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REMOVAL OF CHLOROFORM AND MTBE FROM WATER BY ADSORPTION ONTO GRANULAR ZEOLITES: EQUILIBRIUM, KINETIC, AND MATHEMATICAL MODELING STUDY

A Dissertation in

Civil & Environmental Engineering

By

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Submitted in Partial Fulfillment

Of the Requirements for the Degree of

Doctor of Philosophy

November, 12th 2010

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Abstract

Many parts of the world are facing water crises due to the lack of clean drinking water. Growing industrialization in many areas and extensive use of chemicals for various concerns has increased the burden of deleterious contaminants in drinking water especially in developing countries. It is reported that nearly half of the population in developing countries suffers from health problems associated with lack of potable drinking water as well as the presence of microbiologically contaminated water [1]. Synthetic and natural organic contaminants are considered among the most undesirable contaminants found in water. Various treatment processes are applied for the removal of organic contaminants from water including reverse osmosis membranes, ion exchange, oxidation, nanofiltration, and adsorption. The adsorption process is a widely-used technology for the removal of organic compounds from water. In this work, the adsorption of chloroform and methyl tertiary butyl ether (MTBE) onto granular zeolites was investigated. Zeolites were specifically chosen because they have shown higher efficiency in removing certain organics from water than granular activated carbon (GAC).

Batch adsorption experiments to evaluate the effectiveness of several granular zeolites for the removal of MTBE and chloroform from water were conducted and the results compared with GAC performance. Results of these batch equilibrium experiments showed that ZSM-5 was the granular zeolite adsorbent with the greatest removal capacity for MTBE and chloroform from water, and outperformed GAC.

Fixed-bed adsorption experiments with MTBE and chloroform were performed using granular ZSM-5. Breakthrough curves obtained from these column experiments were used to understand and predict the dynamic behavior of fixed bed adsorbers with granular ZSM-5. The
film pore and surface diffusion model (FPSDM) was fit to the breakthrough curve data obtained from the fixed bed adsorption experiments. The FPSDM model takes into account the effects of axial dispersion, film diffusion, and intraparticle diffusion mechanisms during fixed bed adsorption. Generally, good agreement was obtained between the FPSDM simulated results and experimental breakthrough profiles. This study demonstrated that film diffusion is the primary controlling mass transfer mechanism and therefore must be accurately determined for good breakthrough predictions.
Dedicated to

My Mom: Saleema Alyuosef

&

My Dad: the late Ibrahim Abu-Lail
Acknowledgements

I would like to sincerely thank my advisors Professor John A. Bergendahl and Professor Robert W. Thompson for their friendship, support, insights, guidance and inspirations throughout my Ph.D. years in WPI. I would like also to thank Professor James O’Shaughnessy for reviewing my thesis. Many thanks go to Professor John M. Sullivan from the Mechanical Engineering Department for his helpful discussions and Professor Terri Camesano for her friendship and support all the time. I would like also to thank Gerardo Hernandez and Chase Johnson from the Department of Mathematical Sciences for their help in using Matlab, and Donald Pellegrino from the Civil and Environmental Engineering Department for his help with setting up lab experiments. I would like to thank the Department of Civil and Environmental Engineering at WPI for giving me the chance to pursue my doctorate and for providing me with a graduate Teaching Assistantship. The financial support from Triton Systems, Inc. of Chelmsford, MA, and the support by the National Institutes of Health through grant 2R44 ES012784-02 are gratefully acknowledged. My sincere thanks go to all my faithful friends who were always concerned about me. More than all, I would like to thank my family, especially my mom and my sister Nehal, without their support this could not be done. I would like to thank the rest of my family members (Hussein, Omar, Zaina, Seren, Abd-Almajid, Areej, and Alaa) for their love, patience, and encouragement.
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1 Introduction

Removal of a wide range of trace organic contaminants from water to concentrations below USEPA Maximum Contaminant Levels (MCL) remains an important goal for the water industry. Volatile organic compounds (VOCs) and polar organic compounds (POCs) are two classes of organic contaminants that have received increasing attention in the recent years because of the difficulty associated with their removal from water systems and due to the serious health problems they can pose if allowed to enter the human environment. Removal of organic contaminants from water and wastewater has been achieved using several treatment technologies. Examples of such technologies include; advanced oxidation processes, air stripping, reverse osmosis, ultrafiltration, and adsorption. In particular, there is a growing interest in the application of adsorption processes for the removal of organic compounds from aqueous solutions. Adsorption processes can be successfully used when contaminants are not amenable to biological degradation. Granular activated carbon (GAC) is the most widely used adsorbent material for the removal of organic contaminants in water and wastewater applications [2-5]. However, the design and operation of fixed-bed GAC systems can be complicated by the presence of dissolved natural organic matter in the water stream being treated [6].

In addition, bacterial growth on the carbon grains, which can be enhanced by the adsorbed organic substrates, can lead to relatively high operational maintenance associated with frequent replacement or reactivation of the GAC bed. Recently, researchers have found that high-silica zeolites, a class of crystalline adsorbents with well defined pore sizes, were shown to be more effective in removing certain organics from water than activated carbon [6-10].
Adsorption processes are usually accomplished in fixed bed contactors because of their lower labor costs and high utilization rate of the adsorbent. In addition, granular materials with relatively large grain sizes are employed in fixed-bed adsorbers to avoid high friction losses which can be associated with passing water through beds of powdered materials.

The design and operation of fixed-bed adsorber systems can be complicated by the variability in the composition of water and the presence of different contaminants which makes the design of a fixed-bed adsorption system site-specific. Hence, integrating process-modeling principles into the design and operation of a treatment system allows the accurate determination of the process mechanisms and variables that are significant for its operation and performance. Once verified, those models can allow savings in time and expense that is usually associated with pilot studies and can be used to examine the effects of changing process variables other than those directly measured.

In this study, the removal of chloroform and methyl tertiary butyl ether (MTBE) as two examples of VOCs and POCs, respectively, from water using various granular zeolites was investigated. Additionally, a model that describes the physics of the adsorption process in fixed-bed adsorbers that is derived from fundamental mass continuity relationships was developed.

This dissertation is arranged into five chapters; the first and last chapters are the introduction and conclusions chapters, respectively, and the other three chapters corresponded to the body of the study. The second chapter focused on studying the adsorption of MTBE onto granular zeolites. In particular, equilibrium and kinetic adsorption of MTBE onto several types of granular zeolites, a coconut shell granular activated carbon (CS-1240), and a commercial carbon adsorbent (CCA) sample was evaluated. In addition, the effect of granular zeolite grain size and the effect of natural organic matter (NOM) on MTBE adsorption were evaluated.
Finally, fixed bed adsorption experiments were performed and the breakthrough results were analyzed with the bed depth service time model (BDST). In the third chapter, the adsorption of chloroform by granular zeolites was evaluated and compared to the adsorption efficiency of a commercial carbon adsorbent and a coconut shell granular activated carbon in batch and kinetic adsorption studies. In addition, the effects of adsorbent grain size and humic acid on chloroform adsorption capacity were also evaluated. Lastly, fixed-bed adsorption experiments of chloroform onto granular zeolite ZSM-5 were performed and fitted to the bed depth service time (BDST) model. In the forth chapter, the single component adsorption of chloroform onto granular zeolite ZSM-5 was evaluated using both batch and fixed-bed adsorption studies. In addition, a model which takes into account the film transfer resistance, intraparticle diffusion resistance, axial dispersion, and linear adsorption was developed and its resulting set of equations were solved numerically and used to fit the experimental breakthrough curves of chloroform adsorption onto granular zeolite ZSM-5.

1.1 Research Objectives

The overall goal of this research was to evaluate the effectiveness of alternative adsorbents for the removal of specific organic contaminants from water. Specific objectives of this study were to:

- Evaluate the effectiveness of several types of granular zeolites to determine the most suitable ones for the adsorption of chloroform and MTBE from water
- Compare chloroform and MTBE adsorption capacities of zeolites to those of two types of granular activated carbons (GAC)
• Study the effect of preloaded natural organic matter (NOM) on the removal capacities of granular zeolites and GAC for chloroform and MTBE from water
• Predict and analyze the adsorption rate using mathematical models which incorporates the equilibrium and kinetics of a given adsorbent-solute system

1.2 Background

1.2.1 Adsorption

Adsorption is the accumulation of a constituent in one phase at the interface between that phase and another (Figure 1-1). Many factors affect the degree of adsorption; adsorbent properties, chemical properties of the adsorbate, and aqueous phase characteristics such as pH and temperature. An adsorption isotherm describes the relation between the mass of adsorbate that accumulates on the adsorbent per unit mass of the adsorbent and the equilibrium aqueous phase concentration of the adsorbate. The most common method for gathering isotherm data is by equilibrating known quantities of the adsorbent material with solutions of the adsorbate. These equilibrium data are then matched into an adsorption isotherm model. A variety of models have been developed to characterize the equilibrium isotherm data. Examples of such models include; the linear model, the Langmuir model, the Freundlich model, and the BET model [11]. The Freundlich model is one of the most frequently used models in the design of adsorber systems because it usually fits single-solute experimental data and acknowledges the surface heterogeneity of the adsorbent [11]. The Freundlich isotherm model has the following form

\[ q_e = K_f C_e^{1/n} \]

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 \( K_f \) and \( (1/n) \) are characteristic constants [11].
1.2.2 Adsorbents

Two types of adsorbents were used in this study; activated carbon and zeolites. A description of their structure, properties and applications is given below.

1.2.2.1 Activated Carbons

Activated carbons can be prepared from almost any carbonaceous material by heating it in the absence of air to liberate carbon from its associated atoms. This step is called carbonization and it is followed by activation. Activation occurs by passing a mildly oxidative gaseous steam or carbon dioxide through the carbon at elevated temperatures (315-925°C) [12]. This process causes the formation of tiny fissures or pores. The typical range of GAC pore volume is around 0.85-0.95 ml/g and its apparent dry density ranges from 22-50 g/100 ml [12]. The surface areas of commercial GACs range from 600-1600 m²/g. Activated carbons adsorption has been used in the water treatment industry for a wide range of applications from taste and odor control to removal of specific organic contaminants such as aliphatic and aromatic hydrocarbons [12].

1.2.2.2 Zeolites

Zeolites are microporous inorganic crystalline materials with uniform pore dimensions. The zeolite framework consists of TO₄ tetrahedra units, where T is predominantly either a Si⁴⁺ or Al³⁺ atom located at the center of the tetrahedron. Other T-atoms such as (Fe, Ti, Ge, Ga, and Se) can be incorporated usually in small amounts, or as impurities, and for special purposes. Tetrahedra units are joined together in various regular arrangements through shared oxygen atoms, to form an open crystal lattice containing pores of molecular dimensions into which guest molecules can penetrate. Since the microstructure is determined by the crystal lattice it is precisely uniform with no distribution of pore size. This pore size regularity makes zeolites
different from other molecular sieves such as the microporous charcoal and amorphous carbon. Zeolite pore openings range from 3 to > 7 Å depending on the framework structure [13].

The crystalline zeolite framework carries a negative charge, and its magnitude depends on the amount of isomorphically substituted Al$^{3+}$. This charge is balanced by cations localized in non-framework positions (incavities or channels) to obtain a neutral net charge of the structure. Typical cations include the alkaline (Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$) and the alkaline earth (Mg$^{2+}$, Ca$^{2+}$, Ba$^{2+}$) cations, as well as NH$_4^+$, H$_3$O$^+$, TMA$^+$ (tetramethylammonium) and other nitrogen-containing organic cations [13]. The framework charge and cations are important as they determine the ion exchange properties of zeolites. Zeolites with low Al$^{3+}$ content or constituted exclusively of Si$^{4+}$ in the tetrahedral sites have low negative or neutral framework charge and therefore exhibit a high degree of hydrophobicity and poor ion exchange capacity [13]. The zeolite’s degree of hydrophobicity, which increases with increasing Si$^{4+}$/Al$^{3+}$ ratio of the structure and their pore size and geometry relative to the size of the organic in consideration play a role in determining the suitability of zeolites for the removal of organic contaminants from aqueous solutions [6, 8, 14, 15].

By appropriate choice of framework structure, Si$^{4+}$/Al$^{3+}$ ratio and cationic form, adsorbents with widely different adsorptive properties may be prepared. It is therefore possible, in certain cases, to tailor the adsorptive properties to achieve the selectivity required for a particular application.

Among the zeolite structures presently known, this work focused on four: ZSM-5/silicalite (MFI), Beta (*BEA), Mordenite (MOR), and Y (FAU) zeolites.

1.2.2.2.1 ZSM-5/Silicalite (MFI)

The most important member of the MFI family is the ZSM-5 zeolite because it possess unusual catalytic properties and have high thermal stability [16]. The pure silica form of ZSM-5
zeolite is known as silicalite. The MFI framework is presented in Figure 1-2. Zeolite ZSM-5 is constructed from pentasil units that are linked together in pentasil chains (Figure 1-2). Mirror images of these chains are connected by oxygen bridges to form corrugated sheets with ten-ring channel openings. Figure 1-2 highlights such a corrugated sheet in the y-x plane. Oxygen bridges link each sheet to the next to form a three-dimensional structure with straight ten-ring channels parallel to the corrugations along y intersected by sinusoidal ten-ring channels perpendicular to the sheets along z (Figure 1-2) [17]. The minor and major axis dimensions are 5.1 x 5.5 Å for the sinusoidal channels and 5.3 x 5.6 Å for the straight channels [18].

1.2.2.2 Beta (*BEA) Zeolite
Beta zeolites have well-defined layers comprised of four 5-ring subunits (Figure 1-3) joined by 4-ring subunits that are stacked in a disordered way along the z direction. Despite this disorder, a three-dimensional twelve-ring channel system is formed [17]. The pore dimensions of the channel system are 5.6 x 5.6 Å and 6.6 x 6.7 Å [18].

1.2.2.3 Mordenite (MOR) Zeolite
The Mordenite framework type is formed with four 5-ring subunits as shown in Figure 1-4. These units are linked to one another by common edges to form chains as illustrated in Figure 1-4 and mirror images of these chains are connected by oxygen bridges to form corrugated sheets. The corrugated sheets are connected together to form oval twelve- and eight-ring channels along the z direction (Figure 1-4). These channels are connected by eight-ring channels that are displaced with respect to one another (Figure 1-4). The twelve- and eight-ring channels have dimensions of 6.5 x 7.0 Å and 2.6 x 5.7 Å, respectively [18]. Given the small size of the eight-ring channels, the MOR channel system is effectively one-dimensional instead of two-dimensional [17].
1.2.2.4 Y (FAU) Zeolite

The framework of the faujasite structure can be described as a linkage of TO$_4$ tetrahedra in a condensed octahedron. The condensed octahedron is referred to as the sodalite unit or sodalite cage (Figure 1-5) [13]. In the faujasite structure, the sodalite units are linked together at the six-ring ends in a manner that is analogous to the arrangement of C-atoms in diamonds (Figure 1-5). The Y-zeolite (faujasite structure) has circular, 12-ring windows with a diameter of 7.4 Å (or 7.4 x 7.4 Å) and supercages with a diameter of about 13 Å [18].

1.2.3 Adsorbates

1.2.3.1 Methyl Tertiary-Butyl Ether (MTBE)

MTBE was originally introduced in the U.S. fuel supply in the late 1970s to replace the octane-enhancing compound tetraethyl lead. The implementation of the Clean Air Act of 1990 which requires the use of emissions-reducing oxygenated fuels in areas failing to meet national air-quality standards, has led to the increased use of MTBE and ethanol by refiners for producing cleaner-burning gasolines, although ethyl tertiary-butyl ether (ETBE), tertiary-amyl ethyl ether (TAME), diisopropyl ether (DIPE), tertiary-butyl alcohol (TBA), and methanol were also used [19]. Due to its widespread use since the 1980s and its environmental mobility and persistence, reports of MTBE detections in ground and surface water have been increasing. MTBE sources include gasoline leaking from underground fuel-storage tanks, urban runoff, and water craft. Several studies have been conducted to measure the carcinogenicity and taste and odor impacts of MTBE. MTBE was shown to cause cancer in rats and mice, which led some experts to conclude that MTBE poses a potential cancer risk to humans [19, 20]. However, other studies concluded that there is not enough information to classify MTBE as a human carcinogen [21, 22]. Based on the available health data, the U.S. Environmental Protection Agency (USEPA) has not set a health-based maximum contaminant level for MTBE. However, it did issue a drinking
water advisory for MTBE concentrations of 20-40 µg/L based on taste and odor data [19]. The California EPA set a primary health-based MTBE standard of 13 µg/L and a secondary MTBE standard based on taste and odor of 5 µg/L [20].

Given its high aqueous solubility and low volatility (Table 1-1), MTBE removal by traditional treatment technologies, such as air stripping and activated carbon adsorption has been expected to be less effective [23]. The byproducts of advanced oxidation process such as tertiary-butyl alcohol (TBA) have prevented this technique from general application though it is quite effective in removing MTBE [24].

1.2.3.2 Chloroform

In the water industry, chlorine is most often the final disinfectant added to treated water for disinfection purposes before it is conveyed into water distribution systems [25]. On the other hand, reactions between chlorine and organic precursor compounds in water, such as humic and fulvic acid substances results in formation of trihalomethanes (THMs), haloacetic acids (HAAs) and other disinfection byproducts (DBPs). Among DBPs, trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) are known or suspected carcinogens and their presence is not desirable. Consequently, the maximum allowable limit set by the USEPA for all trihalomethanes combined is 80 µg/L [26]. Chloroform as one of the most frequently investigated trihalomethanes has been selected in this study for further investigation (Table 1-1). Beside its production in surface water as a result of the chlorination process, chloroform is also found in groundwater due to the presence of organic solvents containing halogens, which are thought to be leaked from electronic device factories, dry cleaning facilities, and similar sources.
1.2.4 Treatment Technologies for the Removal of Chloroform and MTBE from Water

Various technologies have been applied for the removal of chloroform and MTBE from water such as advanced oxidation, air stripping, and adsorption. Removal of organic substances from water by air stripping involves their transfer from the liquid (water) phase to the gas (air) phase. Air stripping can be an effective process for MTBE removal; however, low mass transfer coefficients are observed for these systems due to the low volatility and high water solubility of MTBE. Consequently, relatively tall packed towers are required to achieve high MTBE removal percentages [27]. Although air stripping can be used for chloroform removal, it has a drawback of transferring chloroform into air creating air pollution concerns.

Advanced oxidation processes, such as UV/H₂O₂, Fe⁰/H₂O₂ and O₃/H₂O₂ have been evaluated for MTBE and chloroform removal. de Arruda et al. [28] evaluated the remediation of groundwater containing chloroform using a reductive system with zero-valent iron, and the reductive process coupled with Fenton’s reagent. Although, their results showed marked reductions in some chlorinated compounds, destruction of chloroform demanded additional treatment. Sutherland et al [27] showed that the O₃/H₂O₂ advanced oxidation process was effective in removing MTBE from groundwater only under conditions of low flow rates, low alkalinity, and at pH 7.0. Additionally, the study found that if the treatment objectives included removal of oxidation byproducts such as TBA, treatment costs were higher than those indicated in their analysis due to the need for a higher oxidant dosage. Beregendahl et al. [29] evaluated the effectiveness of Fenton’s oxidation with Fe⁰ for the removal of MTBE from contaminated water. Their results showed that oxidation reactions were able to degrade over 99% of the MTBE within 10 min.

Adsorption processes have been evaluated for MTBE and chloroform removal from aqueous solutions. Removal of chloroform and MTBE by adsorption on activated carbon has
been widely used as an effective means for water purification [2-5, 30]. For example, Urano et al. [30] investigated the adsorption capacities and rates for adsorption of chloroform and six other chlorinated organic compounds for six commercial GACs. Their results showed that GAC was able to remove these compounds from water; however, the amounts adsorbed were decreased by 10-20% when humic substances coexisted. Similarly, studies have shown that GAC performance in removing MTBE was reduced when other synthetic organic compounds coexisted with MTBE or in the presence of natural organic matter (NOM). For example, Shih et al. [3] studied the impact of NOM on GAC performance for the removal of MTBE from two groundwater sources and one surface water. Their results showed that the higher NOM content of the surface water over the groundwater sources caused a greater competitive-adsorption effect that caused more sites on the GAC to be unavailable to MTBE, thus decreasing the GAC adsorption capacity for MTBE. Additionally, Shih et al. found that a higher TOC content in the water adversely affected MTBE removal because of GAC fouling associated with TOC adsorption [3].

Recently, porous solids other than activated carbons such as zeolites, were found to be interesting alternatives for organic compounds adsorption, they may be in some cases, more efficient because they offer a large range of surface properties [7, 8, 10, 14, 31]. In particular, studies using the adsorptive features of zeolites for the removal of chloroform and MTBE from water were reported and generally suggested that the Si/Al ratio of zeolites played an important role regarding their behavior in adsorbing chloroform or MTBE from water [6, 10, 14]. Zeolites with low Si/Al ratio (i.e., high Al content) are highly hydrophilic and therefore selectively adsorb water rather than chloroform (or MTBE) from aqueous solution. On the other hand, zeolites with
high Si/Al ratio (i.e., low Al content) are hydrophobic and adsorb large amounts of chloroform (or MTBE).

1.2.5 Theory and Design of Fixed-Bed Adsorption Systems

Fixed-bed adsorbers are the usual contacting systems for adsorption in water and wastewater treatment applications. In the design of fixed-bed adsorbers, characterizing the effluent concentration profile as a function of time (breakthrough curve) is considered one of the critical aspects. This profile represents the specific combination of equilibrium and rate factors that control process performance in a particular application. The dynamic behavior of a fixed-bed adsorber can be pictured in terms of an active adsorption zone that is termed the mass transfer zone. The mass transfer zone is the zone in which the solute transfers from the liquid to the solid phase. Above this zone the solute in the liquid phase is in equilibrium with that sorbed on the solid phase. As the sorption zone moves down the bed, the concentration of the solute in the effluent is theoretically zero. Once the sorption zone reaches the bottom of the bed, the effluent solute concentration becomes a finite value and the breakthrough begins, as shown in Figure 1-6. As the sorption zone disappears, the effluent solute concentration increases to the influent solute concentration and the bed is exhausted (Figure 1-6). The rate of adsorption and the shape of a breakthrough curve are affected by several factors, including the physical and chemical properties of both the adsorbate and adsorbent, the depth of the bed, the empty bed contact time, and the rate limiting mechanisms involved [32]. All these factors create a complex system that is difficult to predict and understand without developing a conceptual model that is able to describe the design process and its significant variables and mechanisms. Developing a mathematical model that describes or predicts the adsorption dynamics of fixed-bed adsorber systems can be established by three steps. The first step is to choose an adequate adsorption isotherm model that can accurately describe the equilibrium behavior. The second step is to determine and
characterize the associated rate-limiting mechanisms which control the rate of uptake of the contaminant by an adsorbent. These mechanisms are usually classified into four rate processes that occur in series; bulk transport (fast), film transport (slow), intraparticle transport (slow), and adsorption (fast) [11]. The overall rate of adsorption is then controlled by the step providing the greatest resistance to mass transport. The third step in developing an adsorption model is to apply the principles of continuity and material balance relationships which results in a material balance for each component of interest in both the liquid and solid phases. After establishing the initial and boundary conditions, the resulting set of equations can be solved either analytically or numerically. Several dynamic models that account for both film and intraparticle diffusion mechanisms have been developed to describe the behavior of fixed-bed adsorption systems [2, 33-38]. Variations among such models are distinguished according to the rate limiting mass transport step [33]. Examples of those kinetic models include; the linear driving force model, the surface diffusion model [38], the pore diffusion model [34], and the film pore and surface diffusion model [33, 35]. In this study, the combined film pore and surface diffusion model was applied in predicting the effluent concentration profiles of chloroform adsorption onto granular zeolite ZSM-5.
### Table 1-1: Physicochemical properties and molecular structures of MTBE and chloroform

<table>
<thead>
<tr>
<th></th>
<th>MTBE [19]</th>
<th>Chloroform [6, 26]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight (g/mol)</td>
<td>88.15</td>
<td>119.39</td>
</tr>
<tr>
<td>Aqueous solubility at 25 °C (g/L)</td>
<td>51.26</td>
<td>7.2</td>
</tr>
<tr>
<td>Density at 25 °C (g/cm³)</td>
<td>0.74</td>
<td>1.489</td>
</tr>
<tr>
<td>Log K&lt;sub&gt;ow&lt;/sub&gt;</td>
<td>1.24</td>
<td>1.97</td>
</tr>
<tr>
<td>Henry’s low constant at 25 °C (atm·m³/mol)</td>
<td>5.5 x 10⁻⁴</td>
<td>4.06 x 10⁻³</td>
</tr>
<tr>
<td>Chemical formula</td>
<td>C₅H₁₂O</td>
<td>CHCl₃</td>
</tr>
<tr>
<td>Chemical structure</td>
<td><img src="image" alt="Chemical structure of MTBE" /></td>
<td><img src="image" alt="Chemical structure of chloroform" /></td>
</tr>
</tbody>
</table>
Figure 1-1: A drawing of the adsorption process
Figure 1-2: ZSM-5 framework viewed along (010)[18]
Figure 1-3: Beta framework viewed along (010) [18]
Figure 1-4: Mordenite framework viewed along (001) [18]
Figure 1-5: FAU framework viewed along (111) (upper right: projection down (110)) [18]
Figure 1-6: Dynamic behavior of fixed-bed adsorption systems

Fixed-bed adsorption system

Breakthrough profile

$C_e$ = Effluent concentration of solute
$C_o$ = Influent concentration of solute
$C_{b0}$ = Breakthrough concentration of solute

\[ \frac{C_o}{C_0} \]

\[ \frac{C_{b0}}{C_0} \]

\[ C_e \]

\[ C_0 \]

Time
2 Adsorption of Methyl Tertiary Butyl Ether on Granular Zeolites: Batch and Column Studies

2.1 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.

Keywords: adsorption, activated carbon, MTBE, zeolite
2.2 Introduction

Since the 1970’s, 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) [19]. 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 [19].

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 µg/L may cause adverse health effects [19].

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) [3, 39-41].

Recent studies have demonstrated the ability of powdered zeolites as successful adsorbents for the removal of MTBE from water [9, 42-47]. 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.

2.3 Materials and Methods

2.3.1 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 2.1 lists the supplier, size, SiO$_2$/Al$_2$O$_3$ 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 hours 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).

2.3.2 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 hours at 15 rpm, for adsorption equilibrium to be achieved. A 24 hour equilibration time is based on kinetics testing conducted as part of this work. In addition, previous work on powdered zeolites had shown that 24 hours is sufficient time for MTBE to reach equilibrium [44]. 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 minutes 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.

2.3.3 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.

2.3.4 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 a 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.

2.3.5 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 hours at 300°C. Before immersing the fiber into the aqueous sample (for 30 minutes at 250 rpm), the sample was agitated in the Combi-PAL agitator unit for 10 minutes 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 ºC and 250 ºC, respectively. Nitrogen was 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 ºC for 1 min, ramped to 50 ºC at 7.5 ºC/min, held for 2 min, ramped to 90 ºC at 20 ºC/min, held for 2 min, finally ramped to 200 ºC at 40 ºC/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 ºC for 5 min followed by another 5 min of conditioning in a separate conditioning unit at 300 ºC. The total desorption time of 10 min between successive injections was used to prevent carry-over contamination problems.

2.4 Results & Discussion

2.4.1 MTBE Sorption Isotherms

Batch adsorption experiments were carried out using select granular zeolite samples (Table 2-1), coconut shell GAC (CS-1240) sample, and CCA sample. Figure 2-1 shows MTBE sorption isotherms at room temperature for the granular zeolites listed in Table 2-1. 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 2-2. 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 [48]. 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 [48].

Table 2-2 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) \((K_f = 0.0011 \text{ (mg/g)/(µg/L)}^{1/n}, 1/n = 0.7)\) were different than those reported by Hung et al. [39] \((K_f = 0.14 \text{ (mg/g)/(µg/L)}^{1/n}, 1/n = 0.65)\). 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. [39] (0.0011 vs. 0.14) for MTBE adsorption to mordenite. In addition, the Freundlich isotherm parameters for HISIV 3000 \((K_f = 0.03 \text{ (mg/g)/(µg/L)}^{1/n}, 1/n = 0.57)\) were different from those found by Rossner and Knappe [9] \((K_f = 0.212 \text{ (mg/g)/(µg/L)}^{1/n}, 1/n = 0.87)\) in that the value for \( K_f \) was found to be about one magnitude low than that reported by them. The difference in results could be due to the broader concentration range employed in this study (1,000-100,000 µg/L) which was much greater than that used by Hung et al. and Rossner & Knappe (0.1-1,000 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. Figure 2-1 also shows that in this high concentration range, zeolite beta (with pore dimensions in the range of 6.6-7.7 Å [49]) was better able to remove MTBE from water than mordenite (with pore dimensions of 6.5 x 7.0 Å [49]). 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 2-2). 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 [43] 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 [43]. Erdem-Senatalar et al. [44] observed that dealuminated zeolite Y (DAY) was ineffective in removing MTBE from water at low concentrations. Knappe et al. [50] reported negligible adsorption capacities of zeolite Y. And Giaya et al. [51] observed the same phenomenon for TCE sorption on DAY. Giaya and Thompson [52, 53] and Fleys et al. [54] 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 Figure 2-1), 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 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 [44, 50]. These studies show that silicalite exhibits the greatest affinity for MTBE in the aqueous phase concentration range of 0 to 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 2-2), 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-Senatalar et al. [44], or to the reduced tendency for water molecules to interfere with sorption in the smaller pores, as suggested by Giaya and Thompson [52, 53] and Fleys et al. [54]. 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 µm, (2) 425 → 850 µm, and (3) 850 µm → 1.4 mm. Figure 2-2 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 [55] was followed for comparing the data sets in Figure 2-2. 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=1.8x10^{-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. [56] 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 µm) 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 2-3 summarizes the different constituents which were used in preparing the NOM-containing “challenge” solution.

Figure 2-3 shows the MTBE adsorption isotherms using granular ZSM-5, CS-1240, and CCA adsorbents using both purified water 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 [9, 44].

Figure 2-3 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 [57]. 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 [58]. They found that 100 mg/L humic acid did not significantly affect the performance of Fe-ZSM-5 as a catalyst [58]. 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 [9, 39-41]. 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 [39]. 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 [39-41]. For example, Shih et al. [3] 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.

2.4.2 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 µg/L. Breakthrough curves
generated from MTBE adsorption experiments using the three adsorbent materials are shown in Figure 2-4. 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 µg/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, 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 → 425 µm was evaluated with a fixed MTBE influent concentration of 50 µg/L, and 6, 9, and 12 cm bed depths.
The breakthrough curves are shown in Figure 2-5. Considering the same breakthrough criterion as for previous experiments, it can be seen from Figure 2-5 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 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 [59] and later linearized by Hutchins [60]. 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 [61, 62].

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 [62, 63]. The proposed relation between bed capacity and service time shows a root-time dependence characteristic of diffusional mass transfer-limited adsorption [62]. 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 adsorbers for the removal of heavy metals [62, 64, 65] such as arsenic, lead, nickel, manganese, iron, cadmium, and
copper, and for the removal of acid & base dyes from water [63, 66]. However, some studies have applied the BDST model for organics removal from water [4, 60, 61, 67, 68].

The simplified equation of Bohart and Adams model is as follows [60]:

\[
t = \frac{N_0}{C_0 \cdot u} Z - \frac{1}{k \cdot C_0} \ln \left( \frac{C_0}{C_b} - 1 \right)
\]

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). Equation 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 \(k\).

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

Figure 2-6 shows the BDST curves evaluated at three different MTBE breakthrough concentrations; 2.5, 5, and 7 µg/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 2-4 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 represent 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 2-4.

### 2.5 Conclusions

Several granular zeolites were evaluated for the removal of MTBE from water using batch adsorption experiments from low (\(\mu g/L\)) 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 not 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 µg/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 adsorbers. 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.

2.6 Acknowledgments

The authors acknowledge the financial support from Triton Systems, Inc. of Chelmsford, MA, and the support by the National Institutes of Health through grant 2R44 ES012784-02 (to Triton Systems, Inc.). We appreciate the guidance provided by Arjan Giaya of Triton Systems, Inc. We also thank Donald Pellegrino, WPI, for assistance with the lab experiments.
Table 2-1: Summary of zeolite samples used in the batch adsorption experiments

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Size</th>
<th>Si/Al In</th>
<th>Zeolite %</th>
<th>Company Name</th>
<th>Surface area m²/g [69]</th>
<th>Micropore area m²/g [69]</th>
<th>External area m²/g [69]</th>
<th>Pore dimensions Å [49]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beta</td>
<td>0.0625#</td>
<td>35</td>
<td>80</td>
<td>Engelhard</td>
<td>533.7</td>
<td>266</td>
<td>267.6</td>
<td>6.6 - 7.7</td>
</tr>
<tr>
<td>Mordenite</td>
<td>0.0625#</td>
<td>50</td>
<td>80</td>
<td>Engelhard</td>
<td>472.6</td>
<td>304.3</td>
<td>168.3</td>
<td>6.5 x 7.0</td>
</tr>
<tr>
<td>HISIV 1000</td>
<td>0.0625#</td>
<td>35-40</td>
<td>80</td>
<td>UOP</td>
<td>379.9</td>
<td>247.1</td>
<td>132.8</td>
<td>7.4 x 7.4</td>
</tr>
<tr>
<td>HISIV 3000</td>
<td>0.0625#</td>
<td>800</td>
<td>80</td>
<td>UOP</td>
<td>321.9</td>
<td>230.5</td>
<td>91.4</td>
<td>5.1 x 5.5, 5.3 x 5.6</td>
</tr>
<tr>
<td>Zeolite Y1</td>
<td>0.15</td>
<td>9</td>
<td></td>
<td>Engelhard</td>
<td>158.6</td>
<td>73.4</td>
<td>85.2</td>
<td>7.4 x 7.4</td>
</tr>
<tr>
<td>Zeolite Y2</td>
<td>0.15</td>
<td>14</td>
<td></td>
<td>Engelhard</td>
<td>158.3</td>
<td>58.7</td>
<td>99.6</td>
<td>7.4 x 7.4</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>0.0625#</td>
<td>280</td>
<td>80</td>
<td>Zeolyst</td>
<td>390.8</td>
<td>141.8</td>
<td>249</td>
<td>5.1 x 5.5, 5.3 x 5.6</td>
</tr>
<tr>
<td>Beta</td>
<td>0.0625#</td>
<td>360</td>
<td>80</td>
<td>Zeolyst</td>
<td></td>
<td></td>
<td></td>
<td>6.6 - 7.7</td>
</tr>
<tr>
<td>Mordenite</td>
<td>0.0625#</td>
<td>90</td>
<td>80</td>
<td>Zeolyst</td>
<td></td>
<td></td>
<td></td>
<td>6.5 x 7.0</td>
</tr>
</tbody>
</table>

# Size obtained from manufacturers’ data.
Table 2-2: The Freundlich and Langmuir isotherms parameters

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Langmuir Parameters</th>
<th>Freudlich Parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_a$</td>
<td>$b$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>ZSM-5, Zeolyst</td>
<td>0.67</td>
<td>11.27</td>
<td>0.98</td>
</tr>
<tr>
<td>HISIV 3000, UOP</td>
<td>6.78</td>
<td>0.4</td>
<td>0.96</td>
</tr>
<tr>
<td>Beta, Engelhard</td>
<td>25.06</td>
<td>0.01</td>
<td>1.00</td>
</tr>
<tr>
<td>Mordenite, Engelhard</td>
<td>2.76</td>
<td>0.05</td>
<td>1.00</td>
</tr>
<tr>
<td>Mordenite, Zeolyst</td>
<td>0.08</td>
<td>21.10</td>
<td>0.98</td>
</tr>
<tr>
<td>Beta, Zeolyst</td>
<td>0.02</td>
<td>9.68</td>
<td>0.98</td>
</tr>
</tbody>
</table>
Table 2-3: A list of constituents used in preparing the challenge solution

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural organic matter (NOM)</td>
<td>5</td>
</tr>
<tr>
<td>Mg$^{+2}$</td>
<td>10</td>
</tr>
<tr>
<td>Cl$^{-}$</td>
<td>44.56</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>10</td>
</tr>
<tr>
<td>Ca$^{+2}$</td>
<td>10</td>
</tr>
<tr>
<td>CO$_3^{-2}$</td>
<td>25</td>
</tr>
<tr>
<td>Fe$^{+2}$</td>
<td>10</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>17.2</td>
</tr>
</tbody>
</table>
Table 2-4: 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.

<table>
<thead>
<tr>
<th>Removal %</th>
<th>BDST equation t: d, Z: cm</th>
<th>$R^2$</th>
<th>$N_0$ (g/L)</th>
<th>$k$ (L/g·min)</th>
<th>Service time (d) for 6 cm bed</th>
<th>Volume treated (L) for 6 cm bed</th>
<th>$Z_0$ (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>86</td>
<td>$t = 5.47Z - 24.63$</td>
<td>0.97</td>
<td>2.60</td>
<td>1.02</td>
<td>9.92</td>
<td>74.28</td>
<td>4.5</td>
</tr>
<tr>
<td>90</td>
<td>$t = 4.85Z - 23.5$</td>
<td>0.95</td>
<td>2.31</td>
<td>1.3</td>
<td>7.63</td>
<td>57.13</td>
<td>4.84</td>
</tr>
<tr>
<td>95</td>
<td>$t = 3.96Z - 21.35$</td>
<td>0.94</td>
<td>1.89</td>
<td>1.92</td>
<td>4.17</td>
<td>31.2</td>
<td>5.4</td>
</tr>
</tbody>
</table>
Figure 2-1: 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).
Figure 2-2: MTBE sorption from the aqueous phase onto granular ZSM-5 with three different grain sizes compare to the original ZSM-5 size of 1.6 mm. Initial MTBE concentrations were in the range of 85-7500 μg/L.
Figure 2-3: MTBE sorption from the aqueous phase onto granular ZSM-5, (CS-1240) & 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 μg/L
Figure 2-4: Breakthrough curves of MTBE adsorption onto granular ZSM-5, CCA, & (CS-1240) from the large diameter fixed-bed adsorption experiments ($C_0 = 50 \mu g/L$, flow rate = 32.5 ml/min)
Figure 2-5: Breakthrough curves of MTBE adsorption onto ZSM-5 from the small diameter fixed-bed adsorption experiments using three different bed heights ($C_o = 50 \, \mu g/L$, flow rate = 5.2 ml/min)
Figure 2-6: BDST curves (flow rate = 5.2 ml/min, $C_o = 50 \mu g/L$)
3 Removal of Chloroform from Drinking Water by Adsorption onto Granular Zeolites

3.1 Abstract

The effectiveness of granular hydrophobic molecular zeolites for adsorption of chloroform from water was evaluated and compared to the adsorption efficiency of a commercial carbon adsorbent and a coconut shell granular activated carbon in batch and kinetic adsorption studies. In addition, the effects of adsorbent grain size and humic acid on chloroform adsorption capacity were also evaluated. It was found from the batch equilibrium experiments that granular zeolite ZSM-5 had the greatest chloroform removal capacity among the zeolites that were evaluated. Both batch and kinetic adsorption experiments showed that granular ZSM-5 had a greater capacity for chloroform than the CCA and GAC. The presence of humic acid in water did not significantly affect the ZSM-5 adsorption capacity for chloroform. Results obtained from these fixed-bed experiments were fitted to the bed depth service time (BDST) model and kinetic parameters obtained.

**Keywords:** adsorption, activated carbon, chloroform, zeolite
3.2 Introduction

Chlorination is the most widely used process for disinfection in drinking water treatment plants [26]. However, chlorination can lead to the formation of organo-halides by reaction of chlorine with natural organic matter (NOM) present in water. These organo-halides compounds are called disinfection byproducts (DBPs) and include trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), and others [70]. Trihalomethanes (THMs) and haloacetic acids (HAAs) are the two most commonly identified classes of DBPs in chlorinated drinking water [71] and are regulated by the US Environmental Protection Agency [26] due to their potential health risks.

The US EPA has set the maximum allowable annual average level of the sum of four THMs (i.e., chloroform (CHCl₃), dichlorobromoform (CHCl₂Br), dibromochloroform (CHBr₂Cl) and bromoform (CHBr₃)) to 80 μg/L and has set the maximum allowable annual average level of the sum of five HAAs (i.e., monochloro-, monobromo-, dichloro- [DCAA], dibromo-, and trichloroacetic acid [TCAA]) to 60 μg/L [26]. In addition, the US EPA requires the maximum residual chlorine concentration in drinking water to be below 4 mg/L [26]. These standards are based on the importance of controlling microbial contamination and growth in drinking water through presence of residual disinfectant while limiting the exposure to harmful DBPs like chloroform.

In order to control or limit the formation of DBPs, several alternatives have been utilized: (1) using alternative disinfectants that create fewer DBPs in water, (2) removing or treating precursors to lower their concentrations prior to disinfection, and (3) subsequent treatment to remove DBPs after their formation. Many alternative disinfectants such as ozone, ultraviolet radiation, and chlorine dioxide have been used [72-74], but these disinfectants are usually more
expensive than chlorine. Many studies have focused on the removal of natural organic matter (NOM) to control DBP formation by enhanced coagulation [75, 76], adsorption onto granular activated carbon (GAC) [76-78], or use of membrane filtration [74, 76] prior to disinfection. Other work has focused on the removal of the DBPs [74, 77, 79, 80]. Removal of chloroform has been achieved by adsorption onto activated carbon [74, 81, 82], however, regeneration of activated carbon is energy intensive [83]. Other processes such as air stripping [74], advanced oxidation [84] and nanofiltration [82, 85] also have been applied for the removal of chloroform from drinking water. These processes present some disadvantages such as transferring chloroform into air, the formation of byproducts, and the desorption of chloroform from organic membranes [85].

Hydrophobic zeolites with high silica content (i.e. a high Si/Al ratio) were recently demonstrated to be successful adsorbents for the removal of a wide variety of organic compounds from water [86-92]. Studies have focused on using powdered zeolites for the removal of chloroform from vapor and aqueous phases [87, 93-95]. However, no research has directly evaluated chloroform adsorption from aqueous solutions onto granular zeolites using batch adsorption experiments and fixed bed contactors. Granular zeolites can be employed in fixed-bed adsorbers, and due to the relatively large grain size of granular zeolites, the high friction losses associated with passing water through beds of powdered material can be avoided. The main objective of this work was to evaluate the effectiveness of several granular zeolites for the removal of chloroform from water, and to compare the effectiveness of these zeolites with a commercial carbon adsorbent material (CCA) extracted from a consumer water filtration unit and a coconut shell granular activated carbon (GAC) material. In addition, the effect of adsorbent
grain size and the effect of NOM on chloroform uptake were studied. Finally, kinetic parameters that describe granular zeolite fixed-bed adsorber performance were determined.

3.3 Materials and Methods

3.3.1 Materials

Nine types of granular zeolites were evaluated in this study: Engelhard Beta (Engelhard, Islin, 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). The sources and physical properties of these are listed in Table 3-1. For comparison, a coconut shell GAC (CS-1240)(Res-Kem Corp, Media, PA) sample and a commercial carbon adsorbent (CCA) sample extracted from a commercially available point of use drinking water filter were also evaluated. All granular zeolites were dried in an atmospheric oven at 120 °C for 10-14 hours and then stored in desiccators until use. Chloroform standard solutions were prepared by adding a specified amount of neat chloroform (ACS grade) (HACH Company, Loveland, CO) to purified water from a Barnstead ROpure ST/E-pure water purification system (Barnstead/Thermolyne, Dubuque, IA). Standard solutions of 1,1,2-trichloroethane as an internal standard were prepared using a 98 % pure 1,1,2-trichloroethane (Fisher Scientific, Pittsburgh, PA). Humic acid (Sigma-Aldrich, Saint Louis, MO) was used as the source for NOM in this study.

3.3.2 Batch Adsorption Experiments

Adsorption isotherm experiments for a wide concentration range were obtained at room temperature (22 ± 2 °C) using a fixed sorbent/liquid ratio (0.2 g sorbent/42 ml aqueous solution) and varied initial chloroform concentrations. In all adsorption experiments, the vials were
agitated on a fixed speed rotator for a minimum of 24 hours at 15 rpm for equilibrium to be established, following the procedure in previous work with adsorption to powdered zeolites [90]

In addition, to assure equilibrium was achieved, kinetics experiments were performed which showed that 24 hours was a sufficient time for equilibrium to be reached with these conditions. Following adsorption, the samples were centrifuged for 10 minutes at 3000 rpm to ensure complete separation of the solid and aqueous phases. Then the chloroform in the aqueous supernatant was quantified using gas chromatography as described below.

3.3.3 Fixed-Bed Adsorption Experiments

3.3.3.1 Large Diameter Fixed-Beds

The adsorption kinetics of the sorbent materials was evaluated with fixed bed column tests using a 10 cm long glass column with an internal diameter of 2.5 cm. Each adsorbent material was placed in the column between two layers of glass beads and glass wool. Using a digital peristaltic pump (Cole-Parmer, Vernon Hills, IL), water was passed through the column at a flow rate of 32.5 mL/min for at least an hour to remove air bubbles and to flush any residual fines from the adsorbent granules. Aqueous solution spiked with 450 µg/L chloroform was then passed through the column at a flow rate of 32.5 mL/min (empty bed flow velocity of 6.62 cm/min). Samples at the outlet of each column were collected in 42 ml glass vials at predetermined time intervals.

3.3.3.2 Small Diameter Fixed-Beds

Additional adsorption kinetics experiments with granular ZSM-5 were performed using a 20 cm long glass column (Bio-Rad Laboratories, Hercules, CA) with an internal diameter of 1 cm and an adjustable flow adapter to hold the packed bed in place. Water was passed through the column at a flow rate of 5.2 mL/min for an hour to remove air bubbles and to flush the adsorbent
particles. Adsorption experiments were performed with a flow rate of 5.2 mL/min (empty bed flow velocity of 6.62 cm/min), an influent chloroform concentration of 450 µg/L, and bed heights of 6, 9, and 12 cm. The influent chloroform solution was contained in a Tedlar bag (SKC Inc., Eighty Four, PA) which minimized the head space above the solution and any potential losses due to volatilization. Samples at the outlet of each column were collected in 42 ml glass vials at predetermined intervals of time, and analyzed with gas chromatography as described below.

3.3.4 Gas Chromatography Methodology

Solid phase microextraction (SPME) using a Combi-PAL autosampler (CTC Analytics, Zwingen, Switzerland) was used to extract and concentrate chloroform prior to GC analysis. The SPME fibers were 85 µm film thickness carboxen/polydimethylsiloxane (CAR/PDMS) (Supelco, Bellefonte, PA). Prior to each analysis, the SPME fibers were conditioned in a conditioning unit for one and a half hours at 300°C to prevent any possible carry-over contamination. Fibers typically were used 60 times before they were replaced. The method detection limit was 1 µg/L.

For the GC analysis, 20 ml GC vials were used and contained 18 ml of solution which had been transferred from the 42 ml collection vials. In addition, 0.18 ml of the internal standard solution was added. At the beginning of each analysis, each sample was agitated in the Combi-PAL agitator unit for 10 minutes at 250 rpm, and then the SPME fiber was immersed into the aqueous phase of the sample for 30 minutes with continued agitation. Thermal desorption of the extracted chloroform from the SPME fiber in the GC was effected by inserting it into the GC injector port using the splitless mode at 250 ºC for 5 min followed by another 5 min of conditioning in the conditioning unit at 300 ºC. Total desorption time of 10 min between successive injections was used to prevent carry-over contamination problems.
The concentration of chloroform was measured by a GC Series 6890N (Agilent Technologies, Santa Clara, CA) equipped with an electron capture detector (ECD) and a RTX-5SILMS capillary column (Restek, Bellefonte, PA) 30 m in length and 320 μm in nominal diameter. The inlet and detector temperatures were both 250 °C. Nitrogen served as the carrier gas and makeup gas at a constant flow of 20 ml/min. The GC oven program was as follows: initial temperature was 35 °C for 4 min, increased to 90 °C at 20 °C/min, held for 3 min, ramped to 200 °C at 40 °C/min, and then held for 10 min.

3.4 Results and Discussion

3.4.1 Chloroform Adsorption Isotherms

Equilibrium sorption experiments were conducted using nine different granular zeolites listed in Table 3-1, a coconut shell GAC (CS-1240) sample, and a CCA sample.

3.4.1.1 Chloroform Sorption onto Granular Zeolites

Chloroform adsorption isotherms onto the nine granular zeolites were obtained at room temperature at aqueous phase concentrations up to 100 mg/L. The results are shown in Figure 3-1. The high silica granular zeolites, ZSM-5 and silicalite HISIV 3000, had greater removal capacities for chloroform than the other zeolites tested. ZSM-5 outperformed HISIV 3000 with an average chloroform removal of 97% compared to 93.44 % for HISIV 3000. On the other hand, granular zeolite Y in the three forms tested (HISIV 1000, zeolite Y1, and zeolite Y2) had minimal capacity for chloroform, removing on average 12.4 % chloroform from solution.

The data in Figure 3-1 are in agreement with the trends observed previously by others [87, 90, 92, 94, 96], where the organics were found to adsorb to the greatest extent onto smaller pore high silica zeolites, and adsorb to the least extent onto zeolite Y. For example, Koryabkina et al. [87] found that chloroform adsorbed to a greater extent to powdered silicalite-1 than to
powdered dealuminated zeolite Y (DAY). Also Anderson [92] reported that zeolite Y removed < 1% of chloroform in solution while ZSM-5 was able to remove 78%. Erdem-Senatalar et al. [90] noted that methyl tert butyl ether (MTBE) adsorbed the greatest to powdered silicalite-1, while DAY was ineffective in removing MTBE from water at low concentrations. And Giaya et al. [94] observed similar trends in the adsorption capacity of silicalite and DAY for trichloroethylene. Finally, Tsutsumi et al. [96] found that the amount of chloroform adsorbed from aqueous solution increased with an increase in the Si/Al ratio of the sorbents; i.e. ZSM-5 and mordenite performed better than the low Si/Al zeolites.

The poor efficiency of zeolite Y for removing organic molecules from aqueous solution can be attributed to the presence of liquid water in the large pores of zeolite Y as was corroborated by the computational prediction made by Giaya and Thompson [97] and Fleys et al. [98]. It is believed that the high silica zeolites (such as HISIV 3000 and silicalite-1) provide a favorable environment in the pores for the adsorption of organic molecules. The high silica content (high Si/Al ratio) creates hydrophobic surfaces within the pores.

Figure 3-1 also shows that zeolite beta and mordenite had intermediate capacities for chloroform. However, it can be seen from Figure 3-1 that granular mordenite (Zeolyst) provided for greater removal of chloroform (67%) than granular zeolite beta (Zeolyst) (52%) in the 0-1 mg/L aqueous concentration range. In the 1-100 mg/L concentration range, zeolite beta (Englehard) was superior to zeolite mordenite (Engelhard) in removing chloroform from solution with average removal of 59.9% and 36.8%, respectively.

The higher efficiency of zeolite beta in removing chloroform from solution in the 1 – 100 mg/L range compared to zeolite mordenite could be attributed to the larger pore dimensions
of zeolite beta. Zeolite beta has pore dimensions in the range of 6.6-7.7 Å [18] compared to the smaller pore dimensions of zeolite mordenite, with pore dimensions of 6.5 x 7.0 Å [18]).

In the concentration range of interest for drinking water (below ca. 1 mg/L), the results are in agreement with previous MTBE sorption data [50, 90, 99]. These studies showed that silicalite exhibited the greatest affinity for MTBE in the 0-1 mg/L range, followed by mordenite, and finally by zeolite beta.

The slopes of the adsorption isotherms were evaluated in the low aqueous concentration range (< 1 mg/L) for correlation with the largest pore dimension (Å) and the framework density (# T-atoms/1000 Å³). It was found that the slopes of the adsorption isotherms correlated very well with the largest pore dimension (R² = 0.942) and to a lesser extent with the framework densities (R² = 0.700). Thus, at low chloroform concentrations, granular ZSM-5 with smaller pores and more condensed structures (18.4 T-atoms/1000 Å³) was more efficient in removing chloroform than granular zeolite beta with the larger pores and less condensed structures (15.3 T-atoms/1000 Å³).

In summary, high Si/Al ratio and large pore volumes were the dominant factors in achieving high adsorption capacities at high chloroform concentrations, while at low chloroform concentrations, small pores and high framework densities were the primary factors for attaining high sorption. Because of its superior performance in removing chloroform from water, granular ZSM-5 was selected for further study.

3.4.1.2 Effect of Adsorbent Grain Size

For the purpose of evaluating the effect of sorbent grain size on equilibrium sorption, chloroform sorption isotherms with three different sizes of granular ZSM-5 were obtained, and compared to the isotherm data obtained for the 1.6 mm diameter (size as received) granular
ZSM-5 (Figure 3-2). The three smaller sizes of granular ZSM-5 were obtained by grinding the original granular ZSM-5 material using a ball mill and then by sieving the resultant heterogeneous sized mixture through standard mesh sieves. As shown in Figure 3-2, the adsorption isotherms of the four sizes of granular ZSM-5 in the chloroform aqueous concentration range of 0-300 µg/L were different with the smaller grain sizes providing greater adsorption capacity.

To verify the performance variation with size, the data sets in Figure 3-2 (corresponding to different grain sizes) were statistically compared using the analysis of covariance test. The purpose of the analysis of covariance is to compare two or more linear regression lines by testing two null hypotheses. The first null hypothesis is that the slopes of the regression lines are the same, and the second is that the y-intercepts of the regression lines are the same. If the first null hypothesis is rejected, there is no need to perform the second hypothesis because the lines will cross each other somewhere. In this work, the procedure outlined by Zar [55] was used to test the data sets in Figure 3-2. Following Zar’s procedure, a regression line was found for each grain size data set, and then the slopes of the four regression lines were compared by testing the first null hypothesis that the slopes are all identical. The first null hypothesis was rejected confirming that the slopes are significantly different from each other (P = 0.017), and demonstrating that the observed trend of the increased sorption capacity with decreasing grain size is statistically significant.

Adsorption enhancement from the decrease in grain size can be explained by the fact that the larger zeolites grains were broken into smaller ones. This process produces fractures which are predominately at the boundaries between discrete zeolite grains (the original powder zeolite entities), which results in opening new adsorption sites by exposing pores that were previously
blocked by the binder material. This observation of increased adsorption with smaller grain size was previously reported by Weber et al. [100] in a study of the adsorption of 3-dodecylbenzenesulfonate on three different sizes of Columbia carbon at 30°C. Because of its excellent adsorption capacity for chloroform, granular ZSM-5 with the smallest particle grain size ($250 \mu m < d < 425 \mu m$) was used in the remaining tests.

3.4.1.3 Chloroform Sorption onto Granular ZSM-5, GAC, and CCA Using Purified Water and a Challenge Solution

Equilibrium adsorption experiments with granular ZSM-5 and two reference materials (CS-1240 GAC and CCA) using purified water spiked with chloroform and a more realistic chloroform-spiked “challenge” water were conducted. The “challenge” water contained natural organic matter (NOM) and other constituents that are generally present in natural waters. A summary of the different components used in preparing the challenge solution is presented in Table 3-2. The initial concentration of chloroform employed in these batch adsorption experiments was in the range of 1.4 mg/L-10 mg/L.

Figure 3-3 shows the average chloroform removal percentages using granular ZSM-5, CS-1240, and CCA, for both chloroform-spiked purified water and the chloroform-spiked challenge solution. In chloroform-spiked purified water, granular ZSM-5 and CCA were very similar in their removal efficiencies for chloroform ($P = 0.051$), and more effective than CS-1240. In addition, in the presence of NOM and the other constituents in the challenge water, the chloroform removal efficiencies of granular ZSM-5 and CCA were statistically the same ($P = 0.75$), and higher than the removal efficiency of CS-1240. For example, when 0.2 g of each adsorbent was added to 0.042 L of purified water with an initial chloroform concentration of 3 mg/L, the removal efficiencies with ZSM-5 and CCA were 98.9 % and 99.2 %, respectively, while the removal efficiency with CS-1240 was 96.4%. In general, the three adsorbents removed
chloroform from water to a large extent and differences in their adsorption capacities could be a result of the specific characteristics of each adsorbent material such as type, pore shape, and pore size distributions.

Figure 3-3 also shows that when the results from tests conducted with the challenge water were compared with the results using the chloroform-spiked purified water, there was a reduction in the removal percentages for all three adsorbents in the presence of the constituents in the challenge water, which included 5 mg/L NOM. However, this reduction in the adsorption capacities of the three adsorbents as a result of the constituents in the challenge water was less than 4 %. Therefore, it is believed that for the range of chloroform concentrations employed in this work (initially 1.4 mg/L – 10 mg/L), the additional constituents had minimal effect on the adsorption capacities of ZSM-5, CCA, and CS-1240. Koryabkina et al. [87] also found that the adsorption of chloroform (with an initial concentration of 1 mg/L) to silicalite-1 was not affected by the presence of up to 10 mg/L NOM.

This can be explained as resulting from size exclusion phenomena; NOM molecules are generally expected to have larger molecular sizes than the pore sizes of these adsorbent materials. In addition, Hung et al. [101] hypothesized that high initial contaminant concentrations promote relatively low competition between the contaminant and NOM for adsorption sites. Following this hypothesis, it could be expected that at high initial concentrations such as those employed in this study (mg/L), the organic compound adsorbs much stronger than NOM to the available adsorption sites leading to low competition for adsorption sites, while at low initial concentrations (µg/L or lower) the degree of competition between NOM and the organic compound may increase.
3.4.2 Chloroform Fixed-Bed Adsorption

3.4.2.1 Large Diameter Fixed-Bed Adsorption Experiments

Experiments were performed with chloroform-spiked water using fixed beds of granular ZSM-5, CS-1240, and CCA material in a glass column 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 feed flow rate of 32.5 mL/min, an empty bed contact time (EBCT) of 0.15 minutes, and an influent chloroform concentration of 450 µg/L. Normalized chloroform breakthrough profiles using the three adsorbent materials are shown in Figure 3-4. Chloroform breakthrough was chosen to be 80 µg/L, or 18 % of the influent concentration.

It can be seen from the results that both the CCA and CS-1240 materials allowed breakthrough in less than 20 minutes as a result of the rapid increase in chloroform effluent concentration in that period of time. On the other hand, when using granular ZSM-5, breakthrough occurred after 290 minutes as shown by the slow increase in chloroform effluent concentration with run time.

The results illustrate the higher affinity of granular ZSM-5 for chloroform compared to the less effective performance of CCA and CS-1240 in retaining chloroform. In order to assess the performance of the three adsorbent materials quantitatively, the adsorbent usage rate (AUR) was determined. The AUR was calculated by dividing the mass of adsorbent used in the column by the volume of liquid treated up to the 18 % breakthrough point. The usage rates for granular ZSM-5, CS-1240, and CCA were 0.32 g/L, 6.62 g/L, and 13.8 g/L, respectively, showing a much lower adsorbent consumption for adsorption processes utilizing the granular ZSM-5. However it has been reported [86] that the cost of 1 lb of ZSM-5 is 7 times the cost of 1 lb of either CCA or CS-1240. Yet the higher AURs predicted for CCA (~40 times larger than that associated with
ZSM-5) and CS-1240 (~20 times larger than that associated with ZSM-5) as compared to ZSM-5 will result in higher operating costs for CCA and CS-1240.

In summary, the fixed-bed experiments verified that granular ZSM-5 is more efficient in removing chloroform from water than the CS-1240 and CCA materials since it had a much lower AUR in the column tests.

3.4.2.2 Smaller Diameter Fixed-Bed Adsorption Experiments

In order to better understand the parameters which control the design and selection of a fixed bed adsorber system, additional chloroform fixed bed adsorption experiments with granular ZSM-5 (in the size range 250 µm < d < 425 µm) were performed using three different bed depths (6, 9, and 12 cm). These experiments were set up to operate for longer times before breakthrough using a smaller diameter glass column with an internal diameter of 1 cm and length of 20 cm.

However, 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). As in the preceding experiments, an initial chloroform concentration of 450 µg/L was used and an 18 % breakthrough criterion was selected.

The chloroform breakthrough curves with the three bed depths are shown in Figure 3-5, and show that the three breakthrough profiles reached effluent concentrations identical to their influent concentrations, though at different times. The granular ZSM-5 bed with 6 cm depth had the shortest service life allowing breakthrough in less than 5 days, followed by the 9 cm bed and finally by the 12 cm bed which allowed breakthrough after 10 days. In order to compare the performances of the three columns, data at breakthrough (when the effluent was 18% of the influent concentration) was taken and used to calculate the service time, the volume treated, and
the AURs for the three beds (shown in Table 3-3). In addition, Table 3-3 includes the EBCT values and the amount of chloroform retained in each column calculated by integrating the area above the breakthrough profile, then multiplying the result by the volumetric flow rate and dividing the product by the weight of granular ZSM-5 in each column.

The sorption capacities calculated from the fixed-bed adsorption experiments were compared to the equilibrium data collected from batch adsorption experiments and are illustrated in Figure 3-6. It was found that fixed-bed capacities were close to the equilibrium mass of chloroform adsorbed per mass of adsorbent at the corresponding point of equilibrium concentration (450 µg/L). It also can be seen from Table 3-3 that both the volumes of water treated and the service times at breakthrough increased as the EBCT increased. For example, doubling the EBCT (from 0.91 min to 1.81 min) resulted in threefold increase in the volumes of water treated at breakthrough. In addition, the increase in the volumes of water treated is associated with the observed decrease in the AURs since the two quantities are inversely related. The results are in agreement with the previous work of Capar et al. [102] on GAC adsorption of trihalomethanes.

The capital cost for a column with a large EBCT is higher than a column with a lower EBCT (larger vessel and more adsorbent). However, the service life of the adsorbent in the column with a larger EBCT will increase since the volume of water treated will be greater and the adsorption usage rate will be smaller (compared to columns with lower EBCTs). Thus, the operating costs are reduced. On the other hand, choosing a smaller bed (small volume) with a small EBCT providing lower capital costs will result in high usage rates and a shorter adsorbent service life (increased operating costs). Finally, as can be seen from Table 3-3, chloroform uptake capacities (mass of chloroform adsorbed/mass of granular ZSM-5 (mg/g)) calculated
from the breakthrough profiles were essentially constant for the three runs, as expected. This is an indication that when each column reached its saturation capacity, the amount of chloroform adsorbed in each column per unit mass of granular ZSM-5 added to the column did not vary with the size of the adsorption bed. This result suggests that mass transfer zone formed near the bed entrance, and moved through the column without changing shape, as seen in Figure 3-5. This phenomenon is known as a self-sharpening mass transfer zone, and is generally associated with a favorable isotherm and finite pore resistance to mass transfer. Consequently, choosing an optimum design will depend on the desired effluent water quality, and on the relative importance of capital and operating costs at the particular facility.

3.4.3 BDST model

To predict the effect of bed depth and different breakthrough percentages on granular ZSM-5 service time, the breakthrough data were fitted to the Bed Depth Service Time (BDST) model. The BDST model is based on the irreversible isotherm model by Bohart et al. [103]. Later, Hutchins [104] linearized the model proposed by Bohart et al. assuming that the adsorption zone is moving at a constant speed along the bed and hence, the adsorption capacity \( N_0 \) is constant throughout the bed. The BDST model (as modified by Hutchins) provides useful equations for the prediction of adsorption column design and is physically based on measuring the bed capacity of three column tests with three different bed depths. The BDST procedure has been widely applied in the literature to predict the effects of different bed depths, different feed concentrations, flow rates, and different initial concentrations on the performance of fixed-bed adsorber systems [105-109]. For example, Adak et al. [107] used the BDST model to determine design parameters that describe the adsorption of phenol by surfactant-modified alumina. Also,
Ko et al. [108] used the BDST model to describe the breakthrough profiles of adsorption of metal ions on bone char.

The original model by Bohart et al. can be represented with:

\[ kC_0 t = \ln\left(e^{kN_0Z/u} - 1\right) - \ln\left(\frac{C_0}{C_b} - 1\right) \]  

(1)

Where \( t \) is the service time at breakthrough (min), \( Z \) is the bed depth (cm), \( C_0 \) 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), and \( u \) is the linear flow rate (cm/min).

And Hutchins’ linear relationship between bed depth, \( Z \), and service time, \( t \), which can be obtained from Equation (1) by rearranging it and by assuming the exponential term in Equation (1) to be much greater than unity, so that the 1.0 can be neglected, is as follows:

\[ t = \frac{N_0}{C_0u} Z - \frac{1}{kC_0} \ln\left(\frac{C_0}{C_b} - 1\right) \]  

(2)

In this work, the exponential term in Equation (1) \( (e^{kN_0Z/u}) \) was found to be much larger than unity and hence the application of the Hutchins linear relationship was valid.

Equation (2) has the form of a straight line where the slope is equal to:

\[ \text{slope} = \frac{N_0}{C_0u} \]

and the intercept is:
In addition, setting $t = 0$ and solving Equation (2) for $Z$ yields $Z_0$, which represents the minimum theoretical depth of adsorbent sufficient to achieve the effluent criterion ($C_b$).

Some researchers have found that the linear BDST plots with constant bed capacity ($N_0$) were unable to explain their experimental data points and thus, they developed the extended BDST model which account for changes in the bed capacity as a result of changes in the service time [108, 110]. The extended BDST model suggests that the relation between bed capacity and service time has a root-time dependence characteristic of diffusional mass transfer-limited adsorption [108]. In this work, the authors found the linear BDST model well represented the behavior of the system. This form of the BDST model 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 $k$.

From the breakthrough times (corresponding to $C_b/C_0 = 0.1$) and the exhaust times (corresponding to $C_b/C_0 = 0.9$) for bed depths 6, 9, and 12 cm, the BDST curves were plotted, as shown in Figure 3-7, which showed the bed depth versus service times for 10% and 90% saturation of the columns. The best fitting equations of these two lines are listed in Table 3-4.

It can be seen from Figure 3-7 that the service times for the two BDST curves linearly increased with the increase in bed depths. This linearity as can also be seen from the high values of $R^2$ in Table 3-4 is a good indication of the suitability of the BDST model to represent the adsorption of chloroform in a fixed bed of ZSM-5 zeolite. It can also be observed from Figure 3-7 that the two BDST lines were parallel (with equal slopes) and consequently they should both have same values for bed adsorption capacities ($N_0$). Since the $N_0$ values were constant and did
not vary with changes in the breakthrough values, this is another indication of the validity of the linear BDST model which assumes constant $N_0$.

Additionally, it can be seen from Figure 3-7 that for the same bed, the adsorbent service times increase with increasing the breakthrough percentage. This is expected because with greater breakthrough percentage allowed, more volumes of water can be treated before the bed service limit is reached.

Finally, from the slope and intercept of the 10% saturation line, the design parameters $k$ and $N_0$ were found. The minimum column height ($Z_0$) necessary to produce an effluent concentration of $C_b$ was calculated by setting $t = 0$ and solving Equation (2) for $Z$. The values of $k$, $N_0$, and $Z_0$ were found to be 0.81 L/g.min, 5.02 g/L, and 3.60 cm, respectively.

### 3.5 Conclusions

Batch adsorption experiments using granular zeolites were performed at two ranges of chloroform aqueous concentration. It was found that at low chloroform concentrations (<1 mg/L) the small pores and the high framework densities of granular zeolites were the primary factors to attaining high sorption. While at higher chloroform concentrations, (1-100 mg/L) high Si/Al ratios and large pore sizes were the dominant factors in achieving high adsorption capacities. In addition, using batch adsorption experiments, the effect of ZSM-5 grain size on its adsorption capacity for chloroform and the effect of NOM on the adsorption capacities of ZSM-5, CCA, and CS-1240 for chloroform were evaluated. It was found that ZSM-5 with the smallest grain size (between 250 and 425 µm) was the most effective in removing chloroform from water. The presence of up to 5 mg/L of NOM and other constituents in the solution had minimal effect on
the adsorption capacities of ZSM-5, CCA, and CS-1240. Although batch equilibrium studies using ZSM-5, CCA, and CS-1240 showed that the three adsorbents had similar adsorption capacities for chloroform using purified water, kinetic studies obtained with the three adsorbents in fixed-bed experiments indicated that granular ZSM-5 had a higher adsorption rate. The adsorption capacity of ZSM-5 for chloroform compared well to CCA and CS-1240, as reflected in the values of the AURs of the three adsorbents. This finding suggests that equilibrium adsorption data alone are not sufficient to describe the behavior of chloroform in fixed-bed adsorbers.

Furthermore, chloroform fixed bed adsorption experiments with granular ZSM-5 (diameters between 250 µm and 425 µm) using three different bed depths (6, 9, and 12 cm) were completed. Breakthrough data obtained from the fixed-bed adsorption tests were fitted to the BDST model. The BDST model described the breakthrough data well. The kinetic parameters obtained from the breakthrough curves and the BDST model can be used to optimize the design and operation of fixed-bed adsorbers and to develop preliminary cost information.

### 3.6 Acknowledgments

The authors acknowledge the financial support from Triton Systems, Inc. of Chelmsford, MA, and the support by the National Institutes of Health through grant 2R44 ES012784-02. The authors also appreciate the guidance provided by Arjan Giaya of Triton Systems, Inc. and the assistance provided by Donald Pellegrino with lab experiments.
Table 3-1: Properties of granular zeolites tested in the batch adsorption experiments.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Supplier</th>
<th>Size (in)</th>
<th>Si/Al</th>
<th>Framework density (number of T atoms/1000 Å) [18]</th>
<th>Zeolite %</th>
<th>Micropore area (m²/g) [69]</th>
<th>External area (m²/g) [69]</th>
<th>Surface area (m²/g) [69]</th>
<th>Pore dimensions (Å) [18]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beta</td>
<td>Engelhard</td>
<td>0.0625(^a)</td>
<td>35</td>
<td>15.3</td>
<td>80</td>
<td>266</td>
<td>267.6</td>
<td>533.7</td>
<td>6.6-7.7</td>
</tr>
<tr>
<td>Mordenite</td>
<td>Engelhard</td>
<td>0.0625(^a)</td>
<td>50</td>
<td>17</td>
<td>80</td>
<td>304.3</td>
<td>168.3</td>
<td>472.6</td>
<td>6.5 x 7.0</td>
</tr>
<tr>
<td>HISIV 1000</td>
<td>UOP</td>
<td>0.0625(^a)</td>
<td>35-40</td>
<td>13.3</td>
<td>80</td>
<td>247.1</td>
<td>132.8</td>
<td>379.9</td>
<td>7.4 x 7.4</td>
</tr>
<tr>
<td>HISIV 3000</td>
<td>UOP</td>
<td>0.0625(^a)</td>
<td>800</td>
<td>18.4</td>
<td>80</td>
<td>230.5</td>
<td>91.4</td>
<td>321.9</td>
<td>5.1 x 5.5, 5.3 x 5.6</td>
</tr>
<tr>
<td>Zeolite Y1</td>
<td>Engelhard</td>
<td>0.15</td>
<td></td>
<td>13.3</td>
<td>9</td>
<td>73.4</td>
<td>85.2</td>
<td>158.6</td>
<td>7.4 x 7.4</td>
</tr>
<tr>
<td>Zeolite Y2</td>
<td>Engelhard</td>
<td>0.15</td>
<td></td>
<td>13.3</td>
<td>14</td>
<td>58.7</td>
<td>99.6</td>
<td>158.3</td>
<td>7.4 x 7.4</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>Zeolyst</td>
<td>0.0625(^a)</td>
<td>280</td>
<td>18.4</td>
<td>80</td>
<td>141.8</td>
<td>249</td>
<td>390.8</td>
<td>5.1 x 5.5, 5.3 x 5.6</td>
</tr>
<tr>
<td>Beta</td>
<td>Zeolyst</td>
<td>0.0625(^a)</td>
<td>360</td>
<td>15.3</td>
<td>80</td>
<td></td>
<td></td>
<td></td>
<td>6.6-7.7</td>
</tr>
<tr>
<td>Mordenite</td>
<td>Zeolyst</td>
<td>0.0625(^a)</td>
<td>90</td>
<td>17</td>
<td>80</td>
<td></td>
<td></td>
<td></td>
<td>6.5 x 7.0</td>
</tr>
</tbody>
</table>

\(^a\) Size obtained from manufacturers’ data.
Table 3-2: A list of all constituents used in preparing the challenge solution.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOM</td>
<td>5</td>
</tr>
<tr>
<td>$\text{Mg}^{+2}$</td>
<td>10</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>44.56</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>10</td>
</tr>
<tr>
<td>$\text{Ca}^{+2}$</td>
<td>10</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>25</td>
</tr>
<tr>
<td>Fe$^{+2}$</td>
<td>10</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>17.2</td>
</tr>
</tbody>
</table>
Table 3-3: Comparisons of chloroform column performances at breakthrough (effluent concentration = 18% of influent concentration) obtained from the small diameter fixed-bed adsorption experiments ($C_o = 450 \mu g/L$, flow rate = 5.2 ml/min).

<table>
<thead>
<tr>
<th>Bed depth (cm)</th>
<th>Empty bed contact time (EBCT) (min)</th>
<th>Service time (days)</th>
<th>Volume treated (L)</th>
<th>Adsorbent usage rate (AUR) (mg/L)</th>
<th>Amount adsorbed at saturation (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.91</td>
<td>3.50</td>
<td>26.21</td>
<td>117.13</td>
<td>6.82</td>
</tr>
<tr>
<td>9</td>
<td>1.36</td>
<td>6.76</td>
<td>50.60</td>
<td>92.30</td>
<td>6.70</td>
</tr>
<tr>
<td>12</td>
<td>1.82</td>
<td>11.18</td>
<td>83.72</td>
<td>75.00</td>
<td>7.13</td>
</tr>
</tbody>
</table>
Table 3-4: BDST equations for chloroform adsorption onto granular ZSM-5 at various breakthrough percentages. Flow rate was 5.2 mL/min.

<table>
<thead>
<tr>
<th>Breakthrough ( % )</th>
<th>BDST equation ( t: d, Z: \text{cm} )</th>
<th>( R^2 )</th>
<th>( \exp (kN_0Z/u) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>( t = 1.15Z + 2.36 )</td>
<td>0.99</td>
<td>( 6.23 \times 10^2 - 3.88 \times 10^5 )</td>
</tr>
<tr>
<td>10</td>
<td>( t = 1.17Z - 4.21 )</td>
<td>0.99</td>
<td>( 39.86 - 1.59 \times 10^3 )</td>
</tr>
</tbody>
</table>
Figure 3-1: Chloroform sorption from the aqueous phase onto granular zeolites, using a minimum 24 h equilibrium time.
Figure 3-2: Chloroform sorption from the aqueous phase onto ZSM-5 with three different grain sizes compared to the original ZSM-5 size of 1.6 mm. Lines are best linear fits.
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Figure 3-4: Normalized breakthrough curves of chloroform adsorption onto ZSM-5, CCA, & CS-1240 in the large diameter fixed-bed adsorption experiments ($C_0 = 450$ µg/L, flow rate = 32.5 ml/min, & EBCT = 0.15 min).
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Figure 3-7: BDST curves at various breakthrough points (as percentage of influent concentration) (flow rate = 5.2 ml/min, $C_0 = 450$ ppb). Lines are best fit to respective data.
4 Mathematical Modeling of Chloroform Adsorption onto Fixed Bed Columns of Highly Siliceous Zeolites

4.1 Abstract

The breakthrough curves for adsorption of chloroform onto granular zeolite ZSM-5 in fixed-bed adsorbers was predicted with a film pore and surface diffusion model. Parameters were estimated from published correlations and from data taken from batch adsorption rate studies. It was found that the adsorption rate was enhanced with the decrease in particle size, however, the total adsorption capacity using granular ZSM-5 with different particle sizes remained constant. The film-pore and surface diffusion model (FPSDM) accounted for the effects of axial dispersion, external film transfer resistance, and intraparticle mass-transfer resistances. Generally, good agreement between the simulated results and the experimental data was obtained. Furthermore, a sensitivity analysis was carried out to investigate the relative impact of kinetic parameters on the FPSDM predicted breakthrough profiles and showed that the model calculations were insensitive to either the effective pore diffusivity coefficient ($D_{p,e}$) or the axial dispersion coefficient ($E_z$), but were sensitive to the external mass transfer coefficient ($k_f$). The large impact of $k_f$ on the results and the relatively low Biot numbers determined by the FPSDM indicate that under the experimental conditions employed in the study, film diffusion is the primary controlling mass transfer mechanism. Additionally, a constant value of the effective pore diffusivity coefficient as determined from the batch adsorption rate studies is sufficient to correlate the breakthrough curves accurately.
4.2 Introduction

Chlorination of naturally occurring organic materials found in raw water supplies can lead to the formation of disinfection byproducts (DBPs) which are potentially harmful to humans. Two commonly identified classes of DBPs in chlorinated drinking water are the trihalomethanes (THMs) and haloacetic acids (HAAs). Both exhibit potentially high carcinogenic activity. Commonly found THMs are: chloroform (CHCl$_3$), dichlorobromoform (CHCl$_2$Br), dibromochloroform (CHBr$_2$Cl) and bromoform (CHBr$_3$). In this work, the removal of chloroform from water in fixed bed contactors was mathematically modeled to predict breakthrough in the effluent from these contactors. Chloroform was chosen for this work because of the acute and chronic adverse health effects of chloroform on humans, and it has been classified by the USEPA as a probable human carcinogen [26].

Various treatment methods to remove chloroform have been studied including; air stripping [74], advanced oxidation [84], and adsorption. Of these treatment technologies, adsorption using adsorbents such as activated carbon, activated carbon fiber, have been widely used [2, 4]. It has been recently demonstrated that hydrophobic zeolites with high silica content (i.e. a high Si/Al ratio) may be effective adsorbents for the removal of a wide variety of organic compounds from water [86-92].

Fixed-beds are the most common adsorber configuration used in water and wastewater treatment applications. One critical aspect of the design of a fixed-bed adsorber is the characterization of the breakthrough profile. The shape and rate of appearance of the breakthrough profile, represents the specific combination of equilibrium and rate factors that control the performance and dynamic behavior of a fixed bed adsorber. There are many factors
that affect the behavior of a fixed bed adsorber including; the physical and chemical properties of
the adsorbate and the adsorbent, the particular rate limiting mechanism, the velocity of the flow,
and the depth of the bed. The design of a particular adsorption process is highly specific and
depends on the relative importance of the above factors. Hence, the adsorption dynamics of such
processes and the characteristics of a fixed-bed adsorber breakthrough profile can be explained
and predicted through mathematical modeling. A number of mathematical models that account
for both film and intraparticle diffusion mechanisms have been developed to predict the one-
dimensional transport and adsorption of target contaminants in fixed-bed adsorbers [33-36, 38,
111-115].

Variations among such models are distinguished based on the means for describing the
intraparticle mass transport step. The simplest formulation of the above models is the linear local
equilibrium model that assumes linear adsorption and neglects mass transfer resistances [33]. A
more descriptive analysis of the intraparticle diffusion was then given by the pore transport
model [34, 116] and the surface diffusion model with or without external film resistance [38,
117]. Finally, a more realistic diffusion model was developed which takes into account both
pore and surface diffusivities [33, 35, 114].

For the development of a mathematical model that describes and predicts the adsorption
dynamics, both batch adsorption and fixed-bed adsorption studies are required. Batch adsorption
studies are required to obtain key parameters such as the isotherm constants and the effective
pore diffusivity coefficient. Fixed-bed studies are then used in determining experimental
breakthrough curves to validate the model.
In the present study, batch equilibrium and kinetic experiments and fixed-bed adsorption experiments were performed to quantify the single component adsorption of chloroform onto granular zeolite ZSM-5. In addition, the film pore and surface diffusion model which takes into account the film transfer resistance, intraparticle diffusion resistance, axial dispersion, and linear adsorption was applied. A numerical solution to the film-pore and surface diffusion model (FPSDM) equations was developed and results compared to the experimental breakthrough.

### 4.3 Mathematical Model

The film-pore and surface diffusion model (FPSDM) [33] was used to predict fixed-bed adsorber breakthrough curves for chloroform adsorption onto granular zeolites. The FPSDM is a comprehensive model that takes into account: the external mass transfer resistance (external film diffusion), the internal mass transfer resistance (pore and surface diffusion), and axial dispersion [33].

The FPSDM equations were derived from continuity principles and mass balance expressions for a finite volume in the fixed-bed reactor (Appendix A) as described by Crittenden et al. [33], Hand et al. [38], and Weber and DiGiano [11] resulting in two partial differential equations (PDEs); one describing the liquid-phase mass balance and the other one describing the intraparticle phase. Solving the resulting system of PDEs was performed numerically with the implicit finite difference method using Matlab (Appendix B). The following mechanisms and assumptions were used to formulate the FPSDM: (1) the system operates under isothermal conditions; (2) the adsorbent particles are spherical, uniform in size and density; (3) a local equilibrium exists between the solute adsorbed onto the adsorbent surface and the solute in the intraaggregate stagnant fluid; (4) the adsorption equilibrium can be described by the linear
isotherm equation; (5) no radial concentration gradient in the column and no angular concentration gradient within a particle; (6) the linear velocity of the liquid-phase along the column, and the mass transfer parameters are independent of the solute concentration in the bulk liquid phase; (7) the local liquid-phase mass transfer rate can be described by the linear driving force approximation; (8) the liquid phase is transported through the fixed-bed by constant advection and axial dispersion; (9) the intraparticle mass transfer is due to Fickian diffusion, and is characterized by both pore and surface diffusion (In this paper, the pore diffusion was assumed to be the predominant intraparticle mass transfer mechanism and surface diffusion was set to zero); (10) mass transfer across the boundary layer surrounding the solid particles is characterized by the external film transfer resistance. The equations derived were consistent with those obtained by [33, 38].

The aqueous-phase mass balance in the fixed-bed reactor and its initial and boundary conditions, respectively, are [33]:

\[
\frac{\partial C_b(z,t)}{\partial t} = -V \frac{\partial C_b(z,t)}{\partial z} + E_z \frac{\partial^2 C_b(z,t)}{\partial z^2} \left( -\frac{3k_f (1-\varepsilon)}{R} \right) \left( C_b(z,t) - C_p(r = R, z,t) \right) \tag{1}
\]

\[C_b(z > 0, t = 0) = 0 \tag{2}\]

\[C_b(z = 0, t) = C_0 + \frac{E_z \partial C_b(z = 0, t)}{V} \tag{3}\]

\[\frac{\partial C_b(z=L,t)}{\partial z} = 0 \tag{4}\]

The terms that appear in equation (1) account for the accumulation of the solute in the aqueous phase due to advection, axial dispersion, and transport from the aqueous phase to the stationary phase by liquid phase mass transfer.

The intraparticle mass balance and its initial and boundary conditions, respectively are [33]:
Where

\[ \frac{\partial C_p(r,z,t)}{\partial t} = D_i \left( \frac{\partial^2 C_p(r,z,t)}{\partial r^2} + \frac{2}{r} \frac{\partial C_p(r,z,t)}{\partial r} \right) \]  

Equation (5) accounts for pore and surface diffusion and the accumulation of the solute in the intraparticle phase fluid and on the solid surfaces.

Since the solute in the intraparticle phase fluid is assumed to be in equilibrium with that adsorbed onto the surface, the concentration on the surface is related to the aqueous phase concentration by an equilibrium isotherm equation. In this study, the linear isotherm equation was used to express the assumption of local equilibrium:

\[ q(r,z,t) = K C_p(r,z,t) \]  

Using the linear adsorption isotherm, the pore and surface diffusion can be combined into a single intraparticle diffusion coefficient as shown in equations (9) and (10), respectively.

Equations (1-8) were then converted into their equivalent dimensionless forms using a set of dimensionless variables and parameters. The main dimensionless parameters are defined and summarized in Table 4-1.
In dimensionless form:

\[
\left( \frac{1}{1+D_g} \right) \frac{\partial \tilde{C}_b(\bar{z},T)}{\partial \bar{r}} = - \frac{\partial \tilde{C}_b(\bar{z},T)}{\partial \bar{z}} + \frac{1}{p_e} \frac{\partial^2 \tilde{C}_b(\bar{z},T)}{\partial \bar{z}^2} - 3S_t \left( \tilde{C}_b(\bar{z},T) - \tilde{C}_p(\bar{r} = 1,\bar{z},T) \right) \tag{12}
\]

\[
\tilde{C}_b(0 \leq \bar{z} \leq 1, T = 0) = 0 \tag{13}
\]

\[
\tilde{C}_b(\bar{z} = 0,T) = 1 + \frac{1}{p_e} \frac{\partial \tilde{C}_b(\bar{z} = 0,T)}{\partial \bar{z}} \tag{14}
\]

\[
\frac{\partial \tilde{C}_b(\bar{z} = 1,T)}{\partial \bar{z}} = 0 \tag{15}
\]

\[
\frac{D_g}{1+D_g} \frac{\partial \tilde{C}_p(\bar{r},\bar{z},T)}{\partial \bar{r}} = E_d \left( \frac{\partial^2 \tilde{C}_p(\bar{r},\bar{z},T)}{\partial \bar{r}^2} + \frac{2}{\bar{r}} \frac{\partial \tilde{C}_p(\bar{r},\bar{z},T)}{\partial \bar{r}} \right) \tag{16}
\]

\[
\tilde{C}_p(\bar{r},\bar{z},T = 0) = 0 \tag{17}
\]

\[
\frac{\partial \tilde{C}_p(\bar{r} = 0,\bar{z},T)}{\partial \bar{r}} = 0 \tag{18}
\]

\[
E_d \frac{\partial \tilde{C}_p(\bar{r} = 1,\bar{z},T)}{\partial \bar{r}} = S_t \left( \tilde{C}_b(\bar{z},T) - \tilde{C}_p(\bar{r} = 1,\bar{z},T) \right) \tag{19}
\]

The values of \( E_z \) and \( k_f \) were obtained by fitting the FPSDM to the experimental breakthrough curves and further optimization using the following objective function [118]:

\[
\varphi = \sqrt{\sum_{i=1}^{N} \left( \frac{(C_{b_i}^{\exp} - C_{b_i}^{f(i)})^2}{\sigma_i^2} \right)} \tag{20}
\]

The parameter optimization process stopped when the objective function was a minimum.

### 4.4 Model Parameter Estimation

Table 4-2 summarizes the fixed-bed parameters that were used in formulating the FPSDM. These parameters were measured in the laboratory, derived from direct measurements, calculated using literature correlations, or determined experimentally using batch equilibrium and kinetic studies.
4.4.1 Determining Linear Isotherm Constant (K) and Effective Pore Diffusivity Coefficient (D_{p,e}) in Batch Tests

Batch adsorption equilibrium and kinetic studies of chloroform onto granular zeolite ZSM-5 were performed to determine the linear isotherm constant (K) and the effective pore diffusivity coefficient (D_{p,e}). The linear isotherm constant (K) was found using a least square regression of the isotherm data from the batch equilibrium experiment of chloroform adsorption onto granular zeolite ZSM-5. Batch kinetics experiments of chloroform adsorption onto granular zeolite ZSM-5 were performed using four different granular zeolite ZSM-5 particle sizes. In those experiments, the granular zeolite particles were suspended in a limited volume of chloroform aqueous solution and were well stirred to suppress the effect of external mass transfer resistance. Hence, it is assumed that because of the vigorous agitation, the concentration of solute in the solution is uniform, and that the transport of chloroform is dominated by pore diffusion mechanism only. In order to determine the effective pore diffusivity coefficient (D_{p,e}), the results of batch kinetic studies were interpreted using a pore diffusion with sorption model, assuming that instantaneous local equilibrium exists between the solute adsorbed onto the adsorbent surface and the solute in the intraparticle stagnant fluid, and that the equilibrium sorption can be described by linear isotherm [11].

4.4.1.1 Pore Diffusion-Sorption Model Applied to the Batch Tests

Based on the foregoing assumptions and mechanism, the pore diffusion-sorption model given by Weber and DiGiano [11] can be described for batch adsorption to a spherical particle as:

\[
\frac{\partial c_p}{\partial t} = D_a \left( \frac{\partial^2 c_p}{\partial r^2} + \frac{2\partial c_p}{r \partial r} \right)
\]  

(21)

Where D_a is the apparent diffusivity, defined as:
And the initial and boundary conditions are:

(22)

\[ C_p(r, t = 0) = 0 \] (23)

\[ V_{R,p} \frac{\partial C_p}{\partial t} = 4\pi R^2 D_a \frac{\partial C_p}{\partial r} (r = R) \] (24)

\[ D_a \frac{\partial C_p}{\partial r} (r = 0, t) = 0 \] (25)

Making the distance and time dimensionless, the pore diffusion-sorption model equation and its initial and boundary conditions can be written as:

\[ \frac{\partial C_p}{\partial \bar{r}} = \left( \frac{\partial^2 C_p}{\partial \bar{r}^2} + \frac{2}{\bar{r}} \frac{\partial C_p}{\partial \bar{r}} \right) \] (26)

\[ C_p(\bar{r}, \bar{T} = 0) = 0 \] (27)

\[ \frac{V_{R,p}}{4\pi R^3} \frac{\partial C_p}{\partial \bar{r}} = \frac{\partial C_p}{\partial \bar{r}} (\bar{r} = 1) \] (28)

\[ \frac{\partial C_p}{\partial \bar{r}} (\bar{r} = 0, \bar{T}) = 0 \] (29)

In which

\( \bar{r} = r/R \) and \( \bar{T} = \frac{D_a t}{R^2} \)

The analytical solution of equation (26), for an adsorption that follows linear isotherm from a limited volume of solution is given by Crank [119] as:

\[ M_{fit} = \frac{M_t}{M_\infty} = 1 - \sum_{i=0}^{\infty} \frac{6\varphi_{\nu}(\varphi_{\nu}+1)\exp(-U_{\nu}^2\bar{T})}{9+9\varphi_{\nu}+U_{\nu}^2\varphi_{\nu}^2} \] (30)

Where the fractional uptake \( (M_t/M_\infty) \) is the total amount of solute \( (M_t) \) in the adsorbent particle after time \( (t) \) as a fraction of the corresponding quantity after infinite time, and can be given as:

\[ \frac{M_t}{M_\infty} = \frac{C_t-C_t}{C_t-C_e} \] (31)
where $U_n$ are the non-zero roots of

$$\tan U_n = \frac{3U_n}{3 + \varphi_v U_n^2}$$

(32)

And $\varphi_v = \frac{3V_{r,p}}{4\pi R^3 \rho_s \bar{R}}$ is the ratio between the volumes of solution and the adsorbent particle.

The value of $D_{p,e}$ was then determined by fitting the analytical solution of the pore diffusion-sorption model equation to the experimental batch kinetic results and further optimization using the non-linear regression process. This process minimizes the value of the squared sum of the difference between the data and the fit [120].

4.4.2 Correlations for Estimating the External Film Transfer Coefficient ($k_f$), the Axial Dispersion coefficient ($E_z$), and the Free Liquid Diffusivity ($D_l$)

There are several correlations that were used to estimate the external film transfer coefficient in fixed-bed contactors. Common mass transfer correlations for flow of liquids in packed beds are summarized in Table 3. In this study, a range of external film transfer coefficient values obtained from the correlations summarized in Table 4-3 was used in obtaining an initial approximate range for $k_f$. Three correlations from the literature were used in estimating a range of values for the axial dispersion coefficient ($E_z$). These correlations are summarized in Table 4-3 and were used in obtaining an initial approximate range for $E_z$. Both the external film transfer coefficient and the axial dispersion coefficient depend on the free liquid diffusivity of the solute in water. Table 4-3 summarizes the Wilke-Chang equation which was used to estimate the free liquid diffusivity of chloroform in water.
4.5 Experimental Materials and Procedures

4.5.1 Adsorbent
Granular zeolite ZSM-5 was used as the adsorbent material in the batch and fixed-bed experiments. The physical properties of this material are listed in Table 4-4. Granular zeolite ZSM-5 was dried in an atmospheric oven at 120 °C for 10-14 hours and then it was kept clean and dry in a desiccator until use.

4.5.2 Adsorbate
Neat chloroform (ACS grade) was obtained from (HACH Company Loveland, CO). Stock solutions of chloroform were prepared by adding a specified amount of neat chloroform to purified water from a Barnstead ROpure ST/E-pure water purification system (Barnstead-Thermolyne, Dubuque, IA). 1,1,2-trichloroethane was used in batch adsorption experiments as an internal standard. Stock solutions of 1,1,2-trichloroethane were prepared using 98 % pure 1,1,2-trichloroethane (Fisher Scientific, Pittsburgh, PA).

4.5.3 Procedures
4.5.3.1 Batch Adsorption Experiments
For the determination of adsorption isotherm parameters, batch adsorption experiments were performed at room temperature (22 ± 2 °C) using glass vials with 42 ml of aqueous solution and varied initial chloroform concentrations containing a known mass (0.2 g) of granular zeolite ZSM-5 (250 μm < d_p < 425 μm). The vials were agitated on a fixed speed rotator for a minimum of 24 hours at 15 rpm for equilibrium to be established. Following adsorption, granular ZSM-5 was separated by centrifugation at 3000 rpm for 10 minutes and then chloroform in the aqueous supernatant was analyzed by gas chromatography.
4.5.3.2 Batch Kinetic Experiments

Batch kinetic experiments were performed using four sizes of granular ZSM-5. The four sizes were; (original size with \(d_p = 1.6\) mm), (850 \(\mu m < d_p < 1400\) \(\mu m\)), (425 \(\mu m < d_p < 850\) \(\mu m\)), and (250 \(\mu m < d_p < 425\) \(\mu m\)). Granular ZSM-5 with \(d_p = 1.6\) mm is the original material and the other three sizes of granular ZSM-5 were obtained by grinding the original granular ZSM-5 material using a ball mill followed by passing the resultant heterogeneous sized mixture through standard mesh sieves. The experiments were performed at room temperature (22 ± 2 °C) using glass vials with fixed sorbent/liquid ratio (0.2 g sorbent/42 ml aqueous solution) and containing a constant chloroform concentration of 10,000 \(\mu g$/L. Agitation of the vials started at time zero using a fixed speed rotator at 15 rpm and the first samples were taken at time zero and at predetermined time intervals thereafter until equilibrium was reached. Following adsorption, the samples were centrifuged for 10 minutes at 3000 rpm to ensure complete separation of the solid and aqueous phases. Then the chloroform in the aqueous supernatant was quantified using gas chromatography.

4.5.3.3 Fixed-Bed Experiments

Fixed-bed experiments using granular zeolite ZSM-5 (250 \(\mu m < dp < 425\) \(\mu m\)) were carried out in a 20 cm long glass column with an internal diameter of 1 cm and an adjustable flow adapter to hold the packed bed in place. Water was passed through the column at a flow rate of 5.2 mL/min for an hour to remove air bubbles and to flush the adsorbent particles. Adsorption experiments were performed with a flow rate of 5.2 mL/min (empty bed flow velocity of 6.62 cm/min), an influent chloroform concentration of 450 \(\mu g$/L, and bed heights of 6, 9, and 12 cm. Chloroform feed solution was contained in a Tedlar bag (SKC Inc., Eighty Four, PA) which minimized the head space above the solution and any potential losses due to volatilization and was introduced to the column using a digital peristaltic pump (Cole-Parmer, Vernon Hills, IL).
Samples at the outlet of each column were collected in 42 ml glass vials at predetermined intervals of time, and analyzed with gas chromatography. Details on the gas chromatography methodology are given in [121].

4.6 Results and Discussion

4.6.1 Batch Adsorption Equilibrium Isotherm

Single-solute adsorption isotherm curves of chloroform onto granular zeolite ZSM-5 were obtained over a wide range of chloroform aqueous phase concentrations by plotting the mass of the solute adsorbed per unit mass of adsorbent \( q_e \) against the equilibrium aqueous phase concentration of the solute \( C_e \). Chloroform adsorption isotherm data onto granular zeolite ZSM-5 were correlated with the linear isotherm model \( R^2 = 0.97 \) and typical equilibrium data are shown in Figure 4-1. From the best fit line (Figure 4-1), the value of the adsorption capacity constant \( K \) was found to be 10.5 L/g.

4.6.2 Batch Adsorption Rate Studies

4.6.2.1 Effect of Particle Sizes and the Pore Diffusion-Sorption Model

The effect of ZSM-5 granular size on chloroform adsorption is shown in Figure 4-2. It can be seen from Figure 4-2 that equilibrium was reached faster with smaller ZSM-5 particles than with the larger particle sizes, and that chloroform adsorption rate increased with the decrease in ZSM-5 particle sizes. Smaller particles have a shorter diffusion path and hence they allow the adsorbate to penetrate deeper into the adsorbent particle more quickly, which results in a higher rate of adsorption. This behavior has been previously noticed by other researchers [122, 123]. Although the rate of adsorption is different for different particle sizes, the total adsorption capacity for the different particle sizes is the same because their total internal pore area is expected to be constant. It can be observed also from Figure 4-2 that the experimental data
correlated well with the pore diffusion-sorption model curves expressed by the solid lines in Figure 4-2. In fitting the analytical solution of the pore diffusion-sorption model equation (equation 30) to the experimental batch kinetic results, the value for the apparent diffusivity ($D_a$) was optimized using a non-linear regression technique which minimizes the value of the squared sum of the difference between the data and the predicted value [120]. The value of the effective pore diffusivity coefficient ($D_{p,e}$) was then calculated from ($D_a$) using equation 22. For the four different particle sizes, the value of the effective pore diffusivity coefficient ($D_{p,e}$) was constant and equal to $5.83 \times 10^{-4}$ cm$^2$/sec. The finding of constant effective pore diffusivity with particle size is expected since highly porous adsorbents such as granular zeolites ZSM-5 have most of their surface area in the internal pore structure, which is approximately constant for the different particle sizes. This result supports our assumption that pore diffusion is the dominant intraparticle mass transfer mechanism.

Although the effective pore diffusivity coefficient ($D_{p,e}$) was used to represent the controlling intraparticle mass transfer mechanism, an equivalent surface diffusivity coefficient ($D_s$) was calculated to determine whether using a surface diffusivity coefficient instead of the pore diffusivity coefficient would alter the FPSDM results. Estimation of the surface diffusivity coefficient ($D_s$) was completed using the following equation by Crittenden et al. [33]:

$$D_s = \frac{D_{p,e}e_pC_0}{\rho_eK_0}$$

(33)

The value of ($D_s$) calculated based on equation (33) was found to be $(1.17 \times 10^{-8}$ cm$^2$/sec) which is four orders of magnitude lower than the $D_{p,e}$ value listed in Table 4-3. This finding indicates that surface diffusion can be neglected in comparison with pore diffusion and justifies the single use of $D_{p,e}$ in the FPSDM calculations.
4.6.3 Fixed-Bed Adsorption Results

4.6.3.1 Effect of Bed Height

The effect of bed height on the breakthrough profiles for the adsorption of chloroform onto granular zeolite ZSM-5 was studied. The experimental and predicted breakthrough profiles obtained at different bed heights (6, 9, and 12 cm), a constant flow rate (5.2 cm$^3$/min), and a constant initial chloroform concentration (450 µg/L) are shown in Figure 4-3. The resulting plots showed the typical ‘S’ shape of a packed-bed adsorption system with an initial period of negligible solute, followed by gradual breakthrough that slowly approached the solute influent concentration. The “S” shape profile in fixed-bed adsorption is generally associated with solutes of smaller molecular weight and simple structure, and is not observed in adsorbates with larger molecular weights such as dyes [66, 124]. It is obvious from Figure 4-3 that an increase in bed height increases the breakthrough time, resulting in longer service time. This is because of the increase in the amount of adsorbent mass, which results in greater adsorption sites with increasing bed height. For example, an extension of the service time from 3.5 days to 11.18 days was obtained at 18% breakthrough upon increasing the bed height from 6 cm to 12 cm at a flow rate of 5.2 ml/min.

4.6.3.2 FPSDM Results

In solving the FPSDM equations, the mass transport parameters $E_z$ and $k_f$ are required as system inputs. These parameters were estimated initially from correlations listed in Table 4-3. Then, using the correlations in Table 4-3, a range of values for both $k_f$ and $E_z$ parameters was obtained ($1.74 \times 10^{-3}$ cm/sec < $k_f$ < $6.12 \times 10^{-3}$ cm/sec) and ($7.67 \times 10^{-3}$ cm$^2$/sec < $E_z$ < $1.11 \times 10^{-1}$ cm$^2$/sec) and used in obtaining the FPSDM predicted breakthrough curves. Both $E_z$ and $k_f$ mass transport correlations depend on the free liquid diffusivity of chloroform in water ($D_l$). The value
of (D_i) was estimated using the Wilke-Chang correlation (Table 4-3) and found to be 6.86 x 10^{-6} cm^2/sec.

Further optimization using the simplex method (equation 20) was performed on the experimental and predicted breakthrough curves for the three beds with different heights until a minimum sum of the objective function for the three beds with different heights was fulfilled. The best fit values of E_z and k_f for the three beds with different heights obtained by fitting the mathematical model to the experimental breakthrough curves and further optimization using the above criterion were E_z = 4.95 x 10^{-2} cm^2/sec and k_f = 5.2 x 10^{-3} cm/sec. The values of E_z and k_f were used in creating the predicted breakthrough profiles shown in Figure 4-3. The equivalent values of E_z, k_f, and D_{p,e} in dimensionless form, P_e, S_t, and E_d, for the three beds with different heights are summarized in Table 4-5. In general, good agreement was obtained between the experimental and theoretical breakthrough profiles. This implied that the FPSDM could be used to predict the breakthrough kinetics of chloroform adsorption onto granular zeolites. However, in the case of the 12 cm bed, the theoretical prediction underestimated the experimental profile at high C/C_0 values. This deviation between experimental and predicted breakthrough profiles could possibly be attributed to the dissimilarities between bed adsorption capacities determined by batch and column studies as previously reported by other researchers [115, 125]. Bed capacities as calculated from batch isotherm studies could be different from those calculated by column experiments due to the incomplete achievement of equilibrium in the case of batch adsorption. The solid phase equilibrium adsorption capacity for the chloroform-ZSM-5 system calculated by the linear isotherm equation was found to be 5.60 mg/g, while the bed capacities calculated from the breakthrough profiles were essentially constant for the three runs with different heights and equal to 6.88 mg/g.
Under the conditions investigated in this work, both the external mass transfer coefficient \( (k_f) \) and the axial dispersion coefficient \( (E_z) \) remained constant with varying bed heights. Since the hydraulic loading remained constant in the beds with different heights, it is expected that both the film resistance to mass transfer and axial dispersion effects will remain unchanged. By looking at the values of the dimensionless mass transport parameters listed in Table 4-5, it can be seen that increasing the bed height at constant flow rate and constant initial solute concentration increased the values of Peclet number \( (P_e) \), Stanton number \( (S_t) \), and the intraparticle diffusion modulus \( (E_d) \). However, Biot number \( (B_i) \) which is defined as the ratio of the external mass transfer to the intraparticle mass transfer remained constant for the three beds with different heights. As \( B_i \) increases, the liquid-phase mass transfer becomes faster than the intraparticle mass transfer indicating a decrease in the mass transfer resistance compared to the intraparticle mass transfer resistance. Hence, for large \( B_i \) values (larger than 30 \cite{38} ), the intraparticle mass transfer controls the adsorption rate. On the other hand, at low \( B_i \) values, less than 0.5 \cite{38}, the liquid mass transfer controls the adsorption rate. The low Biot number \( (B_i = 0.65) \) values for the system under investigation indicates that film diffusion rather than intraparticle diffusion is the controlling mechanism. These results are in agreement with those obtained by \cite{126}.

### 4.6.4 Sensitivity Analysis

A sensitivity analysis to assess the relative impact of changes in kinetic parameters on the concentration profiles calculated by the FPSDM was performed (Figure 4-4, 4-5, and 4-6). The model parameters that were examined include: film transfer coefficient \( (k_f) \), effective pore diffusivity coefficient \( (D_{p,e}) \), and axial dispersion coefficient \( (E_z) \). The baseline utilized the initial parameters reported in Table 4-2. The model parameters \( k_f, D_{p,e}, \) and \( E_z \) were varied by ±25% and the percent sensitivity was determined by dividing the change in the concentration profile for
±25% variation in $k_f$ or $D_{p,e}$ or $E_z$ by the total change in the concentration profile for ±25% variation in the three parameters [38]. The predicted profiles were most sensitive to $k_f$ (% sensitivity = 100%), followed by $E_z$ (% sensitivity = 25%), and least sensitive to $D_{p,e}$ (% sensitivity = 2%). This indicates that ($k_f$) has a greater impact on the model calculations than both $E_z$ and $D_{p,e}$ and suggests that mass transfer for chloroform onto granular zeolite ZSM-5 would be limited by film diffusion which is consistent with the estimated $B_i$ values. Therefore, accurate estimation of the film diffusion coefficient is important for accurate breakthrough prediction. While the correlations used to estimate $E_z$ and the batch adsorption experiments used to estimate $D_{p,e}$ were satisfactory in determining these parameters.

The greater influence of film diffusion on chloroform breakthrough could be explained by the relatively low concentrations of chloroform used in this study. For low solute concentrations, it is expected that as soon as the solute reaches the outer surface of the adsorbent it penetrates through its pores and that undergoes a low intraparticle mass transfer resistance [127]. Hence, the major mass transport resistance is between the liquid-solid interface and the bulk solution.

4.7 Conclusions

The film pore and surface diffusion model (FPSDM) describing single solute adsorption in a fixed-bed using linear isotherm was applied to adsorption of chloroform onto granular zeolite ZSM-5 in fixed bed columns. The model, which consists of a system of partial differential equations (PDEs), accounts for the effects of axial dispersion, film diffusion, and internal diffusional mass-transfer resistances. Solution of the resulting PDEs was achieved with Matlab using the implicit finite difference method. The numerical simulation was satisfactory in predicting the experimental fixed-bed adsorption data. However, some deviations were found
between the experimental and predicted breakthrough curves, which could be due to differences between batch and column adsorption capacities.

A sensitivity analysis to determine the relative importance of different kinetic parameters on the FPSDM calculations was performed and showed that a ±25% change in $k_f$ had a greater impact on the breakthrough results than that caused by a ±25% variation in either $E_z$ or $D_{p,e}$. This result is in agreement with the values for Biot number calculated from the FPSDM which were smaller than 1 ($B_i = 0.65$), indicating high film resistance. Therefore, in this study, film diffusion is demonstrated to be the primary controlling mass transfer mechanism, and must be accurately determined for good breakthrough predictions. Accurate estimation of the film diffusion coefficient can be attained experimentally by running short fixed-bed adsorbers under hydrodynamic conditions similar to those expected in practice.

Finally, a single value of the effective diffusivity coefficient was obtained by fitting batch adsorption kinetics to the theoretical curves of a pore diffusion with sorption model and found to be sufficient in predicting the model breakthrough profiles accurately.

### 4.8 Acknowledgements

The authors acknowledge the financial support from Triton Systems, Inc. of Chelmsford, MA, and the support by the National Institutes of Health through grant 2R44 ES012784-02. The authors also acknowledge the financial support from the Civil & Environmental Engineering Department at WPI. The authors appreciate the assistance provided by Gerardo Hernandez and Chase Johnson from the Department of Mathematical Sciences at WPI and the assistance provided by Donald Pellegrino with lab experiments.
4.9 Nomenclature

\( C_0 \) = initial liquid phase concentration (for the fixed-bed adsorber), \( \mu g/cm^3 \)

\( C_b \) = bulk liquid phase concentration in the column, \( \mu g/cm^3 \)

\( C_e \) = the equilibrium liquid phase concentration of solute in the batch reactor solution (for the pore diffusion-sorption model), \( \mu g/cm^3 \)

\( C_i \) = the initial liquid phase concentration of solute in the batch reactor solution (for the pore diffusion-sorption model), \( \mu g/cm^3 \)

\( C_p \) = liquid phase concentration inside the pores, \( \mu g/cm^3 \)

\( C_t \) = the liquid phase concentration of solute in the batch reactor solution at time \( t \) (for the pore diffusion-sorption model), \( \mu g/cm^3 \)

\( D_a \) = apparent pore diffusivity, \( cm^2/sec \) (for the pore diffusion-sorption model)

\( D_i \) = combined intraparticle diffusivity coefficient, \( cm^2/sec \)

\( D_l \) = free liquid diffusivity coefficient, \( cm^2/sec \)

\( D_{pe} \) = effective pore diffusivity coefficient, \( cm^2/sec \)

\( D_s \) = surface diffusivity coefficient, \( cm^2/sec \)

\( D_{sp} \) = apparent pore diffusivity that takes surface diffusivity into account, \( cm^2/sec \)

\( d_c \) = column diameter, \( cm \)

\( d_p \) = mean particle diameter, \( cm \)

\( E_z \) = axial dispersion coefficient, \( cm^2/sec \)

\( K \) = linear isotherm capacity constant, \( L/g \)

\( k_f \) = external film transfer coefficient, \( cm/sec \)

\( L \) = length of the column, \( cm \)

\( M_t \) = the total amount of solute in the adsorbent particle after time \( t \) (for the pore diffusion-sorption model)

\( M_e \) = the total amount of solute in the adsorbent particle after infinite time (for the pore diffusion-sorption model)
Q = flow rate, cm³/min
q = solid phase concentration, µg/g
qₑ = solid phase concentration in equilibrium with C₀, equal to KC₀, µg/g
R = particle radius, cm
r = radial position inside particles, cm
Tₑₚₚ = Temperature in (K) (used in the Wilke-Chang equation)
t = time, sec
V = interstitial velocity, cm/sec
Vₛ = discharge velocity, cm/sec
Vₐ = molal volume of solute, cm³/mol (used in the Wilke-Chang equation)
Vₚ = pore volume per mass of adsorbent cm³/g (used in estimating the solid density of the adsorbent)
V₋ₐ₋ₚ = the volume of solution in the batch reactor served by each spherical granular zeolite particle, cm³ (for the pore diffusion-sorption model)
z = axial position in column, cm

Dimensionless Variables and parameters:

Bᵢ = Sᵢ/Eₐ = Biot number

\( \tilde{C}_b = C_b/C₀ = \) dimensionless liquid phase concentration

\( \tilde{C}_{bi}^{exp} = \) dimensionless liquid phase concentration at point (i) used in the estimation of \( \phi \)

\( \tilde{C}_{bi}^{fit} = \) the FPDSM value of the dimensionless liquid phase concentration at point (i) used in the estimation of \( \phi \)

\( \tilde{C}_p = C_p/C₀ = \) dimensionless liquid phase concentration inside the pores

Dₙ = solute distribution ratio

Eₐ = intraparticle diffusion modulus

Mᵣ = the value of the solute fractional uptake calculated from (equation 30)

N = number of experimental values used in the estimation of \( \Phi \)
P_e = Peclet number
R_e = Vd_p/ν = Reynolds number
\( \tilde{r} = r/R \) = dimensionless radial position inside particles
S_c = ν/D_t = Schmidt number
S_t = Stanton number
T = t/τ(1+D_g) = dimensionless time (for the FPDSM)
\( \tilde{T} = D_a t/R^2 \) = dimensionless time (for the pore diffusion-sorption model)
U_n = the non-zero roots of \( \tan U_n = \frac{3U_n}{3+\varphi_s U_n^2} \) which is used in the calculation of M_fit (equation 30)
W_{g,mo,s} = molecular weight of solvent (used in the Wilke-Chang equation)
\( \tilde{z} = z/L \) = dimensionless axial position in column

Greek Letters:
\( \varepsilon \) = fixed-bed void fraction
\( \varepsilon_p \) = particle void fraction
\( \rho_a \) = apparent particle density, g/cm\(^3\)
\( \rho_b \) = bulk particle density, g/cm\(^3\)
\( \rho_s \) = Solid particle density, g/cm\(^3\)
\( \nu \) = liquid kinematic viscosity, cm\(^2\)/sec
\( \mu \) = liquid dynamic viscosity, g/cm.sec
\( \mu_v \) = liquid dynamic viscosity in (centipoises) (used in the Wilke-Chang equation)
\( \tau \) = L/V = fixed-bed contact time
\( \varphi \) = objective function for optimization (equation 20)
\( \varphi_s \) = solvent association term which equals 2.6 for water (used in the Wilke-Chang equation)
\( \varphi_v \) = the ratio between the volumes of solution and the adsorbent particle (for the pore diffusion-sorption model)
### Table 4-1: Dimensionless parameters.

<table>
<thead>
<tr>
<th>Dimensionless Parameters</th>
<th>Equation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_p$ (Solute distribution)</td>
<td>$\frac{(1 - \varepsilon)e_p}{\varepsilon} + \frac{(1 - \varepsilon)p_a q_e}{\varepsilon C_0}$</td>
<td>Mass of solute contained in the intraparticle phase at equilibrium with the influent concentration</td>
</tr>
<tr>
<td>$Pe$ (Peclet number)</td>
<td>$\frac{VL}{E_x}$</td>
<td>Rate of transport by advection</td>
</tr>
<tr>
<td>$St$ (Stanton number)</td>
<td>$\frac{k_f \tau (1 - \varepsilon)}{R \varepsilon}$</td>
<td>Rate of transport by external film transfer</td>
</tr>
<tr>
<td>$Ed$ (Intraparticle diffusion modulus)</td>
<td>$\frac{D_g D_i \tau}{R^2}$</td>
<td>Rate of transport by intraparticle diffusion</td>
</tr>
<tr>
<td>$Bi$ (Biot number)</td>
<td>$\frac{S_t}{Ed} = \frac{k_f R (1 - \varepsilon)}{\varepsilon D_g D_i}$</td>
<td>Rate of transport by intraparticle diffusion</td>
</tr>
</tbody>
</table>
Table 4-2: FPSDM parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Definition</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_0$</td>
<td>Initial chloroform concentration</td>
<td>450.0 µg/L</td>
<td></td>
</tr>
<tr>
<td>$d_c$</td>
<td>Column diameter</td>
<td>1.0 cm</td>
<td></td>
</tr>
<tr>
<td>$K$</td>
<td>Linear isotherm parameter</td>
<td>10.5 L/g</td>
<td>Estimated from batch reactor data</td>
</tr>
<tr>
<td>$q_e$</td>
<td>Solid phase concentration in equilibrium with $C_0$</td>
<td>4725 µg/g</td>
<td></td>
</tr>
<tr>
<td>$R$</td>
<td>Particle radius</td>
<td>0.017 cm</td>
<td></td>
</tr>
<tr>
<td>$d_p$</td>
<td>Mean particle diameter</td>
<td>0.034 cm</td>
<td></td>
</tr>
<tr>
<td>$v$</td>
<td>Kinematic viscosity</td>
<td>$1.0 \times 10^{-2}$ cm$^2$/sec</td>
<td></td>
</tr>
<tr>
<td>$\mu$</td>
<td>Dynamic viscosity</td>
<td>$1.0 \times 10^{-2}$ g/cm$\cdot$sec</td>
<td></td>
</tr>
<tr>
<td>$Q$</td>
<td>Flow rate</td>
<td>5.2 cm$^3$/min</td>
<td></td>
</tr>
<tr>
<td>$V_s$</td>
<td>Discharge velocity</td>
<td>$1.1 \times 10^{-1}$ cm$\cdot$sec</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Fixed-bed void fraction</td>
<td>0.4</td>
<td>Measured in the laboratory</td>
</tr>
<tr>
<td>$V$</td>
<td>Average interstitial velocity</td>
<td>$2.76 \times 10^{-1}$ cm$\cdot$sec</td>
<td></td>
</tr>
<tr>
<td>$\rho_b$</td>
<td>Bulk density of adsorbent</td>
<td>0.66 g/cm$^3$</td>
<td>Measured in the laboratory</td>
</tr>
<tr>
<td>$\rho_a = \rho_b(1- \varepsilon)$</td>
<td>Apparent density of adsorbent</td>
<td>1.1 g/cm$^3$</td>
<td></td>
</tr>
<tr>
<td>$\rho_s = 1/((1/\rho_a)- V_p)$</td>
<td>Solid density of adsorbent</td>
<td>1.43 g/cm$^3$</td>
<td></td>
</tr>
<tr>
<td>$\varepsilon_p = 1-( \rho_s/ \rho_a)$</td>
<td>Particle void fraction</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>$D_l$</td>
<td>Free liquid diffusivity</td>
<td>$6.86 \times 10^{-6}$ cm$^2$/sec</td>
<td>Estimated from literature correlation</td>
</tr>
<tr>
<td>$D_a$</td>
<td>Apparent diffusivity</td>
<td>$1.17 \times 10^{-8}$ cm$^2$/sec</td>
<td>Estimated by fitting batch kinetic experiments to the pore-sorption diffusion model</td>
</tr>
<tr>
<td>Parameter</td>
<td>Description</td>
<td>Value</td>
<td>Notes</td>
</tr>
<tr>
<td>-----------</td>
<td>--------------------------------------------------</td>
<td>--------------</td>
<td>--------------------------------------------</td>
</tr>
<tr>
<td>D&lt;sub&gt;p,e&lt;/sub&gt;</td>
<td>Effective pore diffusivity coefficient</td>
<td>5.83 x 10&lt;sup&gt;-4&lt;/sup&gt; cm&lt;sup&gt;2&lt;/sup&gt;/sec</td>
<td></td>
</tr>
<tr>
<td>D&lt;sub&gt;s&lt;/sub&gt;</td>
<td>Surface diffusivity coefficient</td>
<td>0.0</td>
<td>Estimated by fitting breakthrough data to the FP-SDM</td>
</tr>
<tr>
<td>k&lt;sub&gt;f&lt;/sub&gt;</td>
<td>External mass transfer coefficient</td>
<td>5.2 x 10&lt;sup&gt;-3&lt;/sup&gt; cm/sec</td>
<td>Estimated by fitting breakthrough data to the FP-SDM</td>
</tr>
<tr>
<td>E&lt;sub&gt;z&lt;/sub&gt;</td>
<td>Axial dispersion coefficient</td>
<td>4.95 x 10&lt;sup&gt;-2&lt;/sup&gt; cm&lt;sup&gt;2&lt;/sup&gt;/sec</td>
<td></td>
</tr>
</tbody>
</table>
Table 4-3: Correlations for obtaining external mass transfer coefficient, axial dispersion coefficient, and free liquid diffusivity.

<table>
<thead>
<tr>
<th>Correlations and references</th>
<th>Equation</th>
<th>limits</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frossling, 1938 [128]</td>
<td>$k_f = \frac{D_l}{d_p} \left(2 + 0.6R_e^{1/2}S_c^{1/3}\right)$</td>
<td>$1.74 \times 10^{-3}$ cm/sec</td>
<td></td>
</tr>
<tr>
<td>Wilson &amp; Geankoplis, 1966 [129]</td>
<td>$k_f = \frac{D_l}{d_p} \left(\frac{1.09}{\varepsilon_B} R_e^{0.333} S_c^{0.333}\right)$</td>
<td>$0.0016 &lt; R_c &lt; 55$</td>
<td>$6.12 \times 10^{-3}$ cm/sec</td>
</tr>
<tr>
<td>Williamson, 1963 [130]</td>
<td>$k_f = \frac{D_l}{d_p} (2.4R_e^{0.34}S_c^{0.42}\varepsilon_B)$</td>
<td>$0.08 &lt; R_c &lt; 125$</td>
<td>$4.06 \times 10^{-3}$ cm/sec</td>
</tr>
<tr>
<td>Gnielinski, 1978 [131]</td>
<td>$k_f = \frac{D_l}{d_p} \left(2 + 0.644R_e^{0.5}S_c^{0.333}\right)$ $[1 + 1.5(1 - \varepsilon_B)]$</td>
<td>$R_e &lt; 100$</td>
<td>$3.49 \times 10^{-3}$ cm/sec</td>
</tr>
<tr>
<td>Dwivedi &amp; Upadhyey, 1977 [111]</td>
<td>$k_f = \frac{V_s}{\varepsilon} (1.1068R_e^{0.72}S_c^{-0.667})$</td>
<td>$R_e &lt; 10$</td>
<td>$2.50 \times 10^{-3}$ cm/sec</td>
</tr>
<tr>
<td>Tang &amp; Fan, 1990 [132]</td>
<td>$E_z = (0.575V_s^{1.28})$</td>
<td></td>
<td>$1.11 \times 10^{-1}$ cm$^2$/sec</td>
</tr>
<tr>
<td>Chung &amp; Wen, 1968 [133]</td>
<td>$E_z = \left(\frac{R_e}{R_{emf}}\right) \left(\frac{\mu}{\rho}\right) \frac{R_e}{0.2 + 0.011R_e^{0.48}} \left(\frac{R_e}{R_{emf}}\right) = 1$</td>
<td></td>
<td>$4.42 \times 10^{-2}$ cm$^2$/sec</td>
</tr>
<tr>
<td>Fried, 1975 [134]</td>
<td>$E_z = D_l \left(0.67 + 0.5 \frac{2RV}{D_l}\right)^{1/2}$</td>
<td>$6 &lt; \left[2RV\right] &lt; 260$</td>
<td>$7.67 \times 10^{-3}$ cm$^2$/sec</td>
</tr>
<tr>
<td>Wilke-Chang, 1955 [135]</td>
<td>$D_l = 7.4 \times 10^{-8} \left(\varphi_3 W_{g,mo,s}\right)^{0.5} \frac{T_{tem}}{\mu \nu^{0.6}}$</td>
<td></td>
<td>$6.86 \times 10^{-6}$ cm$^2$/sec</td>
</tr>
</tbody>
</table>
Table 4-4: Characterization of the adsorbent.

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Zeolyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size</td>
<td>(250 µm &lt; d_p &lt; 425 µm)</td>
</tr>
<tr>
<td>Si/Al</td>
<td>280</td>
</tr>
<tr>
<td>Zeolite %</td>
<td>80</td>
</tr>
<tr>
<td>Pore dimensions (Å)</td>
<td>5.1 x 5.5, 5.3 x 5.6</td>
</tr>
</tbody>
</table>
Table 4-5: The values of dimensionless mass transport parameters at different bed heights.

<table>
<thead>
<tr>
<th>Bed height (cm)</th>
<th>Peclet number ((P_e))</th>
<th>Stanton number ((S_t))</th>
<th>Intraparticle diffusion modulus ((E_d))</th>
<th>Biot number ((B_i)) = ((S_t/E_d))</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>33.44</td>
<td>10.05</td>
<td>15.44</td>
<td>0.65</td>
</tr>
<tr>
<td>9</td>
<td>50.16</td>
<td>15.08</td>
<td>23.16</td>
<td>0.65</td>
</tr>
<tr>
<td>12</td>
<td>66.88</td>
<td>20.11</td>
<td>30.88</td>
<td>0.65</td>
</tr>
</tbody>
</table>
Figure 4-1: Adsorption isotherm for chloroform onto ZSM-5 zeolite. The line represents the linear isotherm model.

\[ y = 10.5 x \]

\[ R^2 = 0.97 \]
Figure 4-2: Comparison of the measured concentration-time data with that predicted by the pore-sorption diffusion model for the adsorption of chloroform onto four sizes of granular zeolite ZSM-5 in batch adsorber.
Figure 4-3: The experimental and predicted (by the FPSDM) breakthrough curves for the adsorption of chloroform onto granular ZSM-5 at different bed heights.
Figure 4-4: Sensitivity analysis of the FPSDM to the film diffusion coefficient ($k_f$) for the 6 cm bed.
Figure 4-5: Sensitivity analysis of the FPSDM to the film diffusion coefficient ($E_z$) for the 6 cm bed.
Figure 4-6: Sensitivity analysis of the FPSDM to the film diffusion coefficient ($D_{p,e}$) for the 6 cm bed.
5 Conclusions and Recommendations for Future Work

5.1 Conclusions

Clean drinking water is one of the implicit requisites for a healthy human population. However, growing industrialization and extensive use of chemicals for various concerns, has increased the burden of unwanted contaminants in drinking water. Synthetic and natural organic chemicals are considered among the most undesirable contaminants found in drinking water. These compounds include taste and odor causing synthetic organic chemicals, pesticides, gasoline additives, disinfection by products, pharmaceuticals, and personal care products, some of which may be carcinogenic or pose other health risks.

As a consequence of this ever-increasing number of emerging compounds that provide potential environmental threats, methods for their identification, evaluation and removal are progressively under research. In particular, this study was focused on evaluating the adsorption process for removing specific organic contaminants, as adsorption is one of the most effective methods to remove organic contaminants from water. More specifically, the removal of chloroform and MTBE from water by adsorption onto granular zeolites was evaluated using batch and fixed-bed adsorption studies. In addition, a computational model that describes the dynamic behavior of the adsorption process in fixed-bed adsorbers was applied. This study was performed in three parts; the first two parts were done experimentally (chapter 2 and chapter 3), and the third part was done through computational modeling (chapter 4).

Chapter 2 focused on evaluating the equilibrium and kinetic adsorption of MTBE onto granular zeolites, a coconut shell granular activated carbon (CS-1240), and a commercial carbon adsorbent (CCA). In addition, the effect of natural organic matter (NOM) on MTBE adsorption
was evaluated. Equilibrium studies determined that MTBE can be effectively removed from water using granular zeolite ZSM-5. The adsorption capacity of ZSM-5 granular zeolite for MTBE was influenced by the adsorbent hydrophobicity and large pore sizes at high aqueous phase MTBE concentrations and by the adsorbent’s small pore sizes (at low MTBE concentrations). Furthermore, it was observed that the MTBE rate of adsorption increased with decreasing granular size of the zeolite. Further equilibrium and kinetic experiments verified that granular ZSM-5 was 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. In order to further understand and predict the dynamic behavior of MTBE adsorption onto granular ZSM-5, fixed-bed adsorption experiments were performed and the effect of bed height on the breakthrough results was evaluated through the application of the bed depth service time model (BDST). It was found that the MTBE breakthrough profiles were well characterized by the BDST model.

Chapter 3 addresses the evaluation of the efficiency of granular zeolites, a coconut shell granular activated carbon (CS-1240), and a commercial carbon adsorbent (CCA) for adsorption of chloroform from water. In addition, the effects of adsorbent grain sizes and natural organic matter (NOM) on chloroform adsorption capacity were evaluated. The primary factors affecting the efficiency of adsorption of chloroform on granular zeolites were (at low chloroform concentrations) the small pore size and the high framework densities of granular zeolites and (at high chloroform concentrations) the high Si/Al ratios and large zeolite pore size. Among all the granular zeolites that were tested, ZSM-5 with the smallest grain size (between 250 and 425 µm) was the most effective in removing chloroform from water. The presence of up to 5 mg/L of
NOM and other constituents in water had minimal effect on the adsorption capacities of ZSM-5, CCA, and CS-1240. Further kinetic studies obtained with ZSM-5, CCA, and CS-1240 in fixed-bed adsorbers indicated that granular ZSM-5 had a higher adsorption rate of chloroform than both CCA, and CS-1240. Finally, the effect of bed height on the adsorption of chloroform in fixed-bed adsorption experiments with granular ZSM-5 (diameters between 250 µm and 425 µm) was evaluated using three different bed heights (6, 9, and 12 cm). The BDST model was used to analyze the breakthrough data obtained from the fixed-bed adsorption tests and found to provide a good description of the breakthrough data.

Chapter 4 focused on developing a mathematical model for describing the dynamic response for adsorption of chloroform in fixed-bed adsorption systems using linear adsorption isotherms. The model equations which take into account the effects of axial dispersion, film diffusion, and intraparticle diffusion mechanisms were derived using continuity principles and mass balance relations. Because of their highly non-linear nature, the resulting set of partial differential equations was solved numerically using the implicit finite difference method in Matlab. In general, the simulated results obtained from this model agreed well with the experimental chloroform breakthrough profiles. Furthermore, a sensitivity analysis was carried out to investigate the relative impact of kinetic parameters on the predicted breakthrough profiles and showed that the model calculations were insensitive to either the effective pore diffusivity coefficient ($D_{p,e}$) or the axial dispersion coefficient ($E_z$) and were sensitive to the external mass transfer coefficient ($k_f$). In addition, Biot number which measures the ratio of external to internal mass transfer resistances within the column was found to be low ($B_i = 0.65$) indicating a film diffusion controlled process.
Lastly, the effective pore diffusivity coefficient \( (D_{p,e}) \) which was determined by fitting a pore diffusion-sorption model to chloroform rate adsorption results, and the axial dispersion coefficient which was estimated from literature correlations, were found to be sufficient in predicting the model breakthrough profiles. However, the film diffusion coefficient \( (k_f) \) needs to be determined more accurately since it has a greater impact on the model breakthrough profiles than both \( E_z \) and \( D_{p,e} \).

Overall, this research has illustrated that granular zeolites have high potential for removing chloroform and MTBE from water. However, the cost could inhibit their ultimate implementation. To reduce overall system costs, studies are being done to evaluate the possibility of regenerating the zeolites with minimal loss of their sorption ability. In addition, the comprehensive model developed herein is useful in the design and analysis of fixed-bed adsorbers treating single component solutes, where all mass-transfer resistances of intraparticle and film diffusion and axial dispersion are taken into account.

### 5.2 Recommendations for Future Work

There several topics that can be addressed in continuation to this work. A brief discussion of these issues is presented below.

#### 5.2.1 Regeneration of Zeolite-Bound Contaminants by Advanced Oxidation

After the removal of chloroform and MTBE from water by adsorption onto zeolites, their complete or partial destruction can be achieved by advanced oxidation. Following the work by Koryabkina et al. [87], regenerating the zeolite-bound contaminants with \( \text{H}_2\text{O}_2 \) based advanced oxidation is possible. In advanced oxidation processes, the reactions lead to the formation of hydroxyl radicals which have the ability to mineralize organic compounds.
5.2.2 Study the Effects of Solution Flow Rate, Initial Solute Concentration, and Adsorbent Particle Size on Fixed-Bed Adsorption Systems

In the study, the effect of bed height on the adsorption of chloroform and MTBE in fixed-bed adsorbers was studied. However, studying the effects of changing other operating conditions such as the solution flow rate, initial solute concentration, and adsorbent particle size can be very useful in the design of adsorption columns. Once fixed-bed adsorption experiments are performed using different flow rates, adsorbent particle sizes, and initial concentrations, the resulting breakthrough profiles can be compared with the FPSDM predicted breakthrough profiles. These results will improve our understanding of adsorption phenomena with respect to the limiting adsorption step (film diffusion or intraparticle diffusion) and will be very useful in enhancing the reliability of the FPSDM in predicting complex systems encountered in real applications.
6 References


[128] Frossling, N., Evaporation of Falling Drops, Geophysics 52 (1938)


7 Appendices

7.1 Appendix A: Supplementary Equations for Chapter 4

Derivations of equation (1) and equation (5) in chapter 4:

The liquid-phase mass balance for a control volume $z \rightarrow z + \Delta z$ in a fixed-bed reactor is:

\[ \text{Accumulation} = \text{Flux in (z)} - \text{Flux out (z + Δz)} + \text{generation} \]  \hfill (A.1)

\[ \frac{\partial C_b(z,t)}{\partial t} A.\Delta z = N.\dot{A}(z) - N.\dot{A}(z + \Delta z) - \tau_i A.\Delta z \text{, dividing by (A.Δz) yields:} \]  \hfill (A.2)

\[ \frac{\partial C_b(z,t)}{\partial t} = \frac{N}{\Delta z} (z) - \frac{N}{\Delta z} (z + \Delta z) - \tau_i \text{, take the limit as Δz → 0} \]  \hfill (A.3)

\[ \frac{\partial C_b(z,t)}{\partial t} = -\frac{\partial N(z,t)}{\partial z} - \tau_i \text{, where N accounts for flux by advection and dispersion} \]  \hfill (A.4)

\[ N = V C_b(z,t) - E_z \frac{\partial C_b(z,t)}{\partial z} \text{, substitute back into (A.4) yields:} \]  \hfill (A.5)

\[ \frac{\partial C_b(z,t)}{\partial t} = \frac{\partial}{\partial z} \left( V C_b(z,t) - E_z \frac{\partial C_b(z,t)}{\partial z} \right) = \tau_i \]  \hfill (A.6)

Including the porosity of the bed (\varepsilon) in the first two terms and (1-\varepsilon) in the third term yields

\[ \varepsilon \frac{\partial C_b(z,t)}{\partial t} = \varepsilon \left[ -V \frac{\partial C_b(z,t)}{\partial z} + E_z \frac{\partial^2 C_b(z,t)}{\partial z^2} \right] = \left( 1 - \varepsilon \right) \tau_i \text{, where} \ \tau_i = \rho_s \frac{\partial q}{\partial t} \]  \hfill (A.7)

Substituting the expression of \tau_i back into (A.7) and dividing by \varepsilon yields:

\[ \frac{\partial C_b(z,t)}{\partial t} = -V \frac{\partial C_b(z,t)}{\partial z} + E_z \frac{\partial^2 C_b(z,t)}{\partial z^2} = \frac{(1-\varepsilon)}{\varepsilon} \rho_s \frac{\partial q}{\partial t} \]  \hfill (A.8)

The sorption term \frac{\partial q}{\partial t} can take a variety of forms representing different rate and equilibrium components.

For film diffusion \frac{\partial q}{\partial t} = \frac{3k_f}{R\rho_s} \left( C_b(z,t) - C_p(r = R, z,t) \right) \hfill (A.9)

Substituting the film diffusion expression back into (A.8) yields:

\[ \frac{\partial C_b(z,t)}{\partial t} = -V \frac{\partial C_b(z,t)}{\partial z} + E_z \frac{\partial^2 C_b(z,t)}{\partial z^2} = \frac{3k_f}{R} \frac{(1-\varepsilon)}{\varepsilon} \left( C_b(z,t) - C_p(r = R, z,t) \right) \]  \hfill (A.10)
Note that equation (A.10) derived in this section is the same equation as equation (1) in chapter 4.

The intraparticle mass balance in the radial direction accounting for pore and surface diffusion is:

$$- \left( \frac{\partial N}{\partial r} + \frac{2}{r} N \right) = \varepsilon_p \left( \frac{\partial C_p}{\partial t} \right) + \rho_s \frac{\partial q}{\partial t} \quad \text{(A.11)}$$

Where $N$ accounts for the pore and surface diffusional flux

$$N = N_s + N_p \quad \text{(A.12)}$$

$$N_s = -\rho_s D_s \frac{\partial q}{\partial r} \quad \text{(A.13)}$$

$$N_p = -\varepsilon_p D_p,e \frac{\partial C_p}{\partial r} \quad \text{(A.14)}$$

And for linear isotherm with $1/n=1$, $q(r,z,t) = K C_p(r,z,t)^{1/n}$, hence, equation (A.12) becomes:

$$N = - \left( \rho_s D_s K + \varepsilon_p D_p,e \right) \frac{\partial C_p}{\partial r} \quad \text{(A.15)}$$

Where, $\frac{\partial q}{\partial C_p} = K$ and equation (A.15) becomes:

$$N = - \left( \rho_s D_s K + \varepsilon_p D_p,e \right) \frac{\partial C_p}{\partial r} \quad \text{(A.16)}$$

By calling $\rho_s D_s K + \varepsilon_p D_p,e = D_{s,p}$ equation (A.16) becomes:

$$N = - D_{s,p} \frac{\partial C_p}{\partial r} \quad \text{(A.17)}$$

Substituting the expression for $N$ back into equation (A.11) yields:

$$- \left( \frac{(-D_{s,p}) \frac{\partial^2 C_p}{\partial r^2} - \frac{2}{r} (D_{s,p}) \frac{\partial C_p}{\partial r}}{1} \right) = \varepsilon_p \left( \frac{\partial C_p}{\partial t} \right) + \rho_s \frac{\partial q}{\partial t} \quad \text{(A.18)}$$

Rearranging and using $\frac{\partial q}{\partial t} = K \frac{\partial C_p}{\partial t}$ for linear isotherm yields:

$$\left( D_{s,p} \right) \left( \frac{\partial^2 C_p}{\partial r^2} + \frac{2}{r} \frac{\partial C_p}{\partial r} \right) = \varepsilon_p \left( \frac{\partial C_p}{\partial t} \right) + \rho_s K \frac{\partial C_p}{\partial t} \quad \text{(A.19)}$$

Introducing $D_t = \frac{D_{s,p}}{\varepsilon_p+\rho_s K}$ and rearranging equation (A.19) becomes:
\[
\frac{\partial C_p(r,x,t)}{\partial t} = D_t \left( \frac{\partial^2 C_p(r,x,t)}{\partial r^2} + \frac{2}{r} \frac{\partial C_p(r,x,t)}{\partial r} \right)
\]  
(A.20)

Note that equation (A.20) derived in this section is the same equation as equation (5) in chapter 4.

7.2 Appendix B: The Matlab Program for the FPSDM Model in Chapter 4

```matlab
% solving the film Pore and Surface Diffusion Equations via Implicit Finite Difference Method (run as a % script)

clc
clear all  % clear all variables previously defined in the workspace
T=3;  % Time window
samp=2;
dt = 1e-2;

numr = 101;  % number of grid points in r
numt = (T/dt)+1;  % number of time steps to be iterated.
numz = 101;  % number of grid points in z

dr = 1/(numr-1);  % define step sizes for all three variables
dz = 1/(numz-1);

D_g = 1.73e4;  % Define various constants
P_e = 33.45;
S_t = 10.05;
E_d = 15.44;
F = E_d*(1+D_g)/D_g;
B_i = S_t/E_d;

tau=21.75;

% load experimental data
load data
T_exp=Time*60/(tau*(1+D_g));

% X = zeros(numr,numz,2);  % Initialize everything to zero
% C = zeros(numr,2);
Final_X = zeros(numr,numz,2);
Final_C = zeros(numz,2);
C=Final_C(:,1);
X=Final_X(:,:,1);

% The coeff. to construct the first matrix
equ_1_left=(-dt*(D_g+1)/(2*dz))+(dt*(D_g+1)/(P_e*(dz^2)));
equ_1_right=(dt*(D_g+1)/(2*dz))-(dt*(D_g+1)/(P_e*(dz^2)));
equ_1_middle=1+(2*dt*(D_g+1)/(P_e*(dz^2)))+(3*S_t*dt*(D_g+1));

% The diagonal vectors
```
Diag_left = equ_1_left * ones(numz,1);
Diag_left(numz,1) = equ_1_left + equ_1_right;

Diag_middle = equ_1_middle * ones(numz,1);
Diag_middle(1,1) = equ_1_middle - (equ_1_left * (2 * dz * P_e));

Diag_right = equ_1_right * ones(numz,1);
Diag_right(1,1) = equ_1_right + equ_1_left;

% The coeff of the second matrix
r = [0:dr:1]'; r(1) = 1;
Diag2_left = ((dt * F)./(dr * r)) - ((dt * F)./(dr^2));
Diag2_left(numr,1) = -(2 * dt * F)/(dr^2);

Diag2_right = ((-dt * F)./(dr * r)) - ((dt * F)./(dr^2));
Diag2_right(1,1) = -(2 * dt * F)/(dr^2);

alpha_middle = 1 + ((2 * dt * F)/(dr^2));
Diag2_middle = alpha_middle * ones(numr,1);
Diag2_middle(numr,1) = Diag2_middle(numr,1) - (2 * dr * S_t * Diag2_right(numr,1))/(E_d);

count = 1;
for tt = 2:numt
    RHS2 = Final_X(:, :, 1);
    RHS2(numr, :) = RHS2(numr, :) - (Diag2_right(numr) * 2 * dr * (S_t/E_d) * (Final_C(:, 1)'));
    Final_X(:, :, 2) = thomas_modified(Diag2_left, Diag2_middle, Diag2_right, RHS2, numr);

    RHS = Final_C(:, 1) + 3 * S_t * dt * (D_g + 1) * (Final_X(numr, :, 2)');
    RHS(1) = RHS(1) - equ_1_left * 2 * dz * P_e;
    Final_C(:, 2) = thomas_modified(Diag_left, Diag_middle, Diag_right, RHS, numz);
    if mod(tt-1, samp) == 0
        count = count + 1;
        C(:, count) = Final_C(:, 2);
        X(:, :, count) = Final_X(:, :, 2);
    end
    Final_C(:, 1) = Final_C(:, 2);
    Final_X(:, :, 1) = Final_X(:, :, 2);
end

t = 0:samp*dt:T;
plot(t, C(numz, :), 'r', T_exp, conc6cm, 'b');
xlabel('t');
ylabel('C(z, t)');