IMPACT OF ACIDIC CONDITIONS AND HIGH SULFATE CONCENTRATIONS ON MTBE MASS TRANSPORT AND MASS TRANSFER IN GAC

By

THOMAS ANDREW HUTSON

Bachelors of Science

East Central University

Ada, Oklahoma

2011

Submitted to the Faculty of the
Graduate College of the
Oklahoma State University
in partial fulfillment of
the requirements for
the Degree of
MASTER OF SCIENCE
August, 2014

IMPACT OF ACIDIC CONDITIONS AND HIGH SULFATE CONCENTRATIONS ON MTBE MASS TRANSPORT AND MASS TRANSFER IN GAC

Thesis Approved:

Dr. Gregory G. Wilber

Thesis Adviser

Dr. John N. Veenstra

Dr. Dee Ann Sanders

Dr. Scott G. Huling

ACKNOWLEDGEMENTS

I would like to thank Dr. Scott G. Huling for his invaluable support and expertise. I would also like to thank my committee members (Dr. Gregory G. Wilber, Dr. John N. Veenstra, Dr. Dee Ann Sanders, and Dr. Scott G. Huling) for all the advice, knowledge, and time invested in me. Thanks to the U.S. EPA, Groundwater Ecosystem Restoration Devision (Ada, OK), for their technical assistance in this project. Special thanks to my wife Ashley, and son Jayden for their love and support throughout this entire process.

Acknowledgements reflect the views of the author and are not endorsed by committee members or Oklahoma State University.

Name: THOMAS ANDREW HUTSON

Date of Degree: August, 2014

Title of Study: IMPACT OF ACIDIC CONDITIONS AND HIGH SULFATE CONCENTRATIONS ON MTBE MASS TRANSPORT AND MASS TRANSFER IN GAC

Major Field: CIVIL AND ENVIRONMENTAL ENGINEERING

Abstract: Sodium persulfate (SP) oxidation regeneration of granular activated carbon (GAC) is a developing technology. During SP regeneration of GAC, aggressive oxidative conditions lead to high acidity and the accumulation of sodium persulfate residuals in the GAC. In a previous investigation, this condition was attributed as the cause of a decline in MTBE sorption capacity by limiting MTBE diffusion onto GAC and by physical blockage of sorption sites after SP regeneration (Hutson *et.* al, 2012). This proposed conceptual model was evaluated in this study through MTBE desorption and diffusion experiments, on MTBE-pre-amended GAC. The accumulation of sulfate was primarily responsible for the blockage of sorption sites and hindered MTBE desorption (i.e. desorption + diffusion) in this study. Desorption decline was amplified equally under strong and weak acid condition, indicating pH played a less significant role in limiting MTBE desorption than sulfate pore blockage. Raising the pH in acid-amended reactors and washing with DIW resulted in the removal of residual sulfate and improved MTBE desorption from post-treatment GAC. This indicates the mechanisms responsible for limiting MTBE desorption are partially reversible. These results can be used to optimize future studies involving thermally-activated SP-regeneration of GAC.

TABLE OF CONTENTS

Chapter Page

LIST OF TABLES

Table Page

LIST OF FIGURES

Figure Page

CHAPTER I

INTRODUCTION

1.1. MTBE in Water Supplies

Methyl tert-butyl ether (MTBE) is a volatile, organic chemical. Since 1970, MTBE has been used as an oxygenate to increase octane values in gasoline. This results in more complete combustion of gasoline, and effectively reduces carbon monoxide and ozone precursor emissions. The 1990 Federal Clean Air Act mandated that MTBE, and other oxygenates, be added to gasoline in carbon monoxide and ozone non-attainment areas. Due to its low cost, ease of production, and favorable transfer and blending characteristics MTBE is the most commonly used oxygenates in the United States (Squillace *et al.*, 1995). The result is that MTBE is the second most frequently detected volatile organic compound in shallow groundwater (Squillace *et al.*, 1996). MTBE is found in numerous groundwater and surface water reservoirs throughout the United States (Leahy and Thompson, 1994). There may be as many as 250,000 releases of MTBE associated with leaking underground fuel tanks in the US (Johnson *et al*., 2000). MTBE is a possible human carcinogen at high doses (Church *et al*., 1999). In response to environmental and health concerns a U.S. Energy Bill mandated an end to the additive by 2015 (Cooney, 2005). The Environmental Protection Agency (EPA) has insufficient information to establish a health advisory limit for MTBE, but has issued a drinking water advisory of 20 to 40 ppm to act as a secondary drinking water standard based on taste and odor. MTBE is mobile and persistent in the

environment due to its high water solubility, low Henry's constant, and resistance to degradation (Huang *et al*., 2002). These factors also contribute to the difficulty and expense in treating MTBE contaminated water. There are several possible methods for removing MTBE from water with varying degrees of success and include, but are not limited to, adsorption onto granular activated carbon (GAC), air stripping, advanced oxidation processes (AOP), and biological remediation.

1.2. Granular Activated Carbon Treatment and Regeneration

GAC is a proven technology for treating water contaminated with MTBE. Adsorption of MTBE onto GAC has been extensively studied and the adsorption process is relatively well understood (Keller *et al.,* 1998; Li *et al.,* 2002; Huling, *et al.,* 2005; 2009; 2011; 2012; To *et al.,* 2008b; Kan and Huling, 2009). The adsorption process relies on the affinity of a solid surface for particular chemicals, in this case the affinity of GAC for MTBE. Very high removal efficiencies can be achieved with proper operation of GAC/MTBE treatment systems (Keller et al., 1998).

An important aspect of GAC/MTBE treatment systems is the need to regenerate spent GAC. GAC is "spent" when it becomes saturated with MTBE and effluent target concentrations can no longer be achieved. GAC can be regenerated and reused, or disposed of and replaced with virgin GAC. In most cases involving GAC regeneration, the GAC is thermally regenerated on-site or transported to a thermal regeneration facility and regenerated off-site. However, thermal regeneration involves the transport of the GAC to and from the regeneration facility, and combustion of fossil fuels at high temperatures (500 – 900 ^{o}C) during the regeneration process. Therefore high fossil fuel consumption and the formation and the release of greenhouse gases is a significant characteristic of this process (USEPA, 2000).

An alternative method to thermal regeneration is chemical oxidation regeneration. This process can be performed on-site and/or in-situ. This technology is still developing and additional studies are needed for process optimization and to investigate fundamental mechanisms. In a

preliminary evaluation, a reduction of fossil fuel consumption and production of greenhouse gases can be achieved through on-site chemical oxidation regeneration of spent GAC (data not reported).

1.3. Chemical Oxidation Effects

Activated SP has been demonstrated to regenerate MTBE-spent GAC (Huling et al., 2011). However, SP oxidative treatment negatively impacted post-oxidation MTBE sorption under acidic conditions (pH ≈ 0.8 – 2.1) (Hutson et al., 2012). Hutson *et al.* (2012) also reported that when the acidic pH was adjusted to near-neutral (pH 5.5), these impacts were reversible. Other studies have reported similar losses in sorption after oxidation of spent-GAC (Huling et al., 2005; Liang et al., 2011).

A conceptual model of the mechanism responsible for this result was proposed (Hutson et al., 2012). Specifically, under acidic conditions, the pH of the MTBE solution was lower than the pH at point of zero charge (pH_{PZC}) of the GAC. Specifically, this resulted in a net positive charge on the periphery of the GAC which attracted a disproportionate number of sulfate (SO_4^{2-}) and persulfate anions ($S_2O_8^{2-}$). The decline in MTBE sorption capacity measured under these conditions was attributed to (1) blockage of sorption sites by the anions, and/or (2) blockage of pore throats in the GAC, preventing the diffusive transport of MTBE into the GAC (Hutson et al., 2012).

Acid modification of carbon surfaces may also affect adsorption on GAC by introducing oxygen and decreasing GAC hydrophobicity, thereby reducing contaminant adsorption (Snoeyink *et al., 1974)*. This condition may initiate the sorption of water molecules in the GAC and inhibit the interactions between low-molecular weight hydrophobic contaminants and the carbon surface,

which effectively reduces sorption (Karanfil and Kilduff, 1999). Acid treatment of GAC (pH 0.8) for a long duration (2 weeks) further impacts GAC sorption capacity (Hutson et al., 2012).

A decrease in MTBE diffusion may prevent the practical application of the technology since this would result in the physical separation of the activated oxidant, and the MTBE chemical target. Specifically, MTBE transport from the GAC is restricted and consequently the esides internally in GAC, and persulfate is thermally catalyzed externally of the GAC preventing contact between oxidant and target. There may be no reaction zone that involves the co-existence of MTBE and catalyzed persulfate. Based on these findings, a need exists to better understand the conditions effecting MTBE desorption and diffusion in SP-regenerated GAC.

1.4. Objectives

The objectives of this study are to evaluate this proposed conceptual model and investigate the mechanism(s) by which the post-oxidation MTBE sorption decline occurs as a result of thermally-activated SP oxidation conditions. Specific objectives include: (1) determine the rate of desorption/diffusion of MTBE from GAC under sulfate-free (background pH 6.1), sulfate-rich (Na_2SO_4, pH 5.1) and sulfate-rich acidic (H_2SO_4, pH 1.1) conditions, and (2) contrast the rate of desorption and diffusion for each experimental condition to identify potential mechanisms by which MTBE desorption and diffusion from GAC is limited (e.g. the presence of high anion concentrations, and/or the net positive charge on the periphery of the GAC which attracts disproportionate number of anions effectively blocking sorption sites).

CHAPTER II

LITERATURE REVIEW

2.1. Characteristics of MTBE

The physicochemical properties of MTBE greatly complicate the remediation of contaminated water when compared to other organic contaminants. Organic contaminants in groundwater can be analyzed according to their solubility, volatility, and density with respect to water. As seen in Table 2.1, MTBE is less dense than water, has a high solubility, and a low partitioning constant for sorption onto organic matter in soil. MTBE also has low volatility and a low Henry's Law constant. These factors contribute to the difficulty and expense in treating MTBE contaminated water.

Table 2.1. Literature values of physicochemical properties of MTBE (NSTC, 1997)

Properties at 25^{o} C	Water	MTBE
Vapor Pressure (atm)	0.023	0.330
Aqueous solubility (mg/L)	NA	43,000 to 54,300
Henry's Law Constant (dimensionless)	NA	0.024 to 0.123
Octanol-Water Partitioning Coefficient, K_{ow} (dimensionless)	NA	$10^{1.2}$
Boiling Point (^{o} C)	99.9	55.2
Density (g/mL)	1	0.74
Molecular Weight (g/mL)	18.02	88.15
CAS Number	7732-18-5	1634-04-4

MTBE is highly mobile in the environment due to its high water solubility, and weak partitioning to organic soil, sediments and suspended particles. For these reasons, MTBE is projected to move at the same rate as groundwater flow, with practically no hindrance due to sorption (Keller, 1998). Furthermore, MTBE is resistant to biodegradation in the environment and projected to biodegrade slowly under natural conditions (Borden et al., 1997; Huang et al., 2012).

2.2. Treatment Methods for MTBE-Contaminated Groundwater

Although difficult, inefficient, and time consuming, MTBE contamination in groundwater can be treated using existing technologies (USEPA, 1998). Conventional technologies for treating MTBE in groundwater include adsorption onto GAC, air stripping, advanced oxidation, and biological remediation.

2.2.1. Adsorption

Adsorption onto GAC relies on the affinity of a solid surface for particular chemicals, usually measured in terms of mass of contaminant adsorbed per unit mass of adsorbent (e.g. mg/g). GAC is prepared by pulverizing carbonaceous materials (e.g. coal, coconut shell, peat, or wood) then heating it to high temperatures. This process greatly increases the surface area, and the affinity for organic chemicals. GAC has a high affinity for organic contaminants making it particularly useful in removing contaminants from water. Treatment of MTBE-contaminated water is often achieved using GAC adsorption (Huling et al., 2011). This treatment process involves pumping contaminated water through a bed of activated carbon to rid it of organic compounds such as MTBE. MTBE does not sorb well to carbon, relative to other organic compounds. This may result in fast breakthrough of the MTBE and high GAC utilization rates (Keller, 1998). Consequently, large quantities of GAC are used to treat MTBE-contaminated water relative to other organic compounds exhibiting higher partition coefficients (USEPA, 2012). However, very high removal efficiencies can be achieved with proper operation of

GAC/MTBE treatment systems (Keller, 1998). GAC is a simple technology with high mechanical reliability that can handle relatively large variations in influent MTBE concentrations as well as variations in water flow rate.

2.2.2. Air Stripping

Air stripping involves continuously contacting MTBE-contaminated water with large volumes of air to transform significant fractions of the volatile organic compounds (VOCs) to the air phase. MTBE removal efficiency is a function of the design (e.g. dimensions, flow rate, air/water ratio, and packing media) of the air stripping tower and the contaminants' Henry's constant (Keller, 1998; ITRC, 2005). The most cost-effective air stripping device for MTBE removal is a packed tower (MTBE Research Partnership, 1998). The packing material in a packed tower is designed to maximize the contact area between the water and counter air flow, to increase mass transfer.

Great emphasis is placed on well-designed processes to achieve treatment goals. MTBE has a relatively low Henry's constant at ambient temperatures and therefore is not ideally removed using air stripping techniques (Keller, 1998). Air stripping of MTBE requires very high air-to-water volumetric flow ratios at ambient temperature which can significantly increase tower dimensions, capital cost and operational costs. Consequently, air stripping of MTBE-contaminated water is not often used. Since air stripping involves mass transfer of MTBE from the water to the air phase, additional treatment of the resulting contaminated air may be needed. In many cases GAC is used to control off-gas emissions in air stripping processes. Additionally, if high variations in MTBE concentrations are expected, air stripping may require a post-treatment polishing step using GAC to meet effluent standards (Keller, 1998).

2.2.3. Advanced Oxidation

Advanced oxidation technologies use combinations of ultraviolet light, chemical oxidants (e.g. such as hydrogen peroxide, and persulfate), ozone (O_3), and catalysts to transform contaminants into less toxic byproducts. Oxidation technologies have been demonstrated to oxidize a wide range of organic chemicals, including MTBE (Huling et al., 2009; Hutson et al., 2012; USEPA, 2012). MTBE in water is degraded through the oxidative action of the free radical (OH•, and SO_4^{-}•) (Huling et al., 2009; Hutson et al., 2012) resulting from oxidant activation. Ideally, sufficient free radicals are formed to react completely with the dissolved MTBE and all its byproducts until total mineralization is achieved (ITRC, 2005; Hutson et al., 2012). If total mineralization is not accomplished, competing constituents, such as oxidation byproducts, may create a demand for the radicals - resulting in inefficient MTBE removal (CMRP, 2000). Oxidation reaction byproducts *tert*-butyl formate, and *tert*-butyl acetate may result from chemical oxidation regeneration of MTBE (Vel Leitner et al., 1994). It is important to note that advanced oxidation processes can be utilized to oxidize MTBE sorbed to GAC (Huling et al., 2011).

2.2.4. Biological Treatment

Biological treatment, also known as biodegradation, is based on developing a favorable environment to grow microorganisms that consume MTBE (FRTR 2002). Biodegradation of MTBE is a developing technology with limited number of full-scale applications (ITRC, 2005). Studies have demonstrated MTBE degradation by bacterial and fungal cultures under aerobic (Deeb et al., 2000; Stocking et al., 2000) and anaerobic (Finneran and Lovley, 2001; Wilson et al. 2000) conditions. Laboratory- and full-scale studies have documented both partial degradation of MTBE to metabolic intermediates and complete mineralization to carbon dioxide (ITRC, 2005). MTBE biodegradation can occur either as a primary source of carbon and energy, or following growth on another substrate (ITRC, 2005).

One of the most effective examples of bioremediation technology is an engineered bioreactor. Bioreactors are designed to maximize the quantity of biomass retained in the treatment system (AEHS, 2001). In many cases, bioreactors utilize GAC as a physical and chemical substrate to facilitate the growth of a seeded culture capable of metabolizing MTBE. Biodegradation of MTBE is slow, relative to chemical oxidation; but an advantage of employing GAC is that contaminants are absorbed and then slowly released to the microorganisms for degradation (FRTR, 2002).

2.2.5. Treatment Overview

Because of the physical and chemical properties of MTBE, conventional cleanup technologies are costly and relatively inefficient at removing MTBE from groundwater (Keller, 1998). GAC adsorption and air stripping are generally very expensive when compared to their application for other gasoline products, such as benzene and toluene. Oxidation of MTBE has been proven successful in laboratory and field studies using a variety of oxidizing agents (Raupp and Junio, 1993; Barreto et al., 1995). There are however some concerns with respect to the generation of by-products (Keller, 1998). Biodegradation and mineralization (conversion to carbon dioxide) of MTBE can be accomplished using acclimated bacteria; however the rate of growth of the bacteria is reported to be slow (Guertin, 2000). Based on these findings, a need exists to identify a more effective tool to treat MTBE in groundwater or to improve existing technologies.

GAC is the most cost-effective treatment method if air quality goals must be met and the influent water has low levels of other organic compounds, which is typical of MTBE contaminated water supplies (Keller, 1998).

2.3. GAC Regeneration Methods

The objective of GAC regeneration is to desorb accumulated contaminants and restore the original porous structure with little or no damage to the GAC. There are a variety of methods to regenerate GAC, but the general process remains the same. In most cases, regeneration is accomplished by subjecting the spent-GAC to conditions which favor desorption of adsorbed contaminants, and removal or destruction. The relative process by which regeneration is accomplished is dependent upon the type of adsorption (chemical or physical).

In the case of chemical sorption, a supply of energy greater than the sorptive force is required to break the strong ionic or covalent bonds and shift adsorption equilibrium in favor of desorption. For physical sorption, the shift can usually be accomplished by heating, lowering the pressure, or washing with solvent (Sufnarski, 1999).

The most common method used to regenerate GAC is the thermal process. Other methods used for regeneration include chemical regeneration, bioremediation, wet-air oxidation, and solvent remediation. To remain in context, this paper will focus on thermal, chemical, and biological regeneration techniques. Despite which method is used, it is important to note that the regeneration of GAC is dependent upon the characteristics of the base material, the activation process, and the type of adsorbate.

2.3.1. Thermal Regeneration

Thermal regeneration of spent-GAC is usually accomplished in three stages (e.g. drying, baking, and re-activiation). This process is conducted using multiple-hearth furnaces, rotary kilns, or fluidized-bed furnaces (Cheremisinoff and Morresi, 1978). Thermal regeneration can be conducted on-site or off-site. For large scale operation utilizing large amounts of GAC, it is often more economical for regeneration to be conducted on-site. Many small scale operations, such as municipalities, transport the spent carbon to a thermal regeneration facility for regeneration.

A typical thermal regeneration system will operate in the following stages: (1) a wet slurry of spent GAC is dried in a dewatering bed where it drains by gravity until reaching a moisture content of 50% (McGinnis, 1984), (2) dried GAC is then baked and temperatures are raised to 200 ^{o}C to release volatile organics as gases, then raised again to 400-600 ^{o}C to drive off reversibly adsorbed substances, and decompose irreversibly adsorbed substances to char residue, and finally, (3) reactivation is accomplished by heating the GAC to 870 – 1000 ^{o}C in an atmosphere containing a high concentration of steam or CO_2 that oxidize the char residue (Zanitisch and Stenzel, 1978). In this process, it is important to maintain a combustion-inert system to prevent the combustion of the GAC material. The detention time of the process and the reactivation condition is dependent on the adsorbates present on the GAC (Sufnarski, 1999).

One advantage to thermal regeneration is that it can be used for carbon loaded with heterogeneous mixture of adsorbates. Furthermore, the reactions that occur during reactivation are identical to those in the activation step of GAC production. Combustion conditions in the furnace are controlled to limit oxygen content to effect oxidation of the adsorbate rather than the GAC (Van Vliet, 1991).

A disadvantage however is excessive oxidation of GAC at relatively high temperatures (950 ^{o}C). In most cases there is a 5-10% loss of carbon due to surface oxidation under these conditions (Van Vliet, 1991). Other disadvantages associated with thermal regeneration include high energy requirements, off-gas air pollution problems, and incompatibility of some adsorbates with high temperature operations (e.g. adsorbates such as TNT) (Lyman, 1978).

2.3.2. Chemical Regeneration

Chemical oxidation regeneration involves the addition and activation (i.e., catalysts) of chemical oxidants which are used to oxidize and transform target adsorbates. Two of the most

commonly used chemical oxidation agents are hydrogen peroxide (H_2O_2) and sodium persulfate ($Na_2S_2O_8$).

Chemical oxidation regeneration is a process in which adsorbates are removed and transformed from spent GAC by reactions with strong chemical oxidant reagents. For more information regarding advanced oxidation processes, refer to sections 2.2.3 and 2.4.1. Chemical oxidation involves harsh chemical, physical, and oxidative (e.g. acid or basic pH, exothermic reactions) conditions within reactor vessels. For this reason subsequent washing with water is required to remove the residuals of the regenerating agents.

Chemical regeneration has several advantages over thermal regeneration. Chemical oxidation can be performed on-site and in-situ (Hutson et al., 2012). This eliminates losses due to pumping, transporting, and packing. Furthermore, chemical regeneration avoids the high fossil fuel consumption, and resulting release of greenhouse gases associated with thermal regeneration (USPEA, 2000). Additionally carbon loss associated with thermal regeneration is eliminated using chemical oxidation.

Disadvantages with chemical regeneration include the high costs of reagents, danger of pollution from hazardous chemicals, incomplete regeneration, and formation of oxidation by-products. Loss of sorption capacity for chemically regenerated GAC has also been reported after multiple regeneration cycles (Huling et al., 2005 and Hutson et al., 2012).

2.3.3. Biological Regeneration

Bioregeneration is the renewing of GAC by microbial activities. Bioregeneration occurs by either mixing bacteria with saturated GAC in an off-line system (Scholz and Martin, 1997; Roy et al., 1999; Silva et al., 2004) or in the course of biological treatment such as biological activate carbon (BAC, e.g. biofilm-covered GAC) systems (Jonge et al., 1996; Ha and Vinitnantharat, 2000; Vinitnantharat et al., 2001). Bioremediation can be optimized by varying

the nature of microorganisms, the environmental conditions and the loading on GAC (Vinitnantharat et al., 2001). These conclusions are based on investigations involving off-line bioregeneration, because simultaneous processes cannot easily differentiate between adsorption/desorption and biodegradation effects.

Off-line bioregeneration is a method used to regenerate spent GAC via biological processes and involves removal of adsorbed organic matter from spent GAC through desorption and biodegradation occurring inside a closed batch system (Aktaş and Çeçen, 2007). The process consists of regenerating used activated carbon in a column in which a mixture of acclimated bacteria, nutrients and dissolved oxygen are recirculated to remove adsorbed organic matter (Goeddertz et al., 1988).

An advantage of bioremediation is that regeneration of GAC occurs simultaneously to wastewater treatment during BAC processes (Kim et al., 1997; Seo et al., 1997). Furthermore, operational costs associated with biological treatment are inexpensive relative to thermal oxidation. However, in bioregeneration systems, biofouling caused by excessive microbial growth can considerably hamper the process of regenerating spent GAC (Vuoriranta and Remo, 1994; Scholz and Martin, 1997). Additionally, blockage of pore throats by accumulated biomass may interfere with contaminant diffusion and adsorption in the bioregenerated GAC.

2.4. Background

In a previous study, the impact of acidic pH (0.8, and 2.1), pH adjustment to pH 5.5, and thermally activated SP oxidative treatment on MTBE adsorption in GAC was investigated (Hutson et al., 2012). In this study, it was proposed that under acidic conditions, the pH of the post-oxidation GAC suspension was lower than the pH_{PZC} of the GAC. Specifically, this resulted in a net positive charge on the GAC surfaces which attracted sulfate (SO_4^{2-}) and persulfate ($S_2O_8^{2-}$) anions. The decline in post-treatment MTBE sorption capacity was attributed to blockage of

sorption sites by anions, and/or blockage of pore throats in the GAC preventing the diffusive transport of MTBE from the GAC. Hutson *et al*., 2012, also indicated that at pH 5.5, these impacts were reversible.

Acid modification of carbon surfaces may also affect adsorption on GAC by introducing oxygen and decreasing GAC hydrophobicity, thereby reducing contaminant adsorption (Snoeyink *et al.*, 1974; Karanfil and Kilduff, 1991). This condition may initiate the sorption of water molecules in the GAC and inhibit the interactions between low-molecular weight hydrophobic contaminants and the carbon surface, which effectively reduces sorption capacity. Similarly, acid treatment of GAC (pH 0.8) for a long duration (2 weeks) further impacts GAC sorption capacity (Hutson *et al.*, 2012).

2.4.1. Persulfate Oxidation and Regeneration of GAC

Sodium persulfate ($Na_2S_2O_8$) dissociates in water to form the persulfate anion ($S_2O_8^{2-}$), which is a strong oxidant (E^o = 2.01 V) but kinetically slow in reacting with many organics (Liang et al., 2007). Persulfate anions can be thermally activated (Reaction (1)) to generate the sulfate radical ($SO_4^{-}\bullet$). Sulfate radicals are strong, non-specific, oxidants (2.4 V) that exhibit fast reaction rates and are capable of degrading a wide range of environmental contaminants.

$$S_2O_8^{2-} + \text{heat} \rightarrow 2\ SO_4^{-}\bullet \qquad (1)$$

SP oxidation reactions are acid producing and solution pH is often highly acidic (pH < 2). It has been demonstrated that under acidic conditions (pH < 2 – 3.7), thermally-activated SP can effectively oxidize MTBE (Huling *et al.*, 2011). Other studies have also shown MTBE to be oxidized by activated SP under a range of activation and environmental conditions (Huang et al., 2002; Liang et al., 2010, 2011).

Thermally activated SP was more effective at oxidizing MTBE-spent GAC than either base-activated or hydrogen peroxide (H_2O_2) co-amended SP treatment. Iron activated SP resulted in an accumulation of iron precipitate on the GAC and may explain the additional decrease in GAC surface area relative to iron-free SP activation (Liang et al., 2011). Several process parameters impact oxidation efficiency and include: activation method, SP loading rate, GAC solid:solution ratio, SP concentration (e.g. mass loading), pH, and GAC type (Huang et al., 2002; Huling et al., 2011). Lower volume applications of SP (loading rate), higher solid/solution ratio, and higher SP concentration (mass loading) resulted in greater MTBE oxidation and removal. Furthermore, higher temperatures during thermal activation of SP enhanced MTBE desorption and diffusive transport from the interior of the GAC to the exterior, and allowed greater contact between MTBE and SO_4^{-}• and/or $S_2O_8^{-}$ (Huling et al., 2011). These results are in agreement with Huang et al. (2002) who reported significant enhancement of MTBE degradation with increasing temperature in homogeneous system. Chemical and physical properties of GAC may also impact MTBE removal. SP reaction rate constants declined in successive applications of SP to MTBE-spent GAC under constant thermal conditions. This indicates that SP is partially catalyzed by non-thermal means of activation. Basic surface oxide (BSO) functional groups can catalyze SP through non-productive reactions that do not yield SO_4^{2-}•. BSO functional groups become oxidized under acidic or oxidative conditions during GAC treatment, which in turn, increase oxidation efficiency (Jones, 2007).

2.4.2. Persulfate Oxidation Effects

During thermally-activated SP regeneration of GAC, the SP solution and aggressive oxidative conditions lead to high acidity (pH < 2), and the accumulation of SP residuals (SO_4^{2-}, and $S_2O_8^{2-}$) in GAC (Hutson et al., 2012). Studies have investigated the impact of SP oxidation on the sorption characteristics of MTBE in GAC. Loss of sorption was measured in thermally-activated SP regenerated GAC (Hutson et al., 2012). MTBE sorption loss in GAC, resulting from

thermally-activated SP treatment, is attributed to three potential mechanisms: (1) aggressive oxidative treatment, (2) strongly acidic conditions (e.g. pH = 2.1, 1.2, and 0.8), and potentially, (3) the accumulation of persulfate residuals that could block sorption sites (Hutson et al., 2012). Additional testing was needed to differentiate between these mechanisms.

2.4.3. Acidic Treatment Effects on Sorption

Sulfuric acid treatment of GAC resulted in a decline in MTBE sorption (Hutson et al., 2012). The limited effects on sorption capacity at pH 4.3, indicated the impacts are concentration and/or pH dependent. The decline in sorption was attributed to either acidic effects and/or accumulation of the sulfuric acid residual, sulfate (SO_4^{2-}) (Hutson et al., 2012). Nitric acid was used in a separate test to help distinguish between these two effects. Nitric acid is a strong oxidant and also forms a large amount of acidic surface oxide (ASO) functional groups on GAC, relative to sulfuric acid (Huang et al., 2008). ASOs affect the chemical interactions that govern adsorption on GAC by introducing oxygen and decreasing GAC hydrophobicity (Snoeyink et al., 1974). This process effectively reduces contaminant adsorption. Due to the strong impact of nitric acid treatment on GAC, relative to sulfuric, the results could not be used to distinguish between the effects of sulfuric acid treatment of GAC and accumulation of sulfuric acid and/or SP residuals in GAC.

Similar acidic treatment of GAC (pH 0.8) for a longer duration (2 weeks) resulted in greater loss of MTBE sorption capacity (Hutson et al., 2012). These results suggest that acid treatment can affect GAC sorption through physical processes including the breakdown of carbon surfaces, widening of micropores, a decline in GAC surface area, and ultimately a decline in sorption capacity for organics (Karanfil and Kilduff, 1999). The results of this study suggest that the duration of oxidative treatment under acidic conditions should be limited to minimize acidic effects.

2.4.4. Sulfur Accumulation Effects

Relative to virgin GAC, a greater accumulation of sulfur residuals in GAC was observed with the SP concentrations amended to GAC, and with H_2SO_4 and sodium sulfate amendment to GAC (Hutson et al., 2012). Sodium sulfate-amended GAC resulted in an accumulation of sulfur and sodium species, but limited loss of MTBE sorption relative to SP at 150 g L^{-1} (pH 1.2) (Hutson et al., 2012). This suggests that changes in MTBE sorption characteristics are due partially to the accumulation of sulfate anions on the GAC, but also to the oxidative and acidic effects from SP treatment.

Sodium sulfate was amended to the GAC in quantities equal to the amount of sulfate applied (300 g L^{-1}) during SP oxidation. However, sulfate concentration accumulation in the sodium sulfate amended GAC was lower than the SP GAC. The main variable for these two reactors was pH. This further suggests that factors other than the presence of sulfate species may play a role in the accumulation of inorganic species on post-treatment GAC.

Due to these results, it was proposed that the loss in MTBE sorption in SP-treated GAC may be reversible assuming the sulfur species can be disassociated from the GAC. The pH at point of zero charge (pH_{PZC}) is the pH at which positive and negative surface charges are equal and the GAC surface has a net charge of zero (Hutson et al., 2012). The background pH_{PZC} for the GAC (pH = 5.5) decreased when treated with acid (Huling et al., 2009 Kan and Huling, 2009). Fundamentally, it is proposed that when the pH shifted below the pH_{PZC}, as with SP-oxidation (e.g. pH 0.8 – 2.1), the surface of the GAC carried a net positive charge and electrostatically attracted SO_4^{2-} anions near the surfaces of the GAC (Hutson *et al.*, 2012*)*. Given these very high concentrations at the surface, especially since g L^{-1} concentrations of SP were used, there is massive accumulation of sulfate and persulfate anions at the surface which likely (1) blocked MTBE intra-particle diffusive transport near the surface, (2) blocked MTBE sorption sites near

the surface, (3) and acidic and oxidative treatment increases the ASO's which also block pore throats. Conversely, raising the pH of the SP-oxidized GAC, and thus the pH_{PZC}, the electrostatic attraction between SO_4^{2-} and the GAC surface declined, and released SO_4^{2-} back into solution. Sulfate (SO_4^{2-}) could then be decanted from the GAC slurry, removed from the treatment system, and the MTBE sorption was partially restored to near-virgin GAC conditions (Hutson et al., 2012).

2.4.5. Persulfate Treatment Effects Overview

SP treatment at 40, 150, and 300 g L^{-1} impacted post-oxidation MTBE sorption. The pH associated with these SP concentrations are strongly acidic (pH 0.8, 1.2, and 2.1). These pH ranges facilitate massive accumulation of SO_4^{2-} , and $S_2O_8^{2-}$ anions on the surface of GAC. Very high anion concentrations (g L^{-1} concentrations) are available for accumulation in solution due to SP concentrations used in Hutson *et al.* (2012). Sulfate (SO_4^{2-}) and persulfate ($S_2O_8^{2-}$) anion, accumulation at the surface of GAC will likely: (1) block MTBE intraparticle diffusive transport near the surface of the GAC, (2) and/or block MTBE sorption sites on the GAC. Additionally, acidic and oxidative treatment of the GAC causes increases in acidic surface oxides which may also block pore throats and effect the chemical interactions that govern MTBE adsorption on GAC.

The proposed conceptual model from Hutson et al. (2012) will be evaluated to further assess whether acidic, sulfate-rich conditions, resulting from SP-oxidation are responsible for limiting MTBE diffusion from GAC. A better understanding of this mechanism will allow the development of chemical oxidation regeneration guidelines that identify operational parameters designed to maximize adsorbate diffusion from the GAC during regeneration treatment. Ultimately, these guidelines can be used to assure a reaction zone develops during chemical

oxidation regeneration involving the co-existence of MTBE and catalyzed SP which allows aggressive MTBE oxidation.

CHAPTER III

MATERIAL AND METHODS

3.1. Introduction

It is proposed that thermally-activated SP treatment of GAC results in acidic pH and a net positive charge on the periphery of GAC resulting in the disproportionate number of sulfate (SO_4^{2-}) and persulfate ($S_2O_8^{2-}$) anions near the surface of the GAC. In a previous investigation, this condition was attributed as the cause of a decline in MTBE sorption capacity by limiting MTBE diffusion onto GAC (Hutson *et.* al, 2012). This conceptual model was evaluated through MTBE desorption and diffusion experiments, on MTBE-amended GAC, under independent conditions involving sulfate-free (background pH ≈ 6.1), sulfate-rich (Na_2SO_4, pH ≈ 5.1), and sulfate-rich acidic (H_2SO_4, pH ≈ 1.1) conditions. All sulfate-rich reactors contained the same concentration of sulfate (7 g L^{-1}) amended to GAC with pH as the only variable. The acidic sulfate-rich amended reactor is intended to mimic MTBE desorption that would occur during SP chemical oxidation regeneration (sulfate-rich, acidic pH conditions). The sulfate-rich reactor is used to assess GAC's affinity for sulfate anions under background pH conditions. MTBE desorption and diffusion rates were determined and contrasted for each of the conditions tested.

3.2. Materials

The GAC (URV1, 8×30 mesh) was supplied by Calgon Carbon Corp. (Pittsburgh, Pa), derived from bituminous coal, and activated to minimize H_2O_2 reactivity (Hayden, 2001). The surface area and pore volume of the GAC was 1290 m^2 g^{-1} and 0.64 mL g^{-1}, respectively (Huling *et* al., 2007). The GAC was rinsed with deionized (DI) water, dried in an oven (105 ^oC), sealed with parafilm, and stored until used. GAC was dried and weighed (1g) into each reactor quickly to assure an accurate weight of the GAC. Vials (40 mL) equipped with silicone septa (0.125") caps were purchased from QEC and used as reactors. A SGE gastight syringe (250 µL RN, 25ga., pt#2) was used for MTBE extraction and analysis. MTBE (ACS grade, SigmaAldrich) was used as the sorbate and target compound. Sulfuric acid (ACS grade, Spectrum Corp.) and sodium hydroxide (97.0 %, ACS grade, EMD™) were used to adjust the pH. Sodium sulfate (Na_2SO_4) (99.0 %, ACS grade, Spectrum Corp.) was used to prepare a non-acidic sulfate stock solution.

3.3. Solution Preparation

3.3.1 MTBE Stock Solution

A 20 mg L^{-1} MTBE stock solution was prepared (Eq. 1) and diluted (1:10) to achieve a 2 mg/L solution, that was amended to the GAC (24 hours) and used for the desorption and diffusion study. The density of MTBE is 0.74 g mL^{-1}. The volume of MTBE determined by Eq. 1 was added to 2 L of DI water.

$$\frac{20\ mg\ MTBE}{L} \times \frac{2\ L \times mL}{0.74 g\ MTBE} \times \frac{1\ g}{1{,}000\ mg} = 0.0541 \text{ mL of MTBE} \qquad \text{(Eq. 1)}$$

3.3.2. Sulfuric Acid Desorption Solution

Four milliliters (0.004 L) of concentrated sulfuric acid (H_2SO_4, 18.4 M) was added to one liter (1 L) of DI water to achieve a final aqueous concentration of 7.1 g L^{-1} of sulfate (SO_4^{2-}) based on Eq. 2.

$$\frac{18.4\ mol\ H_2SO_4}{L} \times \frac{1\ mol\ SO_4^{2-}}{1\ mol\ H_2SO_4} \times \frac{96.07\ g}{1\ mol\ SO_4^{2-}} \times \frac{0.004\ L\ H_2SO_4}{1\ L\ DIW} = 7.1\ \text{g L}^{-1}\ \text{of}\ SO_4^{2-} \qquad \text{(Eq. 2)}$$

3.3.3. Sulfate Desorption Solution

A 10.45 g L^{-1} sodium sulfate (Na_2SO_4) solution was prepared to achieve a final aqueous sulfate (SO_4^{2-}) concentration of 7.1 g L^{-1}. Sodium sulfate (10.45 g) was added to one liter (1 L) of DI water as determined by Eq. 3.

$$\frac{7.1\ g\ SO_4^{2-}}{L} \times \frac{142.05\ g\ Na_2SO_4}{96.07\ g\ SO_4^{2-}} = 10.45\ \text{g L}^{-1}\ \text{of}\ Na_2SO_4 \qquad \text{(Eq. 3)}$$

3.4. Experimental Procedures

3.4.1. MTBE Amendment

MTBE (2 mg/L) adsorption onto GAC (1 g) was conducted using glass reactors (40 mL) equipped with Teflon lined septum caps. Prior to desorption experiments, three test reactors containing 1 g of GAC were saturated (24 hours @ 50 ^{o}C) with MTBE (40 mL) (Table 3.1).

Reactor	Adsorption Solution [MTBE] = 2 mg L^{-1}	Desorption Solution		
(Name)	**(mL)**	**(Solution)**	**(mL)**	**(pH)**
Phase 1.				
Sulfate-free (pH 6.1)	40	DI Water	40	6.1
Sulfate (pH 1.1)	40	H_2SO_4	40	1.1
Sulfate (pH 5.1)	40	Na_2SO_4	40	5.1
Phase 2.				
Sulfate-free (pH 7.0)	0	DI Water	40	7.0
Sulfate (Adj. pH 7.1)	0	DI Water	40	7.1
Sulfate (Adj. pH 1.1)	0	H_2SO_4	40	1.1

Table 3.1. Volume of solutions added to each test reactor to be used during desorption and diffusion experiments. The [MTBE] amended to GAC was the same in all three phase 1 reactors (2 mg/L). The [MTBE] varied in phase 2 reactors, it is the remaining [MTBE] not removed from phase 1 desorption and diffusion experiments.

3.4.2. Desorption Solution Amendment

After MTBE amendment was carried out, a desorption solution (40 mL) was added to each of the reactors and allowed to equilibrate (24 hours @ 50 ^{o}C) before conducting desorption experiments (Table 3.1). Desorption Solution amendment took place in two phases (Phase 1 and 2).

Phase 1 MTBE desorption experiments were conducted after MTBE amendment (i.e., adsorption). A desorption solution (40 mL) was added to each of the reactors and allowed to equilibrate (24 hours @ 50 ^{o}C) before conducting desorption experiments (Table 3.1). Following the phase 1 desorption study, each reactor was amended (40 mL) with the respective desorption solution and placed in a hot-water bath (24 hours @ 50 ^{o}C) to ensure consistent treatment of GAC and to stabilize the pH of the GAC slurry before use in phase 2 experiments. Exposing the GAC to the respective desorption solutions, and high temperature (50 ^{o}C) for the additional 24 hours

between phase 1 and 2 experiments may have hindered the ability to compare desorption rate results between phase 1 and 2.

Phase 2 desorption and diffusion reactor preparations involved the same MTBE-saturated GAC and reactors from phase 1 experiments. However, pH adjustment of the sulfate-amended and acidi pH GAC slurries was carried out to investigate mechanism reversibility: [Sulfate-free (pH 7.0)]: received no Sulfate treatment and no pH adjustment, thus serving as a control; [Sulfate (Adj. pH 1.1)]: pH adjustment using H_2SO_4 on post-treatment sulfate (pH 5.1) GAC slurries and MTBE was desorbed using 40 mL of H_2SO_4 solution; [Sulfate (Adj. pH 7.1)]: pH adjustment using NaOH on post-treatment sulfate (pH 1.1)) GAC slurry and desorbed using DIW to elute sulfate species. By the start of phase 2, GAC slurries had been in contact with their respective desorption solution for 96 hours compared to 24 hours in phase 1 experiments.

3.4.2. MTBE Desorption

All desorption experiments involved thermal treatment (50 ^{o}C, 225 min). Prior to desorption and diffusion steps for phase 1 and 2, an initial sample (M_o, 40 mL) was collected from each reactor to determine initial MTBE concentration and mass at equilibrium for each reactor (Sulfate-free (pH 6.1), Sulfate (pH 5.1), Sulfate (pH 1.1), (Sulfate-free (Adj. pH 7.0), Sulfate (Adj. pH 1.1), and Sulfate (Adj. pH 7.1)).

The phase 1 desorption and diffusion experiment was conducted on GAC (1 g) pre-amended with MTBE (40 mL, 2 mg L^{-1}, 48 hours), and desorption solution (40 mL, 24 hours). Phase 2 desorption and diffusion experiment was conducted on GAC (1 g) amended with MTBE (40 mL, 0.74 -1.2 mg/L, 96 hours), and desorption solution (40 mL, 48 hours). For each reactor configuration, the desorption solution was different to maintain experimental conditions (Sulfate-free: [sulfate] = 0 g/L (pH 6.1), H_2SO_4: [sulfate] = 7 g/L (pH 1.1), Na_2SO_4: [sulfate] = 7 g/L (pH 5.1). Desorption and diffusion study was conducted using the fill and draw method. This involved

removing solution (40 mL) in the MTBE-amended GAC reactors and replacing it with MTBE-free solution to facilitate desorption and diffusion of MTBE from the GAC. This was accomplished using the desorption solution for each respective reactor (Table 3.1). The study took place over a four hour period and samples (40 mL) were collected every 15 minutes (225 minute total) and stored at 4^{o}C to be analyzed later.

3.4.3. pH Adjustment of Post-Desorption Reactors

pH adjustment was carried out on the phase 1 reactors to determine if the impacts on MTBE desorption and diffusion, on GAC, are reversible (i.e., phase 2 experiments). Each reactor was collected and the pH was determined. Initial pH following the phase 1 desorption study ranged from 6.1 and 5.1 (DI and Sodium Sulfate reactors) to 1.1 (Acid reactor). The pH adjustment was carried out using either sulfuric acid (Na_2SO_4) or sodium hydroxide (NaOH). The phase 1 sodium sulfate (pH 5.1) reactor was adjusted to pH 1.2 by amendment of 0.074 M (40 mL) sulfuric acid. Phase 1 acidic reactor (pH 1.1) was adjusted to pH 4.8 using sodium hydroxide (1 M, NaOH). A pH adjustment was not carried out on the phase 1 DI reactor (pH 6.1) so that it could be used as a control for later comparison. Each pH-adjusted reactor was placed in a hot-water bath and allowed to equilibrate (24 hours @ 50 ^{o}C) until phase 2 of the desorption study was carried out. During the phase 2 experiment, the desorption and diffusion steps were carried out using the control and pH-adjusted reactors. It should be noted that the phase 2 pH-adjusted reactors were exposed to reactor conditions for approximately 80 hours compared to 24 hours for the original phase 1 reactors.

3.5. Analytical Procedures

3.5.1. MTBE Analysis

MTBE was analyzed using an Agilent 7890B Gas Chromatograph (GC) system with flame ionization detector (FID). The GC was equipped with a Supelco, Equity-5, fused silica

capillary column used for detecting polar compounds. To protect the integrity of the column aqueous samples were not analyzed. Instead, a headspace method for analyzing MTBE was developed. The calibration curve developed from this method is presented below (Fig. A).

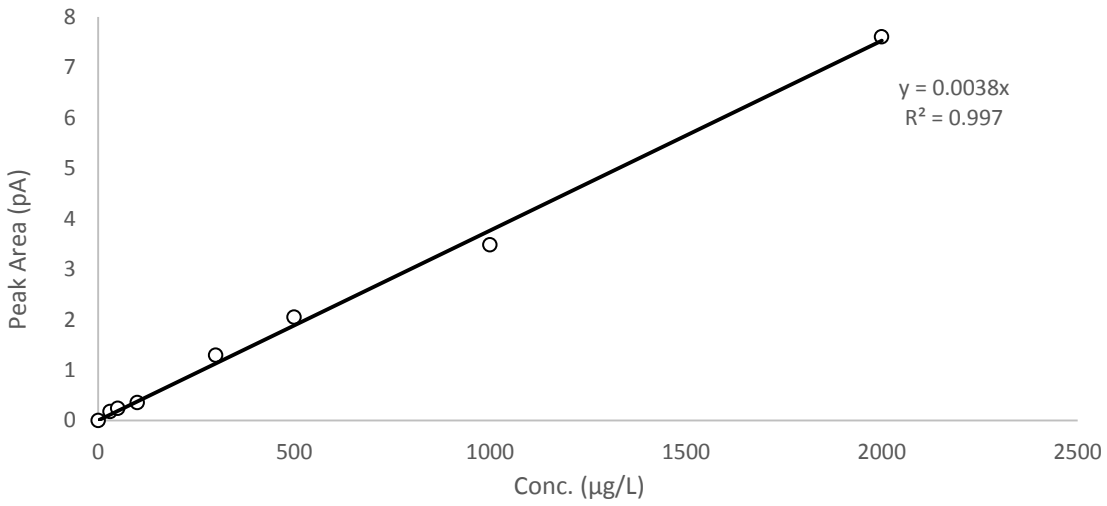


Fig. 1A. Calibration curve for MTBE at various known concentrations (0, 30, 50, 100, 300, 500, and 2,000 mg/L). (Appendix A.)

The headspace method involved an MTBE solution (30 mL) placed in vials (40 mL) that allow headspace samples to be collected when MTBE reaches equilibrium (24 hours) between the gas and liquid phase at a constant temperature. Samples were placed in a constant temperature (50 ^{o}C) hot water bath to weaken hydrogen bonds and initiate volatilization of the MTBE into the gas phase. Headspace samples were collected (100 µL) using a gastight syringe, and directly injected to the inlet of the GC. For the GC parameters used (initial temp. = 40 ^{o}C, at rate of 15 ^{o}C per minute increase), MTBE peak areas resulted at approximately three minutes. Steps were taken to ensure that the calibration curve remained the same for both phases of the study.

3.5.2. Sulfate Analysis

Sulfate anion samples were determined by the EPA, Groundwater Ecosystem Restoration Devision (Ada, OK), using capillary ion electrophoresis with indirect UV detection. Sulfate

analysis was conducted to quantify the concentration of sulfate anions in each reactor and to assess whether this played a role in MTBE desorption and diffusion from GAC. The desorption study took place over a four hour period, and SO_4^{2-} samples (10 mL) were collected every 15 minutes and stored at 4^{o}C to be analyzed later. Samples were injected into a 75-μm-ID silica capillary filled with a buffered electrolyte solution containing a UV-adsorbing anion salt (sodium chromate) and an electro-osmotic flow modifier (OFM). A high voltage, negative power supply is used to separate anions within the capillary. Anions are detected indirectly from the adsorption of chromate at 254 nm. Quality assurance and quality control steps were performed (e.g. blanks, stock standards, duplicates, calibration checks) indicating the proper function of this instrument during analysis.

CHAPTER IV

RESULTS AND DISCUSSION

4.1. Scope of Study

The purpose of this study was to investigate the conceptual model proposed in Hutson *et al.*, which suggest that a decline in MTBE sorption capacity for sodium persulfate (SP) regenerated (55^{o}C, 200 min) GAC was attributed to (1) blocked MTBE intra-particle diffusive transport near the surface, (2) blocked MTBE sorption sites near the surface, and possibly (3) acidic and oxidative treatment increases the ASO's which also block pore throats. This was investigated by MTBE adsorption and desorption experiments under various conditions involving sulfate-free, sulfate-rich, and sulfate-rich acidic solutions. MTBE diffusive transport rates were determined and contrasted for the various conditions. MTBE pre-amended GAC subjected to acidic pH and sulfate-rich (7 g L^{-1}) conditions was used to mimic post-oxidation SP regenerated GAC. Sulfate-rich (7 g L^{-1}) condition was used to investigate the impact of sulfate independent of strong acid pH. Sulfate-free conditions received no sulfate and no pH adjustment, to act as a control. Adjusting pH from phase 1 to 2 was used to determine if impacts might be reversible.

4.2. Phase 1 experimental Results

For each of the three reactors (Sulfate-free, Sulfate pH 5.1, and Sulfate pH 1.1) in phase 1 experiments GAC (1g) was saturated with MTBE to ensure that it was available on the GAC for

desorption. Based on previous experiments, adding 40 mL MTBE solution at 2 mg L^{-1} to URV MOD1 GAC (1 g) resulted in approximately 200 µg L^{-1} MTBE at equilibrium (Hutson *et al.*, 2012). This was confirmed by MTBE concentrations (249, 247 and 256 µg L^{-1}) in solution following 24 hour equilibration (50^{o}C) with 2 mg L^{-1} MTBE, indicating that MTBE adsorbed onto the GAC (Appendix B, C, and D).

MTBE saturated GAC was in contact with desorption solution for 24 hours. This was intended to allow the MTBE on the surface of the GAC to reach equilibrium with the aqueous phase. After the 24 hour washing period, the kinetic study was initiated.

The rate of MTBE mass removal in the sulfate-free verses sulfate (pH 5.1 and 1.1) reactor conditions are plotted versus time (Fig. 2). Each sample analyzed represents an incremental mass of MTBE removed from the GAC relative to the total mass on the GAC at time zero (0). Samples were collected every fifteen minutes over a four hour period and analyzed for MTBE. Since little was known about desorption rates, it was unclear what duration should be used. However, to get enough data to assess the rate of desorption, four hours was considered a good start. It should be noted that four hours was not a sufficient duration to facilitate complete removal of MTBE from the GAC, which resulted in linear data over the 225 minute study, and approximately zero-order behavior. Using this data, phase 1, zero-order MTBE mass removal rates were determined for each experimental condition: (Sulfate-free (pH 6.1) = 0.15 µg min^{-1}, Sulfate (pH 5.1) = 0.08 µg min^{-1}, and Sulfate (pH 1.1) = 0.075 µg min^{-1}) (Fig. 2).

For comparison, MTBE percent removal (($\Sigma M_t/M_o$) ×100) from GAC was plotted (Fig. 3). Presenting data as total incremental mass removed (ΣM_t), relative to initial mass (M_o) at the beginning of the kinetic study, still resulted in zero-order plots. Kinetic, MTBE percent removal rates from GAC were determined: (Sulfate-free = 0.23 min^{-1}, Sulfate (pH 5.1) = 0.12 min^{-1}, and Sulfate (pH 1.1) = 0.11 min^{-1}) (Fig. 3).

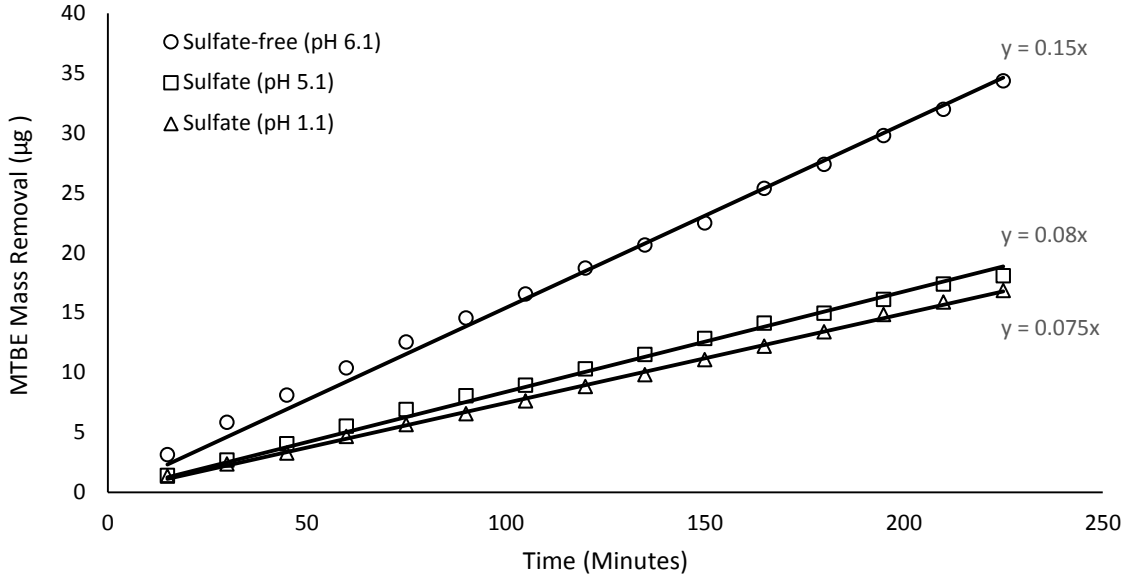


Fig. 2. Phase 1. MTBE mass removal associated with desorption from GAC (1 g) pre-amended with MTBE (2 mg L^{-1}) solution, and treated with various desorption solutions; ○ (Sulfate-free (pH 5.1): received no Sulfate treatment (r^2 = 0.99): □ (Sulfate (pH 5.1): received 40 mL (10.45 g L^{-1}) Na_2SO_4; 7 g L^{-1} SO_4^{2-} equivalence (r^2 = 0.99): △ (Sulfate (pH 1.1): received 40 mL (7.1 g L^{-1}) H_2SO_4 treatment (r^2 = 0.99).

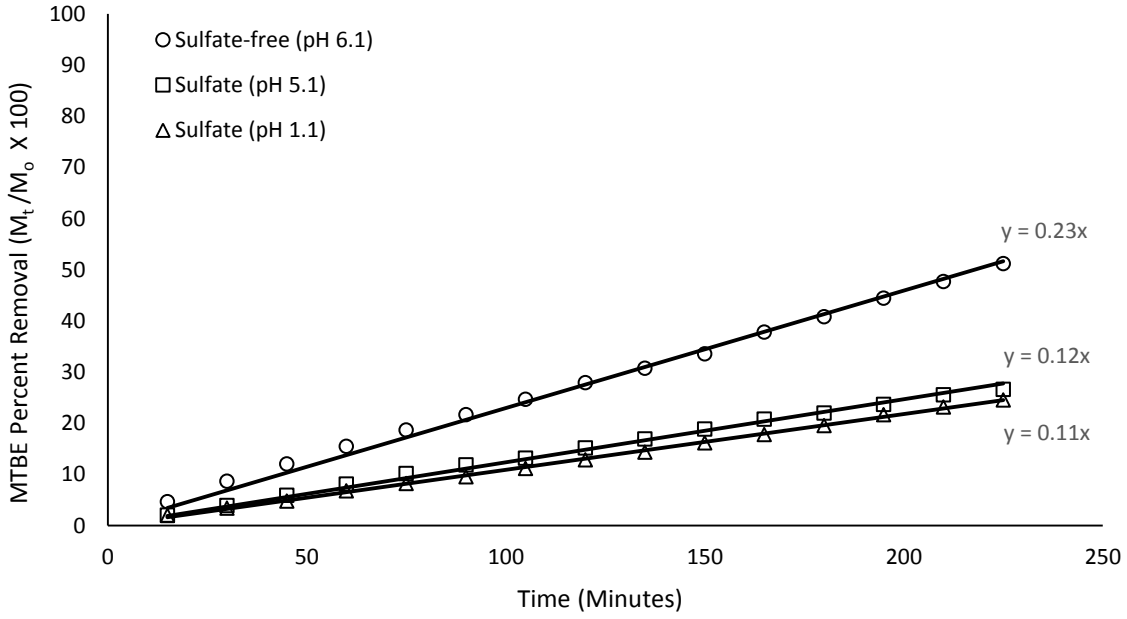


Fig. 3. Phase 1. MTBE mass removal associated with desorption from GAC (1 g) pre-amended with MTBE (2 mg L^{-1}) solution, and treated with various desorption solutions: ○ (Sulfate-free (pH 6.1): received no Sulfate treatment and no pH adjustment (r^2 = 0.99): □ (Sulfate (pH 5.1): received 40 mL (10.45 g L^{-1}) Na_2SO_4; 7 g L^{-1} SO_4^{2-} equivalence (r^2 = 0.99): △ (Sulfate (pH 1.1): received 40 mL (7.1 g L^{-1}) H_2SO_4 treatment (r^2 = 0.99).

The presense of sulfate ions in solution show to retard MTBE desorption rates regardless of pH (Fig. 2 and 3). Decline (53 %) in MTBE desorption rates from GAC in sulfate reactors were relatively consistent relative to sulfate-free reactors. This is somewhat expected since sulfate reactors contained comparable sulfate (7 g L^{-1}) and MTBE (250 µg L^{-1}) concentrations in solution. Since pH was the only variable and [sulfate] remained the same suggests that sulfate is primarily responsible for MTBE desorption decline. These finding are consistent with batch test results on SP (40, 150, and 300 g L^{-1}) and sulfate-treated GAC, which suggested that sulfur species are predominantly responsible for blockage of sorption sites and/or pore throats, and consequently MTBE sorption loss in post-regenerated GAC (Hutson *et al.*,2012). These findings are in general agreement with To *et al.*(2008b) who reasoned that desorption occurred from unblocked pores initially, then desorb slower from blocked pores.

4.3. Phase 2 Experimental Results

For each of the three reactors (Sulfate-free, Sulfate Adj. pH 1.1, and Sulfate Adj. pH 7.1) in phase two experiments, GAC (1g) contained residual MTBE (33, 50, and 52 µg) remaining after phase 1 desorption and diffusion study (Appendices E, F, and G).

MTBE-spent GAC was amended with phase 1 desorption solution for 24 hours following phase 1 study. This was intended to keep the GAC under consistent pH and sulfate conditions. After the 24 hour contact period, the pH was adjusted using either NaOH or H_2SO_4 (24 hours) with phase 2 desorption solution. This was intended to let the GAC fully equilbriate with the phase 2 desorbing solution and to remove sulfate from solution. Following this 24 hour period, phase 2 kinetic study was initiated.

Phase 2, MTBE mass desorption and diffusion rates were calculated for Sulfate-free and Sulfate (Adj. pH 1.1 and 7.1) reactors following pH adjustment: (Sulfate-free (pH 7.0) = 0.065 µg min^{-1}, Sulfate (Adj. pH 1.1) = 0.06 µg min^{-1}, and Sulfate (Adj. pH 7.1) = 0.07 µg min^{-1}) (Fig. 4).

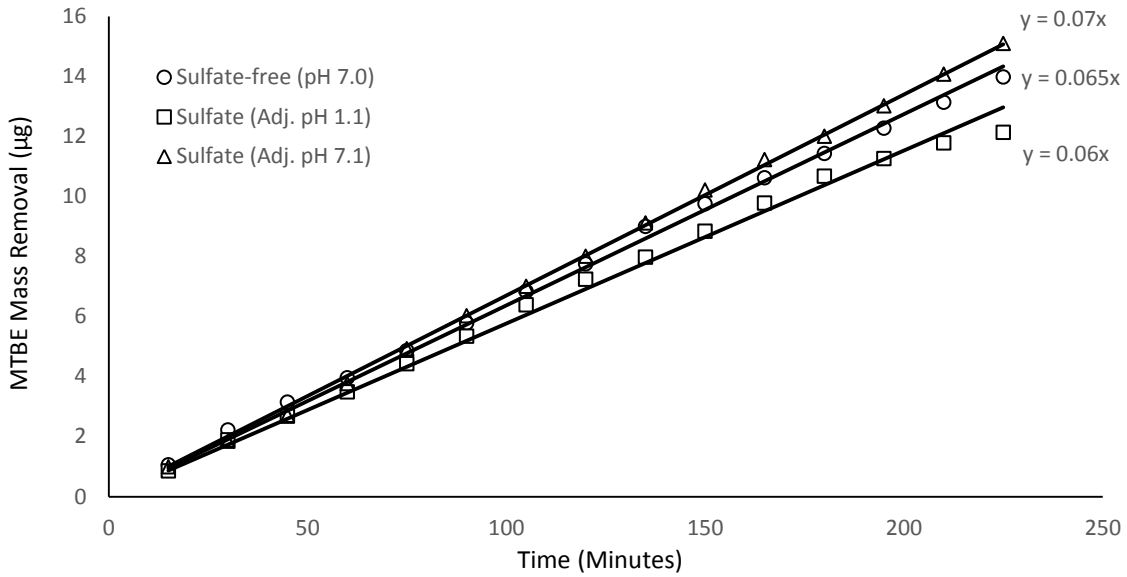


Fig. 4. Phase 2. MTBE mass revoval associated with desorption from pH adjusted GAC (1 g) amended with MTBE (33, 50, and 52 µg), and treated with various desorption solutions: ○ (Sulfate-free (pH 7.0): received no Sulfate treatment and no pH adjustment (r^2 = 0.99): □ (Sulfate (Adj. pH 1.1): post-treatment (Sulfate (pH 5.1)) GAC slurry adjusted to pH 1.1 with 40 mL H_2SO_4 (7 g L^{-1} H_2SO_4 equivlence) (r^2 = 0.99): △ (Sulfate (Adj. pH 7.1): post-treatment (Sulfate (pH 1.1)) GAC slurry adjusted to pH 7.1 with NaOH and desorbed using DIW (r^2 = 0.99).

A clear distinction could not be made between the sulfate-free and sulfate (Adj. pH 7.1) mass removal kinetics. MTBE mass removal rates were relatively the same for all three conditions (Fig. 4). This may have occurred due to differences in initial GAC/MTBE concentrations and resulting concentration gradient. For this reason, percent ($(\Sigma M_t/M_o) \times 100$) MTBE removal rates were plotted to investigate removal effects independent of initial concentration (Fig. 5). Phase 2, percent (M_t/M_o) MTBE desorption and diffusion rates were determined for Sulfate-free and Sulfate (Adj. pH 1.1 and 7.1) reactors following pH adjustment: (Sulfate-free (pH 7.0) = 0.022 min^{-1}, Sulfate (Adj. pH 1.1) = 0.011 min^{-1}, and Sulfate (Adj. pH 7.1) = 0.014 min^{-1}) (Fig. 5).

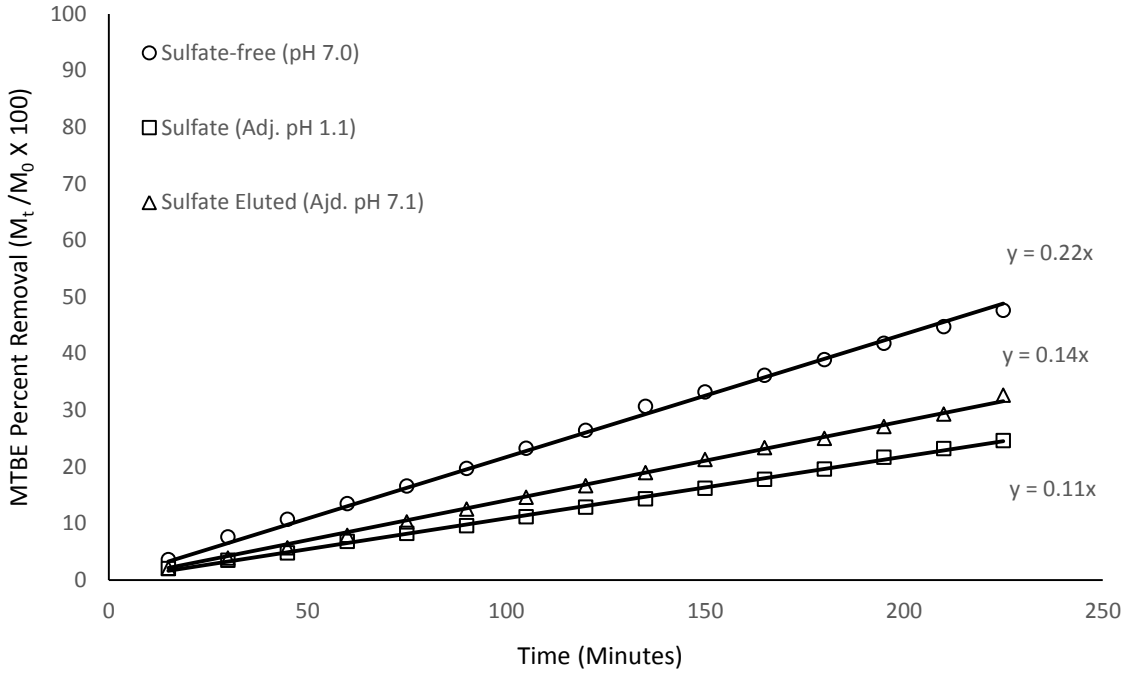


Fig. 5. Phase 2. MTBE mass removal associated with desorption from pH adjusted GAC (1 g) amended with MTBE (33, 50, and 52 µg), and treated with various desorption solutions: ○ (Sulfate-free (pH 7.0): received no Sulfate treatment and no pH adjustment (r^2 = 0.99): □ (Sulfate (Adj. pH 1.1): post-treatment (Sulfate (pH 5.1)) GAC slurry adjusted to pH 1.1 with 40 mL H_2SO_4 (7 g L^{-1} H_2SO_4 equivalence) (r^2 = 0.99): △ (Sulfate (Adj. pH 7.1): post-treatment (Sulfate (pH 1.1)) GAC slurry adjusted to pH 7.1 with NaOH and desorbed using DIW (r^2 = 0.99).

This data further corroborates earlier statements, suggesting that sulfate plays a significant role in MTBE desorption kinetics from GAC. Since initial $[MTBE]_{GAC}$ is no longer a variable (i.e. presented as percent removal), results show a clear separation between sulfate-free and sulfate reactors. During the desorption study, sulfate was removed from solution in the sulfate-eluted reactor (Fig. 6). Furthermore, the removal of sulfate from solution showed to increase (21 %) MTBE desorption and diffusion rates from GAC (Fig. 3 and 5). These results are in agreement with earlier results in phase 1 experiments, which indicate the presence of sulfate in solution plays a significant role in MTBE desorption from GAC. This may explain why removal of excess sulfate in solution improved MTBE desorption and diffusion kinetics from phase 1 to 2.

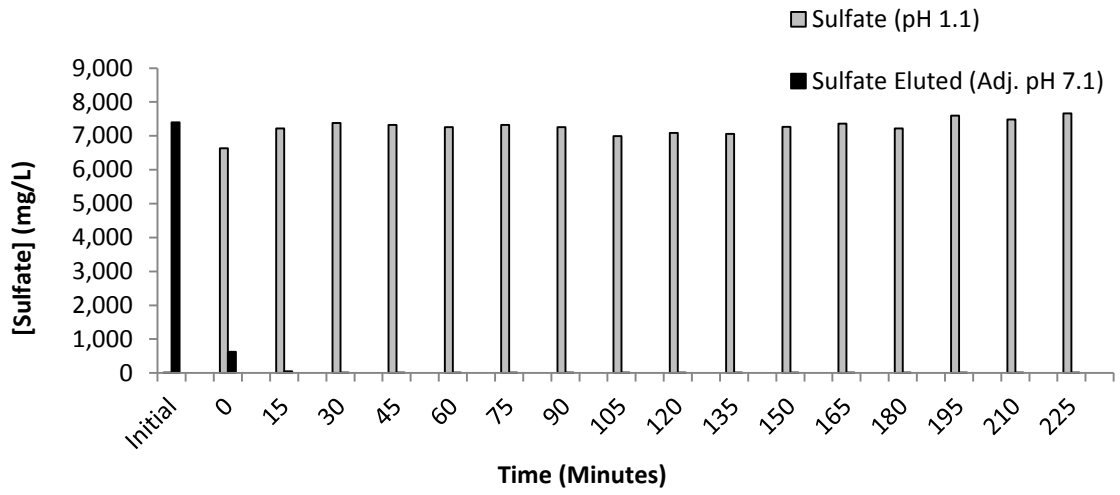


Fig. 5. Sulfate concentrations in solution during desorption and diffusion experiments (50 ^{o}C, 225 min): ☐ (Sulfate (pH 1.1): received 40 mL (7.1 g L^{-1}) H_2SO_4 treatment: ■ Sulfate Eluted (Adj. pH 7.1): post-treatment (Sulfate (pH 1.1)) GAC slurry adjusted to pH 7.1 with NaOH and desorbed using DIW.

4.4. Desorption Kinetics

MTBE desorption kinetics are expected to follow first order reaction rates. All data presented so far have been near linear. Linear data may suggest that the desorption experiment did not take place for a long enough duration to facilitate first-order kinetics, and therefore was in the early stages of a first-order reaction rate. Zero-order behavior would be expected in the early stages of first-order desorption reactions. This hypothesis is somewhat confirmed by plotting combined MTBE mass removal kinetics for both phase 1 and 2, sulfate-free reactors, over 450 minutes, which approaches first-order characteristics as a function of MTBE mass remaining on the GAC (Fig. 7).

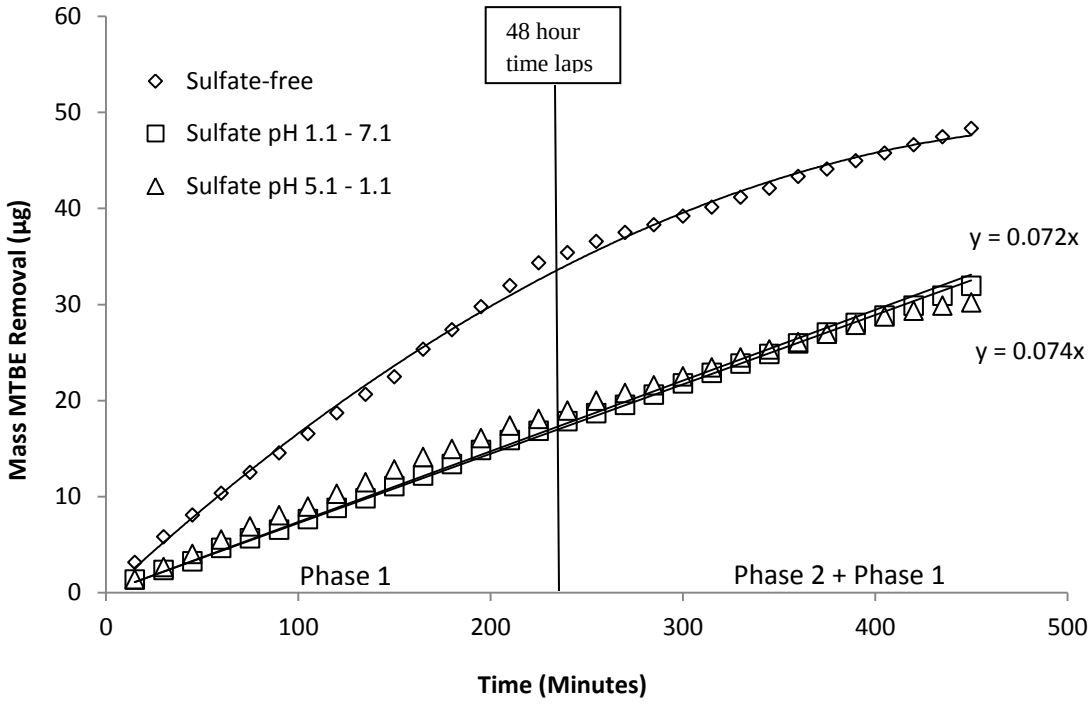


Fig. 7. Phase 1 and 2, MTBE mass removal associated with desorption from pre- and post-pH adjusted GAC (1 g) amended with MTBE and treated with various desorption solutions: ◇ (Sulfate-free): received no Sulfate treatment and no pH adjustment ($r^2 = 0.99$): □ (Sulfate pH 1.1 – 7.1): post-treatment (Sulfate (pH 1.1)) GAC slurry adjusted to pH 7.1 with NaOH and desorbed using DIW ($y = 0.072$, $r^2 = 0.99$): △ (Sulfate pH 5.1 – 1.1): post-treatment (Sulfate (pH 5.1)) GAC slurry adjusted to pH 1.1 with 40 mL H_2SO_4 (7 g L^{-1} H_2SO_4 equivlence) ($y = 0.074$, $r^2 = 0.98$). A 48 hour time laps occurred between phase 1 and 2 data sets.

The reduction in MTBE mass removal rates between phase 1 and 2 sulfate free reactors may indicate that MTBE and sulfate have moved deeper into the GAC and that desorption and diffusion is slower. These results are somewhat intuitive given the current knowledge on MTBE adsorption in GAC. For example, the adsorption process of MTBE onto GAC has been shown to include two stages: external mass transfer at the initial period, then followed by intraparticle diffusion (Chen *et al.*, 2010). It is reasonable to conclude that a MTBE desorption mechanism from GAC would be similar. It is proposed that during the initial stages of desorption, external mass transfer would not be the rate limiting step for sulfate-free conditions due to the high MTBE concentrations and the short diffusion transport distances between GAC surfaces and the

bulk solution. When the amount of MTBE removed from the GAC reached a critical rate of removal (i.e., low [MTBE] and long transport distances), the desorption process may have become intraparicleduffusion-controlled. Intraparticle desorption + diffusion may become the rate limiting step at the later stages of desorption (i.e., slower than external mass transfer), because it involves a longer more tortuous path.

4.5. General Discussion

MTBE percent (M_t/M_o) removal rates (0.023 and 0.022 min^{-1}) were essentially no different in sulfate-free reactors from phase 1 to 2 (Fig. 3 and 5). Both GAC reactors were exposed to the same conditions (DIW, 50 ^oC, 225 min), and therfore negligible changes in percent removal were observed. This was projected since DI water does not contain large amounts of suflate capable of blocking sorption sites.

The pH of solution did appear to have an impact on MTBE desorption and dufusion kinetics from GAC (Fig. 2). Comparing sulfate (pH 5.1 – 1.1) relative to suflate-free conditions, indicates that pH does play some role in MTBE desorption rates, but to a lesser degree than sulfate (Fig. 2). This was somewhat confirmed by comparing (phase 1 vs phase 2) sulfate reactors before and after pH adjustment. Sulfate reactors with similar initial [sulfate] (7 g L^{-1}), and acidic pH (pH 1.1) exhibited reduced MTBE percent removal relative to higher pH conditions (pH 5.1 – 7.1) with comparable [GAC/MTBE] (Fig. 3 and 5). This effect was limited (8 and 21 % reduction) when compared to the effects attributed to sulfate accumulation (57 % reduction). However, it should be noted that strong acid (pH 1.1) conditions exhibit slower MTBE diffusion kinetics than weak acid and neutral (pH 5.1 and 7.1) conditions.

MTBE mass removal rates decreased by 57 % in phase 2 sulfate-free reactor, relative to phase 1 (Fig. 2 and 4). Yet only decreased 25 and 7 % for sulfate reactors between phase 1 and 2 (Fig. 2 and 4). Sulfate reactors contained large quantities of sulfate (7 g L^{-1}), relative to the

sulfate-free condition, yet experienced small changes in MTBE mass removal following pH adjustment. This effect was observed regardless of different initial $[MTBE]_{GAC}$ between phase 1 and 2 (Fig. 7). This data suggests that sulfate played a rate limiting role in MTBE desorption from GAC. Perhaps massive concentrations of sulfate ions in solution are constantly adsorbing and desorbing on the external mass of the GAC, effectively hindering MTBE intraparticle diffusion and thereby controlling the rate at which MTBE can desorb from the GAC. More studies are needed to varify this condition and little data is available for comparison.

CHAPTER V

CONCLUSION

5.1. Conclusions

MTBE adsorption from water onto the surface of GAC was achieved in test reactors carried out under similar baseline conditions (i.e., $[MTBE]_{INITIAL}$, 24 hour contact time). The MTBE-spent GAC was subsequently used in desorption experiments designed to investigate the role of sulfate concentrations and acidic conditions on MTBE desorption from the GAC. MTBE desorption kinetics were determined by measuring [MTBE] in solution during fill-and-draw experiments. MTBE desorption+diffusion from the MTBE-spent GAC followed zero-order reaction kinetics (Fig. 1-4). Sulfate was primarily responsible for sorption site and pore blockage and MTBE desorption declined under these experimental conditions (i.e. high [sulfate], and acidic pH). Removal of sulfate from the GAC showed to increase MTBE desorption kinetics from GAC under neutral pH. The pH of solution impacted MTBE desorption kinetics from GAC, but to a lesser degree than sulfate. Results suggests the presence of sulfate, under strong and weak acid conditions, plays a rate limiting role in MTBE desorption from GAC.

The results of this study help explain how the presence of sulfate, generated during SP-regeneration of GAC, may contribute to the loss of MTBE adsorption capacity on post-

regenerated carbon. It appears that sulfate is primarily responsible for the reduction in MTBE sorption in post-oxidative treatment of MTBE-spent GAC in Hutson *et al*. (2012). Specifically, sulfate was directly responsible for blockage of pore throats and/or sorption sites in GAC preventing MTBE diffusion and sorption within the GAC. The pH played a role in the decline of adsorption in post-oxidation treatment of the GAC, and that pH adjustment and subsequent GAC contact with DIW eluted sulfate from the GAC permitting increased MTBE mass transfer and transport. Overall, these results support the conceptual model proposed by Hutson *et al.* (2012) indicating that post-oxidation pH adjustment of SP-treated GAC removed sulfur species from the GAC and enhanced MTBE mass transfer and transport and improved MTBE sorption for SP-treated GAC. This indicates that the pH adjustment step is useful in minimizing the impacts of sulfate on post-SP-oxidized GAC.

5.2. Recommendations

5.2.1. Desorption Experiments

Future attempts at improving these experiments should include: 1) conduct desorption kinetic studies over a longer duration than four hours to facilitate complete removal of MTBE from the pre-amended GAC, and 2) When conducting phase 2 experiments, simulate the conditions from phase 1, then adjust the pH and conduct desorption kinetic study. This will eliminate variables like $[MTBE]_{GAC}$ and contact time, and help in the comparison of data between phases 1 and 2. These steps may help to better understand the reversibility of the impact of high sulfate concentrations in GAC. It would also be useful to conduct the experiments using varying [sulfate] to determine if sulfate impacts are concentration dependent.

5.2.2. SP-Regeneration Experiments

When conducting thermally-activated SP-regeneration of MTBE spent GAC, low concentration, frequent applications of SP should be used to minimize sulfate impacts on post

treatment GAC. Furthermore, frequent GAC washing should occur between oxidation events to elute sulfate species from the GAC, and minimize intraparticle diffusion of sulfate onto the GAC.

Following GAC regeneration, GAC should be immediately rinsed and the pH adjusted and allowed to equilibrate for 24 hours. This step should help to remove adsorbed sulfate species from the GAC and into solution, effectively freeing up sorption sites and pore throats for mass transport and transfer of the target compounds. Following this 24 hour period, an additional washing should be conducted on the GAC using DIW. At this point the GAC can be placed back on-line and re-amended with contaminant for later comparison to background adsorption. Similar steps are also applicable in the commercial operation of chemically-regenerated GAC treatment systems.

REFERENCES

Aktaş, Ö., and Çeçen, F., 2007. Bioremediation of activated carbon: A review. Institute of Environmental Science, Boğaziçi University, 34342 Bebek, Istanbul, Turkey. International Biodeterioration and Biodegradation 59, 257-272.

AEHS (Association for Environmental Health and Science), 2001. AEHS Special Oxygenated Fuels Issue, Contaminated Soil Sediment and Water, spring issue.

Borden, R.C., Daniel, R.A., LeBrun, L.E. IV, Davis, C.W., 1997. Intrinsic biodegradation of MTBE and BTEX in a gasoline-contaminated aquifer. Water Resources Res. 33, 1105-1115.

Cheremisinoff, P., Morresi, A., 1978. Carbon Adsorption Applications. Carbon Adsorption Handbook; Cheremisinoff, P.; Ellerbush, F., Eds.; Ann Arbor Science: Ann Arbor, MI, 1978, 1-53.

CMRP, 2000. Treatment Technologies for Removal of Methyl Tertiary Butyl Ether (MTBE) from Drinking Water. Fountain Valley, Calif.: Center for Groundwater Restoration and Protection, National Water Research Institute. California MTBE Research Partnership.

Cooney, C.M., 2005. Water utilities may be stuck with MTBE cleanup/riding along the clear-car corridor. Environ. Sci. Technol., 39, 279A.

Corwin, C.J., Summers, R.S., 2011. Adsorption and desorption of trace organic contaminants from granular activated carbon adsorbers after intermittent loading and throughout backwash cycles. Water Reasearch 45, 417-426.

Deeb, R.A., Nishino, S., Spain, J., Hu, H.-Y., Scow, K., and Alvarez Cohen, L., 2000. MTBE and Benzene Biodegradation by a Bacterial Isolate via Two Independent Monooxygenase-Initiated Pathways, American Chemical Society, Division of Environmental Chemistry, Preprints of Extended Abstracts 40 1, 280-282.

Finneran, K.T., and Lovley ,D.R., 2001. Anaerobic Degradation of Methyl tert-Butyl Ether (MTBE) and tert-Butyl Alcohol (TBA). Env. Sci. Tech. 35 9, 1785-16.

FRTR, 2002. Remediation Technologies Screening Matrix and Reference Guide. Vers. 4. http://www.frtr.gov/.

Guertin, J., Herron C., Jacobs J.A., MTBE: Effects on Soil and Groundwater Resources. CRC Press, Sep 28, 2000 - Technology and Engineering, 54-64.

Hayden R., 2001. Personal Communication. Calgon Carbon Corporation, Pittsburgh, PA.

Huang, K.C., Couttenye, R.A., Hoag, G.E., 2002. Kinetics of heat-assisted persulfate oxidation of methyl *tert*-butyl ether. Chemosphere 49, 413-420.

Huang, C.C., Li, H.S., Chen, C.H., 2008. Effect of surface acidic oxides of activated carbon on adsorption of ammonia. J. Hazard. Mater. 159, 523-527.

Huling, S.G., Jones, P.K., Els, W.P., Arnold, R.G., 2005. Repeated reductive and oxidative treatments of granular activated carbon. J. Environ. Eng. 131, 287-297.

Huling, S.G., Jones ,P.K., Lee, T.R., 2007. Iron optimization for Fenton-driven oxidation of MTBE-spent granular activated carbon. Environ. Sci. Technol. 41, 4090-4096.

Huling, S.G., Kan, E., Wingo, C., 2009. Fenton-driven regeneration of MTBE-spent granular activated carbon—Effects of particle size and iron amendment procedures. J. Appl. Catal. B: Environ. 89, 651-657.

Huling, S.G., Ko, S., Park, S., Kan, E., 2011. Persulfate oxidation regeneration of MTBE-and chloroform-spent granular activated carbon. J. Hazard. Mater. 192 3, 1484-1490.

Huling, S.G., Kan, E., Caldwell, C., Park, S., 2012. Fenton-driven chemical regeneration of MTBE-spent granular activated carbon – A pilot study. J. Hazard. Mater. 205-206, 55-62.

ITRC, 2005. Overview of Groundwater Remediation Technologies for MTBE and TBA. Interstate Technology and Regulatory Council. MTBE and Other Fuel Oxygenates Team. Technology Overview, 39-63.

Johnson, R., Pankow, J., Bender, D., Price, C., Zogorski, J., 2000. MTBE – to what extent will past releases contaminate community water supply wells? Environ. Sci. Technol. 34, 210A–217A.

Jones, P.K., 2007. Impact of surface chemistry modification on Fenton regeneration of activated carbon. Master thesis, University of Oklahoma, Department of Environmental Science and Engineering.

Jonge, R.J. de, Breure, A.M., Andel, J.G. van, 1996a. Bioregeneration of powdered activated carbon (PAC) loaded with aromatic compounds. Water Research 30, 875-882.

Kan, E., Huling, S.G., 2009. Effects of temperature and acidic pre-treatment on Fenton-driven oxidation of MTBE-spent granular activated carbon. Environ. Sci. Technol. 43, 1493-1499.

Karanfil, T., Kilduff, J.K., 1999. Role of granular activated carbon surface chemistry on the adsorption of organic compounds. I: Priority pollutants. Environ. Sci. Technol. 33, 3217-3224/

Keller, A.A., Sandall, O.C., Rinker, R.G., Mitani, M.M., Bierwagen, B., Snodgrass, M.J., 1998. Cost and performance evaluation of treatment technologies for MTBE-contaminated water. UC Toxics Research and Teaching Program. Report to the governor of California.

Kim, D., Miyahara, T., Noike, T., 1997. Effect of C/N ratio on the bioregeneration of biological activated carbon. Water Science and Technology 36, 239-249.

Leahy, P.P., Thompson, T.H., 1994. US Geological Survey National Water Quality Assessment Program. USGS Open-File Report 94-70, USGS, Reston, VA.

Li, L., Quinlivan, P.A., Knappe, D.R.U, 2002. Effects of activated carbon surface chemistry and pore structure on the adsoprion of organic contaminants from aqueous solution. Carbon 40, 2085-2100.

Liang, C., Wang, Z., Bruell, C.J., 2007. Influence of pH on persulfate oxidation of TCE at ambient temperatures. Chemosphere 66, 106-113.

Liang, C., Guo, Y.Y., Chien, Y.C., Wu, Y.J., 2010. Oxidative degradation of MTBE by pyrite activated persulfate: proposed reaction pathways. Ind. Eng. Chem. Res. 49, 8858-8864.

Liang, S.H., Kao, C.M., Kuo, Y.C., Chen, K.F., 2011. Application of persulfate-releasing barrier to remediate MTBE and benzene contaminated groundwater. J. Hazard. Mater. 185, 1162-1168.

Lyman, W., 1978. Applicability of Carbon Adsorption to the Treatment of Hazardous Industrial Wastes. Carbon Adsorption Handbook; Cheremisinoff, P.; Ellerbusch, F., Eds.; Ann Arbor Science: Ann Arbor, MI, 131-165.

McGinnis, F., 1994. Thermal Regeneration of Activated Carbon. Pollution Eng. (16) 1, 40-42.

MTBE Research Partnership, 1998. Evaluation of Treatment Technologies for Removal of Methyl tertiary-Butyl Ether (MTBE) from Drinking Water: Air stripping, Advanced Oxidation Processes (AOP), Granular Activated Carbon (GAC). Association of California Water Agencies, 910 K Street, Suite 100, Sacramento, CA 95814-3577.

NSTC, 1997. Interagency assessment of oxygenated fuels. Executive Office of the President of the United States, National Science and Technology Council, Committee on Environment and Natural Resources.

Roy, G., Maillacheruvu, K., Mouthon, J., 1999. Bioregeneration of granular activated carbon loaded with 2,4-D. Jour. of Env. Sci. and Health 34, 769-791.

Scholz, M., Martin, R.J., 1997. Ecological equilibrium on biological activated carbon. Water Reasearch 31, 2959-2968.

Seo, G. T., Ohgaki, S., Suzuki, Y., 1997. Sorption characteristics of viological powdered activated carbon in BPAC-MF (biological powdered activated carbon-microfiltration) system for refractory organic removal. Water Science and Technology 35, 163-170.

Silva, M., Fernandes, A., Mendes, A., Manaia, C.M., Nunes, O.C., 2004. Preliminary feasibility study for the use of an adsorption/bioregeneration system for molinate removal from effluents. Water Research 38, 2677-2684.

Snoeyink, V.L., Lai, H.T., Johnson, J.H., Young, J.F., 1974. Symposium on the chemistry of water supply, treatment, and distribution. Ann Arbor Science Publisher, Ann Arbor, Mich., 232-252.

Stocking, A., Deeb, R.A., Flores, A., Stringfellow, W., Talley, J., Brownell, R., and Kavanaugh, M., 2000. Bioremediation of MTBE: A Review from a Practical Perspective. Biodegradation 11 2-3, 187-201.

Sufnarski, M. D., 1999. The Regeneration of Granular Activated Carbon Using Hydrothermal Technology. Master thesis, University of Texas at Austin, 30-42.

To, P.C., Mrinas, B.J., Snoeyink, V.L., Ng, W.J., 2008b. Effect of strongly competing background compounds on the kinetics of trace organic contaminant desorption from activated carbon. Environ. Sci. Technol. 42 (7), 2606-2611.

USEPA, 1998. MTBE Fact Sheet #2. Remediation of MTBE Contaminated Soil and Groundwater. EPA 510-F-97-015, Office of Solid Waste and Emergency Response, United States Environmental Protection Agency, Washington, DC.

USEPA, 2000. Wastewater Technology Fact Sheet. Granular Activated Carbon Absorption and Regeneration. EPA 832-F-00-017, Office of Water, United States Environmental Protection Agency, Washington, DC, 2000.

USEPA, 2012. Clean Up and Treatment. Methyl Teriary Butyl Ether (MTBE). US EPA. www://epa.gov/mtbe/clean.htm. Last updated, December 27, 2012.

Van Vliet, B., 1991. The Regeneration of Activated Carbon. J.S. Afr. Inst. Min. Metalt. 1991, 91 5, 159-167.

Vel Leitner, N.K., Papailhou, A.L., Croue, J.P., Peyro,t J., Dore, M., 1994. Oxidation of Methyl tert-Butyl Ether (MTBE) and Ethyl tert-Butyl Ether (ETBE) by ozone and combined ozone/hydrogen peroxide. Ozone Science and Eng., 16, 41-54.

Vinitnantharat, S., Baral, A., Ishibashi, Y., Ha, S.R., 2001. Quantitative bioregeneration of granular activated carbon loaded with phenol and 2,4-dichlorophenol. Env. Tech. 22, 239-246.

Vuoriranta, P., Remo, S., 1994. Bioregeneration of activated carbon in fluidized GAC bed treating bleached kraft mill secondary effluent. Water Science and Technology 29, 239-246.

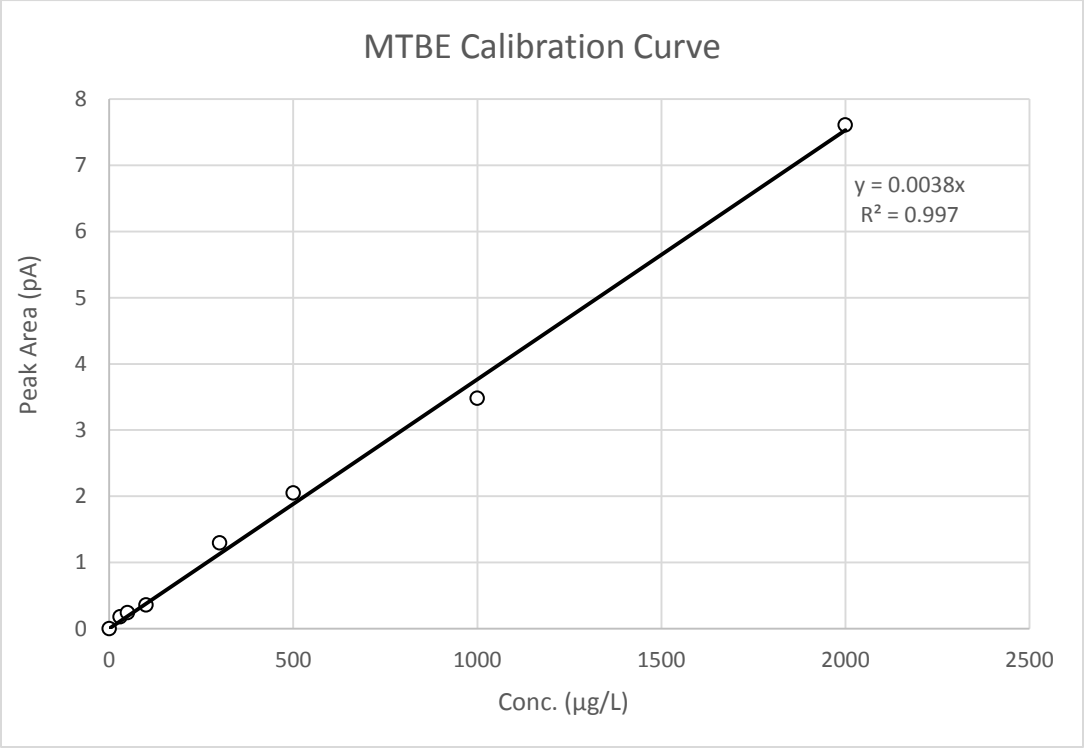
Wilson, J.T., Cho, S. Wilson, B.H., and Vardy, J.A., 2000. Natural Attenuation of MTBE in the Subsurface under Methanogenic Conditions. EPA/600/R-00/006. Washington, D.C: U.S. Environmental Protection Agency, Office of Research and Development.

APPENDICES

A) MTBE Calibration Curve

The analysis used in this experiment are presented in Section 3.5.1. Both phases of the experiments had similar calibration curves. The calibration curve presented is from phase 1 of the experiments.

Reactor	Area	Avg. Area	Conc. (µg/L)
Blank-A	0	0	0
Blank-B	0		
30-A	0.2	0.175	30
30-B	0.15		
50-A	0.21	0.24	50
50-B	0.27		
100-A	0.37	0.355	100
100-B	0.34		
300-A	1.18	1.295	300
300-B	1.41		
500-A	2.01	2.05	500
500-B	2.09		
1000-A	3.56	3.48	1000
1000-B	3.4		
2000-A	8	7.605	2000
2000-B	7.21		



B) Sulfate-free (pH 6.1); Desorption Data (Stock Desorption Solution pH = 5.18)

[MTBE] Initial = 2,036 µg/L = 2 mg/L												
Mass [MTBE] Initial = 81.4 µg = 0.81 mg												
Sample	Area	pH	Average Area	Concen-tration	MTBE Mass Removed	SUM (MTBE Mass Removed)	%(MTBE Mass Removed)	Time	[Sulfate]			
	(pA)		(pA)	(µg/L)	(µg)	(µg)	(%)	(min.)	(mg/L)			
MTBE-0A	0.964	6.29	0.945	248.553	9.942	9.940	12.211	Initial	16.2			
MTBE-0B	0.925	6.29										
DI-0A	0.415	5.39	0.419	110.263	4.411	14.353	17.632	0	5.95			
DI-0B	0.423											
DI-1A	0.297	6.43	0.298	78.289	3.132	3.132	4.671	15	0.961	←	MTBE Init. =	67.05 µg
DI-1B	0.298											
DI-2A	0.255	6.24	0.255	67.105	2.684	5.816	8.674	30	0.588			
DI-2B	0.255											
DI-3A	0.232	6.15	0.216	56.842	2.274	8.089	12.065	45	0.759			
DI-3B	0.200											
DI-4A	0.224	5.81	0.216	56.711	2.268	10.358	15.448	60	0.557			
DI-4B	0.207											
DI-5A	0.206	5.94	0.206	54.211	2.168	12.526	18.682	75	0.481			
DI-5B												
DI-6A	0.192	5.78	0.192	50.526	2.021	14.547	21.696	90	0.487			
DI-6B												
DI-7A	0.160	5.73	0.190	50.000	2.000	16.547	24.679	105	0.252			
DI-7B	0.220											
DI-8A	0.158	5.94	0.206	54.079	2.163	18.711	27.905	120	0.251			
DI-8B	0.253											
DI-9A	0.182	5.64	0.182	47.895	1.916	20.626	30.763	135	0.182			
DI-9B												
DI-10A	0.168	5.98	0.176	46.316	1.853	22.479	33.526	150	0.181			
DI-10B	0.184											
DI-11A	0.273	6.59	0.273	71.842	2.874	25.353	37.812	165	0.266			
DI-11B												
DI-12A	0.221	5.48	0.191	50.132	2.005	27.358	40.802	180	0.112			
DI-12B	0.160											
DI-13A	0.229	7.72	0.229	60.263	2.411	29.768	44.397	195	0.190			
DI-13B												
DI-14A	0.209	7.46	0.209	55.000	2.200	31.968	47.678	210	0.220			
DI-14B												
DI-15A	0.225	6.02	0.225	59.211	2.368	34.337	51.211	225	0.137	←	MTBE Final =	32.713 µg
DI-15B												
	Avrg pH =	6.14										

C) Sulfate (pH 1.1); Desorption Data (Stock Desorption Solution pH = 1.59)

[MTBE] Initial = 2,036 µg/L = 2 mg/L												
Mass [MTBE] Initial = 81.4 µg = 0.81 mg												
Sample	Area	pH	Average Area	Concen-tration	MTBE Mass Removed	SUM (MTBE Mass Removed)	%(MTBE Mass Removed)	Time	[Sulfate]			
	(pA)		(pA)	(µg/L)	(µg)	(µg)	(%)	(min.)	(mg/L)			
MTBE-0A	1.14	6.11	0.937	246.579	9.863	11.947	14.677	Initial	16.1			
MTBE-0B	0.734	6.11										
Acid-0A	0.292	1.17	0.287	75.526	3.021	12.884	15.828	0	6,630			
Acid-0B	0.282											
Acid-1A	0.14	1.12	0.128	33.684	1.347	1.347	1.966	15	7,220	←	MTBE Init. =	68.52 µg
Acid-1B	0.116											
Acid-2A	0.13	1.12	0.095	25.000	1.000	2.347	3.426	30	7,380			
Acid-2B	0.06											
Acid-3A	0.048	1.08	0.087	22.763	0.911	3.258	4.755	45	7,320			
Acid-3B	0.125											
Acid-4A	0.132	1.07	0.132	34.737	1.389	4.647	6.782	60	7,260			
Acid-4B												
Acid-5A	0.077	1.11	0.094	24.737	0.989	5.637	8.227	75	7,320			
Acid-5B	0.111											
Acid-6A	0.099	1.07	0.087	22.895	0.916	6.553	9.563	90	7,260			
Acid-6B	0.075											
Acid-7A	0.105	1.09	0.103	26.974	1.079	7.632	11.138	105	6,990			
Acid-7B	0.1											
Acid-8A	0.13	1.08	0.112	29.474	1.179	8.811	12.858	120	7,090			
Acid-8B	0.094											
Acid-9A	0.095	1.09	0.095	25.000	1.000	9.811	14.318	135	7,060			
Acid-9B												
Acid-10A	0.12	1.08	0.120	31.579	1.263	11.074	16.161	150	7,270			
Acid-10B												
Acid-11A	0.1	1.11	0.105	27.632	1.105	12.179	17.774	165	7,360			
Acid-11B	0.11											
Acid-12A	0.14	1.06	0.115	30.263	1.211	13.389	19.541	180	7,220			
Acid-12B	0.09											
Acid-13A	0.14	1.08	0.138	36.184	1.447	14.837	21.653	195	7,600			
Acid-13B	0.135											
Acid-14A	0.099	1.08	0.099	26.053	1.042	15.879	23.174	210	7,480			
Acid-14B												
Acid-15A	0.092	1.07	0.091	23.947	0.958	16.837	24.572	225	7,660	←	MTBE Final =	51.683 µg
Acid-15B	0.09											
	avr pH =	1.09										

D) Sulfate (pH 5.1); Desorption Data (Stock Desorprtion Solution pH = 5.78)

[MTBE] Initial = 2,036 µg/L = 2 mg/L												
Mass [MTBE] Initial = 81.4 µg = 0.81 mg												
Sample	Area	pH	Average Area	MTBE Concen-tration	MTBE Mass Removed	SUM (MTBE Mass Removed)	%(MTBE Mass Removed)	Time	[Sulfate]			
	(pA)		(pA)	(µg/L)	(µg)	(µg)	(%)	(min.)	(mg/L)			
MTBE-0A	0.824	5.92	0.972	255.789	10.232	10.232	12.570	Initial	15.5			
MTBE-0B	1.12	5.92										
SO4-0A	0.375	4.37	0.307	80.789	3.232	13.463	16.540	0	7,130			
SO4-0B	0.239											
SO4-1A	0.13	4.8	0.133	34.868	1.395	1.395	2.053	15	7,400	←	MTBE Init. =	67.94 µg
SO4-1B	0.135											
SO4-2A	0.116	5.2	0.121	31.711	1.268	2.663	3.920	30	7,640			
SO4-2B	0.125											
SO4-3A	0.128	5.21	0.130	34.079	1.363	4.026	5.926	45	7,580			
SO4-3B	0.131											
SO4-4A	0.14	5.32	0.140	36.842	1.474	5.500	8.095	60	7,420			
SO4-4B												
SO4-5A	0.132	5.23	0.132	34.737	1.389	6.889	10.141	75	7,470			
SO4-5B												
SO4-6A	0.107	5.25	0.110	28.816	1.153	8.042	11.837	90	7,390			
SO4-6B	0.112											
SO4-7A	0.089	5.18	0.085	22.368	0.895	8.937	13.154	105	7,380			
SO4-7B	0.081											
SO4-8A	0.128	5.17	0.128	33.684	1.347	10.284	15.137	120	7,480			
SO4-8B												
SO4-9A	0.107	5.3	0.115	30.132	1.205	11.489	16.911	135	7,510			
SO4-9B	0.122											
SO4-10A	0.127	5.21	0.127	33.421	1.337	12.826	18.879	150	7,400			
SO4-10B												
SO4-11A	0.123	5.25	0.123	32.368	1.295	14.121	20.785	165	7,340			
SO4-11B												
SO4-12A	0.069	5.28	0.079	20.789	0.832	14.953	22.009	180	7,210			
SO4-12B	0.089											
SO4-13A	0.106	5.16	0.107	28.158	1.126	16.079	23.666	195	7,250			
SO4-13B	0.108											
SO4-14A	0.138	5.19	0.122	32.105	1.284	17.363	25.557	210	7,290			
SO4-14B	0.106											
SO4-15A	0.074	5.05	0.068	17.895	0.716	18.079	26.610	225	7,330	←	MTBE Final =	49.861 µg
SO4-15B	0.062											
	avrg pH =	5.14										

E) Sulfate-free (Adj. pH 7.0); Desorption Data (Stock Desorption Solution pH = 5.18)

[MTBE] Initial = 818 µg/L = 0.82 mg/L

Mass [MTBE] Initial = 32.7 µg = 0.033 mg

	Sample	Area	pH	Average Area	Concen-tration	MTBE Mass Removed	SUM (MTBE Mass Removed)	%(MTBE Mass Removed)	Time	[Sulfate]				
		(pA)		(pA)	(µg/L)	(µg)	(µg)	(%)	(min.)	(mg/L)				
pH-	MTBE-0A	0.176	5.86	0.157	41.184	1.647	1.647	5.037	Initial	1.62				
pH-	MTBE-0B	0.137	5.86											
pH-	DI-0A	0.160	5.78	0.159	41.711	1.668	3.316	10.140	0	1.38				
pH-	DI-0B	0.157												
pH-	DI-1A	0.123	6.41	0.100	26.316	1.053	1.053	3.584	15	0.389	←	MTBE Init.	29.38	µg
pH-	DI-1B	0.077												
pH-	DI-2A	0.122	7.39	0.111	29.211	1.168	2.221	7.560	30	0.362				
pH-	DI-2B	0.100												
pH-	DI-3A	0.100	7.30	0.088	23.158	0.926	3.147	10.713	45	0.338				
pH-	DI-3B	0.076												
pH-	DI-4A	0.071	6.91	0.077	20.132	0.805	3.953	13.453	60	0.393				
pH-	DI-4B	0.082												
pH-	DI-5A	0.099	6.85	0.087	22.895	0.916	4.868	16.571	75	0.264				
pH-	DI-5B	0.075												
pH-	DI-6A	0.087	7.24	0.087	22.895	0.916	5.784	19.688	90	0.120				
pH-	DI-6B													
pH-	DI-7A	0.127	7.80	0.100	26.316	1.053	6.837	23.270	105	0.750				
pH-	DI-7B	0.073												
pH-	DI-8A	0.087	7.03	0.087	22.895	0.916	7.753	26.387	120	0.298				
pH-	DI-8B													
pH-	DI-9A	0.146	6.83	0.119	31.184	1.247	9.000	30.633	135	0.293				
pH-	DI-9B	0.091												
pH-	DI-10A	0.074	6.95	0.072	18.947	0.758	9.758	33.213	150	0.158				
pH-	DI-10B	0.070												
pH-	DI-11A	0.082	7.75	0.082	21.579	0.863	10.621	36.151	165	0.197				
pH-	DI-11B													
pH-	DI-12A	0.070	6.74	0.077	20.263	0.811	11.432	38.909	180	0.279				
pH-	DI-12B	0.084												
pH-	DI-13A	0.063	8.26	0.080	21.053	0.842	12.274	41.776	195	0.225				
pH-	DI-13B	0.097												
pH-	DI-14A	0.082	5.95	0.082	21.579	0.863	13.137	44.714	210	0.317				
pH-	DI-14B													
pH-	DI-15A	0.077	5.91	0.081	21.184	0.847	13.984	47.598	225	0.161	←	MTBE Fina	15.396	µg
pH-	DI-15B	0.084												
		avr pH =	6.94											

F) Sulfate (Adj. pH 7.1); Desorption Data (Stock Desorption Solution pH = 1.59) (Desorbed using DIW)

[MTBE] Initial = 1,292 µg/L = 1.3 mg/L

Mass [MTBE] Initial = 51.7 µg = 0.052 mg

	Sample	Area	pH	Average Area	Concen-tration	MTBE Mass Removed	SUM (MTBE Mass Removed)	%(MTBE Mass Removed)	Time	[Sulfate]			
		(pA)		(pA)	(µg/L)	(µg)	(µg)	(%)	(min.)	(mg/L)			
pH-	MTBE-0A	0.15	1.13	0.175	46.053	1.842	1.842	3.563	Initial	7,400			
pH-	MTBE-0B	0.2	1.13										
pH-	Acid-0A	0.177	4.79	0.169	44.474	1.779	3.621	7.004	0	630			
pH-	Acid-0B	0.161											
pH-	Acid-1A	0.081	4.26	0.094	24.737	0.989	0.989	2.057	15	46.8	←	MTBE Init.	48.08 µg
pH-	Acid-1B	0.107											
pH-	Acid-2A	0.077	6.3	0.082	21.447	0.858	1.847	3.842	30	14.3			
pH-	Acid-2B	0.086											
pH-	Acid-3A	0.086	7.6	0.082	21.579	0.863	2.711	5.638	45	8.35			
pH-	Acid-3B	0.078											
pH-	Acid-4A	0.091	7.26	0.101	26.447	1.058	3.768	7.838	60	4.87			
pH-	Acid-4B	0.11											
pH-	Acid-5A	0.095	7.67	0.111	29.079	1.163	4.932	10.257	75	3.48			
pH-	Acid-5B	0.126											
pH-	Acid-6A	0.085	6.75	0.104	27.237	1.089	6.021	12.523	90	3.46			
pH-	Acid-6B	0.122											
pH-	Acid-7A	0.084	7.92	0.094	24.737	0.989	7.011	14.581	105	2.39			
pH-	Acid-7B	0.104											
pH-	Acid-8A	0.1	7.79	0.095	24.868	0.995	8.005	16.650	120	2.12			
pH-	Acid-8B	0.089											
pH-	Acid-9A	0.098	8.13	0.106	27.763	1.111	9.116	18.960	135	1.65			
pH-	Acid-9B	0.113											
pH-	Acid-10A	0.099	6.9	0.105	27.632	1.105	10.221	21.258	150	1.36			
pH-	Acid-10B	0.111											
pH-	Acid-11A	0.076	7.57	0.096	25.132	1.005	11.226	23.349	165	1.40			
pH-	Acid-11B	0.115											
pH-	Acid-12A	0.057	7.4	0.074	19.474	0.779	12.005	24.969	180	1.02			
pH-	Acid-12B	0.091											
pH-	Acid-13A	0.096	8.36	0.096	25.263	1.011	13.016	27.071	195	1.05			
pH-	Acid-13B												
pH-	Acid-14A	0.081	8.47	0.101	26.579	1.063	14.079	29.282	210	1.09			
pH-	Acid-14B	0.121											
pH-	Acid-15A	0.11	6.69	0.097	25.526	1.021	15.100	32.627	225	0.93	←	MTBE Fina	32.980 µg
pH-	Acid-15B	0.084											
		avr pH =	7.12										

G) Sulfate (Adj. pH 1.1) Desorption Data (Stock Desoprtion Solution pH = 5.78)

[MTBE] Initial = 1,247 µg/L = 1.3 mg/L
Mass [MTBE] Initial = 49.9 µg = 0.05 mg

	Sample	Area	pH	Average Area	Concen-tration	MTBE Mass Removed	SUM (MTBE Mass Removed)	%(MTBE Mass Removed)	Time	[Sulfate]		
		(pA)		(pA)	(µg/L)	(µg)	(µg)	(%)	(min.)	(mg/L)		
pH-	MTBE-0A	0.218	5.24	0.238	62.500	2.500	2.705	5.421	Initial	7,440		
pH-	MTBE-0B	0.257	5.24									
pH-	SO4-0A	0.219	1.19	0.222	58.421	2.337	4.837	9.693	0	7,030		
pH-	SO4-0B	0.225										
pH-	SO4-1A	0.0834	1.07	0.081	21.237	0.849	0.849	1.884	15	7,140	←	MTBE Init. 45.06 µg
pH-	SO4-1B	0.078										
pH-	SO4-2A	0.066	1.06	0.099	26.053	1.042	1.892	4.198	30	7,200		
pH-	SO4-2B	0.132										
pH-	SO4-3A	0.063	1.03	0.075	19.737	0.789	2.681	5.950	45	7,430		
pH-	SO4-3B	0.087										
pH-	SO4-4A	0.08	1.05	0.077	20.263	0.811	3.492	7.749	60	7,360		
pH-	SO4-4B	0.074										
pH-	SO4-5A	0.078	1.05	0.089	23.421	0.937	4.428	9.828	75	7,730		
pH-	SO4-5B	0.1										
pH-	SO4-6A	0.093	1.04	0.087	22.895	0.916	5.344	11.860	90	7,510		
pH-	SO4-6B	0.081										
pH-	SO4-7A	0.065	1.08	0.099	26.053	1.042	6.386	14.173	105	7,520		
pH-	SO4-7B	0.133										
pH-	SO4-8A	0.07	1.01	0.081	21.316	0.853	7.239	16.065	120	7,320		
pH-	SO4-8B	0.092										
pH-	SO4-9A	0.058	1.05	0.071	18.553	0.742	7.981	17.712	135	7,740		
pH-	SO4-9B	0.083										
pH-	SO4-10A	0.093	1.06	0.082	21.579	0.863	8.844	19.628	150	7,290		
pH-	SO4-10B	0.071										
pH-	SO4-11A	0.056	1.06	0.089	23.421	0.937	9.781	21.707	165	7,520		
pH-	SO4-11B	0.122										
pH-	SO4-12A	0.1	1.07	0.085	22.237	0.889	10.671	23.681	180	7,420		
pH-	SO4-12B	0.069										
pH-	SO4-13A	0.022	1.02	0.056	14.737	0.589	11.260	24.989	195	7,310		
pH-	SO4-13B	0.09										
pH-	SO4-14A	0.04	1.08	0.050	13.158	0.526	11.786	26.157	210	7,480		
pH-	SO4-14B	0.06										
pH-	SO4-15A	0.026	1.01	0.033	8.684	0.347	12.134	26.928	225	7,420	←	MTBE Fina 32.926 µg
pH-	SO4-15B	0.04										
		Avrg pH=	1.06									

VITA

Thomas Andrew Hutson

Candidate for the Degree of

Master of Science

Thesis: IMPACT OF ACIDIC CONDITIONS AND HIGH SULFATE CONCENTRATIONS ON MTBE MASS TRANSPORT AND MASS TRANSFER IN GAC

Major Field: Civil and Environmental Engineering

Biographical:

Education:

Completed the requirements for the Master of Science in Civil and Environmental Engineering at Oklahoma State University, Stillwater, Oklahoma in August, 2014.

Completed the requirements for the Bachelor of Science in Environmental Health and Science at East Central University, Ada, Oklahoma in 2011.

Completed the requirements for Minor of Math and Chemistry at East Central University, Ada, Oklahoma in 2011.

Experience:

May, 2013 – July, 2014. Accurate Environmental LLC. (Accurate Engineering Services).

May, 2011 – September, 2011. Environmental Protection Agency (Physical Science Technician), R.S. Kerr Environmental Research Center, Ada OK.

May, 2009 – April, 2011. R.S. Kerr Environmental Research Center, Environmental Research Apprenticeship Program, East Central University, Ada OK.