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Remediating MTBE Contamination with Hydrophobic Membranes and Chemical Oxidation

A Major Qualifying Project to be submitted to the faculty of
Worcester Polytechnic Institute in partial fulfillment of the requirements for the
Degree of Bachelor of Science

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ABSTRACT

Volatile organic compounds (VOC) have been contaminating lakes, streams and groundwater since the onset of the industrial era. Methyl tert-butyl ether (MTBE), a component of gasoline, has been introduced to the environment in large quantities over the last past few decades. It presents a hazard to the health and welfare of communities across the United States. Several remediation techniques have been put into place; however, they are both inefficient and costly. Hydrophobic media have been proven to offer selective filtering of MTBE from water. A panel of hydrophobic polymer membranes was investigated for the ability to resist degradation when exposed to aggressive oxidizing solutions that can be used to decompose MTBE while fostering selective-permeation by MTBE. These two properties propose new options for the remediation of MTBE contamination when taken in concert.

ACKNOWLEDGEMENTS

The project group would like to acknowledge the groups and individuals that contributed to this project, making its completion possible.

First, the team wishes to thank the Worcester Polytechnic Institute Departments of Chemical Engineering and Civil & Environmental Engineering. The Civil & Environmental Engineering Department was kind enough to make laboratory space and equipment available to us. The faculty members and teaching assistants that operate the lab were not only willing to give us access to their facilities, but they also took the time to answer any and all questions that we asked of them. It was a pleasure to conduct our research in such a clean and well organized environment. The Chemical Engineering Department also devoted crucial resources and support to the project.

Graduate student Man Phewluangdee aided the group in the completion of goniometer derived contact angle measurements. He allowed us access to his lab and equipment each time we requested his help. Perhaps more notably, he took a significant amount of time to teach us the procedures for making the much needed measurements.

The project would have experienced serious setbacks without the time, energy, and advice of the aforementioned people and organizations. In each case, busy individuals with tight schedules devoted themselves to meeting our needs, and for that we are truly appreciative.

The team also wishes to thank Professor John A. Bergendahl of the Civil & Environmental Engineering Department. Professor Bergendahl , beyond giving us access to his laboratory, went out of his way to provide us directly with polymer membrane samples and essential testing supplies. Beyond those contributions, Professor Bergendahl's own research added a great deal to the inspiration for and the success of the project.

Finally, the group wishes to thank Professor Robert W. Thompson, the project advisor. At the onset of the project, Professor Thompson devised and established our aims. Despite his very busy schedule, Professor Thompson took the time to provide the team with key advice and direction over the course of the project in weekly meetings, as well as outside of normal business hours. It was only through his vision, enthusiasm and guidance that the conclusion to the project was realized.

EXECUTIVE SUMMARY

Background

In 1981, the Environmental Protection Agency authorized use of up to ten percent, by volume, Methyl tert-Butyl Ether (MTBE) in gasoline. With this authorization came widespread use of MTBE in the United States. The United States shifted away from lead based fuels in 1979 and began using MTBE as an oxygenate for gasoline, improving both gas mileage and emissions. Accidental releases of gasoline from pipes and underground storage tanks have contaminated water aquifers in numerous communities across the United States. In many cases, the contamination vastly exceeds the health standards by the Environmental Protection Agency. MTBE is highly soluble in water and can easily pass through soil and contaminate groundwater. The methods currently being used to remediate ground water are both inefficient and expensive. Hydrophobic zeolites have shown a propensity for absorbing MTBE from solution. Additionally, strong oxidizing reactions have proven to be able to degrade and mineralize MTBE. Polymer membranes offer a medium for transporting MTBE, in much the same way as zeolites, but in a sustainable manner that can also allow direct remediation by oxidation.

Methodology

A series of objectives were developed at the beginning of the project, each requiring a series of experiments for their realization. The first objective of the project was to prove that the four membranes acquired, all of which were marketed as hydrophobic, could meet the basic requirements for use in the more involved experiments necessary to draw conclusions with regard to the project aim. The second objective of the project was to make solutions of MTBE mirroring those concentrations that appear in MTBE contaminated areas. The third established objective of the project accomplished two aims. Through experiments, the membranes were tested for the ability to pass MTBE and for information allowing a comparison of each membrane's ability to transport MTBE. The fourth objective made use of the membrane providing the most rapid transport of MTBE in the second objective to remove MTBE from solution and transport it into a strong oxidizing solution for mineralization.

The first objective entailed three tests, each designed to address some aspect of membrane viability and the membrane design. Teflon, Nylon, polypropylene, and PVDF membranes were gathered for testing. Drop-wise testing, with drops of water and hydrogen peroxide being placed onto each membrane, was utilized to assess the apparent hydrophobic character of the membranes based on the shape taken on by the liquid s when in contact with the polymer surface. The next test allowed the quantification of the hydrophobic character of the membranes. A goniometer was used to measure the water contact angle for each membrane. The final test for the first objective was to load the membranes into the full apparatus assembly and charge one of the reservoirs (Figure 4). The membrane was tested with water, and then hydrogen peroxide, in one reservoir arm of the apparatus and air in the other arm of the apparatus. The apparatus was then disassembled and inspected for any leaks or transport, a final check of the hydrophobic character of the membranes.

The second objective was reasonably straight forward. Solutions were prepared in keeping with respective calculations.

The third objective was centered on a single series of experiments. Having proven the integrity of the apparatus in the first objective, the entire apparatus was assembled and then charged with a MTBE solution in one reservoir and water on the opposing side. The concentrations were recorded over a thirty minute testing period to allow an analysis of the manner in which the concentration was reduced over time.

Completion of the fourth objective necessitated four experiments. Tests were conducted to ensure that hydrogen peroxide and ferrous iron ions were not able to pass through the membrane tested. The membrane was then tested with MTBE transport across its boundaries, into a strong oxidizing solution. The temperature rise in the individual reservoirs of the apparatus was measured to identify the progress and location of the reaction stemming from the heat of reaction for oxidation of the MTBE. After the membrane had been used in a test involving the oxidation of MTBE at its surface, the water contact angle for the membrane was once again tested to identify any degradation.

Results and Discussion

When we started, we had four membranes for which were run through a series of tests to properly determine the membrane which would eventually be used in Fenton's oxidation testing. During the dropwise testing, Polyvinylidene difluoride was removed as a potential candidate because of the lack of hydrophobic nature it exuded. During the flux testing, the Teflon membrane was the membrane that best approached half of the original concentration of MTBE. From this test, the Teflon membrane was chosen. Although, when the Teflon membrane was tested using the goniometer. The Teflon membrane was not the membrane that gave the highest contact angle. We remained with the Teflon membrane because the flux testing was the most important experiment that had been run to this point. From there, we began the Fenton's oxidation testing using the Teflon membrane.

The effective removal of the MTBE was proven in the full scale test combining the use of Fenton's oxidation reagents and Teflon membranes. The oxidizing reagents acted quickly upon contact with the MTBE with most of the removal taking place within the first 5 minutes. Within 30 minutes of the experiment, the MTBE concentration within the reservoir had effectively removed close to 80 percent of the initial concentration for two trial runs.

Conclusions and Recommendation

The Teflon, Nylon and polypropylene membranes all fostered MTBE transport, and so other membranes resistant to strong solutions should be tested for the ability to rapidly transport MTBE, possibly outpacing the transport through Teflon. Independent of the which hydrophobic polymer is ultimately found to have the greatest capability to rapidly transport MTBE, various industrial scale remediation systems should be investigated to identify the best way to implement a scheme involving MTBE transport through a hydrophobic membrane into an oxidizing solution.

BACKGROUND

Methyl Tert-Butyl Ether

Methyl tert-Butyl Ether (MTBE) is an additive to gasoline that allows a cleaner and more efficient combustion in common gasoline burning engines. Use of MTBE began in 1979, displacing lead-based additives that were used throughout the industry. In 1990, the Clean Air Act Amendments (CAAA) were passed into law requiring that gasoline oxygenates be used in any urban area where there are unhealthy levels of smog and pollution (Environmental Protection Agency, *Gasoline*, 2007).

The synthetic molecule was initially used in low concentrations, from 0.5 to 3.5 percent by volume (Napoli, Kaiser, Bern & Associates, 2000). In 1981, the Environmental Protection Agency authorized use of up to ten percent by volume MTBE in gasoline and in 1988, two years before use of oxygenates were mandated, the acceptable level of MTBE in gasoline was increased to 15 percent (Napoli, Kaiser, Bern & Associates, *A History of MTBE*, 2000). In 1993, "MTBE was the second most produced organic compound (second only to gasoline) in the U.S." (McCaulou, D.R. & Slater, J.C., *MTBE in Groundwater: Physical Properties and Regulatory Outlook* , 2002).

The oxygen in MTBE reduces the amount of pollution rendered by the combustion of gasoline, by increasing the oxygen-to-fuel ratio and enhancing the octane rating of the gasoline. A study prepared by Systems Application International, Inc., has shown that the use of oxygenated fuels in the concentrations made available to consumers reduces the carbon monoxide production by up to 14 percent (Howard, C. J., Russell, A., Atkinson, R., & Calvert, J., *AIr Quality Effects of the Winter Oxyfuel Program,* 1996). Given the stoichiometry of combustion, the oxygen enrichment of the mixture improves gas mileage, and reduces the amount of hydrocarbon contained carbon that is converted into carbon monoxide (Howard, C. J., Russell, A., Atkinson, R., & Calvert, J., *AIr Quality Effects of the Winter Oxyfuel Program* , 1996).

Many oil refineries across the United States continue to rely on MTBE to help achieve the standards set-forth by the Federal Clean Air Act, which, since 1963, has limited various types of atmospheric emissions throughout the United States in an effort to protect the environment. Eighty-seven percent of the gasoline that is reformulated includes oxygenates containing MTBE (Environmental Protection Agency, *Gasoline*, 2007). Because of the high concentrations of MTBE in gasoline and the large quantities of gasoline distributed, stored and sold across the country, tremendous volumes of MTBE are at large.

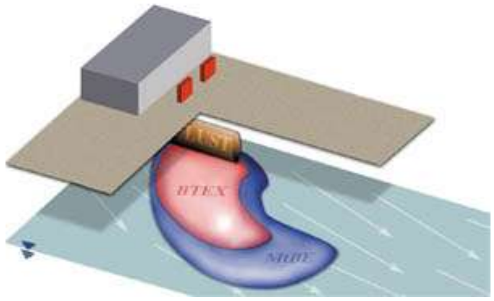


Figure 1: MTBE Spill and Expansion from LUST. MTBE spread compared to BTEX

MTBE is highly soluble in water and so MTBE released into the environment associates with ground water to a large extent. “At 25 degrees Celsius the water solubility of MTBE is about 5,000 milligrams per liter for a gasoline that is 10 percent MTBE by weight” (Paul J. Squillace, *Environmental Behavior and fate of Methyl tert-Butyl Ether(MTBE)*, 1998). This means that any time there is a leak of MTBE, a significant portion of it dissolves into the aqueous environment. The high water-solubility and low sorption of MTBE also results in a significantly faster spread of the compound when compared to other organic components of gasoline when released. This differential in speed of dissemination is depicted in Figure 1, with the movement of MTBE over a given time being compared to that of BTEX, a combination of volatile organic compounds.

Underground Storage of MTBE

Gasoline is stored in liquid underground storage tanks (LUSTs) at gas stations across the United States. For decades, these tanks were constructed out of steel that was not resistant to corrosion. While the addition of MTBE does not make stored fuels more corrosive (California Environmental Protection Agency, *Compatibility and Permeability of Oxygentated Fuels to Materials in Underground Storage and Dispensing Equipment*), many of these tanks are not properly maintained and, over the course of decades of neglect, they deteriorate.

The storage tanks leak their contents into the ground water in the areas around gas stations. In California, "more than twenty public drinking water wells…have ceased water production for this reason" (Happel, A., *Sleuthing MTBE with Statistical Data*, 1999). Even those tanks that are not in a state of disrepair may leak gasoline due to improper installation, hardware malfunction or tank overflows or spills.

Storage tank leaks have been identified across the country. "In the United States alone, releases of gasoline containing MTBE may have occurred from more than 250,000 leaking underground storage tanks, potentially threatening over 9000 community water supply wells" (Nada Al Ananzeh et. al., *Kinetic Model for the Degradation of MTBE by Fenton's Oxidation*, 2005) Another report puts the number of confirmed leaking UST sites at 539,623. Of the half-million sites recognized by that report, it is estimated that twenty-five percent of the sites include the release of MTBE (Sweet, F., Kauffman et Al., *An Estimate of the National Cost for Remediation of MTBE Releases…, 2005).*

MTBE Releases

Pascoag, Rhode Island

In Pascoag, Rhode Island, the rock aquifer that the town sits upon and which permeates the town's water supply is completely contaminated by MTBE. Since 2001, MTBE levels in the town's ground water have exceeded the maximum allowable MTBE level set in Rhode Island by a dramatic margin. The limit of 40 µg/L was established by the state branch of the Department of Health. In some cases, tests have yielded concentrations up to 15,000 µg/L. The MTBE level is measured in terms of grams per liter because the measurement is taken as the water is pumped from the subterranean reservoir beneath the town.

Pascoag's drinking water is drawn from a single well and so, with the contamination of that well, the people of Pascoag have been cut off from a "water source of their own" (Allen, J., & Boving, T., *MTBE Drinking Water Contamination in Pascoag, RI* , 2006). The town is being driven toward bankruptcy because the situation with their ground water has forced the townspeople to ship in bottled water and to purchase water from a neighboring town. The purchase of water represents a financial burden of more than $1,000,000.00 a year.

The source of the contamination in Pascoag was a single abandoned gas station. The leak spread gasoline from beneath the gas station and contaminated an area covering nearly twenty acres and over 100 feet into the ground. Since the problem was identified, the EPA – New England Region has appropriated almost two and a half million dollars to the cleanup of MTBE at the Pascoag site. The money has been devoted, in large part, to the installation of on- and off-site remediation equipment. A pilot-scale Biomass Concentrate Reactor (BCR) has been installed in Pascoag as a proof of concept (Environmental Protection Agency, *Underground Storage Tanks, 2004*). The reactor is capable of treating a flow of five gallons-per-minute and reducing the MTBE levels to within the RI EPA standard of 20-40 parts per billion.

Over the course of the cleanup and remediation efforts, the EPA and the Department of Environmental Management have removed the source of the leak and several thousand yards of heavily contaminated soil. More than eight million gallons of contaminated groundwater have been pumped through the remediation system, which operated almost constantly from 2003 to October 2007. The MTBE from 3,000 gallons of gasoline have been extracted from contaminated groundwater (Department of Environmental Management, *Pascoag Fact Sheet 2007*, 2007).

Santa Monica, California; Charnock Sub-basin

In addition to the large-scale release of MTBE in Pascoag, Rhode Island another large spill of MTBE has contaminated wells in Santa Monica, California. The city receives its drinking water from well-fields which are supplemented by water from the Colorado River. Leaks from underground gasoline storage tanks, above ground storage tanks, and pipelines have contaminated seven of the wells in two of these well-fields. The contamination was discovered in the Arcadia Well-field and the Charnock Sub-basin in 1995 during water sampling by the city.

The concentrations of MTBE in the well-water in the Acadia Well-field are much lower than in the Pascoag groundwater, ranging from levels between 20 ppb to 86.5 ppb (Environmental Protection Agency, *MTBE Project*, 1998). The regional branch of the EPA directed Mobil Oil, the proprietors of the

USTs, the above ground tanks, and pipelines, to fund and lead a cleanup of the contaminated area. The gas station to which the leaking tanks and pipelines were connected was removed, along with several thousand cubic yards of contaminated soil. An activated carbon bed remediation system began pumping MTBE laced groundwater in October, 1997. The water containing MTBE passes through three beds of activated carbon before being reintroduced to the public water system, meeting EPA standards.

The Charnock Sub-basin experienced significantly more contamination, around 610 ppb within the wells. Twenty-six leaking USTs and two leaking pipelines have been removed in connection with MTBE contamination of the Charnock Sub-basin. Contaminated soil was also removed from the site.

Dallas Texas; Lake Tawakoni

Dallas, Texas has also suffered from the effects of MTBE being introduced into the environment in large quantities. In March of 2000, a gasoline pipeline, the Explorer Pipeline, was found to have a rupture 50 inches long that was leaking into East Caddo Creek. East Caddo Creek is a tributary for Lake Tawakoni, running twenty-eight miles from the site of the gasoline pipe rupture to the lake inlet. Steps were immediately taken to limit the spread and impact of the spill; floating and cofferdams were used in conjunction with vacuums to staunch the flow of the gasoline and remove it from the watershed. However, runoff rainwater served as a driving force to disseminate the spilled gasoline. Within three days of the discharge, the gasoline had traveled almost thirty miles.

Lake Tawakoni was used as a source of water for the Dallas Water Utilities (DWU) which is responsible for distributing water to millions of people within the limits of the City of Dallas

(Odencrantz, J. E. , *Environmental Impacts from Largest MTBE Release in History*, 2004). The gasoline contained MTBE and upon discovery of that fact, the lines pumping water from the lake were turned off. The best estimate offered by the DWU for the volume released from the pipe rupture is a half-million gallons of gasoline, which left the DWU a deficit of 190 million gallons each day. The problem was solved at significant expense through the construction of an underground pipeline to another lake, Lake Ray Hubbard (Odencrantz, J. E. , *Environmental Impacts from Largest MTBE Release in History*, 2004.)

Health Effects

The health effects of MTBE are not yet completely understood and it is not yet certain whether or not it should be classified as an imminent human health risk. It is categorized by the EPA as a possible carcinogen to humans. Prolonged exposure to highly concentrated MTBE vapors has resulted in cancerous polyp formation on the kidneys in rats as well as displaying other, non-cancerous, complications. MTBE has a number of less severe effects on humans, ranging from nose and throat irritation to headaches to nausea and vomiting. In Pascoag, RI many of these symptoms were exhibited throughout the community. Individuals suffered from migraine-grade headaches. Other denizens began to develop respiratory problems, wheezing heavily and often. In some of the worst cases of exposure, victims developed open sores and blisters on their lips.

MTBE contamination of soil and ground water is occurring throughout the country. The issue is being addressed in an effort to assuage the problems that a good portion of the population is experiencing with regard to one of their basic needs, drinking water. Degradation of MTBE by advanced oxidation offers a means of rectifying the problem. Fenton's oxidation has proven to be very effective in breaking down MTBE into a number of different products.

Remediation

Unfortunately, the problem of MTBE contamination in ground water and wells across the United States will not rectify itself. MTBE is resistant to biodegradation and does not break down to a large extent over time. MTBE is also highly soluble in water and so does not readily precipitate out of solution.

Several techniques are currently being used to cleanse MTBE contamination from ground water and soil. Soil vaporization extraction (SVE) forces air through contaminated aquifers, volatizing the contaminants. The vaporized MTBE is then collected by a vacuum for treatment by air stripping and disposal. When MTBE is dissolved in water, it must be pumped out of the wells for treatment. Granular activated carbon (GAC) beds can be used to remove MTBE from solution, however, MTBE does not have much affinity for organic compounds, and so must be flushed through the bed numerous times to yield sufficiently low concentrations (Environmental Protection Agency, *Clean Up and Treatment*, 2007.)

Advanced oxidation processes have been shown to oxidize up to 99% of MTBE within five minutes of the onset of treatment (Nada Al Ananzeh, J. A., *Kinetic Model for the Degradation of MTBE by Fenton's Oxidation,* 2005.) This method is one of the more promising means of dealing with and destroying MTBE, but it requires the separation of MTBE from the water supply so that the oxidizing agents and the products of oxidation do not remain in the water stream.

Zeolite Separation

New technologies are being developed and investigated in an effort to deal with the problem of MTBE contamination. Zeolites, which are "nano-porous, crystalline alumino-silicates with framework structures containing silica and alumina tetrahedra, "(N. Koryabkina et Al., *Adsorption of Disinfection Byproducts on Hydrophobic Zeolites…*, 2007) have been explored as a means of selectively removing MTBE from a water stream. Hydrophobic and organophillic zeolites repel water while allowing the transport of MTBE. The hydrophobic nature of the compounds comes from the particular arrangement of the silica tetrahedra, relative position to alumina, and the amount of alumina tetrahedra in the structure. Silicate structures are comprised of two types of groups, silanol sites, which is a silicon group bonded to an hydroxyl group (ΞSiOH,) and a pair of silicon atoms bonded to an oxygen atom(Ξ Si – O – Si Ξ.) The silicon-oxygen-silicon bonds are not polarized and so should repel polarized water molecules. This repulsion of water molecules from the surface of the crystalline silicates creates hydrophobic zeolite particles. The rigid crystalline structure of the zeolites offers pores that can adsorb organic compounds, such as MTBE. In experiments, hydrophobic zeolites have performed better in terms of MTBE adsorption and removal than granular activated carbon beds (Adsorption of disinfection…, Feb 2007). Once saturated with organic MTBE, the zeolite bed can be cleansed through advanced oxidation by hydroxyl radicals, extracting and mineralizing the targeted compound (N. Koryabkina et Al., *Adsorption of Disinfection Byproducts on Hydrophobic Zeolites…*, 2007).

This zeolite technology is not, however, the direct answer to the problem of cleansing MTBE contaminated water. The transition from laboratory experiments to industrial scale use of zeolites belies a major flaw in the technology. The same nano-porous structure and small particle size which allows a bed of hydrophobic zeolite to selectively attract MTBE prevents the passage of a stripping agent during remediation. Prohibitively large pressure drops are experienced across these beds, due to energetic demands and other inefficient operating parameters. Pressure drop in a packed tower is determined by Equation 1:

Equation 1: Pressure Drop in a Packed Tower

$$\frac{dp}{dL} = \frac{150\mu\upsilon(1-\varepsilon)^2}{(\Phi_s D_p)^2\varepsilon^3}$$

dp/dL defines the pressure drop per unit length. μ represents the viscosity of the filtrate through the zeolite particle bed. U represents the linear velocity of the filtrate based on the area of the filter. ε is the porosity of the zeolite particles, dependent upon the ratio of alumina to silica. The factors determined relating to sphericity or shape and particle size are Φ_S and D_p. Because the particle size is accounted for in the denominator as a squared term, the very small size of the zeolite particles offers a tremendous pressure drop across a scaled-up bed for the removal of MTBE from a water supply. Pumps must be operated at a sufficiently high rate to overcome this pressure drop, yielding the aforementioned prohibitive energetic demands of such a large-scale effort.

Membrane Separation

Filtration on a molecular-scale, which is termed ultrafiltration, is possible through the use of semi-permeable membranes. Membranes can effectively retain a particular solute or solvent while a free-energy disparity caused by concentration gradient drives another solute from one side of the barrier to the other. Pore-size limits what molecules can actually pass through the membrane, along with the chemical makeup of the membrane and the solute of interest. Just as a molecule that is too large to pass through a membrane will be maintained on a particular side of the membrane, a molecule that is repelled by the surface chemistry will not pass through. Hydrophobic membranes prevent the transmission of water molecules across the diaphragm of interest. Organophillic membranes allow the passage of organic compounds. Polymer membranes offer a platform where the properties of hydrophobicity and organophillicity can be combined. Such a combination theoretically allows for the development of a means for selectively removing MTBE from a water source, while making use of materials that are chemical resistance to aggressive solutions.

Hydrophobicity

The hydrophobic nature of a material is primarily governed by several factors. The first of those factors is the chemical makeup of the membrane and the polarity of the bonds within the molecules. The molecular structure within the membrane also plays part in the determination of the hydrophobicity of a material. Further hydrophobic nature is realized through the topography of the membrane surface (Lei Zhai, F. C. , *Stable Superhydrophobic Coatings from Polyelectrolyte Multilayers*, 2004).

The electronegativity difference between the oxygen and hydrogen in water molecules creates a pair of dipole moments and a molecule that is, overall, polar. The positive hydrogen dipoles within water molecule tend to associate with the negative oxygen dipoles, forming what are termed *hydrogen bonds* (Zumdahl, S., & Zumdahl, S. , *Chemistry,* 2003). The energetic stability derived from the formation of hydrogen bonds leads to a tendency for the maximum number of such bonds to form. The

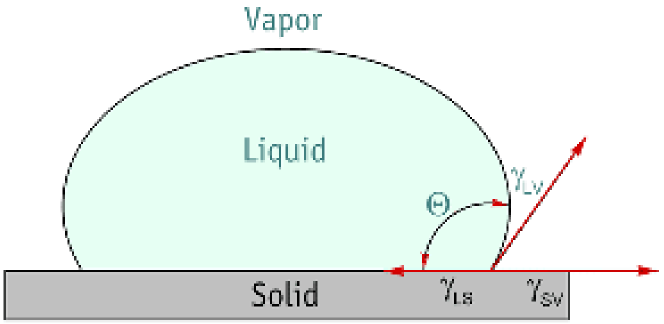


Figure 2: Contact Angle Measurement
“Wafer Bumper”

presence of non-polar molecules among polar molecules prevents the formation of hydrogen bonds, developing a repulsive force between two such phases. It is partially this repulsive force that lends hydrophobic character to a material. “The liquid will bead up on the surface to minimize the solid-liquid interfacial area” (*Contact Angle Measurement*, 2001).

If a molecule has polar as well as a non-polar portions, the structure must arrange and orient the molecules in a manner sufficient to prevent the interaction of water with the hydrophillic regions. Hydrophilic molecules on the membrane surface increase the wettability of the membrane as a substrate (*Contact Angle Measurement*, 2001). Additionally, formation of hydrophilic channels through the membrane would foster the movement of water through the membrane, countering the effect of the hydrophobic regions.

The microscopic surface topography of a membrane can increase the hydrophobicity of a material by allowing further reduction in the size of the interfacial area between the liquid and the membrane. Roughness is characterized by either “peaks” or “pillars” of varying size on the membrane. It is well known that increasing the roughness of a hydrophobic surface can increase its hydrophobicity dramatically” (Lei Zhai, F. C. , *Stable Superhydrophobic Coatings from Polyelectrolyte Multilayers*, 2004). A water droplet will rest on top of the peaks or pillar tops of a rough surface, allowing air to fill the valleys between the membrane surface and the water droplet. The limited surface contact allows the formation of increasingly spherical beads of water.

The degree of hydrophobicity exhibited by a membrane can be measured in terms of water wetting contact angle between the surface and a line tangential to the drop, as can be seen in Figure 2. A hydrophilic surface yields a contact angle less than 90 degrees while hydrophobic surfaces display contact angles greater than 90 degrees (*Contact Angle Measurement*, 2001). Surfaces with contact angles in excess of 150 degrees are considered to be superhydrophobic (Lei Zhai, F. C. , *Stable Superhydrophobic Coatings from Polyelectrolyte Multilayers*, 2004).

Organophilicity

Organophilic character is a measure of how readily a material associates with organic compounds. Hydrophobic compounds are also organophilic because of the non-polarity of the molecules and the organics (Mortland, Stephen A. Boyd and Max M., *Enzyme Interactions with Clays and Clay-Organic Matter Complexes*). This characteristic is of significant import, because MTBE is an organic compound, and so, for it to permeate membrane a membrane that membrane must be organophilic.

Polymer Membranes

Teflon – Teflon, or polytetrafluoroethylene (PTFE), was developed in 1938 by Roy Plunkett in an attempt to develop a new refrigerant. Plunkett was working for Kinetic Chemicals; a company absorbed by E. I. du Pont de Nemours & Co., Inc., in their Jackson Laboratory in New Jersey. The substance was used industrially throughout World War II and was released for commercial consumption by DuPont in 1945. Because of its rather unique characteristics, Teflon is used in a wide variety of applications.

Many of Teflon's properties suit it for use in a membrane designed to foster the transport of MTBE while restricting the passage of water. It is also well-suited for use with aggressive solutions such as the oxidizing solutions that will be necessary for the destruction of the MTBE after it has crossed the membrane substrate. PTFE is chemically inert, which means that it does not readily react to or interact with other substances which can help to prevent its degradation while oxidation is taking place. It also has a high resistance to heat that will allow it to maintain its form when heat is evolved from oxidation-reduction reactions (Gangal, S. V., *Perfluorinated Polymers, Polytetrafluoroethylene*, 2002). These characteristics offer a PTFE surface that is non-corrosive.

Teflon is comprised of a chain of non-polar monomers bearing the formula $–(C_nF_{2n})$-. The non-polar monomer lends itself to a non-polar and therefore, hydrophobic and organophilic, polymer chain. The contact angle for PTFE ranges from 98.5 degrees (James R. Fleming et Al., Material of Construction for Pharmaceutical and for Biotechnology for Processing) to 105 degrees depending upon the manufacturing technique used in the development of the Teflon, as different techniques offer different surface topographies. Teflon resin can be precipitated, from aqueous solution, in a granular form if a dispersing agent is not used. If a dispersing agent is used in solution in conjunction with agitation, a particulate form of the resin develops (Gangal, S. V., *Perfluorinated Polymers, Polytetrafluoroethylene*, 2002). Either form carries the characteristics necessary for allowing the transport of MTBE while resisting destruction at by strong oxidizing agents.

Nylon - Nylon was discovered, in 1935, by Dr. Wallace Carothers, a research scientist in the employ of the DuPont Corporation. Dr. Carothers made his discovery while investigating the polymerization of amides, which exhibit a significant resistance to aggressive environments. DuPont developed nylon as an artificial fiber for use in the manufacture of hosiery and leggings. During World War II, the polymer was used in parachutes as well as in other parts of the war effort (E.I. du Pont de Nemours and Company, *1935: Nylon* ,2003.)

Nylon is naturally hydrophilic with a water contact angle of 70 degrees (Tokoro, T., Recovery of Hydropohobicity of Nylon Aged by Heat and Saline Water, 1996). It is a crystalline polyamide polymer. The crystalline network of the polymer offers a degree of strength to membranes made from it. Nylon is resistant both to heat and a variety of chemicals, including weak acids (E.I. du Pont de Nemours and Company, *1935: Nylon* ,2003). Nylon, however, is attacked by strong acids and in some cases dissolves in the presence of such solutions (Huntingdon Fusion Techniques Limited, *Nylon Chemical Resistance and Technical Dat*a). The surface chemistry of nylon membranes can be altered in order to render it hydrophobic (GE OEM Labstore, *Hydrophobic Membranes for Strong or Aggressive Solvents, Acids, Bases and Venting,* 2008). Contact angles of around 120 degrees are possible with nylon membranes that have received such treatment (Molly K. Phariss*, Evaluation of Peel-Ply…*, 2007).

Polyvinylidene Diflouride – Polyvinylidene diflouride, or PVDF, is a fluoropolymer resistant to chemical, including strong acids, and thermal degradation (The TexLoc Closet, *PVDF Detailed Properties, 2008*). The polymer chain is comprised of – (CH2CF2)n- monomers. The wetting contact angle for 18MΩ water on PVDF is 71.8 degrees. This means that the surface of a PVDF membrane exhibits slightly hydrophilic behavior and, for comparison, “Teflon…is more than 137% less water-wettable than is PVDF” (James R. Fleming et Al., Material of Construction for Pharmaceutical and for Biotechnology for Processing).

Polypropylene – Polypropylene was first developed after the Second World War. It was created in resin form, by a Spanish research scientist, Giulio Natta, in 1957 (Lenntech, *Polypropylene*, 2008). The polymer was discovered by a number of other parties in close succession, resulting in long-running legal battle that was not settled for nearly thirty years. Ultimately, Paul Hogan and Robert Banks, chemists employed by Phillips Petroleum were accredited with the patent for the discovery of polypropylene.

Polypropylene is formed by the linkage of – (C_2H_{2n}) - component monomers, which elongates in a linear fashion when propylene gas is introduced to an appropriate solid catalyst (Lenntech, *Polypropylene*, 2008). It is hydrophobic with a contact angle of 105 degrees (Jochen Frank, F. S., *Characterization of the Interfacial Properties of Modified Polypropylene,* 1999) and chemically resistant to attack by strong acidic solutions. However, polypropylene is susceptible to solutions containing strong oxidizing agents and so may degrade in the presence of such solutions (Inteplast Group, *Technical Properties of Polypropylene (PP) IntePro,* 2006).

Fenton’s Oxidation

There are a several different advanced oxidation processes used commercially. These processes make use of hydrogen peroxide or titanium dioxide and ultraviolet radiation, ozone or iron to generate hydroxyl radicals. The hydroxyl radicals are of sufficiently high oxidation state to oxidize organic compounds, such as MTBE, degrading them to benign products. The Fenton oxidation process is a specific reaction that utilizes hydrogen peroxide and ferrous iron at low pH values (pH~3) to produce the desired hydroxyl radicals (Nada Al Ananzeh, J. A., *Kinetic Model for the Degradation of MTBE by Fenton's Oxidation,* 2005).

Equation 2

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^-$$

Equation 3

$$FeOH^+ + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + 2OH^-$$

The hydroxyl radicals then react with the MTBE that is in the solution. The primary reactions of hydroxyl radicals with MTBE are as follows.

Equation 4

$$(CH_3)_3COCH_3 + \bullet OH \rightarrow (CH_3)_3COCH_2^{\bullet} + H_2O$$

Equation 5

$$(CH_3)_3COCH_3 + \bullet OH \rightarrow CH_2(CH_3)_2COCH_3 + H_2O$$

There are a number of other reactions that occur in solution with the Fenton oxidation reagents. Hydrogen peroxide and ferrous iron interact with the other components of the solution in up to thirty different minor reactions. The hydroxyl radicals also participate in up to twenty-seven different minor reactions. The major products of the degradation of MTBE by hydroxyl radical oxidation include tert-butyl formate, tert-butyl alcohol, acetone, methyl acetate, and formaldehyde (Nada Al Ananzeh et Al, *Kinetic Model for the Degradation of the MTBE by Fenton's Oxidation,* 2005.)

The reaction of Fe $^{2+}$ with hydrogen peroxide occurs quite rapidly. However, the Fe $^{3+}$ that is produced by this reaction also reacts with hydrogen peroxide in a much slower reaction to produce hydroxyl radicals.

Equation 6

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+}$$

Equation 7

$$Fe^{III}(HO_2)^{2+} \rightarrow Fe^{2+} + HO_2^{+}$$

Equation 8

$$Fe^{III}(HO)(HO_2)^{2+} \rightarrow Fe^{2+} + HO_2^{\bullet} + OH^{-}$$

As the reaction progresses, the degradation of MTBE slows considerably as Fe 2+ begins to compete with the byproducts of the minor reactions for hydrogen peroxide and the much slower reaction of Fe3+ with hydrogen peroxide. With fewer hydroxyl radicals available, fewer oxidation reactions can occur. Additionally, the products of the various reactions compete with the MTBE to react with what hydroxyl radicals are available. Because of this, the degradation of MTBE slows quickly after the beginning of the reaction, breaking down up to 99% of the MTBE in the first five minutes of latency time, but never completely eradicating the contaminant.

METHODOLOGY

Objective 1: Membrane Viability

The characteristics of each polymer membrane acquired for the purpose of this investigation had to be tested to ensure that they were appropriate for the separation of MTBE from a water supply while also preventing the transport of the oxidizing solution into the water supply. The membranes were tested for hydrophobic character, ability to maintain hydrogen peroxide on one side of the membrane, and ability to prevent the passage of iron ions. The experiments were carried out in a progression designed to evaluate properties in keeping with a logical hierarchy of importance to the goal of the project. Such a progression served to identify membranes not fit for use at the earliest possible juncture.

Four polymer membranes were obtained for testing over the course of the project. Samples of polyvinylidene diflouride membrane tubing were procured from the stores of the Worcester Polytechnic Institute Civil Engineering Department. Three other membranes were ordered from the General Electric Osmonics Labstore. PTFE (Teflon) laminated membranes, Nylon, and polypropylene were purchased. Each of the membranes purchased from GE Osmonics were marketed as hydrophobic as well as having a high resistances to aggressive solutions. The Teflon membranes ordered were disks 25mm in diameter and had 0.45 micron pores. The part and model number were 1215492 and F04LP02500 respectively. The Nylon membrane ordered were also disks with 0.45 micron pores, but were 47mm in diameter, which had to be cut down for use in the apparatus. The part and model numbers were 1237909 and R04SH04700 respectively. Polypropylene membrane was purchased in sheets. The pores, as with the other membranes, were 0.45 microns in diameter. The part and model numbers were 1225933 and M04WP320F5 respectively.

Hydrophobicity

The polymer membranes had to have a series of tests done in order to assess how each of four membranes interacts with liquid water. Teflon, Nylon, polypropylene, and PVDF membranes were tested. All of the membranes were marketed as having hydrophobic character. The wettability of the membranes was tested from a macroscopic standpoint through a drop-wise test. It was also quantified in terms of the water contact angles of the membranes, which were measured by a goniometer.

Drop-Wise Testing

The first test conducted was run to visually evaluate the wettability of the membranes with water as well as a hydrogen peroxide solution. This base level investigation was used to identify, at the earliest possible stage, if any of the membranes was actually hydrophilic. The experiment allowed conclusions to be drawn about the membrane wettability based on the shape of the water bead on the membrane surfaces.

A 1-to-200 μL pipette was used to uptake and deposit 2 μL droplets of water onto each of the membranes, which had been placed onto a flat countertop. Observations about the droplets on each membrane were recorded in a laboratory notebook. A 30% hydrogen peroxide solution was then used to run the same experiment. Again, observations about the drops were recorded. Procedure 1 was followed to for the execution of the experiment.

Procedure 1: Drop-Wise Testing Procedure

- Place the membranes on the lab surface and ensure that the membranes are flat

- Prepare a 1-to-200 µL pipette by affixing the appropriate size tip and setting it to a volume of 4 µL
- Fill a 50 mL beaker with approximately 25 mL of 18 MΩ E-Pure water
- Draw a sample of water and carefully excrete a droplet onto the surface of the membrane
- Drop several beads of water onto each membrane
- Evaluate and record the shape of the beads of water immediately after deposition
- Allow the beads of water to stand on the membranes for a period of ten minutes
- Record any visible change in the shape of the water beads
- Repeat the entire experiment from the first step with new membranes and a 30% hydrogen peroxide solution

Contact Angle Measurement

In an effort to quantify the hydrophobicity of the four membranes, the contact angles for the membranes were determined. The contact angle measurements were taken using a goniometer. A goniometer is a piece of equipment that makes use of camera that can magnify and capture the image of a droplet on any desired surface, supported on an adjustable platform between the camera and the opposing lantern. The camera, platform, lantern, and automated water dispensing syringe can be seen in Figure 3. The captured digital image can then be analyzed using computer software to determine the contact angle exhibited by a membrane. The contact angle was measured repeatedly to allow a mean value to be determined.

Figure 3: Sample Goniometer Equipment Setup

Procedure 2: Goniometer testing

- Turn on the computer, camera, pump, and lantern
- Load the automated syringe from a 50 mL beaker filled with 18MΩ E-Pure water
- Place the membrane on the goniometer surface and ensure that the membrane is flat
- Adjust the camera to frame the surface of the membrane
- Enter the desired water droplet size into the computer software interface
- Output a 4 μL water droplet onto the membrane, moving the platform-bound membrane upward or downward as necessary to allow the droplet to release
- Manipulate the computer software to compute the contact angle
- Move the platform laterally to present an unmarred section of membrane fills the camera frame

- Repeat all previous steps until five contact angle measurements have been resolved for each membrane
- On the final droplet for each membrane, take a picture of a droplet to have visual evidence for later reporting

Apparatus-Membrane Seal Testing

Figure 4: Test Apparatus with Two Reservoirs and a Coupling Flange

Another simple test had to be conducted before the designed apparatus, seen in Figure 4, could be used in tests. The apparatus to be tested had two reservoirs, made from two inch PVC piping, to hold test solutions. The reservoirs were capped by screw-on rubber stoppers. The two reservoirs were connected by equal length sections of ¾ inch PVC piping with a threaded flange, displayed in Figure 5, to hold the membrane sample in place and attach the two halves of the apparatus. Each PVC to PVC connection was threaded and the threads were wrapped with latex tape, to ensure tight seals.

To test the seals, throughout the apparatus as well as around the membrane, the apparatus was assembled with a sample membrane loaded. One reservoir was filled with 18 MΩ E-pure water and the other was left empty. The setup was allowed to stand for 5, 10 and 15 minute periods. At the end of each time period the apparatus was drained and disassembled. The side of the membrane not in contact with the water and the ¾ in PVC tubing from the dry side of the apparatus were investigated for moisture. This test offered one final practical check of the hydrophobic character of the membranes while also ensuring the integrity of the entire device. The test was repeated with a hydrogen peroxide solution.

Figure 5: Threaded Flange with Membrane in Place

Procedure 3: Apparatus-Membrane Seal Test

- Seat a membrane onto the black O-ring of the flange
- Screw the two halves of the apparatus together
- Pour 175 mL of 18 MΩ E-pure water into one arm of the apparatus and screw the rubber stopper onto the apparatus.
- Place on a shaker-table to simulate the conditions of future experiments
- Remove the apparatus from the shaker-table after five minutes and empty the reservoirs

- Disassemble the apparatus
- Examine the membrane and the side of the apparatus that was left dry for moisture
- Repeat for 10 and 15 minute intervals
- Repeat the entire experiment with a hydrogen peroxide solution made by adding 670 μL of 30% hydrogen peroxide to 200 mL of 18 MΩ E-pure water for the test solution

Objective 2: Solution Preparations

Several solutions of MTBE in water had to be generated for use in testing. In order to generate a concentration-absorbance curve, from which absorbance measurements could be converted into concentration measurements, varying solutions of calculated concentrations of MTBE had to be developed and then measured for absorbance. Solutions were also necessary for loading into the apparatus during each test. The solutions of MTBE created were 1000, 500, 250, 125 and 50 ppm. The following table will show the total volume of the solution, the amount of MTBE pipetted into the solution and the concentration of the MTBE in parts per million, ppm. All solutions will be prepared in a 300 ml flask and stirred for 20 minutes prior to being placed within the apparatus. Solutions below 50

Table 1: MTBE Solution Preparation

Total Volume	MTBE Volume	Concentration
250 mL	340 µL	1000 ppm
250 mL	170 µL	500 ppm
250 mL	85 µL	250 ppm
250 mL	34 µL	100 ppm
250 mL	17 µL	50 ppm

ppm were not prepared because MTBE levels below 50 ppm approximate the levels set forth by the Environmental Protection Agency as acceptable hazards to individual hazard.

Objective 3: MTBE Transport Across Polymer Membranes

Having determined which of the membranes were hydrophobic and how the different hydrophobic membranes compared to each other, it became imperative to determine if the various polymer membranes could, indeed, transport MTBE across its thickness. The hydrophobic character of the membranes should lend itself to organophilic character, but this assumption needed to be tested. In addition to testing the ability of the membranes to allow and foster the transport of MTBE, a comparison of the ability of the membranes to conduct that transport must be possible from our experiments.

Concentration Profiles for MTBE Transport

The aforementioned aims were accomplished by measuring the concentration of an MTBE solution over time while connected to a reservoir initially containing only water. Experiments were conducted over a period of thirty minutes with samples drawn initially and at five, 15, 25 and 30 minutes. Some experiments were run for longer periods of time. A spectrophotometer was utilized to assess the concentrations of the samples as they were drawn. Well-mixed solutions were maintained by keeping the apparatuses on a shaker-table that oscillated at a constant rate.

Procedure 4: Concentration Profiling for MTBE Transport

- Prepare MTBE solution
- Assemble the apparatus with sample membrane in place
- Pour 175 mL of 1000 ppm MTBE solution into an appropriately labeled arm of the apparatus
- Pour 175 mL of 18 MΩ E-pure water into the opposing arm of the apparatus and screw the rubber stoppers onto each reservoirs after taking an initial sample

- Place the apparatus on the shaker-table, and set the table to a low speed
- Remove the apparatus and draw 3.25 mL samples from each arm of the apparatus at each preset interval; 5, 15, 25 and 30 minutes
- Excrete the samples into individual vials for spectrophotometer analysis
- Screw the rubber stopper onto both arms of the apparatus
- Replace the apparatus on the shaker-table
- At the conclusion of the testing period the MTBE solution must be disposed of in a hazardous waste container and the apparatus must be thoroughly cleaned

Objective 4: MTBE Transport and Fenton's Oxidation

After removing the MTBE contamination from a water source, it must be degraded into lesser forms that do not conflict with health standards. Fenton's oxidation reactions, which are a specific set of oxidation reactions, have been shown to help meet that requirement of a remediation system. However, these reactions are quite aggressive and so these polymer membranes had to be shown to be able to withstand attack by the solution. Only the membrane displaying the most rapid transport of MTBE in the previous round of testing was used in subsequent tests. The polymer membranes were tested via separate experiments to ensure that they did not allow the passage of iron ions or hydrogen peroxide. The non-polar surface of the hydrophobic membrane was expected to repel the two components of interest on similar principles to the repulsion of water.

Fenton's Oxidation in the Apparatus

Fenton's oxidation reactions take place when ferrous iron is in solution with hydrogen peroxide. To create this solution, $FeSO_4 \cdot 7H_2O$ was dissolved in water. Once the salt had completely dissolved, hydrogen peroxide was added. This solution presents two additional possible contaminants to the remediation system. The contamination of the MTBE/water side with iron or hydrogen peroxide is not acceptable and so they must not pass through the membrane. Having tested the membrane's ability to prevent the passage of iron ions and hydrogen peroxide, tests could be conducted with Fenton's oxidation taking place in one reservoir and MTBE transport from the opposing, membrane-separated, reservoir.

Iron Ion Tracking Across Teflon Membrane

The passage of ferrous iron and hydrogen peroxide from one reservior to the other, across the membrane, was tested in a pair of overnight tests. For the iron-based test, a solution of $FeSO_4 \cdot 7H_2O$ in water was created. The combined solution was added to a reservoir on the apparatus. The opposing reservoir was filled with 18 MΩ E-pure water and the two stoppers were put into place to seal the apparatus. The device was placed on a shaker-table for 24 hours to allow a significant opportunity for transport of iron ions across the membrane. The presence of iron ions in the water side of the apparatus at the end of the experiment was tested by adding sodium bicarbonate. From a list of solubility rules it was determined that sodium does not form a precipitate with SO_4^{2-} but Fe^{2+} does form a precipitate with HCO_3^{2-}. Therefore any iron in solution would precipitate out in the presence of the added salt. The same experiment was conducted with a hydrogen peroxide solution. The presence of hydrogen peroxide in the water side of the apparatus at the end of the experiment was tested by adding $FeSO_4 \cdot 7H_2O$, because the addition of hydrogen peroxide to a solution containing ferrous iron generates a clearly distinguishable brown precipitate, 30% hydrogen peroxide was added to the liquid contained in the "water" side of the apparatus with formation of a precipitate signaling iron transport and the absence of a precipitate highlighting the absence of iron.

Brief control experiments were conducted to assess the validity of our claim that precipitates would form in the presence of the added salts. When the down-stream water side solutions were poured from the apparatus into beakers, the up stream solutions were also poured into beakers as well. The upstream solutions contained the compounds of interest for each run. Solutions containing the salts, $FeSO_4 \cdot 7H_2O$ and $NaHCO_3$, were added to the upstream solutions. In each case, a clearly distinguishable precipitate formed and settled out of solution.

Procedure 5: Blocking Ferrous Iron Transport

- Assemble the apparatus with sample membrane in place
- Weigh and add 44.78 grams of $FeSO_4 \cdot 7H_2O$ to 200 mL of 18 MΩ E-pure water
- Allow the solution to mix on a stir plate until all of the iron salt has dissolved
- Pour 175 mL of the iron solution into a reservoir arm on the apparatus
- Fill the opposing side with 175 mL of 18 MΩ E-pure water and secure the rubber stoppers onto each reservoirs
- Place the assembly onto a shaker-table and allow to stand for 24 hours
- At the end of the 24 hour period, remove the apparatus from the shaker-table
- Drain the water side of the apparatus into a 500 mL beaker
- Dissolve 10 grams of $NaHCO_3$ into 50 mL of 18 MΩ E-pure water
- Add the $NaHCO_3$ solution to the to 500 mL beaker
- Look for and make note of any precipitation
- Dispose of the solutions appropriately and thorough cleanse the apparatus

Procedure 6: Blocking Hydrogen Peroxide Transport

- Assemble the apparatus with sample membrane in place
- Add 670 μL of 30% hydrogen peroxide to 200 mL of 18 MΩ E-pure water
- Allow the solution to mix on a stir plate until all salt has dissolved
- Pour 175 mL of the hydrogen peroxide solution into a reservoir arm on the apparatus

- Fill the opposing side with 175 mL of 18 MΩ E-pure water and secure the rubber stoppers onto each reservoirs
- Place the assembly onto a shaker-table and allow to stand for 24 hours
- At the end of the 24 hour period, remove the apparatus from the shaker-table
- Drain the water side of the apparatus into a 500 mL beaker
- Dissolve 5 grams of $FeSO_4 \cdot 7H_2O$ into 50 mL of 18 MΩ E-pure water
- Add the $FeSO_4 \cdot 7H_2O$ solution to the to 500 mL beaker
- Look for and make note of any precipitation
- Dispose of the solutions appropriately and thorough cleanse the apparatus

MTBE Transport into Fenton's Oxidation

Having proven that MTBE can pass through the pores of a particular hydrophobic polymer membrane while preventing the passage of iron ions and hydrogen peroxide in solution, tests with MTBE in being removed from one reservoir to be remediated in the other were possible. A 1000 ppm solution of MTBE was prepared and poured into the assembled apparatus with a membrane loaded. An iron solution was created and hydrogen peroxide was added to it. Samples were drawn over the course of thirty minutes as well as at the end of longer periods of time. The test allowed a comparison of the transfer characteristics of the membrane with and without degradation of MTBE. It also allowed an investigation of attack on the membrane surface by the oxidizing solution as MTBE entered into the remediation solution.

Procedure 7: MTBE Transport into Fenton's Oxidation

- Assemble the apparatus with a sample membrane loaded
- Prepare MTBE and $FeSO_4 \cdot 7H_2O$ solutions
- Pour 175 mL of desired MTBE solution into the right arm of the apparatus
- Pour 175 mL of $FeSO_4 \cdot 7H_2O$ solution into the left arm of the apparatus (1-to-56.18 molar MTBE/ $FeSO_4 \cdot 7H_2O$ ratio)
- Pipette 670 µL of H_2O_2 into the left arm of the apparatus (1-to-10.06 molar MTBE/$H_2 0_2$ ratio)
- Screw the rubber stopper onto the right arm of the apparatus
- Cover the reservoir on the left arm of the apparatus with Para-film
- Place the apparatus on a shaker-table set at a low speed
- Remove the apparatus and draw 2.50 mL samples from each arm of the apparatus at each preset interval; 5, 15, 25 and 30 minutes
- Excrete the samples into individual micro COD testing vials
- Replace the reservoir covers on both arms of the apparatus
- Replace the apparatus on the shaker-table
- Shake the micro COD vial
- Analyze the solution using micro COD testing (APPENDIX A)
- Dispose of the solutions appropriately and thorough cleanse the apparatus

Tracking Temperature Change in the Reservoirs

The concentration of MTBE in the reservoir containing Fenton's oxidizing agents could not be measured because of the presence of the other components in solution. Therefore, the removal of

MTBE from the MTBE reservoir could not be tracked into the opposing reservoir. The oxidation of MTBE has a heat of reaction, and so, if the MTBE was oxidized the temperature of the oxidizing solution would increase as the reaction progressed. If the MTBE is evaporating over the course of the reaction, a corresponding temperature decrease might be exhibited. By measuring the temperatures of the two constituent solutions, of MTBE and hydrogen peroxide with ferrous iron, we can assume that if there is a temperature change when the two are separated by a membrane, it is because of MTBE transport and oxidation.

Procedure 8: MTBE and 18 MΩ E-pure water Heat of Reaction testing

- Assemble the apparatus with a membrane loaded
- Make 175 mL of 1000 ppm MTBE solution and let it come to room temperature. Pour into the right arm.
- Obtain 175 mL of 18 MΩ E-pure water and let it come to room temperature and then pour it into the left arm of the apparatus.
- Cover each reservoir with parafilm and poke a hole in the center of the parafilm
- Place a thermometer in each hole of the parafilm
- Record temperature readings at 5, 10 and 15 minutes
- Dispose of the solutions appropriately and thorough cleanse the apparatus

Procedure 9: Fenton's solution and 18 MΩ E-pure water Heat of Reaction testing

- Assemble the apparatus with a membrane loaded
- Obtain 175 mL of 18 MΩ E-pure water and let it come to room temperature. Pour into the right arm of the apparatus
- Make 175 mL of $FeSO_4{\cdot}7H_2O$ solution
- Pipette 670 µL of 30% H_2O_2 into iron solution
- Let the solution come to room temperature and then pour it into the left arm of the apparatus
- Cover each reservoir with parafilm and poke a hole in the center of the parafilm
- Place a thermometer in each hole of the parafilm
- Record temperature readings at 5, 10 and 15 minutes
- Dispose of the solutions appropriately and thorough cleanse the apparatus

Procedure 10: MTBE and Fenton's solution Heat of Reaction testing

- Assemble the apparatus with a membrane loaded
- Make 175 mL of 1000 ppm MTBE solution and let it come to room temperature
- Pour the solution into the right arm of the apparatus
- Make 175 mL of $FeSO_4{\cdot}7H_2O$ solution and add to it 670 µL of H_2O_2
- Allow the solution to come to room temperature before pouring it into the left arm of the apparatus
- Cover each reservoir with parafilm and poke a hole in the center of the parafilm
- Place a thermometer in each hole of the parafilm
- Record temperature readings at 5, 10 and 15 minutes
- Dispose of the solutions appropriately and thorough cleanse the apparatus

Contact Angle Measurement After Prolonged Exposure to Fenton's Oxidation

The experiments progressed from the initial tests to; assure the hydrophobicity of the polymer membranes, to a full test of the remediation of a MTBE contaminated solution by a strong oxidizing solution separated by one of those same membranes. However, destruction of the membrane by the oxidizing solution presents a serious threat to the viability of hydrophobic polymer use in industrial-scale remediation efforts. Each membrane was investigated visually for degradation after each exposure to the Fenton's oxidation solution. In an effort to quantify the potential breakdown of the membrane by the oxidizing agent, a post-use goniometer-based contact angle measurements were conducted for comparison to the initial values.

Procedure 11: Contact Angle Measurement After Exposure to Oxidation

- Load the apparatus with a membrane and 1000 ppm MTBE solution and Fenton's oxidation solution
- Allow the apparatus to stand on a shaker-table for a full 48 hour period
- Remove the apparatus from the shaker-table and drain the reservoirs
- Disassemble the apparatus, remove and cleanse the membrane with 18 MΩ E-pure water
- Follow all steps of Procedure 2

RESULTS AND DISCUSSION

Objective 1: Membrane Viability

The characteristics of each polymer membrane acquired for the purpose of this investigation had to be tested to ensure that they were appropriate for the separation of MTBE from a water supply while also preventing the transport of the oxidizing solution into the water supply. The membranes were tested for hydrophobic character, ability to maintain hydrogen peroxide on one side of the membrane, and ability to prevent the passage of iron ions. The experiments were carried out in a progression designed to evaluate properties in keeping with a logical hierarchy of importance to the goal of the project. Such a progression served to identify membranes not fit for use at the earliest possible juncture.

Hydrophobicity

For use in the separation of MTBE from a water supply, it was paramount to the continuation of research that the polymer membranes have the property of hydrophobicity. If the membranes allowed the passage of water, then the water supply undergoing remediation would be able to pass into the oxidizing solution used to decompose the MTBE and the water in the oxidizing solution would be able to pass into the water supply to achieve equilibrium with regard to the MTBE concentration gradient. The pores of the membrane must be large enough to allow the passage of MTBE and so can not be small enough to restrict the movement of water molecules. Therefore, the membrane chemistry and surface topography must repel water.

The first round of testing conducted served to directly address the issue of the hydrophobic nature in the membranes. Through these tests we sought to identify the membranes as either hydrophilic or hydrophobic. We also investigated the hydrophobic character of the membranes relative to one another.

Drop-Wise Testing

The drop-wise testing experiment was used to identify the wettability of the membranes from a macroscopic viewpoint. Water-droplets 4 μL in size were pipette onto each of the membranes. The shape of each bead was then evaluated by the naked eye immediately after the drop was placed, and then again after a period of ten minutes to see if exposure to water had increased the wettability.

Four membranes were tested over the course of the experiment; a Teflon membrane, a polypropylene membrane, a polyvinylidene diflouride, and a Nylon membrane. As reported in Table 1, the Teflon, polypropylene, and Nylon membranes all displayed limited wettability. This conclusion was drawn from the spherical form of the beads of water; the droplets placed on each of the aforementioned membranes were repelled from the surface and limited the solid-liquid interface by taking on such a shape. The results of the PVDF membrane test, however, stood in stark contrast to those of the other membranes.

While the water droplet that was placed onto the PVDF membrane took on a definite form, it did not approximate a sphere. The water-bead on the PVDF membrane took on the shape of a hemisphere. Given that the amount water deposited on each membrane was the same and the different structure of the two types of beads observed, it could be concluded that there was a significantly larger solid-liquid interfacial area for the polyvinylidene diflouride (PVDF) membrane when compared to the others. The shape of the water droplet on the PVDF membrane suggests that the membrane was more hydrophilic and less hydrophobic than the other membranes tested. A more definitive assessment could not be conducted due to the small scale and observations based on the unaided eye.

Table 2: Drop-Wise Testing Results

Drop-Wise Testing				
Test Membrane	Test Liquid - 4 µL Drop			
	18 MΩ E-Pure Water		30 % H_2O_2	
	After Drop	10 Min. Elapse	After Drop	10 Min. Elapse
0.45 µm Pore Nylon	Well-Defined Drop, Limited Wetting	Well-Defined Drop, Limited Wetting	Well-Defined Drop, Limited Wetting	Well-Defined Drop, Limited Wetting
0.45 µm Pore Teflon	Well-Defined Drop, Limited Wetting	Well-Defined Drop, Limited Wetting	Well-Defined Drop, Limited Wetting	Well-Defined Drop, Limited Wetting
0.45 µm Pore Polypropylene	Well-Defined Drop, Limited Wetting	Well-Defined Drop, Limited Wetting	Well-Defined Drop, Limited Wetting	Well-Defined Drop, Limited Wetting
0.45 µm Pore Polyvinylidene Diflouride	Visual Wetting, Poorly Formed Drop	Visual Wetting, Poorly Formed Drop	Visual Wetting, Poorly Formed Drop	Visual Wetting, Poorly Formed Drop

Four drops were placed on each membrane and allowed to stand for ten minutes. No difference was observed from one drop to the next on a particular membrane. Time exposure did not appear to affect the form of the beads or the wettability of the individual surfaces. The membranes were also tested with a hydrogen peroxide solution with the same results. The observations about the droplet shapes and apparent wettability of the membranes are reported in Table 2. In order to determine if the PVDF membrane was hydrophobic or not and to allow a comparison of the membranes that had demonstrated hydrophobic character, the contact angle of a bead of water on each of the membranes had to be measured.

Contact Angle Measurement

A goniometer was utilized to measure the contact angle of water droplets placed onto the polymer membranes. A measurement was calculated for five drops per membrane, allowing a mean contact angle to be determined. The calculated contact angles as well as the mean values are reported in Table 3. Care was taken to use forceps to place the membranes on the measuring platform so that no skin oils would alter the results.

Table 3: Contact Angle Measurement from Goniometer Testing

Goniometer Contact Angle Measurements				
Test Membrane	**0.45 µm Pore Nylon**	**0.45 µm Pore Teflon**	**0.45 µm Pore Polypropylene**	**0.45 µm Pore Polyvinylidene Diflouride**
Trial 1	121.0	127.2	118.8	74.6
Trial 2	119.8	107.3	126.7	96.7
Trial 3	119.7	124.2	127.8	89
Trial 4	122.4	115.7	136.9	N/A
Trial 5	125.5	126.7	139.4	N/A
Average	121.7	120.2	130.7	86.8

As reported in Table 3, the testing of the Nylon membrane yielded a range of contact angles from 119.7 to 125.5 degrees. The mean value for the five measurements was 121.7 degrees, which is greater than 90, reaffirming the hydrophobic character observed in the drop-wise test. Falling halfway between ninety degrees and 150 degrees, the cutoff for superhydrophobic character, Nylon exhibits significant hydrophobic behavior.

The Teflon membrane offered contact angle measurements from 127.2 degrees to 107.3. The mean value for the contact angle of Teflon was 120.2 degrees. The hydrophobic nature of the Teflon membrane was essentially equivalent to that of the Nylon membrane.

The polypropylene membrane rendered the highest contact angle and, therefore, the greatest hydrophobic character. Individual measurements ranged from 118.8 degrees to 139.4 degrees and the mean value was 130.7 degrees.

Only three measurements could be taken for the PVDF membrane. Those measurements ranged from 74.6 degrees to 96.7 degrees. The average value of the PVDF contact angle was 86.8 degrees. Based on those measurements, the PVDF membrane that was tested was not hydrophobic.

The polypropylene membrane has the greatest ability to resist the wetting of its surface, however, that classification does not, in and of itself, make the polypropylene membrane the best suited for use in removing MTBE from a water source. Because of the slightly hydrophilic nature of the PVDF membrane, it was not used in any further tests.

Apparatus-Membrane Seal Testing

Before other characteristics of the membranes could be resolved, the apparatus to be used for our experiments had to be tested with the membranes in place. The apparatus was assembled with the membranes seated between the two flanges of the juncture. A reservoir was then filled with 18MΩ E-pure water and allowed to sit with an empty reservoir on the opposite side of the membrane. The test was run for five, 10, and 15 minutes intervals. At the end of each test, the apparatus was drained and disassembled. Once disassembled, it was inspected.

Table 4: Apparatus-Membrane Seal Test Results

Apparatus -Membrane Seal Testing		
Setup	**Time**	**Result**
18 MΩ E-Pure Water vs. Air	5 Min.	No Visible Transport or Leaking
	10 Min.	No Visible Transport or Leaking
	15 Min.	No Visible Transport or Leaking
30% H_2O_2 vs. Air	5 Min.	No Visible Transport or Leaking
	10 Min.	No Visible Transport or Leaking
	15 Min.	No Visible Transport or Leaking

The countertop that the experiment was run on was checked for any drops of water to ensure that the apparatus was not leaking. The side of the membrane that was not in contact with the filled reservoir was inspected for moisture. The channel on the portion of the apparatus that was left empty was inspected for moisture as well. As reported in Table 4, there was no observed leaking in any portion of the apparatus or transport of water across the membrane barrier. The test was also run with a hydrogen peroxide solution to once again check for leaks and conduct a final test of the membranes impermeability to water and hydrogen peroxide. The results, which can be found in Table 3, were the same as those for the water test.

Objective 2: MTBE Transport Across Polymer Membranes

The ability of the membranes to transport MTBE was not necessarily tied exclusively to the hydrophobic character of the membranes. While hydrophobic character suggests organophilicity and therefore the ability to pass organic compounds, the hypothesis had to be tested. Beyond that, a comparison of the abilities of the membranes to carry out the transport of MTBE had to be developed. To do this, concentration measurements were taken over a period of time as MTBE moved from across the apparatus bound membrane.

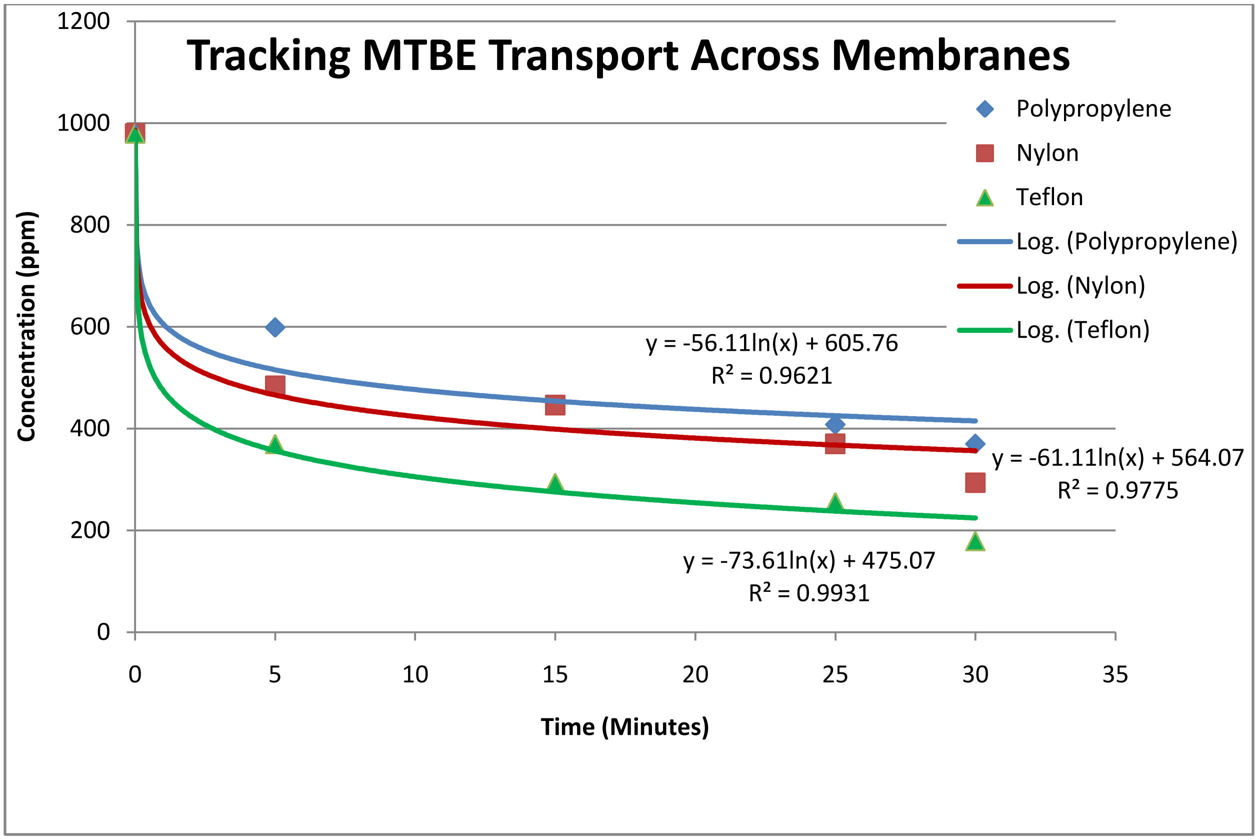
MTBE Transport Across Membranes

The polypropylene, nylon and Teflon membranes were tested over a thirty minute interval for their ability to selectively transport MTBE from a reservoir containing MTBE in solution to a reservoir containing only 18 MΩ E-pure water. 3.25 mL samples of the solution in the MTBE reservoir were taken and the concentrations were measured via a spectrophotometer.

The results of those tests are reported in Figure 6. As is clearly demonstrated by the data points for each membrane, the concentration in the MTBE reservoir decreased over time in all cases. This led to the conclusion that MTBE transport was possible and taking place through each membrane.

The rate of MTBE transport, the reduction in MTBE concentration per unit time, was expected to decrease over the course of the experiments. The driving force for the transportation of the MTBE across the membrane was the differential in concentration between the reservoirs. As the MTBE concentration in the upstream reservoir decreased and it increased in the downstream reservoir, the difference in concentration would also decrease. The smaller differential is tied directly to a smaller driving force and a decreased rate of MTBE transport. With decreasing rate of transport, the differential between the two reservoirs would decrease at ever lower rates, and so, as the system approached some equilibrium between the two reservoirs, the concentration was expected to asymptotically approach a level. The measured values for the experiments appeared to follow this rationale. Linear, polynomial, and exponential trend lines were generated for the data, but the fit with the highest R^2 was a logarithmic trend line. From these lines of best fit, a comparison of the permeabilities of the three membranes to MTBE was made possible.

Figure 6: Tracking MTBE Transport Across Polymer Membranes



As seen in Table 5, polypropylene transport MTBE at the slowest rate, with a logarithmic factor of -56.1. Nylon transports MTBE at a higher rate, with a logarithmic factor of -61.1, but it is Teflon that exhibits the highest rate of transport. The logarithmic factor for Teflon, as calculated from our experimental results, was -73.6. Because Teflon displayed the highest rate of MTBE transport, the focus of the remainder of the project shifted to the Teflon film alone. The other membranes, nylon and polypropylene were not used in any subsequent tests.

Table 5: Logarthmic Lines of Best Fit for MTBE Transport to Water

Logarthmic Lines of Best Fit for MTBE Transport to Water Reservoir			
Membrane	**Equation**	**Logarithmic Factor**	**R^2- value**
Nylon	y = -61.1ln(x) + 564.0	-61.1	0.977
Polypropylene	y = -56.1ln(x) + 605.7	-56.1	0.962
Teflon	y = -73.6ln(x) + 475.0	-73.6	0.993

Objective 3: Fenton's Oxidation in the Apparatus

Polymer membrane use in the remediation of MTBE contamination will almost certainly require the use of aggressive solutions that are capable of degrading the organic compound, and perhaps attacking the membranes. The membranes must be able to resist the chemical attack, whether it is oxidation or acidic or alkaline in nature. For our investigation of the use of polymer membranes, Fenton's oxidation reactions were used to decompose MTBE. The membranes in use therefore had to be able to contain the solutions components, maintain its integrity over a testing period, and also maintain its ability to repel water while transporting MTBE.

Isolated Solution Transport for Teflon Membrane

The Teflon membrane was tested to ensure that it was capable of blocking the passage of ferrous iron ions as well as hydrogen peroxide, the two components of Fenton's oxidation solution. Individual aqueous solutions of ferrous iron and hydrogen peroxide were allowed to stand in the apparatus for a 24 hour period. The opposing reservoir was filled with water and at the end of the testing period; the water-side solution was tested for the presence of the respective component. The presence of iron or hydrogen peroxide was tested by adding to the solution a salt that would result in the formation of precipitate in combination with the component of interest. As displayed in Table 6, the salts added to the hydrogen peroxide-based test and the ferrous iron-based test were $FeSO_4 \cdot 7H_2O$ and $NaHCO_3$ respectively. The addition of the salt did not evolve a precipitate in either case and so we concluded that no transport of hydrogen peroxide or iron was taking place across the membrane boundary. Therefore, in a test involving Fenton's oxidation solution, the components would be restricted to the reservoir that they were initially poured into and would not contaminate the solution in the other reservoir.

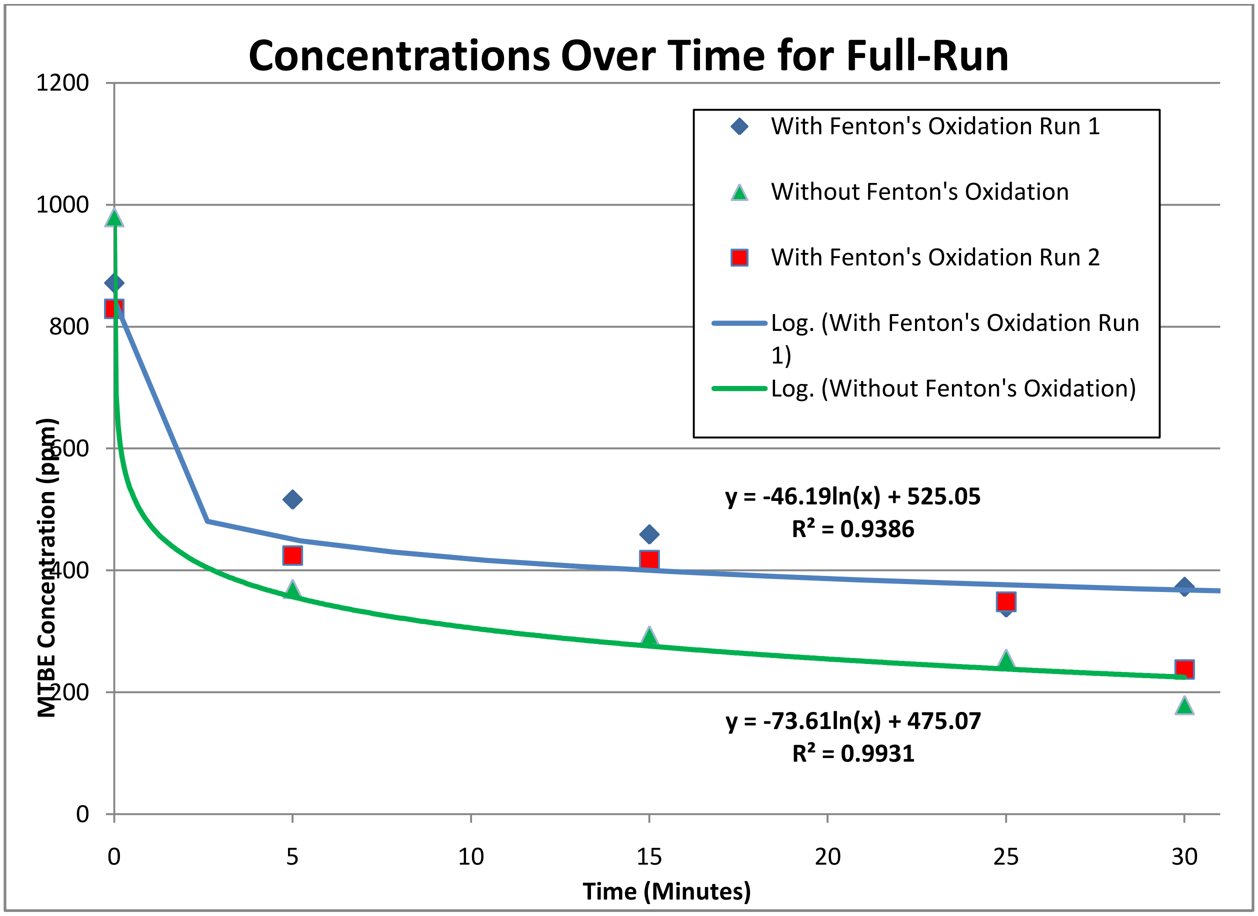
Table 6: Transport of Fenton's Oxidation Solution Components

Apparatus - Isolated Solution Transport Testing for Teflon Membrane			
Solution	**Additive**	**Reaction**	**Conclusion**
30% H_2O_2 in 18 MΩ E-Pure Water	$FeSO_4 \cdot 7H_2O$	No Reaction	No Transport
$FeSO_4 \cdot 7H_2O$	$NaHCO_3$	No Reaction	No Transport

MTBE Transport into Fenton's Oxidation

A full proof of concept run was conducted to ensure that MTBE transport was indeed possible from a MTBE solution reservoir into a reservoir containing Fenton's oxidation solution. The test was conducted over the same span of time, with samples drawn at the same intervals in the previous experiments. Theoretically, as the MTBE transported across the polymer membrane, it should have been destroyed by the oxidizing agents in the down-stream reservoir, maintaining only a very small concentration of MTBE in that reservoir. This effect should have provided for a linear declination of the driving force between the two reservoirs due to concentration gradient. However, as shown in Figure 7, the removal of MTBE from the solution occurred in along a logarithmic trend line, much the same way that the transport occurred in the in the absence of the Fenton's oxidation solution. The trend line plotted Figure 7 was calculated from the values from four runs. Two pairs of runs were conducted, with each of the duplicate apparatuses created for experimentation being utilized. The values measured for the two apparatuses were averaged, leaving two sets of data points to be plotted. The logarithmic coefficient for the equation of the trend line generated for the data points was significantly lower than that generated in the previous objective. The value generated for MTBE into water was -46.19 and the value for MTBE in Fenton's oxidation solution was -73.61. There was some reddish-brown staining on some of the membranes at the conclusion of the tests. The stains may well have been deposited iron that had the effect of clogging the pores of the membrane and therefore slowing the transport of MTBE across the polymer boundary.

Figure 7: Concentrations Over time for Full-Run



Tracking Temperature Change in the Reservoirs

The tests involving both MTBE and Fenton's oxidation solution, in separate reservoirs of the same apparatus, suggested that MTBE transport and oxidation of that MTBE were occurring in conjunction with one another. However, to be lend credence to the conclusion that the only reaction taking place during the testing period was oxidation of MTBE, the temperatures of the solutions over the course of the experiment were compared to baseline values, with changes in temperature suggesting reactions generating heats. Temperature readings were taken over a twenty-five minute period.

Table 7: Heat of Reaction Test Results

Apparatus - Heat of Reaction Test			
Setup	**Time**	**Temperature (˚C)**	
		Side 1	**Side 2**
18 MΩ E-Pure Water (1) vs. Fenton's Oxidation Solution (2)	5 Min.	21.7	21.7
	10 Min.	21.7	21.7
	15 Min.	21.7	21.7
18 MΩ E-Pure Water (1) vs. 1000 ppm MTBE Solution (2)	5 Min.	21.7	21.7
	10 Min.	21.7	21.7
	15 Min.	21.7	21.7
Fenton's Oxidation Solution (1) vs. 1000 ppm MTBE Solution (2)	5 Min.	21.7	21.7
	10 Min.	22.2	21.7
	15 Min.	22.5	21.7
	20 Min.	22.6	21.7
	25 Min.	22.6	21.7

No change in temperature was experienced when a MTBE solution was allowed to sit in the apparatus with a membrane separating it from a reservoir containing water. The same result was seen when Fenton's oxidation solution was allowed to stand in the same setup as the MTBE solution. When the Fenton's oxidation solution and MTBE solutions were both loaded into the apparatus, in different reservoirs, a temperature change of approximately one degree was seen over the twenty-five minute timeframe. These results are summarized in Table 7 and they led to the conclusion that the oxidation of MTBE occurring.

Contact Angle Measurement after Prolonged Exposure to Fenton's Oxidation

The Teflon membranes, after exposure to a strong oxidizing solution for a period of time no less than 48 hours, were tested again for the ability to repel water. The hydrophobic nature of the membranes was characterized by the contact angle measured for a drop of 18MΩ E-pure water on the membrane surface. The range for the contact angle measurements of the Teflon membrane after exposure was 109.2 to 135.9 degrees. The mean contact angle, for the four measured values was 120.5 degrees, which closely compares to the initial value mean contact angle of 120.2 degrees, certainly well within the standard deviation of the measurements. Because of the close agreement of the two values, it can be concluded that no change in the hydrophobicity of the membrane occurred.

Table 8: Conact Angle Measurements for Teflon Membrane after Fenton's Oxidation Exposure

Goniometer Contact Angle Measurements after Fenton's Oxidation Exposure	
Test Membrane	**0.45 µm Pore Teflon**
Trial 1	109.2
Trial 2	118.4
Trial 3	135.9
Trial 4	118.4
Average	120.5

CONCLUSIONS AND RECOMMENDATIONS

Of the four polymer membranes that were initially procured for testing, only three actually exhibited hydrophobic character. The Teflon, Nylon, and polypropylene membranes, which were proven to be hydrophobic, were tested for the ability to be permeated by MTBE. All three selectively transported MTBE and a comparison of the concentration reductions over time highlighted the Teflon membrane as having the greatest permeability to the contaminant. The Teflon membranes, when bound between an oxidizing solution, of ferrous iron ions and hydrogen peroxide, and MTBE in water, maintained their semi permeable characteristics. However, the concentration of MTBE in the MTBE solution was not reduced as drastically when paired with the oxidizing solution, as when paired with water. Staining was displayed on the membranes at the end of the test cycles involving the oxidizing solution containing iron. Given this phenomenon, the conclusion was drawn that iron deposits were clogging the polymer pores, limiting transport of MTBE. The deposition of iron onto the polymer membrane surface and the manner in which it reduces the membrane permeability to MTBE should be investigated further. A simply means of cleansing the membrane surface of deposition may be possible.

The concentrations of solutions for all experiments were determined based on the absorbance of light by solution samples. The concentration values were calculated from a standardization curve of the absorbance values measured for solutions of known concentration. A spectrophotometer was used to measure absorbance. The spectrophotometer utilized was inconsistent and on occasion, would report wildly different values for a single solution. In such cases, the system would need to be restarted or revisited later. A more reliable piece of equipment should be used in further experimentation.

The PTFE (Teflon) membrane used, while supported, was rather frail due to its thickness. The limitations of using thicker, more structurally sound forms of the membrane must be investigated for the development of an industrial scale remediation effort. A multiple pass tube exchanger would offer a large surface area for MTBE transport, as well as a dedicated area for the oxidizing solution. However, the Teflon tubes would have to be able be structurally sound enough to maintain form while also maintaining functionality.

The Teflon, Nylon and polypropylene membranes all fostered MTBE transport, which supports the tie between hydrophobic character and organophilic character. Other membranes resistant to strong solutions should be tested for the ability to rapidly transport MTBE, possibly outpacing the transport through Teflon.

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APPENDICES

Appendix A: MicroCOD Testing Procedure

- Preheat the MicroCOD incubator to 150°C
- Appropriately label a COD testing vial
- Draw a 2.5 mL sample using a 1-to- 5 μL pipette
- Excrete 2.5 mL of test solution into a MicroCOD vial.
- Shake the MicroCOD vial vigorously
- Place the vial within the COD incubator and set the timer for 2 hours
- Remove the MicroCOD vial from the incubator
- Unscrew vial cap and draw a 3.25 mL sample
- Excrete the sample into a spectrophotometer blank
- Zero the spectrophotometer using an empty blank
- Take a spectrophotometer reading
- Record the reading

Appendix B: Membrane Procurement Contact Information

Teflon, Nylon, Polypropylene: GE Osmonics Labstore:

Address:

5951 Clearwater Dr
Minnetonka, MN 55343
Phone Number:
(800-444-1212)
952-988-6665
Website:

http://www.osmolabstore.com/

Polyvinylidene Diflouride: John Andrew Bergendahl

Position:

Associate Professor

Civil and Environmental Engineering

Worcester Polytechnic Institute

Office:

Kaven Hall 117B

Worcester Polytechnic Institute

Phone Number:
1-508-831-5772
Email:

jberg@wpi.edu

Appendix C: MTBE/Hydrogen Peroxide Ratio Calculations

MTBE:

$$340\ \mu\mathrm{L} \times \frac{10^{-3}\,\mathrm{mL}}{1\ \mu\mathrm{L}} \times \frac{0.74\ \mathrm{g}}{1\ \mathrm{mL}} \times \frac{\mathrm{mole}}{88\ \mathrm{g}} = 2.859 \times 10^{-3}\ \mathrm{moles}$$

Hydrogen Peroxide

$$670\ \mu\mathrm{L} \times \frac{10^{-3}\,\mathrm{mL}}{1\ \mu\mathrm{L}} \times \frac{1.46\ \mathrm{g}}{1\ \mathrm{mL}} \times \frac{\mathrm{mole}}{34\ \mathrm{g}} = 2.877 \times 10^{-2}\ \mathrm{moles}$$

The ratio is $\frac{Hydrogen\ Peroxide}{MTBE} = \frac{2.877 \times 10^{-2}\ moles}{2.859 \times 10^{-3}\ moles} = 10.06$

For every mole of MTBE, there are 10.06 moles of Hydrogen Peroxide

APPENDIX D: MTBE/ $FeSO_4{\cdot}7H_2O$ Solution Ratio Calculations

1000 ppm solution of MTBE:

$$340\ \mu\text{L} \times \frac{10^{-3}\text{mL}}{1\ \mu\text{L}} \times \frac{0.74\ \text{g}}{1\ \text{mL}} \times \frac{\text{mole}}{88\ \text{g}} = 2.859 \times 10^{-3}\ \text{moles}$$

$FeSO_4{\cdot}7H_2O$ solution:

$$44.78\text{g} \times \frac{\text{mole}}{277.9\ \text{g}} = 0.161\ \text{moles}$$

The ratio is $\frac{\text{MTBE}}{\text{FeSO4}\cdot\text{7H2O}} = \frac{2.859\ \times 10^{-3}\ \text{moles}}{0.161\ \text{moles}} = 0.0178$

For every mole of a 1000 ppm solution of MTBE, there are 56.18 moles of $FeSO_4{\cdot}7H_2O$.

APPENDIX E: Hydrogen Peroxide/ $FeSO_4{\cdot}7H_2O$ Solution Ratio Calculations

Hydrogen Peroxide:

$$670\ \mu\text{L} \times \frac{10^{-3}\text{mL}}{1\ \mu\text{L}} \times \frac{1.46\ \text{g}}{1\ \text{mL}} \times \frac{\text{mole}}{34\ \text{g}} = 2.877 \times 10^{-2}\ \text{moles}$$

$FeSO_4{\cdot}7H_2O$ solution:

$$44.78\text{g} \times \frac{\text{mole}}{277.9\ \text{g}} = 0.161\ \text{moles}$$

The ratio is $\frac{\text{Hydrogen Peroxide}}{\text{FeSO4}\cdot\text{7H2O}} = \frac{2.877 \times 10^{-2}\ \text{moles}}{0.161\ \text{moles}} = 0.179$

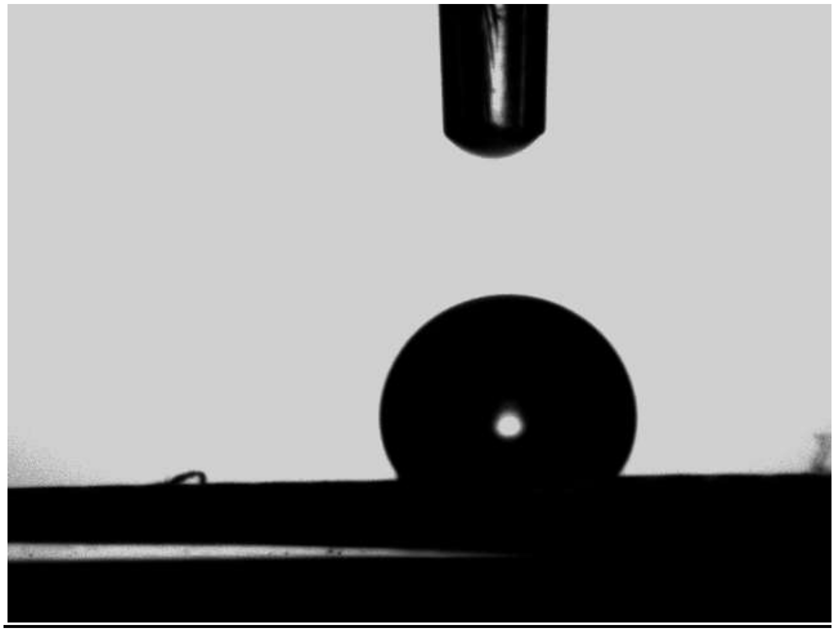
For every mole of a Hydrogen Peroxide, there are 5.59 moles of $FeSO_4{\cdot}7H_2O$.

Appendix F: Goniometer Pictures

Pre-Oxidation

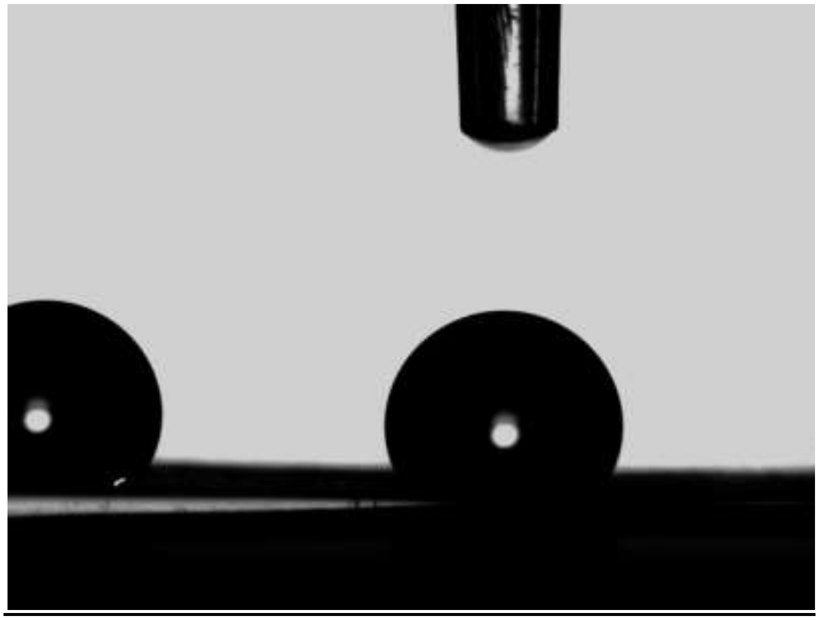
Teflon

Figure 8: Teflon Pre-Oxidation Picture



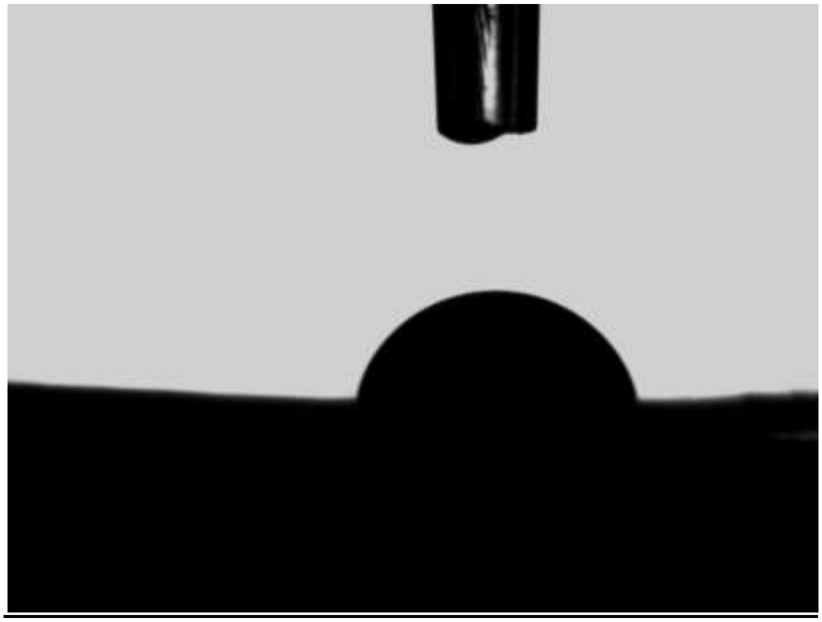
Nylon

Figure 9: Nylon Pre-Oxidation Picture



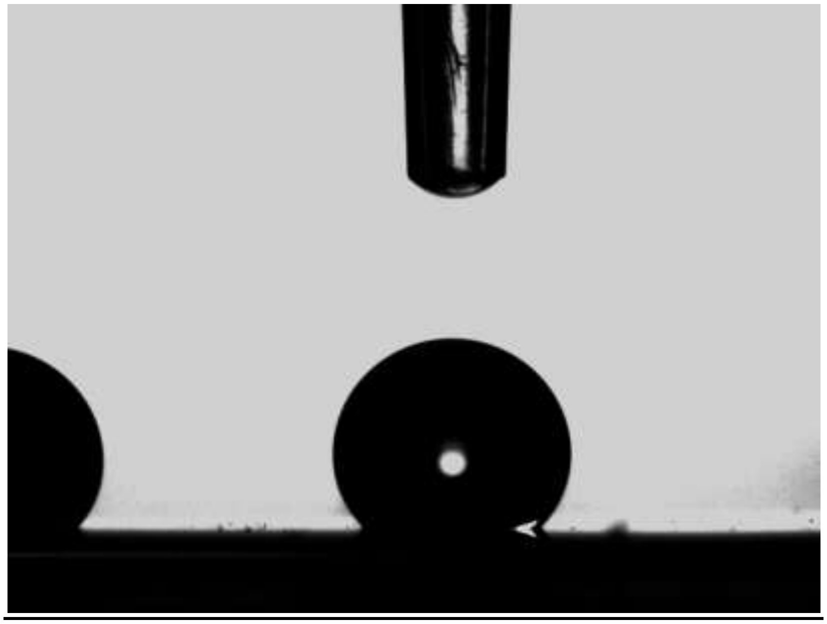
PVDF

Figure 10: PVDF Pre-Oxidation Picture



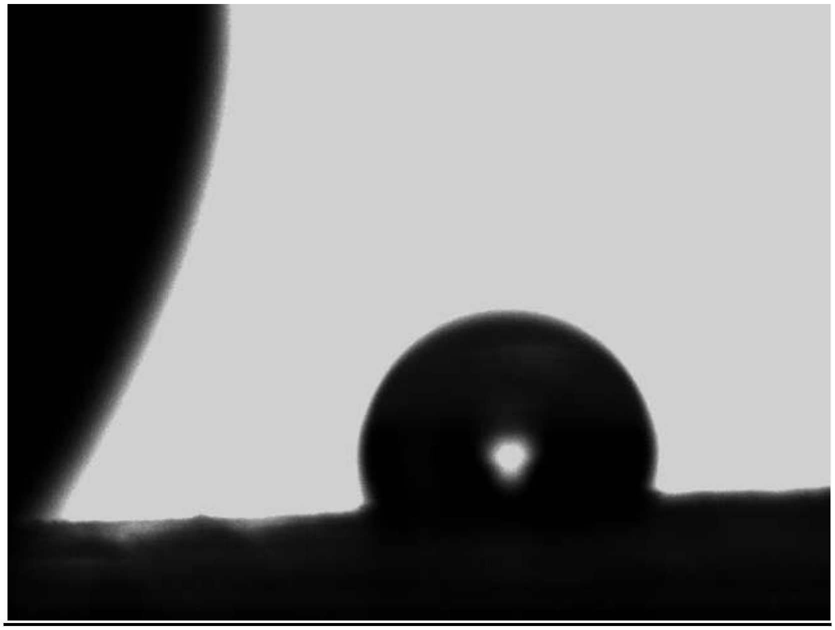
Polypropylene

Figure 11: Polypropylene Pre-Oxidation Picture



Post-Exposure: Teflon

Figure 12: Teflon Post-Oxidation Picture

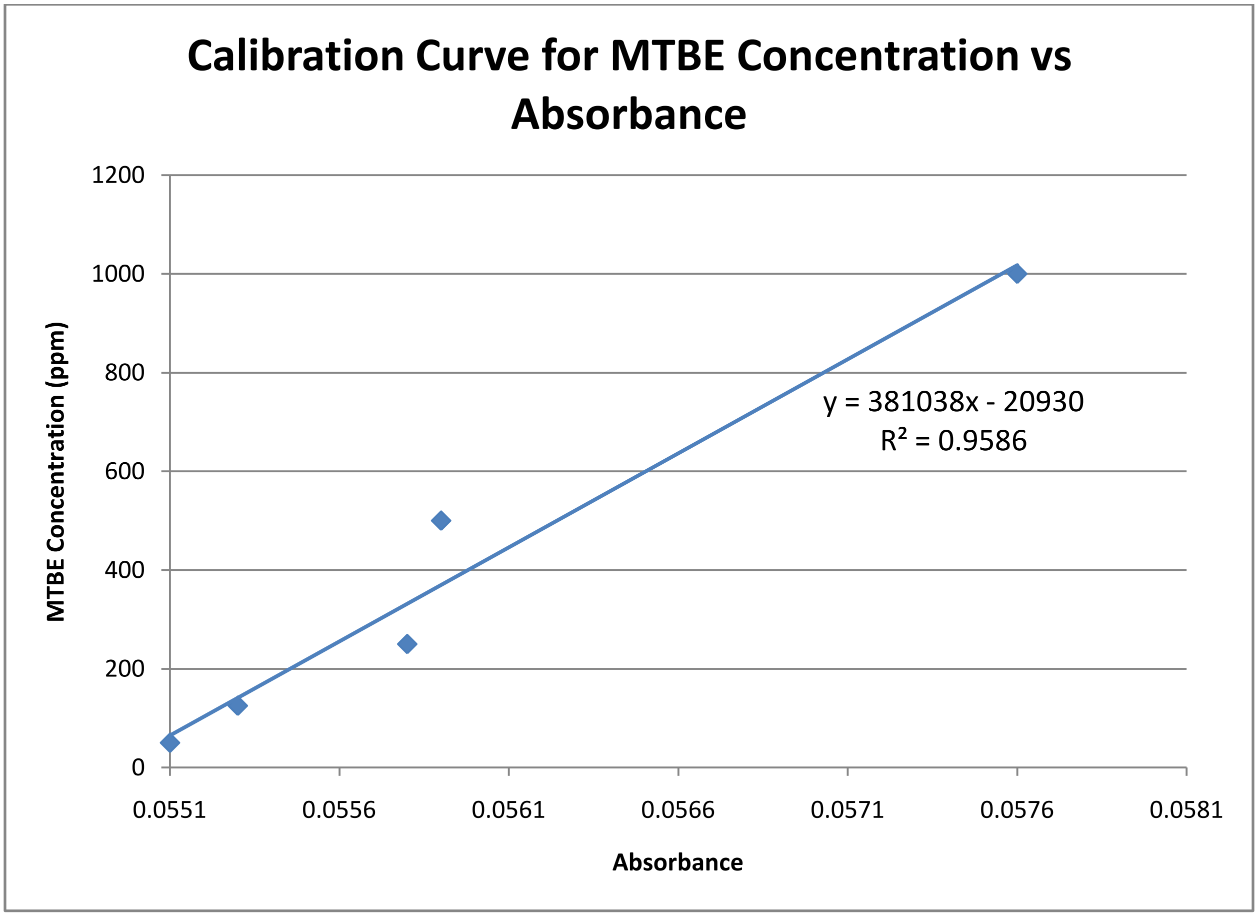


APPENDIX G: MTBE Concentration to Absorbance Calibration Curve

Table 9: Calibration Curve for MTBE Concentration vs Absorbance

Calibration Curve for MTBE Concention vs Absorbance	
Concentration (ppm)	**Absorbance**
1000	0.0576
500	0.0559
250	0.0558
125	0.0553
50	0.0551

Figure 13: Calibration Curve for MTBE Concentration vs Absorbance



APPENDIX H: MicroCOD MTBE Concentration to Absorbance Calibration Curve

Table 10: COD Testing Absorbance vs MTBE Concentration

COD Testing Absorbance vs MTBE Concentration Curve	
Concentration of MTBE(ppm)	**Absorbance**
1000	0.84
500	1.326
250	1.8251
125	3.663
50	4.3665
0	4.49

Figure 14: MicroCOD Absorbance vs MTBE Concentration