



## Adsorption of methyl tertiary butyl ether on granular zeolites: Batch and column studies

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### ABSTRACT

Methyl tertiary butyl ether (MTBE) has been shown to be readily removed from water with powdered zeolites, but the passage of water through fixed-beds of very small powdered zeolites produces high friction losses not encountered in flow through larger sized granular materials. In this study, equilibrium and kinetic adsorption of MTBE onto granular zeolites, a coconut shell granular activated carbon (CS-1240), and a commercial carbon adsorbent (CCA) sample was evaluated. In addition, the effect of natural organic matter (NOM) on MTBE adsorption was evaluated. Batch adsorption experiments determined that ZSM-5 was the most effective granular zeolite for MTBE adsorption. Further equilibrium and kinetic experiments verified that granular ZSM-5 is superior to CS-1240 and CCA in removing MTBE from water. No competitive adsorption effects between NOM and MTBE were observed for adsorption to granular ZSM-5 or CS-1240, however there was competition between NOM and MTBE for adsorption onto the CCA granules. Fixed-bed adsorption experiments for longer run times were performed using granular ZSM-5. The bed depth service time model (BDST) was used to analyze the breakthrough data.

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### 1. Introduction

Since the 1970s, methyl tertiary butyl ether (MTBE) has been widely used as a gasoline additive in the United States, initially as an octane-enhancing replacement for lead. As a result of the Clean Air Act (CAA) requirements in 1990, MTBE use as a fuel oxygenate increased to higher concentrations (up to 15% by volume) [1]. More specifically, in 1995 the CAA required that Reformulated Gasoline (RFG) meet a 2.0% (by mass) oxygen content requirement and MTBE was the primary oxygenate used by refiners to meet this requirement [1].

While the use of MTBE as a gasoline additive has significantly helped to reduce air emissions of smog-forming pollutants, it has also caused widespread and serious contamination of the nation's drinking water supplies. MTBE is highly soluble in water, and thus can partition out of gasoline into water. Consequently, contamination of drinking water sources can occur in a number of ways: leakage from gasoline storage tanks and distribution systems, spills, emissions from marine engines into lakes and reservoirs, and to a lesser extent from air deposition. MTBE presence in drinking water sources is of concern to the public due to its offensive taste and

odor, and because of the uncertainty regarding the level of risk to public health from the exposure to low levels of MTBE in drinking water. Because of the above concerns, the U.S. Environmental Protection Agency (EPA) issued a non-regulatory advisory for MTBE in drinking water. According to the advisory, MTBE concentrations above 20–40  $\mu\text{g/L}$  may cause adverse health effects [1].

Adsorption is a proven technology for treating water contaminated with anthropogenic organic compounds. Granular activated carbon (GAC) is the most commonly-used adsorbent in water treatment, and has been successfully used to remove MTBE from water. However, GAC performance in removing MTBE was observed to be reduced when other synthetic organic compounds coexist with MTBE or in the presence of natural organic matter (NOM) [2–5].

Recent studies have demonstrated the ability of powdered zeolites as successful adsorbents for the removal of MTBE from water [6–12]. However, the high friction loss associated with passing water through powder beds precludes use of powdered adsorbents in treatment systems. Few studies have directly evaluated granular zeolites in batch adsorption experiments and fixed-bed contactors [9]. In this work, the effectiveness of several granular zeolites for the removal of MTBE from water was evaluated and compared with removal by CS-1240 and a CCA. In addition, the effect of NOM on MTBE uptake was studied, and equilibrium and kinetic parameters that describe the adsorption of MTBE onto granular zeolites were determined.

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**Table 1**  
Summary of zeolite samples used in the batch adsorption experiments.

| Sample name | Size (in)           | Si/Al | Zeolite % | Company name | Surface area (m <sup>2</sup> /g) [35] | Micropore area (m <sup>2</sup> /g) [35] | External area (m <sup>2</sup> /g) [35] | Pore dimensions (Å) [14] |
|-------------|---------------------|-------|-----------|--------------|---------------------------------------|---|--|--------------------------|
| Beta        | 0.0625 <sup>#</sup> | 35    | 80        | Engelhard    | 533.7                                 | 266                                     | 267.6                                  | 6.6–7.7                  |
| Mordenite   | 0.0625 <sup>#</sup> | 50    | 80        | Engelhard    | 472.6                                 | 304.3                                   | 168.3                                  | 6.5 × 7.0                |
| HISIV 1000  | 0.0625 <sup>#</sup> | 35–40 | 80        | UOP          | 379.9                                 | 247.1                                   | 132.8                                  | 7.4 × 7.4                |
| HISIV 3000  | 0.0625 <sup>#</sup> | 800   | 80        | UOP          | 321.9                                 | 230.5                                   | 91.4                                   | 5.1 × 5.5, 5.3 × 5.6     |
| Zeolite Y1  | 0.15                |       | 9         | Engelhard    | 158.6                                 | 73.4                                    | 85.2                                   | 7.4 × 7.4                |
| Zeolite Y2  | 0.15                |       | 14        | Engelhard    | 158.3                                 | 58.7                                    | 99.6                                   | 7.4 × 7.4                |
| ZSM-5       | 0.0625 <sup>#</sup> | 280   | 80        | Zeolyst      | 390.8                                 | 141.8                                   | 249                                    | 5.1 × 5.5, 5.3 × 5.6     |
| Beta        | 0.0625 <sup>#</sup> | 360   | 80        | Zeolyst      |                                       |   |  | 6.6–7.7                  |
| Mordenite   | 0.0625 <sup>#</sup> | 90    | 80        | Zeolyst      |                                       |   |  | 6.5 × 7.0                |

<sup>#</sup> Size obtained from manufacturers' data.

## 2. Materials and methods

### 2.1. Materials

The granular zeolites evaluated were Engelhard Beta (Engelhard, Iselin, NJ), Engelhard Mordenite (Engelhard), HISIV 1000 (UOP, Des Plaines, IL), HISIV 3000 (UOP), Zeolite Y1 (Engelhard), Zeolite Y2 (Engelhard), ZSM-5 (Zeolyst, Valley Forge, PA), Zeolyst Beta (Zeolyst), and Zeolyst Mordenite (Zeolyst). Table 1 lists the supplier, size, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio, zeolite %, surface area, micropore area, external area, and pore dimensions for each zeolite. For comparison purposes, a coconut shell GAC sample (CS-1240) obtained from Res-Kem Corp (Media, PA) and a commercial carbon adsorbent (CCA) sample (extracted from a commercially-available drinking water filter for residential use) were used as received. Prior to experiments, zeolite samples were dried in an atmospheric oven at 120 °C for 10–14 h and then samples were kept clean and dry in a desiccator. MTBE standard solutions were prepared using purified water from a Barnstead ROpure ST/E-pure water purification system (Barnstead/ThermoLyne, Dubuque, IA) and MTBE (HPLC grade; Fisher Scientific, Pittsburgh, PA). Natural organic matter (NOM) was used as received (humic acid, Sigma–Aldrich, Saint Louis, MO).

### 2.2. Batch adsorption experiments

To obtain adsorption equilibrium isotherm data with the granular sorbents, aqueous phase adsorption experiments were performed in 42 mL glass vials using a fixed sorbent/liquid ratio (0.2 g sorbent/42 mL aqueous solution) and varied concentrations of MTBE initial solutions. In all experiments, the vials were agitated on a fixed speed rotator at room temperature (22 ± 2 °C) for a minimum of 24 h at 15 rpm, for adsorption equilibrium to be achieved. A 24 h equilibration time is based on kinetics testing conducted as part of this work. In addition, previous work on powdered zeolites had shown that 24 h is sufficient time for MTBE to reach equilibrium [8]. Beside the adsorption experiments, control experiments with MTBE using blanks with no adsorbent material were performed periodically and ensured that no MTBE losses occurred during the experiments. Following adsorption, solid–liquid separation was done by centrifugation for 10 min at 3000 rpm and MTBE in the aqueous supernatant samples was quantified using gas chromatography (GC) with solid phase micro extraction (SPME). When necessary, dilution was made in order to keep the measurements within the linear range of the standard curves.

### 2.3. Large diameter fixed-bed adsorption experiments

A glass column with a length of 10 cm and an internal diameter of 2.5 cm was used in the fixed-bed adsorption experiments. A digital peristaltic pump (Cole-Parmer, Vernon Hills, IL) supplied the feed. The adsorbent material was placed in the glass column and

held in place using glass beads and glass wool. For approximately one hour, water was passed through the column at a flow rate of 32.5 mL/min to remove air bubbles and to flush the adsorbent granules. Finally, MTBE solution passed through the column at a flow rate of 32.5 mL/min and a feed concentration of 50 µg/L.

### 2.4. Small diameter fixed-bed adsorption experiments

Adsorption column experiments with granular ZSM-5 were performed using a glass column (Bio-Rad Laboratories, Hercules, CA) of 1 cm internal diameter and 20 cm long with an adjustable flow adapter to hold the packed bed in place. Experiments were performed with a fixed solution flow rate of 5.2 mL/min, an influent MTBE concentration of 50 µg/L, and bed heights of 6, 9, and 12 cm. Water was passed through the column at a flow rate of 5.2 mL/min for an hour to remove air bubbles and to rinse the adsorbent particles. After flushing, MTBE solution flowed from a Tedlar bag (SKC Inc., Eighty Four, PA) into the fixed-bed at a flow rate of 5.2 mL/min with the use of a peristaltic pump (Cole-Parmer, Vernon Hills, IL). The use of a Tedlar bag to contain the MTBE feed solution minimized the head space above the solution and any potential losses due to volatilization.

Samples from both the small diameter fixed-bed adsorption experiments and the large diameter fixed-bed adsorption experiments were collected in 42 mL glass vials at the outlet of each column at predetermined intervals of time. Sample sizes of 18 mL were transferred from each 42 mL vial to GC autosampler vials, isopropyl alcohol as an internal standard was added (99.5%, A.C.S. grade; Aldrich, Saint Louis, MO), and then the samples were analyzed using the GC.

### 2.5. Gas chromatography methodology

A Combi-PAL autosampler (CTC Analytics, Zwingen, Switzerland) combined with a solid phase microextraction (SPME) system was used to extract and concentrate MTBE prior to GC analysis. SPME was used to extract MTBE from the aqueous phase of each sample using carboxen/polydimethylsiloxane (CAR/PDMS) 85 µm film thickness fibers (Supelco, Bellefonte, PA). The method detection limit was 1 µg/L and the average service life of the fibers was around 65 injections.

At the beginning of each analysis, the SPME fiber was conditioned in the Combi-PAL conditioning unit for one and a half hour at 300 °C. Before immersing the fiber into the aqueous sample (for 30 min at 250 rpm), the sample was agitated in the Combi-PAL agitator unit for 10 min at 250 rpm. A GC (Series 6890N Agilent Technologies, Santa Clara, CA), equipped with a flame ionization detector (FID) and a DB-624 capillary column 30 m in length and 317 µm in nominal diameter (J&W Scientific, Folsom, CA), was used to analyze the MTBE in aqueous solution. The inlet and detector temperatures were 220 and 250 °C, respectively. Nitrogen was

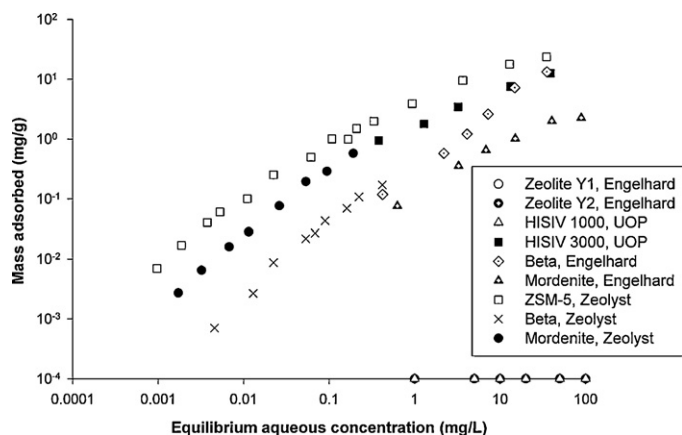


Fig. 1. MTBE sorption from the aqueous phase onto granular zeolites, using a minimum of 24 h equilibration time. Initial MTBE concentrations were in the range of (0.01–150 mg/L).

used as the carrier gas at a constant flow of 45 mL/min. Hydrogen and air were used to maintain the detector flame at flows of 40 and 450 mL/min, respectively. The GC oven program was as follows: 35 °C for 1 min, ramped to 50 °C at 7.5 °C/min, held for 2 min, ramped to 90 °C at 20 °C/min, held for 2 min, finally ramped to 200 °C at 40 °C/min and held for 10 min. The MTBE on the SPME fiber was thermally desorbed in the GC inlet using the splitless mode at 220 °C for 5 min followed by another 5 min of conditioning in a separate conditioning unit at 300 °C. The total desorption time of 10 min between successive injections was used to prevent carry-over contamination problems

### 3. Results and discussion

#### 3.1. MTBE sorption isotherms

Batch adsorption experiments were carried out using select granular zeolite samples (Table 1), coconut shell GAC (CS-1240) sample, and CCA sample. Fig. 1 shows MTBE sorption isotherms at room temperature for the granular zeolites listed in Table 1. The MTBE aqueous phase concentrations spanned over a wide range (up to 100 mg/L), which might be encountered in a significant MTBE spill and in impacted drinking water sources.

MTBE sorption isotherms were fitted to the Langmuir and Freundlich equilibrium models and the parameters for both models are summarized in Table 2. The Langmuir adsorption isotherm model is frequently used to describe adsorption data and is written as  $q_e = \frac{Q_a b C_e}{1 + b C_e}$ , where  $q_e$  (mg/g) is the mass of solute adsorbed per unit mass of adsorbent at equilibrium,  $C_e$  (mg/L) is the aqueous phase concentration, and  $Q_a$  (mg/g) and  $b$  (L/mg) are coefficients related to the properties of the adsorbent [13]. The Freundlich isotherm model has the following form  $q_e = K_f C_e^{1/n}$  where  $K_f$  and  $(1/n)$  are characteristic constants [13].

Table 2 clearly shows that both the Langmuir and Freundlich isotherm models were appropriate in describing the equilibrium as reflected by the high values for the correlation coefficients,  $R^2$ . In comparison with other studies, the Freundlich isotherm parameters found in this work for mordenite (Engelhard) ( $K_f = 0.0011$  (mg/g)/(μg/L) $^{1/n}$ ,  $1/n = 0.7$ ) were different than those reported by Hung et al. [3] ( $K_f = 0.14$  (mg/g)/(μg/L) $^{1/n}$ ,  $1/n = 0.65$ ). Specifically, the value for  $K_f$ , a measure of the adsorbent capacity, in this work was found to be over two orders of magnitude lower than found by Hung et al. [3] (0.0011 vs. 0.14) for MTBE adsorption to mordenite. In addition, the Freundlich isotherm parameters for HISIV 3000 ( $K_f = 0.03$  (mg/g)/(μg/L) $^{1/n}$ ,  $1/n = 0.57$ ) were different from those found by Rossner and Knappe [9] ( $K_f = 0.212$  (mg/g)/(μg/L) $^{1/n}$ ,  $1/n = 0.87$ ) in that the value for  $K_f$  was found to be about one order of magnitude lower than that reported by them. The difference in results could be due to the broader concentration range employed in this study (1000–100,000 μg/L) which was much greater than that used by Hung et al. and Rossner and Knappe (0.1–1000 μg/L). The data in the high concentration range (1–100 mg/L) showed that ZSM-5, a silicalite zeolite, had the highest adsorption capacity for MTBE among the other zeolites tested. HISIV 3000 which is also a silicalite zeolite was the second most effective adsorbent for MTBE in this range. The high sorption capacity of ZSM-5 and HISIV 3000 for MTBE could be attributed to their high silica content which creates hydrophobic surfaces within the pores of the adsorbent making it a favorable environment for adsorption of organic molecules. Fig. 1 also shows that in this high concentration range, zeolite beta (with pore dimensions in the range of 6.6–7.7 Å [14]) was better able to remove MTBE from water than mordenite (with pore dimensions of 6.5 × 7.0 Å [14]). The Freundlich isotherm parameter,  $K_f$ , which is primarily related to the specific capacity of the adsorbent for the adsorbate, correlated very well with the above results in that it would be expected that a greater capacity would be associated with a larger  $K_f$  value (Table 2). The other three materials (HISIV 1000, zeolite Y1, and zeolite Y2) had minimal capacities for MTBE. The low affinity of organics for zeolite Y has been previously noticed. For example, Anderson [7] found that zeolite Y removed only 5% of MTBE in solution. Anderson attributed his findings to both the large pore size and the high Al content of zeolite Y compared to other zeolites looked at [7]. Erdem-Senatalar et al. [8] observed that dealuminated zeolite Y (DAY) was ineffective in removing MTBE from water at low concentrations. Knappe et al. [15] reported negligible adsorption capacities of zeolite Y. And Giaya et al. [16] observed the same phenomenon for TCE sorption on DAY. Giaya and Thompson [17,18] and Fleys et al. [19] suggested from simulations that the poor efficiency of zeolite Y for removing TCE from aqueous solution was likely due to the presence of liquid water in the large pores of zeolite Y.

MTBE adsorption isotherms at room temperature and at low range of MTBE aqueous phase concentrations (0–1 mg/L in Fig. 1), were obtained using the following granular zeolites; ZSM-5 (Zeolyst), HISIV 3000 (UOP), zeolite beta (Zeolyst), and zeolite mordenite (Zeolyst). Zeolites beta and mordenite tested at this range were from another supplier (Zeolyst) due to the unavailability of

Table 2  
The Freundlich and Langmuir isotherms parameters.

| Adsorbent            | Langmuir parameters |            |       | Freundlich parameters        |       |       |
|----------------------|---------------------|------------|-------|------------------------------|-------|-------|
|                      | $Q_a$ (mg/g)        | $b$ (L/mg) | $R^2$ | $K_f$ (mg/g)/(mg/L) $^{1/n}$ | $1/n$ | $R^2$ |
| ZSM-5, Zeolyst       | 0.67                | 11.27      | 0.98  | 3.21                         | 0.78  | 0.97  |
| HISIV 3000, UOP      | 6.78                | 0.4        | 0.96  | 1.64                         | 0.57  | 1.00  |
| Beta, Engelhard      | 25.06               | 0.01       | 1.00  | 0.28                         | 1.11  | 0.99  |
| Mordenite, Engelhard | 2.76                | 0.05       | 1.00  | 0.14                         | 0.7   | 0.97  |
| Mordenite, Zeolyst   | 0.08                | 21.10      | 0.98  | 4.52                         | 1.14  | 1.00  |
| Beta, Zeolyst        | 0.02                | 9.68       | 0.98  | 0.68                         | 1.23  | 0.99  |

large quantities of these zeolites from the first supplier (Engelhard). The data in this range once more shows that granular ZSM-5 had the highest adsorption capacity for MTBE among the other tested granular zeolites. However, data in the low aqueous phase concentration range showed that zeolite mordenite had a greater adsorption capacity for MTBE than zeolite beta. The results are in agreement with previous data [8,15]. These studies show that silicalite exhibits the greatest affinity for MTBE in the aqueous phase concentration range of 0–1 mg/L followed by zeolite mordenite, and finally by zeolite beta. Since the isotherms in the low aqueous concentration range were approximately linear (as reflected by the  $1/n$  values close to 1 in Table 2), the slopes of the isotherms were correlated with the sorbent properties. It was found that the slope of the adsorption isotherm correlated very well with the granular zeolite average pore dimension ( $R^2 = 0.98$ ). Thus, at low MTBE concentrations, the smaller pore zeolites like ZSM-5 were more effective in removing MTBE than the more open ones like zeolite beta. This could be due to the stronger MTBE-pore wall interaction energy with smaller pores, as suggested by Erdem-Senatarlar et al. [8], or to the reduced tendency for water molecules to interfere with sorption in the smaller pores, as suggested by Giaya and Thompson [17,18] and Fleys et al. [19]. In summary, at high MTBE concentrations, hydrophobicity and large pore sizes were important to obtain high capacities, while at low MTBE concentrations the small hydrophobic pores were the dominant factor to achieving high sorption. Since ZSM-5 was the best adsorbent to remove MTBE both at high and low aqueous phase concentrations, ZSM-5 was selected for further study.

MTBE sorption isotherms using three sizes of granular ZSM-5 were evaluated to discern the effect of the sorbent grain size on equilibrium sorption. The original granular ZSM-5 material that was used in the previous experiments with granular size of 1.6 mm was ground using a ball mill and the resultant heterogeneous mixture of sizes was fractionated into three size ranges using standard mesh sieves. The three size ranges were: (1) 250 → 425  $\mu\text{m}$ , (2) 425 → 850  $\mu\text{m}$ , and (3) 850  $\mu\text{m}$  → 1.4 mm. Fig. 2 shows the MTBE isotherm data using the selected three different sizes of granular ZSM-5 compared to the isotherm data obtained using the original granular ZSM-5 size of 1.6 mm. To ascertain with confidence that differences existed between the performances of the different grain sizes, an analysis of covariance test was applied. The analysis of covariance is a statistical test used to compare the slopes and intercepts of two or more regression lines and to determine whether the regression lines are significantly different or not. The procedure described by Zar [20] was followed for comparing the

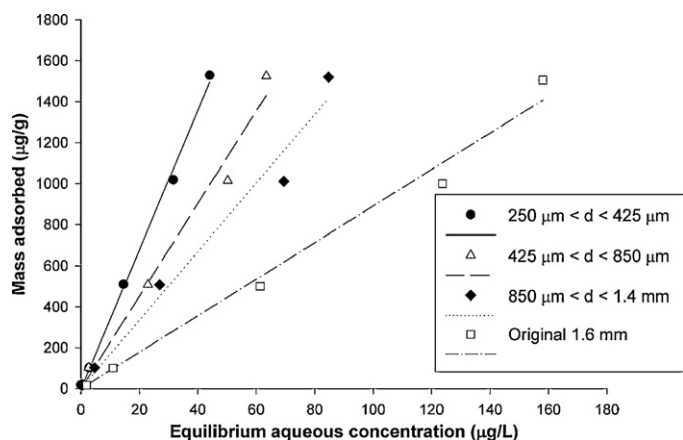


Fig. 2. MTBE sorption from the aqueous phase onto granular ZSM-5 with three different grain sizes compared to the original ZSM-5 size of 1.6 mm. Initial MTBE concentrations were in the range of 85–7500  $\mu\text{g/L}$ .

Table 3

A list of constituents used in preparing the challenge solution.

| Constituent                  | Concentration (mg/L) |
|------------------------------|----------------------|
| Natural organic matter (NOM) | 5                    |
| $\text{Mg}^{2+}$             | 10                   |
| $\text{Cl}^-$                | 44.56                |
| $\text{Na}^+$                | 10                   |
| $\text{Ca}^{2+}$             | 10                   |
| $\text{CO}_3^{2-}$           | 25                   |
| $\text{Fe}^{2+}$             | 10                   |
| $\text{SO}_4^{2-}$           | 17.2                 |

data sets in Fig. 2. First, a regression line was found for each grain size data set. Next, the slopes of the four regression lines were compared. The test results showed that the slopes are significantly different from each other ( $P = 1.8 \times 10^{-9}$ ), demonstrating that the sorption capacity increased with decreasing grain size. This trend is expected since the process of breaking the larger grains to form smaller ones will most likely increase the available specific surface area of the material, providing additional surface area and sites favorable for adsorption. It can be expected that the fracturing that occurred in the process of obtaining smaller zeolite grain sizes would occur preferentially at grain boundaries (where the individual zeolite grains are held together with binder as larger grains). This would provide a somewhat larger surface area for adsorption by exposing pores which were previously blocked by binder with the larger grain sizes. A similar trend was previously observed by Weber et al. [21] in their equilibrium adsorption data of 3-dodecylbenzenesulfonate on three different sizes of Columbia carbon at 30 °C. Due to the superior performance, granular ZSM-5 with the smallest particle grain size (250 → 425  $\mu\text{m}$ ) was used in the remaining tests.

To allow the comparison between granular ZSM-5 and other available adsorbents for MTBE adsorption capacity, batch adsorption experiments were performed using granular ZSM-5, CS-1240 and CCA as the adsorbent materials. In addition, to evaluate the effect of NOM on MTBE uptake of the three selected adsorbent materials, batch adsorption experiments were carried out in a solution which had a mixture of NOM and other constituents that are generally present in many waters. Table 3 summarizes the different constituents which were used in preparing the NOM-containing “challenge” solution.

Fig. 3 shows the MTBE adsorption isotherms using granular ZSM-5, CS-1240, and CCA adsorbents using both purified water

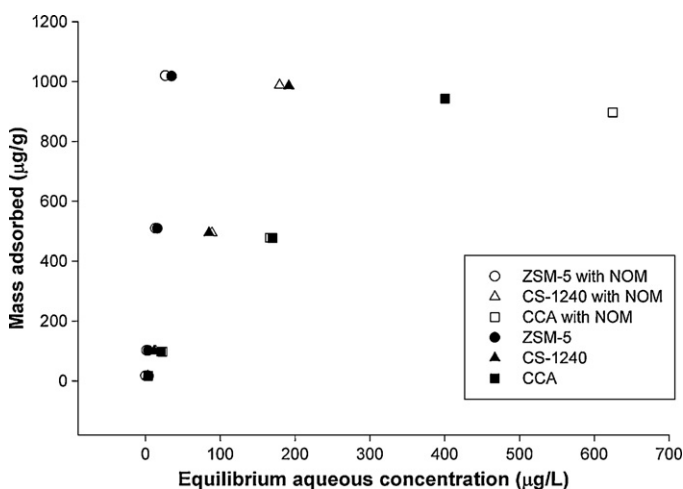


Fig. 3. MTBE sorption from the aqueous phase onto granular ZSM-5, (CS-1240) and CCA with and without the presence of natural organic matter (NOM = 5 mg/L) in the solution. Initial MTBE concentrations were in the range of 85–5000  $\mu\text{g/L}$ .

and the NOM-containing water. Using both purified water and the NOM-containing water, granular ZSM-5 was found to be the most effective adsorbent and CCA was the least effective. For example, when 0.2 g granular ZSM-5 was added to 0.042 L of purified water with 2.5 mg/L initial MTBE concentration, the removal efficiency was 99.37%. However, when the same liquid/solid ratio was used with CS-1240 and CCA, their removal efficiencies were 96.6% and 93.21%, respectively. These data agree with previously reported MTBE adsorption data using similar ranges of MTBE aqueous phase concentrations [8,9].

Fig. 3 also shows that, when the MTBE/ZSM-5 isotherms using purified water and the NOM-containing water were compared, the isotherms were identical; this indicates that NOM molecules did not compete with MTBE for ZSM-5 adsorption sites. The NOM molecular size is expected to be much larger than the pore size of ZSM-5 and hence, the NOM molecules are excluded from the ZSM-5 pores [22]. Gonzalez-Olmos et al. came to the same conclusion in their work on the degradation of MTBE with hydrogen peroxide, catalyzed by the iron-containing zeolite (Fe-ZSM-5) in the presence of humic acid [23]. They found that 100 mg/L humic acid did not significantly affect the performance of Fe-ZSM-5 as a catalyst [23]. In addition, the MTBE/CS-1240 isotherm data using purified water and NOM-containing water were identical, suggesting that MTBE adsorbs much stronger to the sites of CS-1240 than NOM in the MTBE concentration range investigated in this work. This finding is in contrast to several previous studies with GAC which showed that NOM decreased the rate of adsorption of MTBE to GAC and its capacity for MTBE [3–5,9]. The reason for these discrepancies among MTBE/GAC systems could be due to differences in the types and concentrations of NOM used, the specific type of GAC and its pore size distribution, and the MTBE concentrations considered [3]. On the other hand, the adsorption of MTBE onto CCA was lowered in the presence of NOM, especially at the higher MTBE aqueous phase concentrations. This result is in agreement with previous studies which showed that GAC performance for MTBE removal from water was adversely affected by the presence of NOM in water [3–5]. For example, Shih et al. [2] suggested that NOM can reduce GACs adsorption capacity for trace organics by pore blockage or by the competition between NOM and the target organics for adsorption sites, thus reducing the total available adsorption sites.

### 3.2. MTBE fixed-bed adsorption

Adsorption of MTBE onto granular ZSM-5, coconut shell GAC (CS-1240), and CCA material was evaluated using a fixed-bed contactor with a length of 10 cm and an internal diameter of 2.5 cm. The adsorption experiments were carried out in the up-flow direction using a flow rate of 32.5 mL/min, and a feed MTBE concentration of 50  $\mu\text{g/L}$ . Breakthrough curves generated from MTBE adsorption experiments using the three adsorbent materials are shown in Fig. 4. The results show that the CCA material was the first adsorbent to allow breakthrough, retaining almost no MTBE, followed by CS-1240, and lastly by granular ZSM-5. The results were used to determine the adsorbent utilization rate (AUR), which is defined as the mass of adsorbent used per volume of liquid treated at breakthrough for granular ZSM-5, CS-1240, and CCA using a 10% MTBE breakthrough criterion which corresponds to an effluent MTBE concentration of 5  $\mu\text{g/L}$ . It was found that the utilization rate for CS-1240 is 10 times that of granular ZSM-5 and the utilization rate for CCA is 12 times that of granular ZSM-5. These results are in agreement with the AURs obtained by Rossner and Knappe [9], for which they found that silicalite had the smallest AUR and GAC had the greatest AUR among the adsorbents that they tested. In this work, trends in removal efficiency found from equilibrium and kinetic studies on the three tested adsorbents were in agreement,

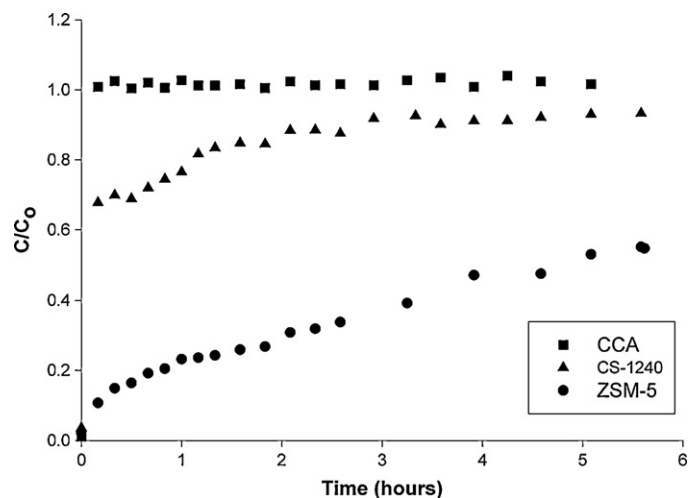


Fig. 4. Breakthrough curves of MTBE adsorption onto granular ZSM-5, CCA, and (CS-1240) from the large diameter fixed-bed adsorption experiments ( $C_0 = 50 \mu\text{g/L}$ , flow rate = 32.5 mL/min).

and they verify that granular ZSM-5 is more efficient in removing MTBE from water than CS-1240 and CCA materials tested.

To further understand and predict the fixed-bed adsorber dynamics of MTBE adsorption onto granular ZSM-5, and to facilitate the design of a full-scale fixed-bed adsorber system using granular ZSM-5, fixed-bed adsorption experiments providing for longer times before breakthrough were performed using smaller diameter adsorption columns with variable lengths. These columns had an internal diameter of 1 cm and length of 20 cm. In order to keep the superficial velocity identical to the previous experiments (6.62 cm/min), the smaller diameter columns were operated at a lower flow rate (5.2 mL/min). Granular ZSM-5 with particle diameter 250  $\rightarrow$  425  $\mu\text{m}$  was evaluated with a fixed MTBE influent concentration of 50  $\mu\text{g/L}$ , and 6, 9, and 12 cm bed depths.

The breakthrough curves are shown in Fig. 5. Considering the same breakthrough criterion as for previous experiments, it can be seen from Fig. 5 that the granular ZSM-5 bed with 6 cm depth reached the breakthrough point in less than 10 days. However, it took the ZSM-5 bed with 12 cm depth more than 40 days to reach the breakthrough point. It was expected that the bed with the shortest length would breakthrough first, since it had a smaller amount of adsorbent mass compared to the longer beds and hence, this bed

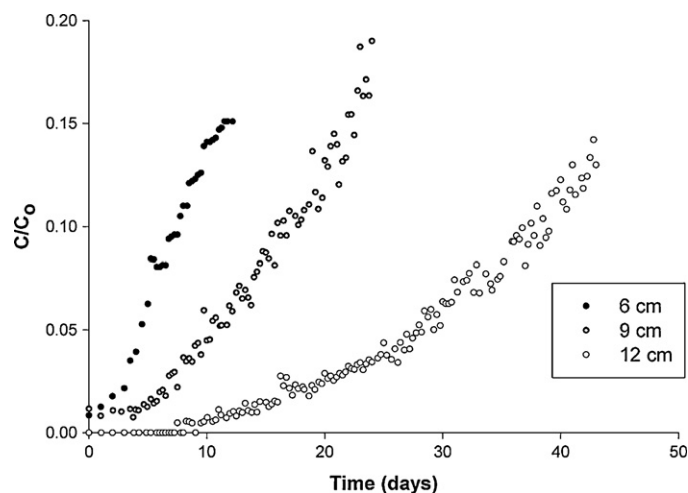


Fig. 5. Breakthrough curves of MTBE adsorption onto ZSM-5 from the small diameter fixed-bed adsorption experiments using three different bed heights ( $C_0 = 50 \mu\text{g/L}$ , flow rate = 5.2 mL/min).

**Table 4**  
BDST equation parameters, adsorption capacity ( $N_0$ ), adsorption rate constant ( $k$ ), service time, volume treated for different MTBE removal percentages and the minimum depth of adsorbent required to achieve the effluent criterion ( $Z_0$ ). Flow rate was 5.2 mL/min.

| Removal % | BDST equation $t$ : $d$ , $Z$ : cm | $R^2$ | $N_0$ (g/L) | $k$ (L/g min) | Service time (d)<br>for 6 cm bed | Volume treated<br>(L) for 6 cm bed | $Z_0$ (cm) |
|-----------|------------------------------------|-------|-------------|---------------|----------------------------------|------------------------------------|------------|
| 86        | $t = 5.47Z - 24.63$                | 0.97  | 2.60        | 1.02          | 9.92                             | 74.28                              | 4.5        |
| 90        | $t = 4.85Z - 23.5$                 | 0.95  | 2.31        | 1.3           | 7.63                             | 57.13                              | 4.84       |
| 95        | $t = 3.96Z - 21.35$                | 0.94  | 1.89        | 1.92          | 4.17                             | 31.2                               | 5.4        |

will have the least available adsorption sites. To evaluate the effect of bed depth on the breakthrough time, the breakthrough data were interpreted using the Bed Depth Service Time (BDST) model.

The BDST model was originally proposed by Bohart and Adams [24] and later linearized by Hutchins [25]. The model assumes that the adsorption zone is moving at a constant speed along the column. Thus, the bed adsorption capacity,  $N_0$ , will be constant throughout the bed and a linear relationship between the bed depth and service time should be obtained. With this assumption the linearized model by Hutchins works well, and offers a simple approach for analyzing fixed-bed adsorption data and determining adsorption column design parameters for changes in the system parameters such as flow rate and initial concentrations [26,27]. However, some researchers found that the linear BDST model with constant  $N_0$  was unable to explain their experimental data and they extended the BDST model to account for changes in the bed capacity as a result of changes in the service time [27,28]. The proposed relation between bed capacity and service time shows a root-time dependence characteristic of diffusional mass transfer-limited adsorption [27]. The BDST technique requires three column tests with three different bed depths to collect the necessary data. The BDST model has been widely applied in the literature to predict the performance of fixed-bed adsorbents for the removal of heavy metals [27,29,30] such as arsenic, lead, nickel, manganese, iron, cadmium, and copper, and for the removal of acid and base dyes from water [28,31]. However, some studies have applied the BDST model for organics removal from water [25,26,32–34].

The simplified equation of Bohart and Adams model is as follows [25]:

$$t = \frac{N_0}{C_0 u} Z - \frac{1}{k C_0} \ln \left( \frac{C_0}{C_b} - 1 \right) \quad (1)$$

where  $C_0$  is the influent solute concentration (g/L),  $C_b$  is the effluent solute concentration at breakthrough (g/L),  $N_0$  is the dynamic adsorption capacity (g/L),  $k$  is the adsorption rate constant (L/g min),  $Z$  is the bed depth (cm),  $u$  is the linear flow rate (cm/min), and  $t$  is the service time at breakthrough (min). Eq. (1) can be used to determine the service time,  $t$ , of a column of bed depth  $Z$ , given the values of  $N_0$ ,  $C_0$ , and  $k$ .

Eq. (1), plotted as  $t$  vs.  $Z$ , has the form of a straight line where the slope is  $\frac{N_0}{C_0 u}$  and the intercept is  $\frac{1}{k C_0} \ln \left( \frac{C_0}{C_b} - 1 \right)$ .

Fig. 6 shows the BDST curves evaluated at three different MTBE breakthrough concentrations; 2.5, 5, and 7  $\mu\text{g/L}$ . The three breakthrough points correspond to 95%, 90%, and 86% removal percentages, respectively. The results indicated a decline in the slopes of the BDST curves with increasing removal percentages of MTBE, and consequently lower values of  $N_0$ . With the increase in removal percentage, the effluent requirements become more stringent and result in lower adsorbed MTBE mass per unit volume of adsorbent values. Additionally, Table 4 shows that for the same flow rate, the dynamic adsorption capacity ( $N_0$ ), the adsorbent service time, and treated water volumes were all reduced with increased removal percentages. The results indicate that for the same bed, greater removal percentages are associated with higher operating costs as a result of the reduced treated water volumes and more frequent bed regeneration. On the other hand, critical bed depths ( $Z_0$ ), which rep-

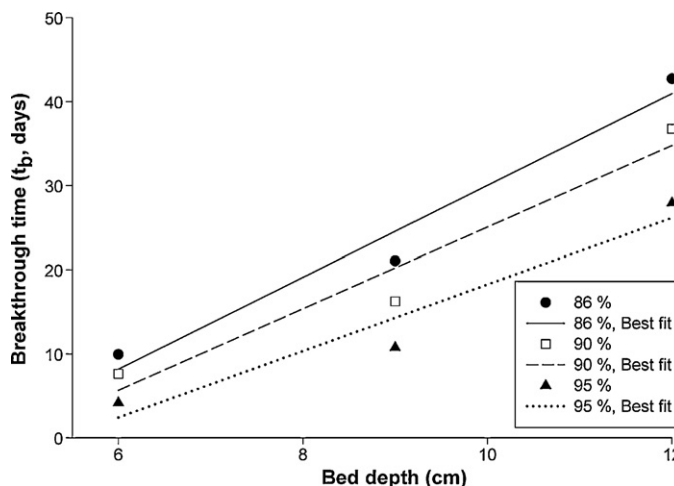


Fig. 6. BDST curves (flow rate = 5.2 mL/min,  $C_0 = 50 \mu\text{g/L}$ ).

resent the minimum depths of adsorbent required to achieve the effluent criterion ( $C_b$ ) and which can be calculated from the lines best fitting equations by letting  $t = 0$  and solving for  $Z$ , were found to increase with increasing MTBE removal percentages, as shown in Table 4.

#### 4. Conclusions

Several granular zeolites were evaluated for the removal of MTBE from water using batch adsorption experiments from low ( $\mu\text{g/L}$ ) to high (mg/L) solution concentrations. ZSM-5 granular zeolite had the highest adsorption capacity at the low and high range of concentrations compared with the other granular zeolites tested. At high MTBE concentrations, hydrophobicity and large pore sizes were found to be the important factors to obtain high capacities, while at low MTBE concentrations, the small pore sizes were the dominant factor to achieving high sorption.

MTBE adsorption isotherms on granular ZSM-5 were compared to the MTBE adsorption isotherms on coconut shell GAC (CS-1240) and CCA materials in the presence and absence of NOM. Using both purified water (without NOM) and a “challenge” water (amended with NOM), granular ZSM-5 was the most effective adsorbent and CCA was the least effective. Furthermore, in the presence of NOM, the ZSM-5 capacity for MTBE was not adversely affected, while the adsorption capacity of CCA for MTBE was lowered. This is an indication that NOM did not compete with MTBE for the ZSM-5 adsorption sites within the zeolite pores because of the large size of the NOM molecules. However, NOM did compete with MTBE for the CCA adsorption sites.

Column adsorption experiments of MTBE removal from water using granular ZSM-5, coconut shell GAC (CS-1240), and CCA material in packed beds were carried out. For the three adsorbent materials using a flow rate of 32.5 mL/min, a feed MTBE concentration of 50  $\mu\text{g/L}$  and a 10% MTBE breakthrough criterion, CCA material was the first adsorbent to allow breakthrough, followed by CS-1240, and lastly by granular ZSM-5. Correspondingly, the AURs

evaluated for the three adsorbents showed that the utilization rate for CS-1240 was 10 times that of granular ZSM-5 and the exhaustion rate for CCA was 12 times that of granular ZSM-5.

To further understand and predict the fixed-bed adsorber dynamics of MTBE adsorption onto granular ZSM-5 and to evaluate the effect of bed depth on the breakthrough time, granular ZSM-5 with particle diameters between 250 → 425 μm was evaluated with a fixed flow rate of 5.2 mL/min, a fixed influent MTBE concentration of 50 μg/L, and 6, 9, and 12 cm bed depths. The breakthrough data were fitted to the linear BDST model which can be used to aid in full-scale design for fixed-bed adsorbents. Overall, this research evaluated the performance of granular ZSM-5 in batch and column experiments and showed it to be an efficient adsorbent for the removal of MTBE from water.

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