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Experimental investigation of methyl *tert*-butyl ether dissolution in saturated porous media[☆]

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ABSTRACT

This study aims to investigate methyl *tert*-butyl ether (MTBE) dissolution in saturated porous media. A series of 1D column experiments were conducted in laboratory to obtain MTBE dissolution data with different groundwater velocity, initial MTBE saturation and grain size of porous medium, and in the presence of other nonaqueous liquids. Results indicate that higher groundwater velocity increases MTBE dissolution rate and higher initial MTBE saturation reduces effective permeability to slow MTBE dissolution rate. Smaller grain size medium gives higher MTBE dissolution rate because of higher permeability. The addition of trichloroethylene enhances MTBE dissolution, with an optimal mass ratio of 10:2, while the presence of *p*-xylene prolongs complete dissolution of MTBE. Mass transfer correlations are developed for MTBE dissolution rate based on the degree of MTBE saturation S_n . Mass transfer rate is characterized by Re' with a high exponent for $0.3000 < S_n < 0.5482$, while it is related to medium grain size and S_n for $S_n \leq 0.3000$.

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1. Introduction

Nonaqueous phase liquids (NAPLs), such as aromatic hydrocarbon, chlorinated solvents and methyl *tert*-butyl ether (MTBE), are the main contaminants in subsurface environments. The location, prediction, and remediation of NAPL contaminated zones are significantly influenced by NAPL transport process, which mainly includes dissolution and diffusion of NAPL. It is important to understand NAPL dissolution in groundwater. MTBE is once an additive in gasoline, but its effect on groundwater has not received sufficient attention. When MTBE leaks from an oil storage tank or pipeline, it will penetrate water surface quickly and then diffuse because of its high solubility in water [1], leading to wide-range and long-lasting pollution. Its half-life in groundwater is at least two years [2], so it will accumulate in the subsurface. MTBE has been reported [3–5] as a significant pollutant in the aqueous environment.

Several investigations in laboratories and theories were carried out to better understand NAPL transport in porous media. Early experiments with homogenous short column indicated a dependence of dissolution rate on the distribution pattern of entrapped NAPLs and aqueous phase velocity [6], and volumetric NAPL content [7]. Heterogeneous systems with a contaminated coarse sand region surrounded by

fine sand were used to investigate the effect of porous medium on NAPL dissolution [8–10]. Most of experiments have a common characteristic: effluent concentration approaches the NAPL equilibrium concentration at the beginning and gradually decreases to its detection limitation [8–12]. It can be explained by local equilibrium or limited rate assumption of dissolution kinetics [13–16], based on which some Sherwood–Gilliland empirical correlations have been established to evaluate the NAPL mass transfer process [6,7,17,18], which are dependent on the experimental system.

Recently, for the mass transfer of NAPL in aqueous phase, 2D and 3D flow systems were used to investigate the effects of porous medium property and transverse dispersion on flow field heterogeneity [19–23]. The flow in these systems is complicated and affects the NAPL dissolution process. Some mass transfer models were presented to describe the NAPL breakthrough curves with some controlling parameters, such as capillary and mass transfer kinetics in the media [24, 25]. Some experiments with multi-component NAPLs, such as BTEX (benzene, ethylbenzene, toluene and xylene) and gasoline mixture, were performed to explore the interactions and dissolution in porous media. These multi-component NAPLs were considered as ideal mixtures following Raoult's law, which is the driving mechanism of the mass transfer process [26–29]. However, applying Raoult's law in the presence of non-ideal organic compounds such as chlorohydrocarbon and aromatic hydrocarbons will lead to appreciable errors in estimates of NAPL dissolution process in porous media.

These investigations provide valuable insights on NAPL dissolution in subsurface environments, but the study on MTBE is limited [30]. A

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study has revealed that porous medium and fluid properties affect MTBE dissolution and its mass transfer in saturated and unsaturated porous media [31], so the data for MTBE are essential to improve our knowledge of its dissolution in porous media. Since a short column cannot provide a 1D steady flow, a column with length-diameter ratio above 10 is manufactured in this study to obtain MTBE dissolution data in saturated porous media. Some experiments focus on single MTBE to study its dissolution in saturated porous media and mass transfer coefficient correlations dependent on experimental system are developed. Then multi-component NAPL experiments are conducted to explore how other NAPLs (trichloroethylene (TCE) and *p*-xylene) influence MTBE dissolution. MTBE dissolution data are correlated with Sherwood–Gilliland empirical correlations. These data are critical to MTBE pollution treatment, especially in laboratory-scale or larger-scale soil washing [32]. According to the MTBE dissolution mechanism, different flushing flow rates can be used under different conditions, and subsequent extraction and distillation can extract organic compounds from water.

2. Experimental

2.1. Materials

The physical property of MTBE, TCE, and *p*-xylene (chromatographic grade; Tianjin Guangfu Fine Chemical Research Institute) are presented in Table 1.

Table 1
Physical property of organic liquids

Material	Density, $\rho_n/g \cdot cm^{-3}$	Solubility, $C_s/mg \cdot L^{-1}$	Interfacial tension, $\sigma/mN \cdot m^{-1}$	Free liquid diffusivity, $D_l/cm^2 \cdot s^{-1}$	Reference
MTBE	0.741	48,000	19.1	1.5×10^{-5}	[33]
TCE	1.470	1270	30	8.8×10^{-6}	[6]
<i>p</i> -Xylene	0.861	130	35	8.2×10^{-6}	[26]

The porous media were 0.85–2.00 mm, 0.42–0.85 mm, and 0.18–0.30 mm silica sand, sieved, washed and sterilized at high temperature. The basic characteristics are given in Table 2.

Table 2
Properties of experimental silica sand

Silica sand/mm	Average grain size, D_{50}/mm	Sand bulk density, $\rho/g \cdot cm^{-3}$	Porosity, ϕ	Hydraulic conductivity, $K/cm \cdot s^{-1}$	Permeability, k/m^2
0.85–2.00	1.15	0.6000171	0.250345	1.2478	1.24×10^{-9}
0.42–0.85	0.6	0.00161	0.370	0.5714	5.71×10^{-10}
0.18–0.30	0.25	0.00152	0.390	0.0576	5.76×10^{-11}

2.2. Experimental setup

In order to provide horizontal one-dimensional flow, dissolution experiments were conducted with a thin column ($\phi 38 \text{ mm} \times 400 \text{ mm}$) fabricated with normal transparent glass, which will not react with experimental materials. Schematic diagram of 1D dissolution experiments is given in Fig. 1. Both ends of the column are bolted with flange connections, so it is convenient for loading and unloading silica sand. There are four glass ports with screw and screw cap on one side of the column, used for sample injection and sampling, and their distances to the left outlet 2 are 3, 10, 20, and 30 cm. NAPL injection port is in the middle of the 5 cm contaminant zone.

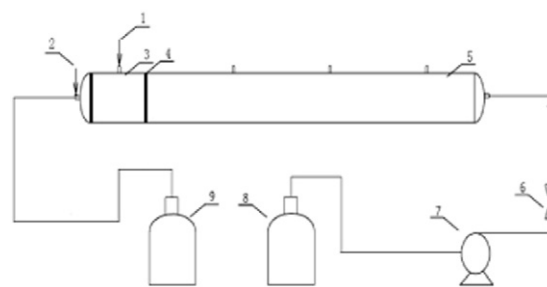


Fig. 1. Schematic diagram of 1D column dissolution experiments. 1 – NAPL injection port; 2 – outlet; 3 – NAPL contaminant zone; 4 – fine sand; 5 – coarse sand; 6 – cut off valve; 7 – peristaltic pump; 8 – influent reservoir; 9 – effluent reservoir.

2.3. Methods

All dissolution experiments were performed in a horizontal sand column. In order to reserve a 5.0 cm length NAPL contaminant zone, the column was filled with coarse sand in a lift of approximately 3.0 cm and 6.0 cm length was left. This layered and tight loading process ensured the soil in the column sufficiently uniform to provide 1D flow. The 5.0 cm length contaminant zone was sandwiched by two layers of 0.5 cm fine sand (0.075 mm) as illustrated in Fig. 1. Because of the difference in medium grain size, a capillary barrier could be produced by the fine sand so that the injected NAPL was retained in the 5.0 cm length contaminant zone. Stainless steel screens were placed inside the two ends of the column to prevent the loss of media. After compaction, the column was saturated by pumping distilled water at a low flow rate to eliminate air. Stable liquid flow was provided by a peristaltic pump (Masterflex, Cole-Parmer Instrument Company).

Before experiments, all compounds were dyed with a small quantity of oil red O ($0.05 \text{ g} \cdot \text{L}^{-1}$; Baihao Biological Technology Chemical) so that MTBE dissolution and transport could be visualized. The contaminant zone was prepared by injecting a known amount of dyed NAPLs. From the observation we could judge whether NAPL distribution in silica sand was uniform and whether NAPL was out of contaminant zone. According to the conservation of mass and silica sand properties, the initial NAPL saturation was estimated [18]. A series of dissolution experiments were conducted under various conditions, i.e., sand grain sizes with D_{50} of 0.025, 0.06, and 0.115 cm, initial NAPL saturations of 0.193, 0.366, 0.579, and 0.602, aqueous velocities of 2, 3, and 4 $\text{ml} \cdot \text{min}^{-1}$, and different initial mass ratios of mixture. Aqueous samples were collected at the outlet of the column in certain time interval until NAPL concentration in the aqueous phase was reduced to below analytical detection limits.

2.4. Chemical analysis

Aqueous effluent samples were analyzed by Autosystem XL gas chromatograph (PerkinElmer, USA) equipped with a capillary column (FFAP, 30 m \times 0.25 mm i.d. \times 1.0 μm), Turbochrom4.1 workstation and Flame ionization detector. The chromatographic conditions for MTBE are as follows: injection temperature of 180 $^{\circ}\text{C}$, oven temperature of 105 $^{\circ}\text{C}$, detector temperature of 210 $^{\circ}\text{C}$, N_2 as the carrier gas with flow rate 0.8 $\text{ml} \cdot \text{min}^{-1}$, H_2 flow rate 45 $\text{ml} \cdot \text{min}^{-1}$, air flow rate 450 $\text{ml} \cdot \text{min}^{-1}$, and split ratio 10:1, injection volume of 1 μl aqueous sample.

3. Results and Discussion

3.1. MTBE dissolution curves in aqueous environment

The dissolution curves at the outlet in the 0.42–0.85 mm silica sand are shown in Fig. 2. The relative concentration undergoes a slight

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