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Adsorption of Methyl Tertiary Butyl Ether on Hydrophobic Molecular Sieves

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ABSTRACT

The use of methyl tertiary butyl ether (MTBE) as a gasoline additive has resulted in serious environmental problems following spills and leaks, primarily due to MTBE's high solubility in water. Remediation technologies have involved air stripping, advanced oxidation, and sorption on granular activated carbons (GAC). In this study, liquid phase sorption on hydrophobic molecular sieves was carried out over a wide range of concentrations of MTBE in water. It was shown that several molecular sieve zeolites significantly outperformed the GAC used as a control, especially in the $\mu\text{g/L}$ concentration range. Silicalite-1, which had the greatest $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and the greatest framework density of the zeolites tested, was the best performer in the low concentration range.

Key words: adsorption; MTBE; remediation; zeolite

INTRODUCTION

METHYL TERTIARY BUTYL ETHER (MTBE) has been used as an automobile gasoline oxygenate at concentrations of up to 15% by volume since approximately 1990. Through various causes, a fraction of the MTBE produced has inevitably been released to the environment. In 1994, a U.S. Geological Survey study found 27%

of 210 wells in urban environments with concentrations of MTBE greater than $0.2 \mu\text{g/L}$, the method detection limit (Squillace *et al.*, 1996). A study was also conducted in Maine investigating MTBE occurrence in drinking water wells (Maine, 1998). Of the 951 tested wells used by private households for drinking water, MTBE was detected in 15.8% of the wells (above $0.1 \mu\text{g/L}$). Over 1% of the private household wells had concentrations above

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Maine's maximum contaminant level (MCL), 35 $\mu\text{g/L}$. Moreover, 16% of 793 public drinking water wells had detectable levels of MTBE, with 6.1% of the tested wells having concentrations between 1 and 35 $\mu\text{g/L}$ (Maine, 1998). This report estimated that between 1,400 and 5,200 privately owned wells in Maine alone may be contaminated with MTBE in excess of 35 $\mu\text{g/L}$. In 1996, drinking water supply wells for Santa Monica, CA, had to be closed because of MTBE concentrations in the groundwater up to 600 $\mu\text{g/L}$ (Johnson *et al.*, 2000). It is not uncommon for spills at automobile gasoline service stations to result in local groundwater contamination levels of MTBE over 100 mg/L . The proximity of known MTBE contamination to drinking water wells points to the possibility of a "significant threat" of MTBE contamination to drinking water sources in the immediate future in the U.S. (Johnson *et al.*, 2000). Currently, MTBE is listed on EPA's Drinking Water Contaminant Candidate List and a drinking water advisory has been set at 20 $\mu\text{g/L}$ for odor concerns and 40 $\mu\text{g/L}$ for taste concerns (EPA, 2002).

The high aqueous solubility and high vapor pressure of MTBE result in a very mobile contaminant in the environment. In addition, it is thought that MTBE is not readily biodegradable due to the lack of carbon branches more than one carbon atom long (Johnson *et al.*, 2000). Various treatment processes may be used to remove MTBE from water. Air stripping will transfer the MTBE from the aqueous to the air phase (NWRI, 2000). However, air stripping is not as effective for removing MTBE from water as it is for compounds with greater Henry's constants, such as the BTEX compounds (benzene, toluene, ethylbenzene, and xylenes). Also, the disposition of the off-gas from stripping is a concern, as it contains appreciable quantities of MTBE.

MTBE may also be removed by adsorption onto surfaces, for example, on granular activated carbon (GAC) (Shih *et al.*, 2003). Adsorption of anthropogenic organic compounds onto GAC is fairly well understood, and there have been many successful full-scale applications (Snoeyink and Summers, 2000). As MTBE has a high aqueous solubility, it does not have a great affinity for GAC. Removal of MTBE with GAC is less effective than for less water-soluble compounds such as benzene, thus requiring much more carbon per unit mass of contaminant removed.

The ability of high-silica zeolites to remove MTBE from water was demonstrated by Anderson (2000). Multicomponent batch sorption experiments with aqueous solutions of MTBE, chloroform, and trichloroethylene were conducted with mordenite, ZSM-5 (silicalite), and dealuminated zeolite Y (DAY), and two activated carbons as the solid adsorbents. It was found that mordenite was able to remove more MTBE from water containing

MTBE, chloroform, and trichloroethylene than the two powdered-activated carbons, one from Fisher Scientific (Pittsburgh, PA) and one from Barnebey-Cheney (Columbus, OH), and the other two zeolites, ZSM-5 and DAY. The concentration of MTBE in a 25-mL solution was reduced from 100 to 4 $\mu\text{g/L}$ with 5 mg of mordenite after 15 min of contact time (96% removal of MTBE). ZSM-5 and DAY were less effective, only removing 63 and 5%, respectively. There was a trend of greater removal of contaminant with the activated carbon with decreasing contaminant solubility (as expected, see Weber, 1972; Snoeyink and Summers, 2000), but no such trend was noticed for removal of the contaminants with zeolites. Based on the higher selectivity of mordenite for MTBE, Anderson prepared a single-component sorption isotherm up to an aqueous MTBE concentration of 300 $\mu\text{g/L}$ using mordenite and the two activated carbons. At 100 $\mu\text{g/L}$, mordenite was observed to adsorb 8 to 12 times more MTBE than the activated carbons. Giaya (2001) also showed that MTBE could be removed by sorption onto hydrophobic zeolites, but he investigated much higher concentrations than in Anderson's work.

On the basis of liquid water and vapor sorption studies (Giaya *et al.*, 2000; Giaya, 2001; Giaya and Thompson, 2002b), it was demonstrated that hydrophobic zeolites could remove chlorinated volatile organic compounds (CVOCs) from water effectively by direct liquid-solid contact. One of the more interesting observations was that the larger pore zeolite DAY appeared to be an inferior performer at very low trichloroethylene (TCE) concentrations, but then the sorbed quantity exceeded the capacity of the other sorbents at higher concentrations. These results are shown in Fig. 1, and illustrate the effect. Giaya and Thompson (2002a, 2002c) argued that this effect was likely due to the competitive interference of water at those low concentrations, and its varying importance in different sized zeolite pores.

Several high-silica zeolites were evaluated as adsorbents for MTBE and compared with a granular activated carbon in this study. The adsorption isotherms for MTBE were developed over a wide concentration range, and the observed adsorption behavior of the adsorbents was related to their properties.

EXPERIMENTAL

The high-silica zeolites tested were silicalite-1, mordenite, zeolite beta, and DAY. Table 1 lists the supplier, $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, and cation form for each zeolite. Table 2 lists some structural information about the zeolite samples used in this study. A granular activated carbon sample used for comparison with zeolites was the Centaur[®]

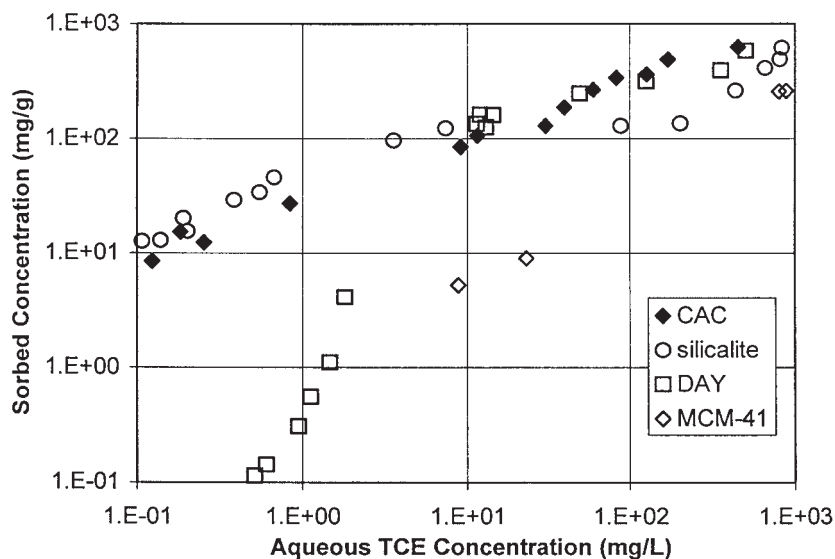


Figure 1. Trichloroethylene (TCE) sorption from the aqueous phase on hydrophobic molecular sieves (from Giaya, 2001). MCM-41 was a wide-pore silica material synthesized using a surfactant template, and provided by Professor Anthony S.T. Chiang, National Central University, Taiwan.

Activated Carbon (CAC) obtained from Calgon Corporation. The silicalite-1 and activated carbon samples were the same as those used previously by Giaya *et al.* (2000). MTBE (HPLC grade, 100%) was purchased from Fisher Scientific, and all water used was purified with a Barnstead ROPure ST/E-pure system.

All adsorbent samples were brought to moisture equilibrium in a saturated humidity atmosphere in a desiccator containing a supersaturated solution of CaCl_2 in water, prior to the experiments. The concentration of the initial MTBE solutions and the liquid/solid ratios were varied during the experiments to obtain isotherm data over a wide concentration range. Adsorption experiments were carried out in 45-mL vials placed on a shaker at room temperature ($20 \pm 2^\circ\text{C}$) for 24 h, for the adsorption equilibrium to be established. A contact time of 24 h was found to be sufficient for equilibrium for trichloroethylene adsorption on similar materials (Hawley, 2003). Shorter contact times of up to 8 h (Anderson, 2000; Giaya, 2001), were observed in preliminary experiments (data not shown) to be insufficient to attain equilibrium in some cases, especially at

high MTBE concentrations, and for adsorbents in the form of granules such as CAC or with narrower pore sizes such as silicalite-1.

Following separation by centrifugation, and dilution when necessary, the supernatants were concentrated by a solid phase microextraction (SPME) technique using CarboxenTM/PDMS fibers (Supelco, Inc., Bellefonte, PA) with 85- μm film thickness and then analyzed by gas chromatography. The GC used (Agilent Technologies, Palo Alto, CA, Series 6890) was equipped with a flame ionization detector (FID), and J&W Scientific (Agilent Technologies) DB-624 capillary column 30 m in length, and 318 μm in nominal diameter. The inlet and detector temperatures were set at 220 and 250 $^\circ\text{C}$, respectively. The oven temperatures were 35 $^\circ\text{C}$ for 1 min, 7.5 $^\circ\text{C}/\text{min}$ ramp to 50 $^\circ\text{C}$ and held for 2 min, 20 $^\circ\text{C}/\text{min}$ ramp to 90 $^\circ\text{C}$ and held for 2 min, followed by a 40 $^\circ\text{C}/\text{min}$ ramp to 200 $^\circ\text{C}$ and held for 7 min.

The fiber was left immersed at room temperature for 25 min in the MTBE solution to be analyzed in the presence of magnetic stirring prior to each GC injection. Fre-

Table 1. Adsorbents used.

Adsorbent	Supplier	$\text{SiO}_2/\text{Al}_2\text{O}_3$ Ratio	Cation form
Silicalite-1	Union carbide	>1000	—
Mordenite (CBV 90A)	Zeolyst	90	H^+
Zeolite beta (CP 811E-150)	Zeolyst	150	H^+
DAY (CBV 780)	Zeolyst	80	H^+

Table 2. Structural information for the adsorbents used.

<i>Zeolite</i>	<i>Ring sizes (number of T atoms)</i>	<i>Framework density (number of T atoms/Å³)</i>	<i>Pore volume (cm³/g)</i>	<i>Largest dimensions of the pores (Å)</i>
Silicalite-1	10	18.4	0.21 ^a	5.6, 5.5
Mordenite	12, 8	17	0.18–0.20 ^b	7.0, 5.7, 4.8
Zeolite beta	12	15.3	0.26 ^b	6.7, 5.6
DAY	12	13.3	0.38 ^a	7.4
Centaur [®] activated carbon			0.51 ^a	7.8 average diameter ^c

^aGiaya *et al.* (2000); ^bSzostak (1998); ^cFor HSV Centaur (Merenov *et al.*, 2000).

quent conditioning of the fiber by baking in the injection port of the GC at 260°C and by rinsing via blank e-pure water injections, was applied. Calibration curves were developed using standard solutions of known concentrations of MTBE in water. The method detection limit was 1 µg/L. The observations on the need for the use of dilution of the solutions and frequent and thorough calibration of the fibers are reported separately (Erdem-Senatalar *et al.*, 2004).

All adsorbents were also characterized by thermogravimetry (TA Instruments TGA 2050 Thermogravimetric Analyzer, New Castle, DE) to follow water loss as a function of temperature and to determine their hydrophobicities. The samples were heated to 400°C at a heating rate of 10°C/min, and were kept at this temperature until constant weight was attained. The hydropho-

bicity was calculated as the ratio of the weight loss up to 150°C to the total weight loss according to the definition proposed previously (Anderson and Klinowski, 1986).

RESULTS AND DISCUSSION

Figure 2 shows the MTBE sorption isotherms at room temperature for all sorbents tested: silicalite-1, mordenite, zeolite beta, DAY, and the Calgon Centaur[®] Activated Carbon (CAC). The aqueous phase MTBE concentrations spanned over five orders of magnitude. The concentrations included the µg/L range (level of concern for drinking water) up to the g/L range, which might be encountered in the event of a major spill.

The data in the low concentration range showed that silicalite-1 has the highest capacity to remediate MTBE-

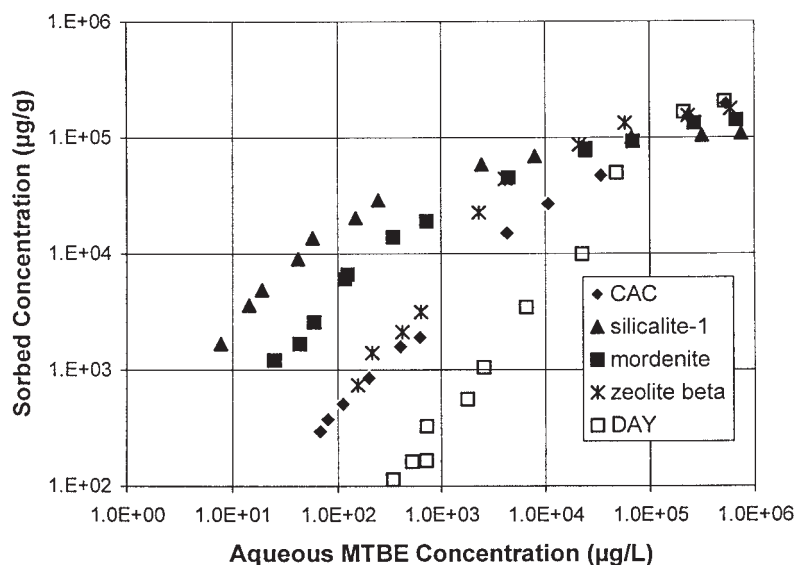


Figure 2. MTBE sorption from the aqueous phase on hydrophobic molecular sieves.

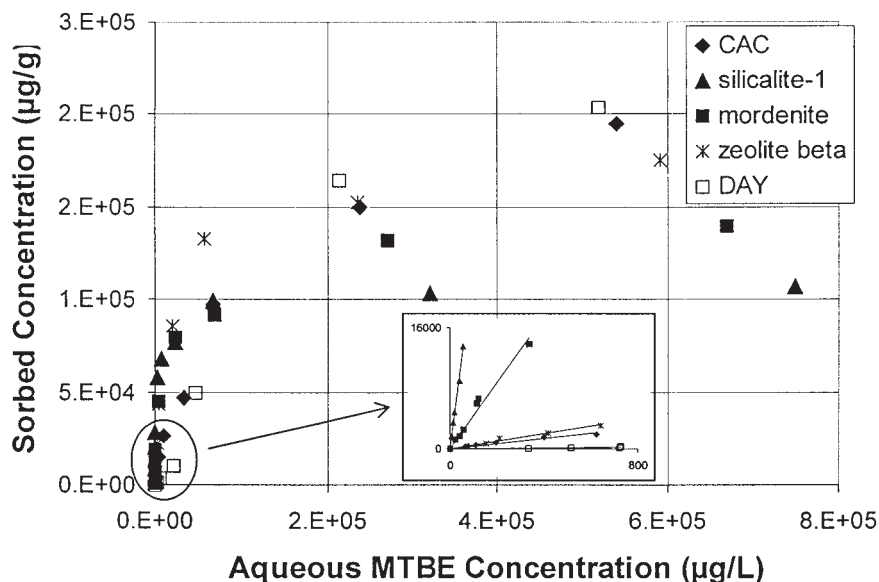


Figure 3. Aqueous phase MTBE sorption in the high concentration range and low concentration range (insert).

contaminated water streams; all other materials underperformed by comparison. In all cases, the isotherms were essentially linear in the low concentration range (see Fig. 3). Additionally, we observed the same behavior for sorption on DAY as was previously shown in the case of TCE sorption in Fig. 1. That is, the DAY sample was a significantly inferior MTBE sorbent at low concentrations, but adsorbed very effectively at higher concentrations. In the case of the CVOCs, this phenomenon was attributed to the likely presence of liquid water in the DAY pores at the lowest organic concentrations (Giaya and Thompson, 2002a, 2002c).

In several recent publications, Caro *et al.* (2000), Noack *et al.* (2000), and Caro *et al.* (2002) reported on transport through a membrane made of silicalite-1 crystals. They noted that MTBE should *not* pass through the silicalite-1 pores, since MTBE has an effective diameter of 0.62 nm, while silicalite-1 has pore diameters of about 0.55 and 0.56 nm. They concluded that any MTBE passing through the membrane must be penetrating through the grain boundaries (defects) between crystals and not the crystal pores. Additionally, despite substantial uptake of MTBE by ZSM-5 (63%), Anderson (2000) stated that MTBE is slightly too large to fit well in the MFI pores (silicalite-I or ZSM-5). Anderson found the slightly larger pores in mordenite to be more conducive for accepting the MTBE molecules, resulting in 96% removal of MTBE from solution. Clearly the data shown in Fig. 2 are in contrast to these conclusions, and demonstrate that MTBE can indeed penetrate the silicalite-1 pores. In fact, the data for relatively lower concentrations demonstrate

that in that range silicalite-1 had the highest affinity for MTBE among the five sorbents tested in this study.

Recently, Cui and Elliott (2002) reported on the development of a multistep potential model, which, among other things, predicts molecular sizes. In their work they focused initially on *n*-alkanes, and later on branched alkanes, alkenes, alkynes, and alcohols (Elliott, 2003). Using their model code (SPEAD), we estimated the dimensions of MTBE to be $0.575 \times 0.593 \times 0.72$ nm. While this may be more informative than a single dimension of 0.62 nm used elsewhere, it still would suggest that MTBE must deform slightly to fit into the pores of silicalite. Alternatively, there may be sufficient defects in the crystalline structure that silicalite crystals can accommodate molecules slightly larger than the nominal pore dimensions, or natural vibrations in the crystal lattice may permit penetration of the MTBE molecule into the pores.

Figure 3 shows the limiting sorption capacities as the aqueous MTBE concentrations were increased to very high levels, far above acceptable drinking water levels. These are levels that may correspond to localized spills. What is observed at very high solution concentrations is that the smaller pore volume materials exhibited lower sorption capacities than those with larger pore volumes. These data are consistent with the single component vapor phase adsorption data with CVOCs reported previously (Giaya and Thompson, 2002b). This trend is due to the limited space available as reflected by the saturation capacity values reported in Table 3, which were computed by assuming that MTBE formed a condensed liquid phase inside the pores (also noted for CVOCs in zeolites by Giaya *et al.*, 2000).

Table 3. Saturation capacities and hydrophobicities of the adsorbents.

<i>Adsorbent</i>	<i>Saturation capacity (μg/g)</i>	<i>Hydrophobicity^c</i>
Silicalite-1	155,400 ^a	0.92
Mordenite	133,200–148,000 ^a	0.87
Zeolite beta	192,400 ^a	0.72
DAY	281,200 ^a	0.89
Centaur [®] activated carbon	~900,000 ^b	0.87

^aUsing pore volumes and liquid density of MTBE at 20°C; ^bExperimental value for PCB GAC of Calgon; ^cBy TGA (weight loss up to 150°C/total weight loss according to the definition of Anderson and Klinowski, 1986).

These results are consistent with the hypothesis that the hydrophobic pores partition the organic molecules between the water phase and the sorbent, favoring the environment created by the hydrophobic pore surfaces. Also, it is noted that the zeolite capacities are approaching their pore volumes, that is, filled with liquid MTBE. The “hydrophobicity” of the pores was indexed by measuring the fraction of water desorbed up to 150°C; the higher the index, the more hydrophobic the pore environment (Anderson and Klinowski, 1986). However, as noted by the “hydrophobicity” values reported for these materials in Table 3, this index alone is not sufficient to explain the sorption behavior. The pore dimensions, which are reflected in the framework densities, also were important in determining the variation of affinities in different concentration ranges.

It is tempting to try to correlate the results in Figs. 2 and 3 with the sorbent properties. The capacities at high concentrations indeed parallel the pore volumes, in general, as mentioned above (the results obtained with mordenite are rather surprising in this context, and will be discussed separately). However, as seen in Table 4, low concentration range sorption (as shown on the insert on Fig. 3) does not correlate well with the inverse of the pore volumes, but very well with the SiO₂/Al₂O₃ ratios and framework densities. Thus, it would appear that the more condensed structures, for example, silicalite-1 with

18.4 T-atoms/Å³, provide more favorable environments for MTBE at low concentrations, than the more open structures, for example, DAY, with 13.3 T-atoms/Å³. This explanation could be due to the reduced tendency for water molecules to interfere, as suggested by Giaya and Thompson (2002a, 2002c), or due to the stronger MTBE-pore wall interaction energy with smaller pores. Thus, at low MTBE concentrations the dominant factors for favorable sorption are high SiO₂/Al₂O₃ ratios and high framework densities—small pores—to disrupt the structure of water and to increase the affinities, while at high MTBE concentrations hydrophobicity and a large pore volume are important to obtain high capacities.

It is worth making the point that zeolite pores have a definite structure that may affect sorption (Breck, 1974; Szostak, 1998). While it is common in the zeolite literature to refer to zeolite pore dimensions as though they were regular cylinders, in actual fact, zeolite pores are far more complex at the molecular level. For example, silicalite-1 has two intersecting channel systems: one straight with dimensions of 0.53 × 0.56 nm, and the other zig-zagged with dimensions 0.51 × 0.55 nm. DAY, with a three-dimensional intersecting pore system, actually has 0.74-nm windows which provide entrance to 1.3-nm cavities, each more or less spherical. Zeolite beta also has a three-dimensional intersecting pore system, with channels of 0.66 × 0.67 nm

Table 4. Correlation of low concentration range adsorption with zeolite properties.

<i>Zeolite properties</i>	<i>Correlation coefficient with slope of low concentration adsorption isotherm [(mg/g)/(mg/L)]</i>
Hydrophobicity	0.562
Pore volume (cm ³ /g)	−0.518
Framework density (# T atoms/Å ³)	0.821
SiO ₂ /Al ₂ O ₃ ratio	0.979
Ave. largest dimensions of pores (Å)	−0.654

running along two crystal axes, and channels of 0.56×0.56 nm running along the third axis. Mordenite has an essentially two-dimensional intersecting pore system with somewhat elliptical apertures. The larger main channels running along one crystal axis are of 0.65×0.70 nm cross-section, and the narrower channels are of 0.34×0.48 nm and 0.26×0.57 nm cross-section. The latter is an example of a highly puckered aperture limiting diffusion. It is therefore surprising, as mentioned above, to observe that the MTBE adsorption capacities obtained at high concentrations for mordenite came close to its total pore volume measured by N_2 adsorption, despite the significant amount of volume resting in the narrower pores. Additionally, pore volumes measured by N_2 adsorption may not reflect the true volume accessible to larger molecules. Therefore, conclusions based on pore "size" must be considered in light of the more complex structures of these materials.

Finally, Fig. 4 shows a comparison of the data collected in this study and the data reported in Giaya (2001). Two of the sorbents (silicalite-1 and CAC) studied here were from the same batches as used in the previous experiments. While the previous DAY sorption data (in this concentration range) were quite similar to the DAY sorption results reported here, the deviation of the other data raised questions. The observation that all of the MTBE sorption data gathered in this study had sorbed concentrations that were higher than those reported previously suggested that 8 h of contact were insufficient for equilibrium to be reached compared to the 24 h used in this investigation. The long equilibration time may have to do with diffusion limitations or the organization of the organic liquid inside the micropores. This will certainly have bearing on MTBE removal in fixed-bed applica-

tions, as shown recently for MTBE adsorption on several activated carbons (Shih *et al.*, 2003).

CONCLUSIONS

Four high silica zeolites, silicalite-1, mordenite, zeolite beta, and DAY, were tested as sorbents for the removal of MTBE from water, and were compared to a granular activated carbon sample as a control. Adsorption isotherms of the sorbents were developed over a wide range of solution concentrations, varying from $\mu\text{g/L}$ to g/L . Several zeolites outperformed the activated carbon up to concentrations on the order of g/L .

At the lower concentrations, ranging from several $\mu\text{g/L}$ to about 10 mg/L , silicalite-1 had the highest capacities, followed by mordenite and zeolite beta. DAY, which performed very poorly at very low concentrations, caught up with and exceeded the MTBE removal capacities of the carbon and other zeolites above concentrations of about 100 mg/L .

Hydrophobicity alone was not sufficient to explain the adsorption behavior. Limiting saturation capacities at high concentrations were observed to approach the micropore volumes of the zeolites, while the affinities at low concentrations correlated well with the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios and framework densities. Since higher framework densities also reflect the presence of smaller pores in the zeolite structures, the high affinity at low concentrations appeared to be promoted by the presence of smaller pores. Varying importance with pore size of the competitive interference of water may be the underlying reason for the observed behavior.

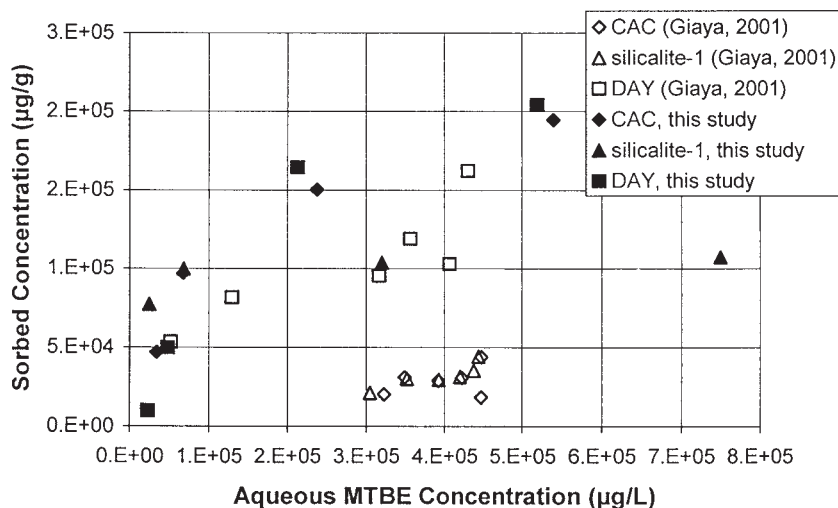


Figure 4. MTBE sorption from the aqueous phase, showing comparison to data reported previously (Giaya, 2001).

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