentonite increases from 100 to 120% of CEC, no additional increase in sorption is observed. Therefore, it appears that

Table 2

Langmuir isotherm parameters for benzene sorption to bentonite exchanged with different amounts of benzyltriethylammonium (BTEA) cations

| Sorbent            | $a$ (mg/kg) | $b$ (l/mg) | Coefficient of determination ( $R^2$ ) |
|--------------------|-------------|------------|--|
| 40%BTEA-bentonite  | 14,300      | 0.0636     | 0.99                                   |
| 70%BTEA-bentonite  | 12,500      | 0.0500     | 0.99                                   |
| 100%BTEA-bentonite | 11,100      | 0.0321     | 0.99                                   |
| 120%BTEA-bentonite | 10,000      | 0.0323     | 0.98                                   |

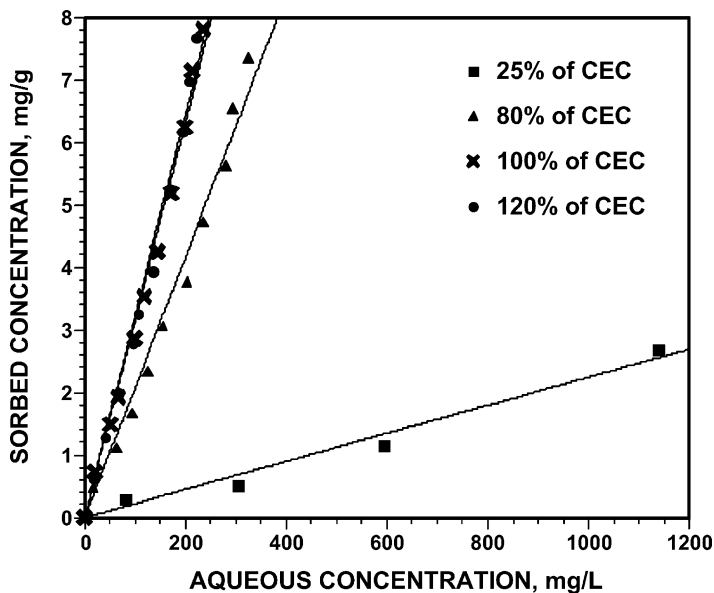


Fig. 2. Equilibrium isotherms for benzene sorption to four hexadecyltrimethylammonium-bentonites from water. Different symbols identify sorbents exchanged with different amounts of organic cations expressed in terms of the bentonite's cation exchange capacity (CEC).

cation loadings greater than 100% will likely not benefit sorption when benzene is the solute.

It is likely that the surface area of the HDTMA-bentonite decreases as the organic-cation loading increases. However, unlike for BTEA-bentonite, higher organic-cation loading does not decrease benzene sorption because the uptake is caused by solute partition into the bentonite's organic matter, not by surface adsorption. The HDTMA-bentonite isotherm data were fit to the linear isotherm model:

$$C_s = K_d C_e \quad (2)$$

where  $K_d$  is the sorption distribution coefficient and equals the slope of the sorption isotherm. The  $K_d$  values for 25, 80, 100, and 120% HDTMA-bentonite are 2.25, 20.8, 31.6, and 32.3 l/kg, respectively. All linear regression correlation coefficients were greater than 0.98.

#### 4. Conclusions

Organobentonites are promising materials for liners beneath underground gasoline storage tanks. When they are water-saturated, they maintain relatively high permeabilities. However, when separate-phase gasoline contacts the liner, the permeabilities are reduced by one to two orders of magnitude, thereby reducing the migration of gasoline into the subsurface. When gasoline constituents such as benzene are dissolved in the water phase, the

organobentonites function as powerful sorbents for the hydrocarbons. Furthermore, benzene sorption to BTEA-bentonite is reduced as the BTEA cation substitution (as a percent of CEC) increases from 40 to 120%. Therefore, some organobentonites may be more effective with respect to contaminant sorption (and less expensive to manufacture) when they have organic cation loadings less than CEC.

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