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Adsorption of MTBE from contaminated water by carbonaceous resins and mordenite zeolite

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Abstract

Equilibrium and kinetic adsorption of methyl *tert*-butyl ether (MTBE) onto two carbonaceous resins and one zeolite was elucidated in this study. The Freundlich isotherm is adequate for describing the adsorption equilibrium of MTBE onto all the tested adsorbents in deionized water and natural waters. The resins of Ambersorb 563 and 572 have the highest adsorption capacity and almost twice the capacity of mordenite in deionized water. A different extent of NOM competition with MTBE was found for the carbonaceous resins in natural waters. For mordenite, no competitive adsorption was observed in natural water. The ideal adsorbed solution theory combined with equivalent background compound (IAST-EBC) model successfully described and predicted the adsorption of MTBE onto the carbonaceous resins in natural waters. The pore diffusion and micropore diffusion model fit the experimental data fairly well and successfully predicted the transport of MTBE within the adsorbent under different operating conditions. The small tortuosity factor between 1.2 and 2.3 of the resins for the diffusion of MTBE was observed, indicating a superior transport property for the carbonaceous resins in natural waters. The intracrystalline diffusivity of MTBE in natural water was much slower than that in deionized water, only 1/10 in STL and 1/3 in FS natural water, since the aperture entrances of mordenite was appreciably hindered by NOM.

Keywords: Adsorption; MTBE; NOM; Resin; Zeolite

1. Introduction

Methyl *tert*-butyl ether (MTBE) is the most common oxygenated fuel additive used to increase the octane rating and to enhance the combustion efficiency of gasoline. Due to its high water solubility, slow biodegradability, low Henry's law constant, and small partition coefficient, MTBE is relatively stable and recalcitrant compared to many other gasoline components such as benzene, toluene, ethylbenzene and xylene (BTEX) in the environment [1–3]. Although the impacts of MTBE on human health are not well understood, it has already been listed as a possible human carcinogen [4]. In addition to the potential health risk, the compound also produces an unpleasant odor at low concentration [5,6].

The adsorption process is one of the promising techniques for the control of synthetic organic compounds (SOCs) in many environmental applications [7]. Granular activated carbon (GAC) is the most popular adsorbent used and the process has been shown to successfully remove MTBE from contaminated water [8–10]. However, poor removal efficiency may be observed in applying carbon adsorption process, especially when other SOCs co-exist with MTBE. Consequently, the carbon adsorption process may not be cost-effective for MTBE removal. The presence of natural organic matter (NOM) may also reduce the adsorption capacity and slow the kinetics while applying activated carbon in natural water [11]. To enhance the performance of adsorption and diminish the adverse effect of NOM, different types of adsorbents, such as carbonaceous resins and mordenite zeolite, were proposed for the removal of MTBE from contaminated waters.

The carbonaceous resins of Ambersorb 563 and 572 have been found to possess a superior adsorption capacity for MTBE in different water matrixes [12–14]. It was found that the two carbonaceous resins, Ambersorb 563 and 572, were promising candidates for the removal of MTBE from aqueous phase. On the other hand, the zeolite with appropriate pore size was also suggested as one of the leading adsorbents for the removal of MTBE from the aqueous phase, such as hydrophobic mordenite,

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12 ring zeolite with 6.5 × 7.0 Å pore size and all-silica β zeolite with 7.1 × 7.3 Å pore size [15,16]. Based on the equilibrium experiments, mordenite and all-silica β zeolite may have better adsorption capacity of MTBE than that of activated carbon in deionized water.

Although promising equilibrium adsorption capacity of MTBE onto the carbonaceous resins and hydrophobic zeolites were verified, most studies focused on simplified water matrix such as deionized water and artificial groundwater. The adsorption behavior of MTBE in natural water is expected to be different from that in deionized water. So far, there has been much less investigation in the competition between MTBE and NOM for the adsorption on carbonaceous resins and zeolite. Additionally, the adsorption kinetics of MTBE on the adsorbents in both deionized water and natural water has been scarcely investigated. To evaluate the effectiveness of adsorption processes on the removal of MTBE-contaminated water, kinetic and equilibrium adsorption of MTBE onto two carbonaceous resins, Ambersorb 563, 572, and one zeolite, mordenite, in both deionized water and natural waters were elucidated in this study. Both kinetic and equilibrium experiments for MTBE onto the adsorbents were conducted. The data were then interpreted with appropriate equilibrium and kinetic models.

2. Materials and methods

2.1. Deionized water and natural waters

Deionized water was prepared using a Milli-Q ultra-pure-water purification system (Bedford, MA, USA). Non-purgeable dissolved organic carbon (NPDOC) for the water is smaller than 0.1 mg/L. Natural waters were collected in a groundwater source from San Tyau Liu (STL) and a surface water source from Feng Shan (FS), both located in south Taiwan. The average pH and NPDOC were 8.0 and 1.2 mg/L for STL groundwater, and were 7.7 and 2.1 mg/L for FS surface water.

2.2. Adsorbents and adsorbate

Two types of adsorbents, carbonaceous resins and mordenite zeolite, were employed in this study. The carbonaceous resins, Ambersorb 563 and Ambersorb 572, obtained from Rohm and Haas Company (Supelco, USA) were used. A mordenite type of zeolite (CBV 90A, Zeolyst International, USA) was chosen as one of adsorbents since the aperture size is comparable to the MTBE kinetic diameter. The SiO_2/Al_2O_3 ratio of the mordenite used is 90. For comparison, the commercial F400 activated carbon from Calgon Carbon, USA was also tested. The surface area, pore volume and pore size distribution was measured by nitrogen adsorption method at 77 K (ASAP 2010, Micromeritics, USA). The physical properties of the adsorbents are listed in Table 1.

MTBE-contaminated water was prepared by adding predetermined amount of reagent-grade MTBE (Janssen Chimica, Belgium) into deionized water or natural water. For analysis, a standard solution of 2000 mg/L MTBE from Supelco, USA was diluted for establishing the analytical calibration curve. Water samples were analyzed for MTBE concentration by the solid-phase micro extraction/gas chromatograph (SPME/GC) method [17]. In the SPME process, a 75 μm PDMS/Carboxen commercial fiber (Supelco, USA) was immersed into the water samples to extract MTBE. During the extraction, the temperature was controlled at 18 °C. The sample volume was 1.6 mL with addition of 25% (w/v) sodium chloride, and the extraction time was set at 60 min. The extracted fiber was injected into a GC (6890 Plus, Agilent, USA) equipped with a flame ionization detector for the determination of MTBE concentration. The detection limit of the method was determined to be 0.5 μg/L.

Table 1
Properties of the tested adsorbents

Properties	Ambersorb 563	Ambersorb 572	Mordenite
Particle density (kg/m^3)	1494[a]	1809[a]	1700[c]
Porosity (%)	52.5[b]	47.6[b]	28.0[c]
BET surface area (m^2/g)	494	958	477
Total pore volume (cm^3/g)	0.58	0.84	0.32
Micropore	0.19	0.38	0.19
Mesopore	0.15	0.22	0.10
Macropore	0.24	0.24	0.04

[a] Measured by water displace method.
[b] Estimated from about the 100 oven-dried carbonaceous resins.
[c] From D.W. Berck, Zeolites Molecular Sieves: Structure, Chemistry and Use, Wiley, New York, USA, 1974.

2.3. Adsorption experiments

The adsorption capacity of MTBE in deionized water and natural water was measured by the bottle-point technology [18]. In the equilibrium experiments, the sizes of resins were used as received (0.297–0.841 mm, or 20–50 US mesh), while that of F400 carbon were pulverized and sieved to 0.037–0.149 mm (100–400 US mesh) to ensure equilibrium status. To simplify the modeling process for the kinetic data, the resins and F400 carbon used in kinetic experiments were sieved to 0.297–0.420 mm (40–50 US mesh). Since mordenite was obtained as a powdered adsorbent, it was directly used in adsorption experiments. The mordenite adsorbent size measured by particle analyzer is 0.76 μm. Preliminary experiments showed that the adsorption capacities of carbonaceous resins and activated carbon at 4 days and 5 days were almost the same, indicating that the adsorption equilibrium may be reached within 4 days. For mordenite adsorbent, the adsorption equilibrium may be reached within 3 h. To assure equilibrium status, the experimental time of all the adsorbents used was set at 5 days. The procedures of kinetic experiment were almost the same as those of the equilibrium experiment except that more samples were taken and analyzed. The bottles were stirred magnetically at 450 rpm to reduce the liquid-phase resistance between the adsorbent and bulk solution. Blank experiments showed that MTBE concentration remained nearly constant (less than 2% of difference) during the time scale of the experimental period, revealing that the volatility of MTBE and its interaction with the bottles can be neglected. The samples of the carbonaceous resins and activated carbon, and mordenite were filtrated with 0.45 and 0.20 μm filter (Advantec MFS,