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Ceramics and Water Purification

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Abstract

The objective of this project was to determine the efficiency of MTBE separation using ceramic membrane filters. The use of advanced oxidation with Fenton's Reagent was also explored to completely degrade the MTBE. The filters were silanated to make them hydrophobic before being placed between samples of both pure and MTBE contaminated water. MTBE successfully passed through the membrane, but the separation involving the use of Fenton's reagent was unsuccessful. It is speculated that the failure resulted from iron precipitate blocking the membrane pores.

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Introduction

In the United States, underground aquifers provide drinking water for many communities. Therefore, it is very important for these sources of drinking water to remain clean. However, there are many chemicals which may contaminate underground aquifers. Although many incidences of contamination occur accidentally, they may nevertheless cause serious environmental and health issues for entire communities.

One example of an important drinking water pollutant is methyl tertiary-butyl ether, also known as MTBE. In the late 1970s, MTBE was introduced as an octane enhancer for gasoline to increase the amount of oxygen in the fuel. The levels of MTBE in gasoline were increased over time since the potential risks of using the chemical were not known. However, gasoline spills and leaking underground storage tanks near gas stations introduced MTBE into the soil, which then contaminated nearby underground aquifers. The reason this was such a large problem was because unlike other volatile organic compounds (VOCs), MTBE is highly soluble in water. This causes MTBE to be very mobile in water and provides little or no retardation when traveling in groundwater systems. Therefore, many remediation methods such as air purging in aqueous systems become ineffective or impractical (Ray & Selvakumar, 2000).

MTBE is not the only VOC that can be found in water. Other toxic compounds such as Benzene, Toluene, Ethylbenzene and Xylenes may be present due to similar spills or leaks into the ground. A variety of treatment methods have been developed to remove these VOCs from water. Advanced oxidation technologies such as ozonation and TiO_2 photocatalysis were first developed to destroy these pollutants. However, these methods were expensive and not very efficient. Fenton's Reagent, a solution of hydrogen peroxide and iron catalyst, later replaced these methods due to a 30% reduction in cost and the fact that it was 25-45 times more efficient than TiO_2 (Fallmann, 1999; Safarzadeh-Amiri, 1996).

The goal of this project was to use a porous ceramic membrane to separate MTBE from water. A hydrophobic surface was created by using alkyltrichlorosilanes to modify the surface chemistry of the anodized aluminum oxide membranes. The hydrophobic membrane was used as a barrier in a liquid-liquid separation system, repelling the MTBE-contaminated water while allowing the VOC to pass through. The addition of Fenton's reagent caused an iron precipitate

to clog the pores of the membrane, which did not allow MTBE to pass through. The inconclusive results did not allow the effectiveness of advanced oxidation in membrane filtration to be determined. The MTBE transport time was on the order of days, and therefore the expensive and extremely fragile filter would require very high surface areas for commercial use.

Background

Methyl *tert*-Butyl Ether

Methyl *tert*-Butyl Ether (MTBE) is a chemical compound made from a chemical reaction between methanol and isobutylene.

In production, *n*-butane is first isomerized to isobutane. The newly formed isobutane is then broken down into isobutylene and hydrogen via dehydrogenation. The isobutylene is finally reacted with the methanol to synthesize Methyl *tert*-Butyl Ether. The chemical structure is shown in Figure 1 (MTBE Production Economics, 2001).

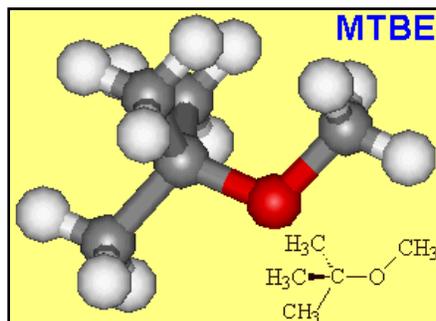


Figure 1: Molecular Configuration of MTBE

Cotton, Simon (2001)

Since the amendment of the Clean Air Act in 1990, MTBE has regularly been added to gasoline in large quantities up to 200,000 barrels a day as an oxygenate to reduce carbon monoxide emissions that result from burning the fuel, as well as improving its performance. The benefits of adding MTBE result from the oxygen present in the molecule which, when added to gasoline, improves combustion (MTBE in Fuels, 2007).

While the addition of MTBE to gasoline is helpful in reducing pollutants, it is harmful to the environment. The consequences of MTBE in drinking water at low concentrations are yet to be fully determined, but it is thought to be a carcinogen. Numerous studies have been conducted on

rats and mice, where cancer formed from exposure to high concentrations of MTBE (Toccalino, 2005).

According to Toccalino, it is not yet known how these test results relate to humans. Current studies have shown that nausea, dizziness, and headaches occurred when people were exposed to gasoline vapor containing MTBE. However, these health effects have not been directly connected to MTBE. In addition, the effects of low concentrations of MTBE over long periods of time have not been proven to cause cancer. Still, due to its possible hazardous side effects, a number of states have banned the use of MTBE as a gasoline additive, using ethanol instead. California became the first state to ban MTBE in 1999, and since then 24 other states have either imposed a partial or a complete ban of MTBE in gasoline (State Actions Banning MTBE, 2007).

MTBE can be introduced to the environment in several ways, the most common being gasoline spills and the incomplete combustion of fuel. Due to its relatively high solubility in water of 42 grams per liter at 25°C, it moves through soil very quickly, making gasoline leaks very hazardous (efoa.org). Not surprisingly, MTBE-contaminated water sources are generally found around gas stations, chemical companies, and parking lots.

If a gasoline leak occurs, MTBE may end up in a community's ground water supply. Its solubility, high resistance to biodegradation and the fact that it does not absorb easily into soil make it extremely difficult to remove from water (Drinking Water, 2007). Various removal methods are described later in the report. In places such as Pascoag, Rhode Island, disasters dealing with MTBE can completely devastate the community's drinking water supply.

According to the EPA, there is not enough of a health risk to quantify health advisory limits for MTBE in drinking water. They have however indicated that if MTBE is consumed in a concentration between 20 and 40 parts per billion, there is little likelihood that any adverse effects will occur. The health effects of MTBE are under a continuous study to determine whether health advisory limits will be set in the future (MTBE Recent Developments, 2002).

MTBE Removal Methods

The removal of MTBE from ground water is vital if it is to become drinking water for human consumption. There are various ways to achieve this removal, some of which are more effective than others depending on the state of the contamination site.

Pump-And-Treat

The pump-and-treat method involves pumping contaminated groundwater into a holding tank above ground where it remains until it passes through a water treatment plant. The treated water can be pumped back into the underground aquifer, used for industrial applications, or blended with clean drinking water (*“Overview of Groundwater Remediation Technologies,” 2005*). If the water is pumped back into the aquifer, the source of pollution must be removed from the aquifer in order to prevent recontamination. Since MTBE dissolves readily in water and does not significantly adsorb to soil (*“Remediation of MTBE,” 1998*), it can be an effective and efficient removal method for MTBE-contaminated groundwater if and only if the source of the MTBE contamination is also cleaned or restricted.

Two types of pump-and-treat methods are available. Restoration techniques work quickly, pumping the water to the treatment plant and flushing the contaminated aquifer with clean water. Containment techniques are used to prevent the spread of contaminants to areas beyond the already contaminated aquifer. These are less costly than restoration techniques because of the lower pumping costs. However, the contaminated water cannot be used. Containment techniques are useful for situations in which contaminated water does not need to be used, but further spreading of the contaminant may cause much larger problems (*“Overview,” 2005*).

Bioremediation

Bioremediation is a term used for the biological degradation of organic contaminants in water. Until the early 90's, MTBE was thought to be entirely resistant to biodegradation. When the possibility of MTBE posing a health threat was discovered, researchers worked to verify this

assumption. As a result, it was found that MTBE could be degraded under aerobic conditions with the addition of certain microbial culture mixtures, or bioaugmentation. The process was slow, most likely due to poor affinity between oxygen and MTBE degrading cultures. Better results were achieved when MTBE samples were oxygenated. Results proved that MTBE can be biodegraded under aerobic conditions, which was not thought to be possible prior to the early 90's. Bioaugmentation has also been found to be more efficient for MTBE biodegradation, particularly when having multiple microorganisms interact with the MTBE (Zanardini, Pisoni, Ranalli, Zucchi, & Sorlini, 2002).

Air Sparging

Air sparging is a method of treating contaminated groundwater, which does not require its removal from an aquifer. Oxygen-enriched compressed air is injected into the underground aquifer, passing through and dissolving into the contaminated groundwater. The oxygen acts as a catalyst for the bioremediation of the contaminant, a process in which microorganisms break down a contaminant, and restores the water to its original clean state. The contaminant volatilizes and is removed by physical contact with the air, adding to the environmental hazard of this operation if the vapors are not contained. This method is both expensive and time-consuming, sometimes lasting one to two years, but effective in removing MTBE.

Ozone-air sparging provides enhanced stripping of volatile organic compounds such as MTBE. Ozone, a highly reactive chemical, is effective in destroying organic chemicals through chemical oxidation. A three step process is necessary for the combination of air and ozone for sparging. First, air is bubbled through the ground water to volatilize any MTBE that is present. Second, the ozone reacts with the MTBE, destroying the vapor that is formed. Last, any oxygen that remains is used in bioremediation to convert the remaining products to carbon dioxide and water. Like other air sparging techniques, this is a long but effective process which can take over two years to complete (Schwartz, 2002).

Chemical Oxidation

The process being explored in this report is chemical oxidation. This technique involves injecting oxidants directly into the contaminated water while it is underground. However, this creates byproducts which must be removed before the water can be used for human consumption (*“Overview,” 2005*). Therefore, this method may involve additional costs beyond the oxidation of MTBE. More information on the byproducts is available under the “Advanced Oxidation” section in this report.

MTBE Remediation Sites

There have been many instances of MTBE contamination reported in the United States. The EPA oversees the cleanup of the contaminated area and makes sure it meets the set regulations. Table 1 describes various MTBE contamination sites, along with the treatment types used at each location.

One of the most recent worst cases of water contamination by MTBE was in Pascoag, Rhode Island. In 2001, Pascoag, Rhode Island’s public drinking water well was shut down due to the high level of MTBE contamination found in the water. Allen and Boving (2006) describe the situation as one the worst in New England and in the country.

Pascoag, Rhode Island has a water district that serves about 5,000 people in the town. This water was pumped from one sixteen inch well and was drawn at a rate of 350 gallons per minute from bedrock and aquifers. About 500 feet from the water well’s source, gasoline over six inches thick was found as a layer on top of the water (*“Pascoag and MTBE,” 2006*). Due to the high concentration of MTBE residing in the aquifers, Pascoag’s drinking water well had to be shut down. A local hockey rink with a separate water supply opened up in response to the drinking water emergency to let residents take showers and fill their water containers.

Table 1: MTBE Remediation Sites and Treatment Methods

Treatment Type	Location	Cost of remediation	Goal (MTBE conc. In µg/L)	Before (µg/L)	After (µg/L)
Bioremediation, Monitored Natural Attenuation	Abandoned Service Station, Boston, MA	\$400,000	70	2,500	20
Air sparging, Soil Vapor Extraction	Department of Defense Housing Facility Site Novato, CA	N/A	13	190,000	2,200
Air sparging, Bioremediation, Free Product Recovery	Harvey Harrelson, Chapin, SC	\$188,000	1,688	2,844,678	13,304
Bioremediation	Main Street Shell, Conway, SC	\$83,540	627	19,527	4,300
Chemical Oxidation, Multi Phase Extraction	SaveWay #2, Hartsville, SC	\$128,300	546	100,000	1,900
Bioremediation, Excavation, Soil Vapor Extraction, Thermal Desorption	Rural Area Disposal Area, TX - B, Liberty, TX	\$950,000	200	3,000	200

(MTBE Treatment Profiles, 2007)

Four months after the problem was discovered, Pascoag residents connected to Harrisville’s water supply. \$400,000 in Federal Grant Funds was reallocated to assist with the initial water treatment costs. Two additional million dollar grants were provided for assessment and remediation (Allen & Boving, 2006).

As of June 2006, over three million gallons of contaminated water has been pumped and cleaned with the current system. MTBE equivalent to 3000 gallons of gasoline was successfully removed over the two years of operation in Rhode Island. Figure 2 displays the change in concentration before and after the treatment.

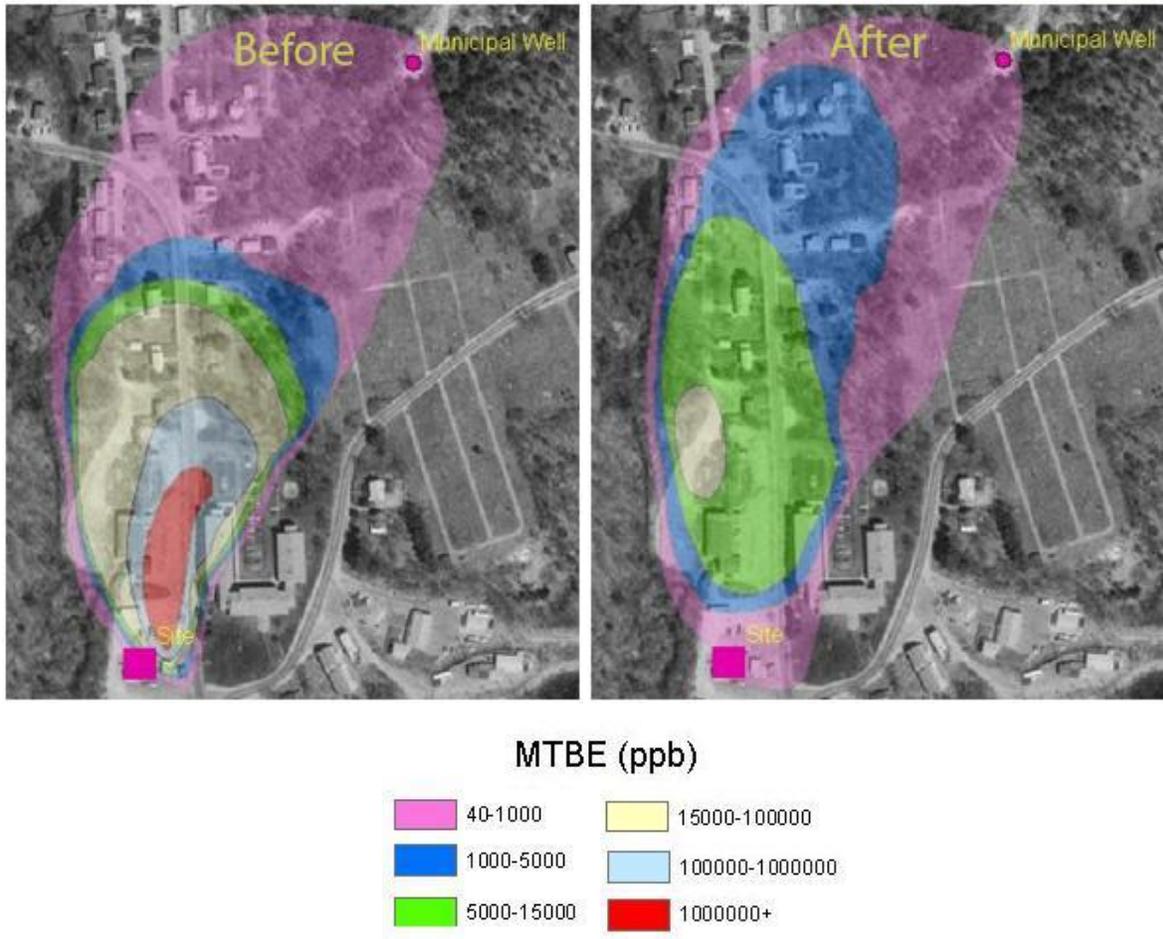


Figure 2: Pascoag, RI : Municipal Well Before & After
("Pascoag and MTBE," 2006)

A four month pump test was performed in 2003 to determine the MTBE concentration after two years of treatment. The concentration was reduced from 700 ppb (in 2001) to 40-70 ppb. A large effort was put into the purification of the water in Pascoag. This procedure only involved the outskirts of the contaminated MTBE area. As of 2006, the Rhode Island Department of

Environment Management was still considering remediation methods for the more concentrated areas.

There are other cases similar to Pascoag, Rhode Island issue with MTBE contamination. Water purification of methyl *tert*-butyl ether is a major concern nationwide and needs to be taken more seriously to deal with future contaminations.

Wicke-Kallenbach Method

A Wicke-Kallenbach diffusion cell employs a technique that is traditionally used to measure the diffusion rates of gases. Two gasses with different compositions flow through a cylinder, each on a different side of a separating membrane. The membrane may be a porous ceramic surface, allowing the two streams to interact. The compositions of the streams leaving the setup after flowing over the membrane are measured and compared to the input concentrations. The diffusion rate of each component through the separation membrane is then calculated.

Although it is traditionally used to separate gases, the Wicke-Kallenbach method can be modified to work with two components in the liquid phase, as shown in Figure 3. A mixture of two liquids flows over one side of the membrane while reactants flow over the other. The inorganic membrane, which can be designed to allow only the undesired liquid to pass through, stops the liquid that is being purified at the surface while the contaminant penetrates the filter. The reactants degrade the contaminant, causing more to diffuse through the filter from the high concentration side. In an ideal case, the contaminated liquid leaves the diffusion cell as one compound, free of impurities, after passing over the membrane.

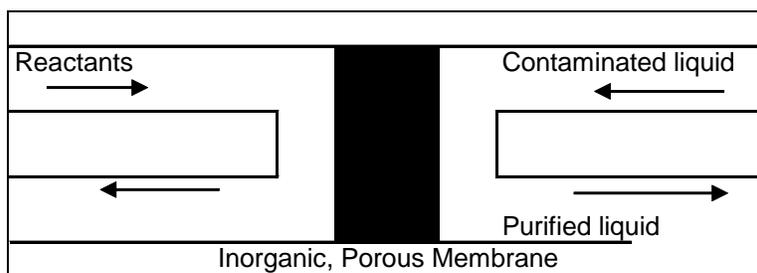


Figure 3: Schematic of Wicke-Kallenbach Diffusion Cell

Another possible design of a system for liquid-liquid separation is one in which the contaminated liquid is run through the porous membrane as opposed to over it. As the membrane has been modified to allow only the contaminant to pass through, the “clean” stream leaves as a contaminant-free output. The undesired liquid, which passes through the filter, is sent through to a cylinder containing reactants where it is broken down and discarded.

Whatman Anodisc Membranes

The Anodisc inorganic membranes used in these experiments were provided by Whatman. The membrane material is composed of a high purity alumina matrix with a honeycomb structure to eliminate chemical crossover between pores. This can be observed when the filter is analyzed with a scanning electron microscope, as shown in Figure 4. Due to the uniform pore structure and narrow pore sizes, these ceramic membranes are ideal for specialty filtration applications such as gravimetric analysis and the ultra-cleaning of solvents.

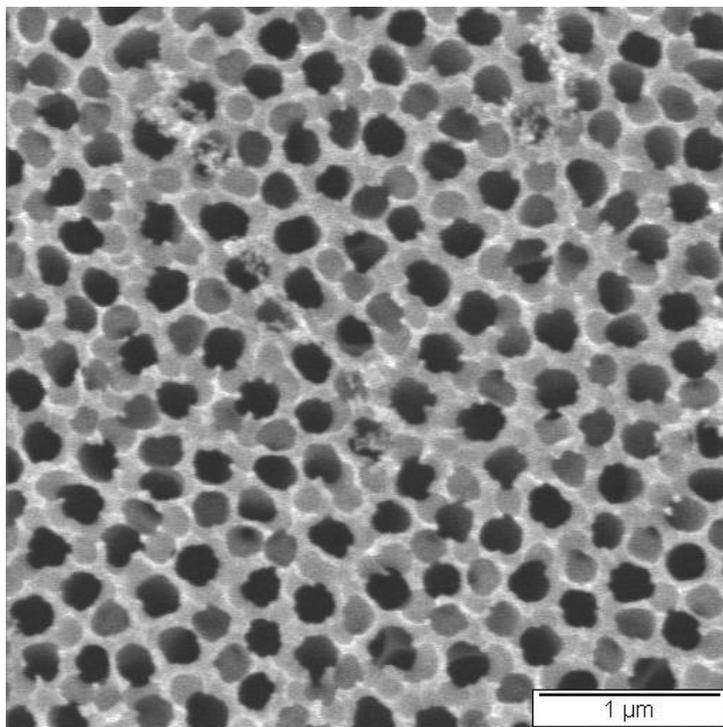


Figure 4: Honeycomb Structure of Anodisc Membrane Filters

Various filter diameters and pore sizes are available. The standard filter diameters of 13mm, 25mm and 47mm are available. However, the actual membrane diameters are 13mm, 21mm and 43mm due to the presence of a polypropylene ring around the two larger sizes. The size of a 25mm filter relative to a United States quarter can be seen in Figure 5.



Figure 5: A 25mm Whatman Anodisc Filter in Comparison to a US Quarter

Due to the extremely fragile nature of the membranes, the peripherally bonded polypropylene ring makes handling the filters much easier, as well as providing reinforcement during pressure filtration. The membranes are also available in three pore sizes of 20nm, 100nm and 200nm (www.whatman.com).

The membrane material is able to withstand high pressures and temperatures. While all varieties of the aluminum oxide membranes can withstand pressures of 65 to 110 psi, the polypropylene ring causes differences in the temperature compatibility. The 13mm membrane can be exposed to temperatures up to 400°C, while the 25mm and 47mm membranes can only withstand temperatures up to 40°C. The inherent problem in all of the membranes is the thickness of the filter, which is just 60µm. Due to the low thickness, the filters must be transported and handled very carefully to avoid cracking the template (www.whatman.com).

The hydrophilic nature of the inorganic membrane allows it to be transparent when wet, which allows a simple qualitative analysis to be conducted to determine whether the membrane has been wetted by a certain liquid. While the membrane itself is compatible with most solvents, the polypropylene ring is much less chemically resistant.

Plasma Cleaning

Plasma is considered to be a fourth state of matter apart from solids, liquids and gases. Boyd and Sanderson (1969) define plasma as “any state of matter which contains enough free, charged particles for its dynamical behavior to be dominated by electromagnetic forces.” While atoms in a normal gas are electrically neutral, the addition of energy to the gas can ionize the atoms, releasing electrons which move around freely. When there is a significant change in the electrical properties of the gas, it is called plasma (What Is Plasma, 2000).

Plasma cleaning is a process used to ultra-clean a surface by removing many contaminants which cannot be removed using other physical or chemical cleaning methods. When a surface is chemically cleaned, waste products are created and potentially reactive residue may be left behind. Physical cleaning methods may leave a thin film of contaminants which cannot be cleaned due to size restraints of the cleaning mechanism. Plasma cleaning is effective at removing very thin films such as oxides (Deiries, Hummel, Iwert, & Lizon, 2006) and does not leave behind solvent which must be discarded or recycled (Ward, 1995).

Plasma cleaning takes place inside a vacuum oven. A gas is fed into the oven at near-vacuum pressures, and a very high voltage anode inside the oven creates plasma at temperatures in the

tens of thousands of degrees Celsius. The choice of gas used for plasma cleaning is important as well, and varies by application. Ambient air is sufficient for cleaning most materials, but hydrogen is a better choice for cleaning noble gases. Stable gases such as Argon bombard the surface being cleaned with atoms and loosen any contaminants present. Oxygen works well for cleaning aluminum and stainless steel, as it operates by oxidation and reduction as shown in Figure 6 (Deiries, et al., 2006).

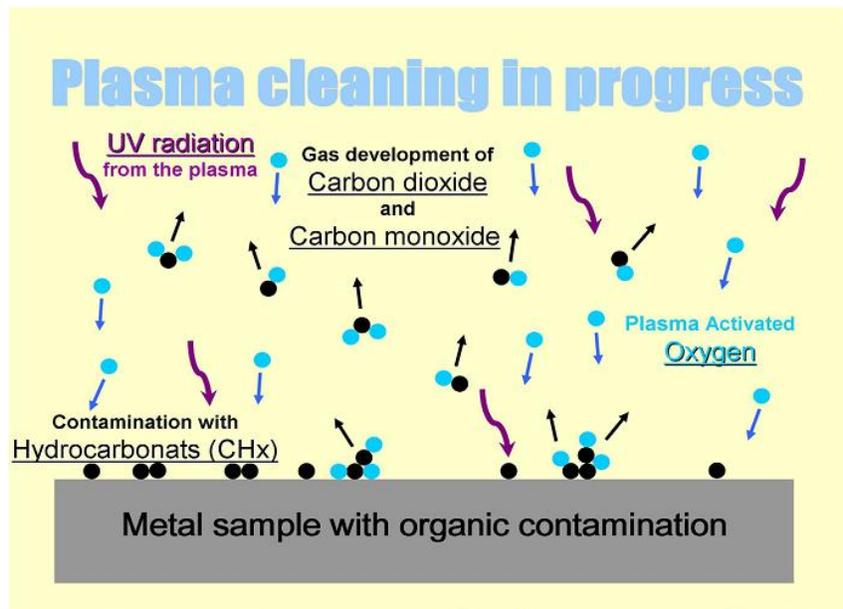


Figure 1. Oxygen ions of the plasma react with hydrocarbon contaminants to produce carbon monoxide and carbon dioxide, which can be pumped away

Figure 6: Plasma Cleaning
(Deiries, et al., 2006)

Hydrophobicity

Hydrophobicity is a physical property of a molecule that causes it to be repelled from a mass of water. This phenomenon is exhibited due to the difference in properties between two components. Water tends to be polar, and solvents such as oils, fats, and hydrocarbon chains tend to be non-polar. As a result, the non-polar molecules will be attracted to the non-polar solvents instead of the water molecules. Additionally, hydrophobic solvents lack the ability to hydrogen

bond and have low surface energy, forming micelles upon clustering. Micelles are aggregates of molecules that form in water, usually forming in spherical shapes. They are formed with the hydrophilic, or “water-loving”, heads of the molecules being in contact with the polar solvent and the hydrophobic tails inside of the sphere (Doshi, Watkins, Israelachvili, & Majewski, 2006).

An example of a commonly used micelle, shown in Figure 7, is soap. Soap is a hydrophobic compound that captures fats and oils in water, since fats and oils would normally not mix with water. Additionally, the soap suspends dirt and other objects so that water can remove them (“How does Soap Work”, 1999).

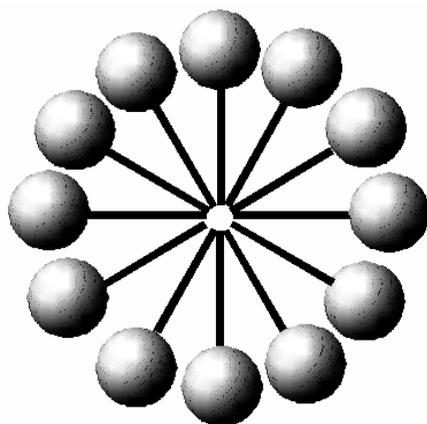


Figure 7: A spherical micelle
(KSV Instruments, 2005)

Applications for Hydrophobic Filters

Hydrophobic filters have many uses in industry, especially in separation processes. These uses range from the separation of water from jet fuel to hydrophobic air filtration.

In the separation of water from jet fuel, the mixture of fuel and water is typically sent through a set of hydrophilic and hydrophobic filters. The mixture first passes through a hydrophilic filter typically made of cotton. The water is absorbed by the filter and exits as large globules with the fuel. The fuel containing the water globules interacts with a hydrophobic filter where the fuel is allowed to pass freely, while the water is retained (“Method and Apparatus”, 2004).

The properties of hydrophobicity may also be exploited in the removal of volatile organic compounds from water by using air stripping techniques. Contaminated water is pumped through a series of hydrophobic, porous hollow fibers. The repulsion of water from the surface of the filter creates a nanoscale layer of air on top of which the water rests. A vacuum is placed outside of the fibers, causing the volatile components to transfer across the membrane in the gas phase. Water and air continuously flow on both sides of the membrane, maintaining a constant concentration gradient and allowing the transfer to occur at a steady rate. This allows for the separation of two liquids using a relatively low-tech process (Jiahan, 2004).

Contact Angle

The contact angle measures the hydrophobicity of a surface. It can be measured simply by adding a drop of water onto the surface of a solid. When the droplet first touches the surface, there are two likely paths the water droplet will take. The droplet may bead up or spread out onto the surface (*Ramé-hart Contact Angle Goniometers*, 2007).

If the water spreads out completely on the surface, the surface is considered to be hydrophilic. If the water forms a droplet that sits on top of the surface without spreading out, the surface is considered to be hydrophobic. A very hydrophobic surface will cause a drop of water placed on it to bend away from the surface, keeping its individuality. This observation is called the wetting phenomena (Lyklema, 2000).

Wetting on the surface of the solid depends on the affinity of the liquid to the solid. If the liquid is water and the solid's surface is hydrophobic, no wetting should occur. The two extremes are being completely hydrophobic or completely hydrophilic. Unfortunately, this isn't enough information to separate all types of surfaces and liquids. "Between these two limits there is a range of intermediate situations, where an equilibrium state is reached, in which the liquid meets the solid surface at a certain angle α , the contact angle [shown in Figure 8] (Lyklema, 2000)."

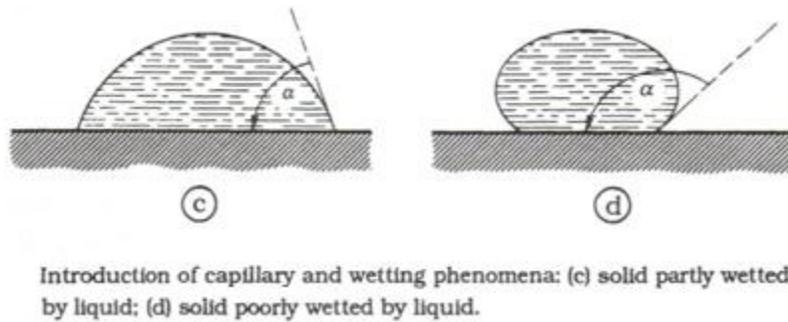


Figure 8: Contact Angle Measurement

(Lyklema, 2000)

Measuring the contact angle is useful for determining the cleanliness of a surface. If organic contaminants are on the surface of the material, wetting will become more difficult and will result in a larger contact angle. As the surface is cleaned the contact angle will gradually decrease as wetting is increased (*Ramé-hart Contact Angle Goniometers*, 2007).

As seen in Figure 9, the contact angle is a quantitative measurement, θ , which is geometrically defined as the angle formed by the liquid at the three phase boundary where a liquid, gas, and solid phase intersect (*Contact Angles*, 2005). This measurement is conducted using a goniometer, shown in Figure 10, in conjunction with software tools to perform, the calculations.

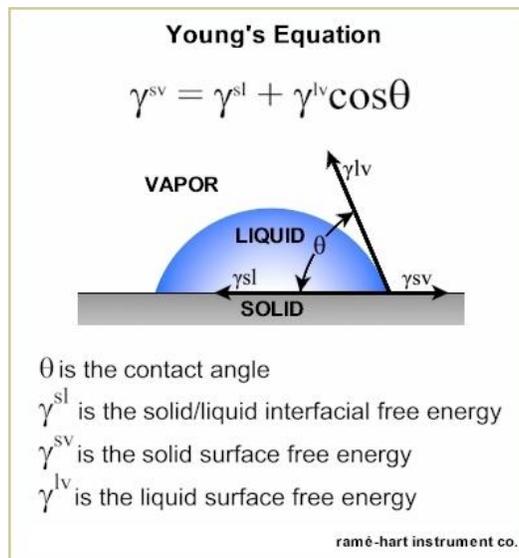


Figure 9: Contact Angle Measurement 2

(*Ramé-hart Contact Angle Goniometers*, 2007)

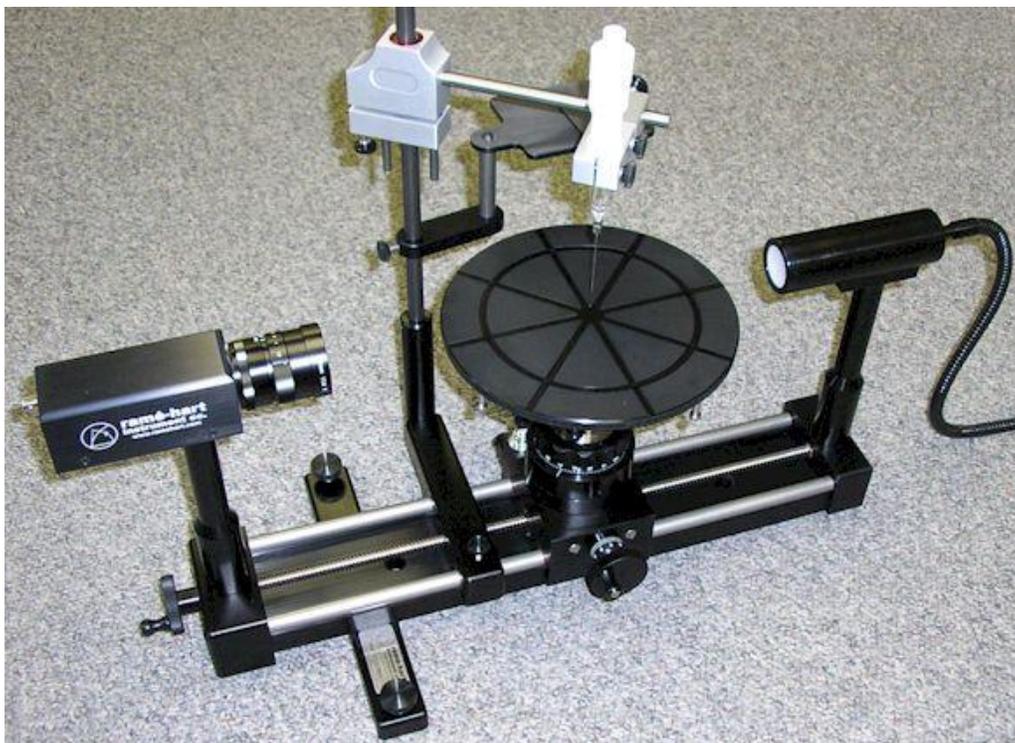


Figure 10: A ramé-hart Goniometer
(*Ramé-hart Contact Angle Goniometers, 2007*)

Silanes and Self-Assembled Monolayers

Silanes are molecules based on the chemical formula SiH_4 , similar to the way hydrocarbons are based on methane, CH_4 . Trichlorosilane, HSiCl_3 , is a modified form of silane containing three chlorine atoms. It is highly reactive in water and is used as a source for silicone polymers, as well as for applications in organic synthesis.

Alkyltrichlorosilanes are trichlorosilanes with an alkyl substituent attached. Octadecyltrichlorosilane (OTS), $\text{C}_{18}\text{H}_{37}\text{Cl}_3\text{Si}$, is an alkyltrichlorosilane containing an 18-carbon chain with 3 chlorine atoms as its terminal group. It has a boiling point of 160°C , and is often used at low pressures because of their use in vapor deposition, which must be conducted at low pressures to avoid heating the samples (Lewis, 2003). A three dimensional representative view of the molecule is provided in Figure 11.

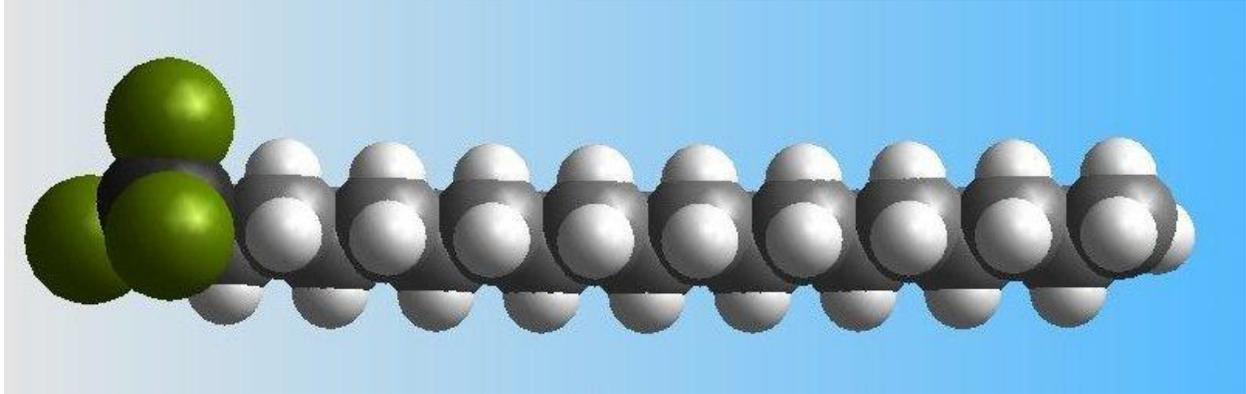


Figure 11: Octadecyltrichlorosilane
(Lewis, 2003)

OTS may be used to modify a surface containing a hydroxyl group, an example of which is a nanoporous alumina template. When OTS comes into contact with a hydroxyl group, one of the chlorine atoms bonds to a hydrogen atom, forming hydrochloric acid. The oxygen group, which becomes negatively charged, bonds to the silicon atom. This reaction allows the OTS molecule to attach itself to a surface.



One possible use for modifying a surface with OTS is to transform a previously hydrophilic surface into a hydrophobic surface. The long carbon chain, ending in a methyl group, helps to repel the polar water molecules from the surface to which the trichlorosilane is attached. As the carbon chain becomes longer, the surface becomes more hydrophobic. In the case of MTBE and water, both liquids are stopped at the silane layer shown in Figure 12. However, due to its high vapor pressure and organophilic character, MTBE volatilizes and passes through the organophilic forest of alkyltrichlorosilanes. The concentration gradient drives the MTBE vapor through the membrane where it condenses and mixes in with the less concentrated liquid.

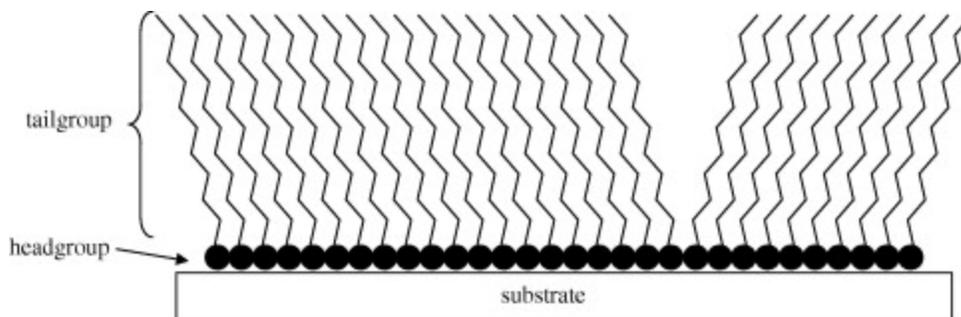


Figure 12: Silanes Bonded to a Surface

(Kirkpatrick, 2007)

To effectively modify a surface with a trichlorosilane, a large majority of the hydroxyl groups on the solid substrate must covalently bond with the silicon atoms. However, this is difficult to achieve without overloading the surface and blocking any pores that may be present on a porous substrate. To overcome this difficulty, self-assembled monolayers (SAMs) may be formed. SAMs are single-layered, ordered molecule assemblies that form on a surface, frequently consisting of long-chain hydrocarbons such as trichlorosilanes (Ulman, 1996). The uniform coverage of the well-organized monolayer ensures that any pores present are not blocked by oversaturation of the surface. By adjusting the length of the hydrocarbon chain and the terminal group, the hydrophobicity, charge, and reactivity of the modified surface can be controlled (Nalwa, 2000).

When attaching a hydrocarbon to a surface, the terminal group plays a large role in the type of bonding that occurs. When a monochlorosilane bonds to a porous silica membrane containing hydroxyl groups, a single covalent bond connects the hydrocarbon to the surface as shown in Figure 13. In addition, the hydrocarbon chain is isolated and does not bond to any adjacent molecules. This type of bonding is not ideal due to the number of hydroxyl groups that are left unbounded. When a dichlorosilane bonds to a silica surface, it may either form two covalent bonds to the surface or polymerize vertically by bonding with other dichlorosilane molecules. This too is not ideal since the formation of large polymers may block the pores on the silica membrane (Fadeev & McCarthy, 2000).

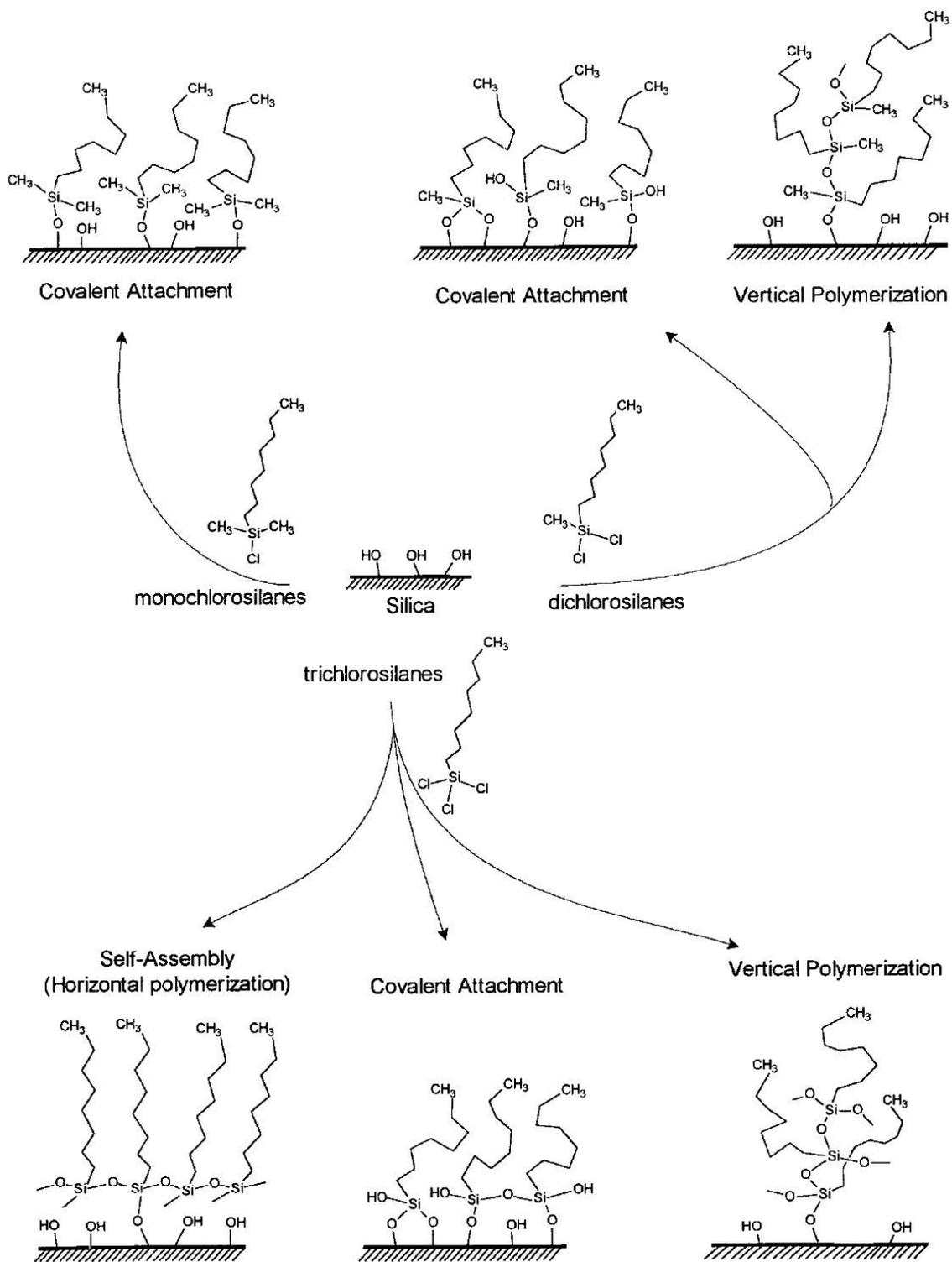


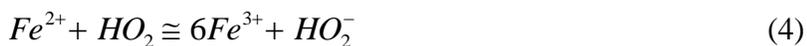
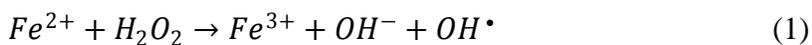
Figure 13: Mono- Di- and Trichlorosilane Bonding on a Silica Surface
(Fadeev, 2000)

The use of trichlorosilanes allows SAMs to form on a silica membrane. One silicon atom bonds to a free hydroxyl group on the surface and proceeds to bond to other trichlorosilanes, forming horizontal polymerization. This is usually the desired outcome because a large portion of the surface is covered by the uniformly polymerized hydrocarbons (Fadeev & McCarthy, 2000).

Advanced Oxidation Processes: Fenton's Reagent

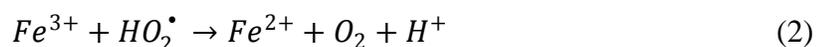
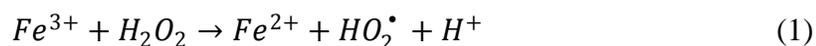
Advanced oxidation processes are used to chemically reduce the concentration of organic pollutants from water (Hubbard, 2001). Fenton's reagent, a solution containing hydrogen peroxide and an iron catalyst (i.e. Fe (II) or Fe (III) salts), is commonly used in the oxidation of MTBE in contaminated water. What makes Fenton's reagent a favorable reaction for the degradation of organic compounds is that the catalyst, hydrogen peroxide, is very inexpensive. Furthermore, the iron compound that is used in the reaction can be recovered and reused by increasing the pH, which in turn precipitates the iron. Fenton's reagent can also oxidize a wide variety of chemical groups such as acids, alcohols, aldehydes, aromatics, amines, and dyes (Nesheiwat, 2000).

The use of hydrogen peroxide allows the creation of hydroxyl (OH·) and perhydroxyl (HOO·) radicals, which are one of the strongest oxidizing reagents besides fluorine (Nesheiwat, 2000). These hydroxyl radicals proceed to react with ferrous ions (Fe²⁺) to form hydroxyl and ferric ions. This process is described by the following equations (Pignatello et al., 1999):



Fe^{2+} and Fe^{3+} express the hydrated species $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$, respectively. Equation (1) is normally considered as the Fenton reaction. This is however not the only reaction that occurs in the Fenton systems. The major factor that causes the degradation of pollutants is the formation of the hydroxyl radical. “Hydroxyl radical is a very strong, nonselective oxidant capable of degrading a wide array of pollutants” (Tarr, 2003).

Aside from the formation of hydroxyl radicals, there are other key steps in the Fenton reagent. The newly formed ferric ions (Fe^{3+}) react with the hydrogen peroxide which produces hydroperoxyl radicals (HO_2^{\bullet}). These then react with the remaining ferric ions and form more ferrous ions which are used in the reaction above. These reactions are shown by the equations below (Pignatello et al., 1999):



During the oxidation of MTBE, four intermediate products of MTBE oxidation can be identified: *tert*-butyl formate, *tert*-butyl alcohol, acetone, and methyl acetate (Siedlecka, 2007). The Fenton’s reagent efficiency is dependent on temperature. An increase in temperature results in an increase in the reaction rate, which is most noticeable at temperatures between 5°C-20°C. As the temperature rises above 50°C, the reaction depends less on temperature due to the rapid degeneration of hydrogen peroxide (Nesheiwat, 2000).

As Nesheiwat mentions, the pH of the Fenton’s reagent is important in determining the states of the ferric ions. At pH values of 3 or less, the ferric ions are in solution with the liquid. A pH of 3-5 would indicate that the ferric ions are in colloidal form, an ideal state for the degradation of MTBE. If the pH rises above 5, Fe_2O_3 precipitate begins to form and settles to the bottom of the liquid.

Methodology

Experimental Design

Although there are currently many methods of separating methyl *tert*-butyl ether (MTBE) from water, this study focused on the separation of a liquid-liquid system using Whatman brand Anodisc filters. Certain criteria also had to be met for the separation to be considered a success. Two bodies of liquid were required to be separated by only a filter to ensure that it was the cause of the separation. The system had to be airtight to prevent the loss of MTBE, since it is a very volatile compound. Finally, the system had to be free of any leaks to avoid any variations in chemical concentrations.

A system that met the set requirements was built using a 1 inch union, two 250ml Nalgene bottles, two $\frac{3}{4}$ inch ID tube connectors, and epoxy. The porous, ceramic membrane filters were held together in the union with the aid of an o-ring gasket, and were used as a barrier between the water contaminated with MTBE and the reactants. The Nalgene bottles were used as liquid storage tanks for the MTBE contaminated water and the Fenton's reagent. A $\frac{3}{4}$ inch hole was drilled on the side of each Nalgene bottle, and the $\frac{3}{4}$ inch tube connectors were attached with epoxy. Teflon tape was used around the connections to prevent leaks. When in use, caps were tightly screwed onto the bottles, and Parafilm was used to seal the caps. The separation unit that was designed is shown in Figure 14.



Figure 14: Separation Unit

Silanation of the Filter

The Anodisc filters, made from aluminum oxide, are hydrophilic in nature. To successfully use them for the separation of MTBE from water, the filters had to be modified to become hydrophobic. The unmodified filter allowed water, MTBE, and the reactants to pass through, while the surface-modified hydrophobic filter would theoretically repel the water and reactants while allowing the MTBE to pass through.

Based on the publication of Sah, Castricum, Blik, Blank, & Elshof (2004), it was determined that silanation was an effective method of modifying the filter's surface chemistry. Octadecyltrichlorosilane (OTS) was selected due to its very polar properties originating from its long, 18-carbon chain with a methyl group at the end. Ease of access was also considered, and

OTS was readily accessible in the laboratory. In addition, based on literature reviews, OTS had been used successfully in the past for similar applications.

Plasma Cleaning

Plasma cleaning was performed on each filter before silanation to remove any contaminants from the ceramic surface. The main power to the plasma cleaner was turned on, and the oxygen supply valve was opened. The plasma cleaner cylinder was removed and 2-4 filters were placed inside, at least one inch apart. The cylinder was inserted into the plasma cleaner and the vacuum pump was turned on. The plasma cleaner was activated, and the power level was adjusted for maximum power. The filters in the first batch were cleaned for 30 seconds. The cleaning time was later reduced to 15 seconds due to some warping of the polypropylene ring around the filter.

Silanation by Vapor Deposition

Vapor deposition was initially used as a method of silanation due to its greater affinity for creating self-assembled monolayers (SAMs) when compared to liquid immersion silanation. This was ideal because an atomic monolayer of silanes provides maximum coverage of the surface while not hindering the movement of MTBE through the pores.

To carry out the vapor deposition, 3-5 drops of octadecyltrichlorosilane were placed on a watch glass in the center of a vacuum desiccator. The filters were spread evenly around the desiccators in plastic petri dishes, at an angle so both sides were exposed. The air in the desiccators was evacuated for one hour using a vacuum pump, and was sealed for 24 hours. The filters were then removed and washed in an ethanol bath, and dried with a stream of nitrogen.

Silanation by Liquid Immersion

Liquid-based silanation of the filters was explored as well. This type of silanation did not require the use of a vacuum desiccator, and was therefore less complicated to perform. It also allowed

more filters to be silanated at one time, since any desiccator space constraints were eliminated. However, any presence of water in the solvent/silane solution would result in the creation of silane polymers, which in turn had the potential to block the membrane's nanopores, hindering the transport of MTBE.

Liquid-based silanation of the filters was carried out using a 1:100 OTS:Hexanes solution. 30ml of hexane and 0.3ml OTS were used. The filters were placed in beakers with the created solution and covered in aluminum foil or parafilm to protect against solvent evaporation and to reduce the interaction with water molecules from the air. The filters were allowed to sit in solution for 24 hours after which they were removed and rinsed with ethanol. While submerged in ethanol, the filters were placed in an ultrasonic cleaner for approximately 2 minutes to remove any silane polymers that may have formed on the surface.

Contact Angle Measurement

To determine the hydrophobicity of the filters, a goniometer was used to measure the contact angle of a water drop on the surface. This was carried out after the initial silination was complete and whenever modifications were made to the procedure. One of each filter type was placed on the goniometer and, using the appropriate software, contact angles of a single drop of water were measured.

Experiment 1: Effects of Water on the Separation Unit

The separation unit, shown in Figure 14, was filled with deionized water without a membrane in the union. The entire system was then placed on a shaker table for 24 hours. Once the allotted time had passed, the water was tested by carrying out a chemical oxygen demand (COD) test. This was done to determine whether any components, such as the epoxy or any residual oils from the connections, did not interfere with the COD testing accuracy.

The water that was exposed to the system for 24 hours had an absorbance value that was identical to fresh, deionized water. This meant that no residual chemicals that would affect the chemical oxygen demand of the system were picked up by the water after 24 hours. Therefore, it was determined that the designed system would not interfere with the COD results in future tests.

It was necessary to determine the minimum absorbance values for the three types of COD vials available. To do this, deionized water was tested in three COD vial ranges: 50-150mg/l, 20-900mg/l, and 100-4500mg/l. The results of this experiment are displayed in the Results and Discussion section.

Experiment 2: Permeability of Hydrogen Peroxide

An experiment was designed to determine whether hydrogen peroxide would permeate the hydrophobic membrane to ensure that the hydrogen peroxide from the Fenton's reagent would not breach the filter in subsequent experiments. The apparatus was set up with 200 ml deionized water in one liquid tank, and a solution of 150ml water and 50ml hydrogen peroxide in the other. A hydrophobic filter was placed in the union connecting the two bottles, and the system was placed on a shaker table for 24 hours.

Cobalt-Ultraviolet Spectrophotometry Method (Belhateche & Symons, 1991) was used to measure the concentration of hydrogen peroxide. This method required the use of a solution of sodium bicarbonate. The solution was created by mixing 25 grams of sodium in bicarbonate in 250ml of water, or proportional amounts depending on the desired volume. The solution was stirred for approximately 45 minutes before the sodium bicarbonate completely dissolved, while

heating the solution helped speed up the process. Approximately half of the solution was transferred to a 25ml volumetric flask. Next, 1.03 ml of cobalt stock solution was added to the flask. The third component added to the flask was 1.0 ml of the sample being tested. Finally, the flask was filled to the 25ml mark with the sodium bicarbonate solution. The mixture was set on a table for 15 minutes to allow the reaction to go to completion. After 15 minutes, the sample was tested in the UV/VIS spectrophotometer at a wavelength of 320nm. A calibration curve, shown in Figure 15, was used to determine the concentration of the hydrogen peroxide based on the absorbance readings.

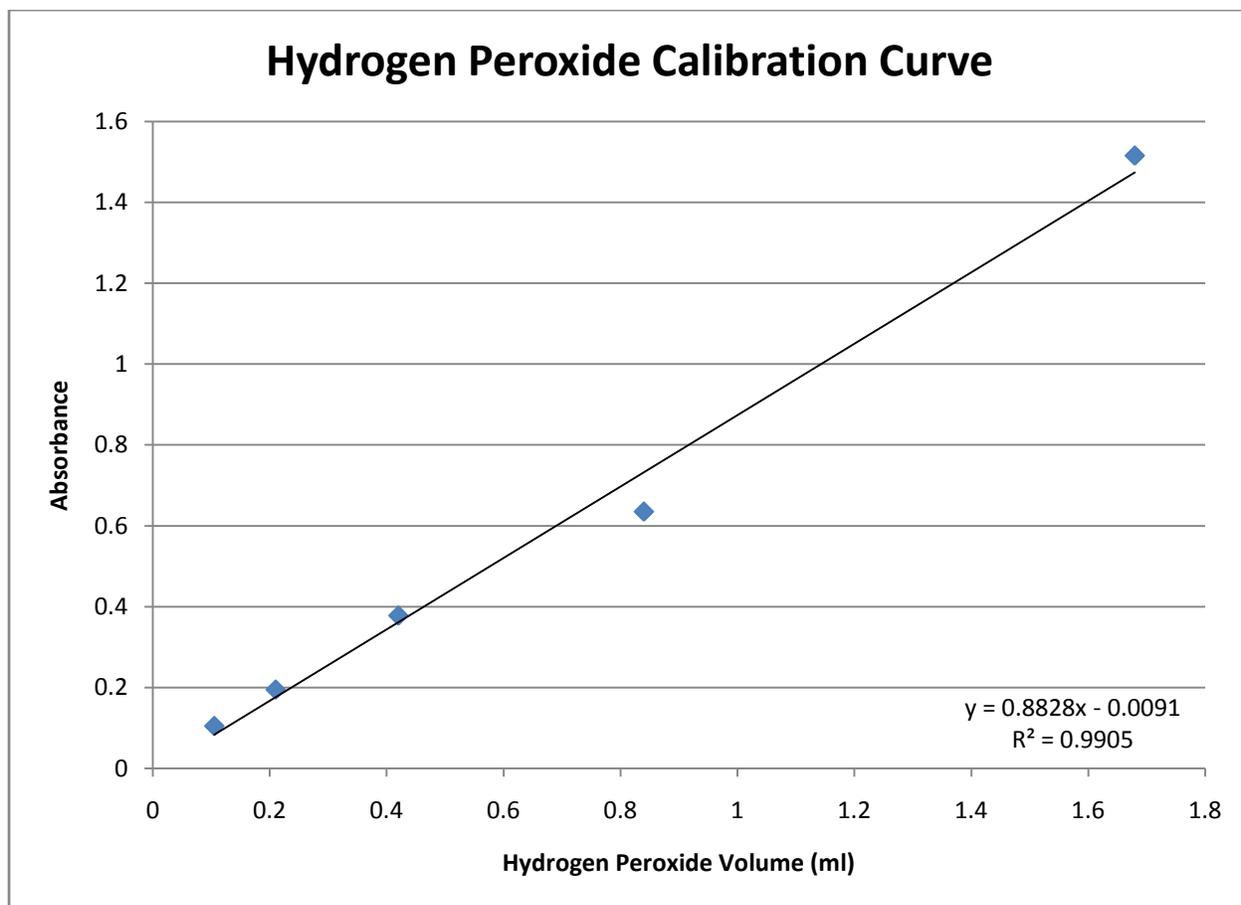


Figure 15: Hydrogen Peroxide Calibration Curve
(Slack, 2004)

Experiment 3: Separation of 1200ppm MTBE from Water (no mixing)

To determine whether MTBE permeated a silanated membrane, a 1200ppm solution of MTBE was created by mixing 810 μ l of MTBE with 500 ml of deionized water. The mixture was stirred using a magnetic stirring bar for 1 hour, and was then stored in a refrigerated amber bottle.

200ml of the MTBE solution was poured into one bottle of the separation unit, and 200ml of deionized water was used in the other bottle. The two sides were separated by a hydrophobic filter and the apparatus sat unmixed. COD testing with 100-4500ppm range vials was conducted on both bottles on the second and fifth days to determine whether MTBE penetrated the filter.

Experiment 4: Separation of 600ppm MTBE from Water (no mixing)

Experiment 3 was repeated with a lower concentration of MTBE and more frequent COD testing. A 200ml mixture of 600ppm MTBE in water was placed in one bottle, while 200ml of deionized water was placed in the other. COD testing was conducted daily for four days to increase the resolution of MTBE transport across the membrane. The COD vials used had a concentration detection range of 100-4500ppm.

To create the mixture of 600ppm MTBE in water, 405 μ l of MTBE were mixed with 500ml of deionized water. The mixture was mixed using a magnetic stirring bar for 1 hour. The mixture was then stored in a refrigerated amber bottle.

Experiment 5: Separation of MTBE from Water (no mixing)

The COD testing in this experiment was also conducted daily for five days. To obtain even greater resolution of the transport of MTBE across the membrane, experiment 4 was repeated with a higher sampling frequency. Samples were collected twice daily for ten days with the separation unit placed in a dark drawer. The same mixture of 600ppm MTBE in water was used for this experiment.

Different COD vials were used to measure the concentration of MTBE in this experiment. Vials with a concentration range of 20-900ppm were used because they provided a more accurate representation of the data when compared to the calibration curve, Figure 16.

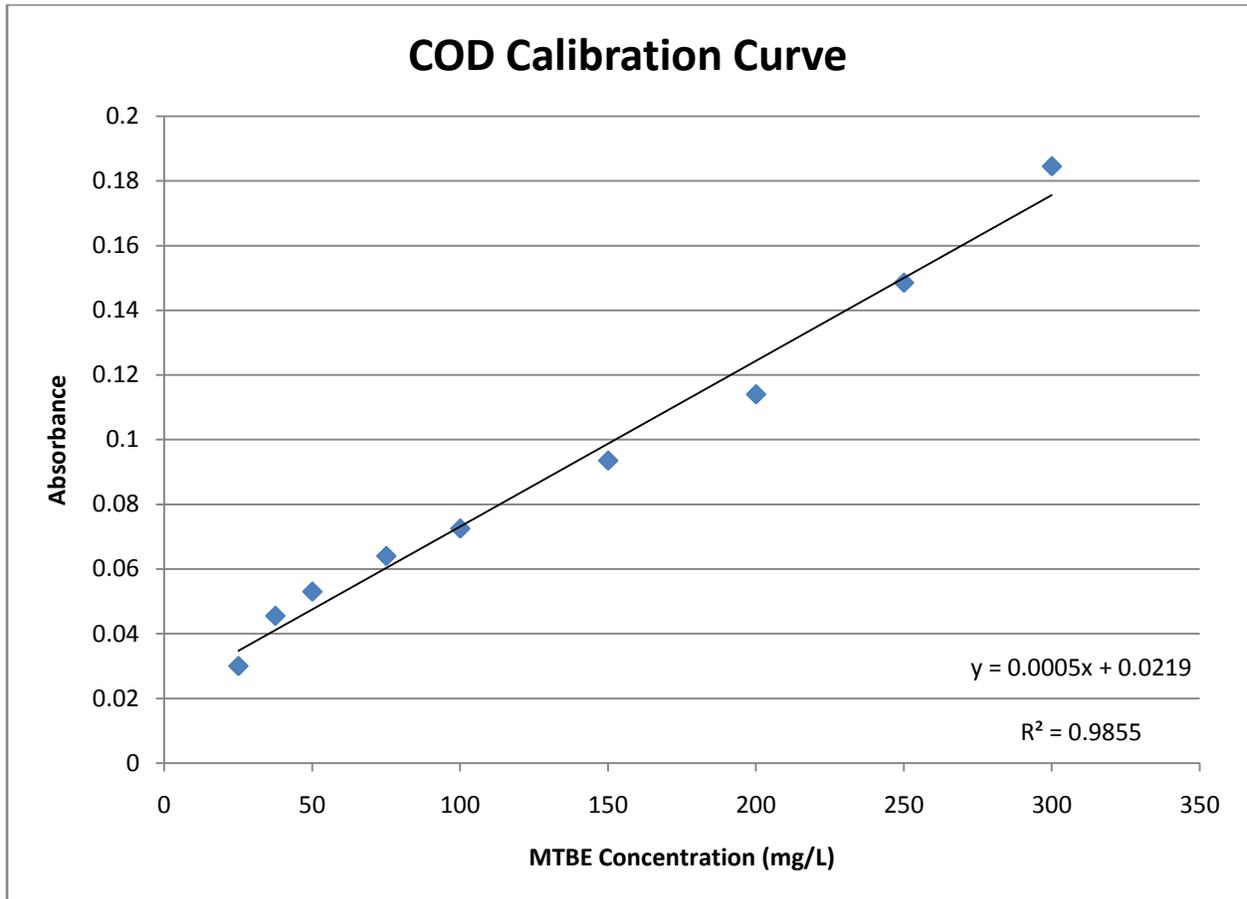


Figure 16: Chemical Oxygen Demand Calibration Curve
(Slack, 2004)

Experiment 6: Separation of MTBE from Water (with mixing)

To determine the effects of mixing on the transport rate of MTBE, magnetic stirrers were placed in each liquid tank. The entire separation unit was placed on two magnetic stirrers on a lab bench. Experiment 5 was repeated, except the liquid in each bottle was stirred for the duration of the experiment to improve the concentration distribution of MTBE in each bottle.

Experiment 7: Fenton's Oxidation

A final experiment was performed with Fenton's reagent and MTBE. The purpose of this experiment was to determine whether the degradation of MTBE, once it passed through the filter, would increase the overall transport rate.

To conduct this experiment, a new mixture of 600ppm MTBE in water was created and 200ml was put in the first bottle. A solution of Fenton's reagent was created by dissolving 44 grams of iron sulfate in 200ml water for 45 minutes, adding 670 μ l hydrogen peroxide and allowing the reaction to complete. 200ml of the solution was placed into the second bottle, and the caps were tightly sealed. The separation unit sat unmixed for four days, and was then placed on magnetic mixers for three more days. Samples were collected daily from the bottle containing MTBE and water.

Results

Experiment 1: Effects of Water on the Separation Unit

Chemical Oxygen Demand (COD) vials with various concentration ranges were tested with deionized water to determine the “zero” values for absorbance at a wavelength of 600nm. The results of these tests are shown in Table 2.

Table 2: COD Absorbances of deionized water at 600 nm

COD Vial Range	Average Absorbance for 0 mg/l at 600nm
5-150 mg/l	.0128
20-900 mg/l	.0160
100-4500 mg/l	.0094

The values for absorbance at 600nm for water were used while determining the concentration of MTBE in future COD tests. The base absorbance values for water were subtracted from any absorbances measured to “zero” the data and to avoid calculating negative concentrations of MTBE.

Silanation of the Filter / Contact Angle

The success or failure of the silanation was based on both quantitative and qualitative results. The behavior of water drops on the filter surface was observed with the naked eye, and a Ramé-Hart goniometer was used to measure the contact angles of the water drops. For each filter, the contact angle test was run at least five times to increase the accuracy. The results of the tests are shown in Table 3, and are reported as averages of the multiple tests.

Table 3: Contact Angle Results

Pore Size (nm)	Plasma Cleaning	Silanation	Average Contact Angle
20,100,200	Yes	No	0
20	No	No	26.3
200	Yes	Vapor Deposition	8.3
20	Yes	Liquid Immersion	140.1
100	Yes	Liquid Immersion	150.4
200	Yes	Liquid Immersion	148.3

As seen in Table 3, the contact angle of an unmodified filter that has been plasma cleaned is immeasurable. The water drop was absorbed by the filter immediately, and no visible water remained on the surface. Since plasma cleaning removes any atomic layers of contamination on a surface, it was expected that the cleaned, unmodified surface would be highly hydrophilic. The surface of the filter is not polar and the nanopores are much larger than molecules of water, so the water flowed through freely.

The filters that did not undergo surface modification and were not plasma cleaned were slightly hydrophobic. This was not due to the nature of the filters, but rather to a buildup of contaminants on the surface of the filter. The plasma cleaned, silanated filters became extremely hydrophobic, causing the water drops to bead up. There was no significant change in hydrophobicity among the 20nm, 100nm and 200nm pore size filters. Therefore, the middle size of 100nm was chosen for future experiments.

Two methods of silanation, both vapor deposition and liquid immersion, were explored in the initial silanation experiments. After 24 hours, a white powder coated the insides of the desiccators used to carry out the vapor deposition. However, the very low contact angles measured using the goniometer after vapor deposition showed that the surface was poorly coated. This can be attributed to OTS' very high boiling point of 160°C, which is difficult to achieve in a

vacuum desiccator. The majority of the filter's surface remained very hydrophilic after vapor deposition was attempted.

The liquid immersion silanation returned excellent results. The contact angles were very high for all three filter varieties, with very little difference between the 20, 100 and 200nm pore size filters. The 100nm pore size filter had the largest measured contact angles, with the 20nm pore size filter having the smallest. The water droplets on all three surfaces immediately formed beads due to the polar water molecules being repelled by the polar methyl groups at the ends of the OTS chains, as shown in Figure 17 and 18. The surfaces became so hydrophobic that the water droplet had a greater affinity to the dropper than to the surface, and getting the drop to remain on the filter was difficult. Figure 17 illustrates this phenomenon.

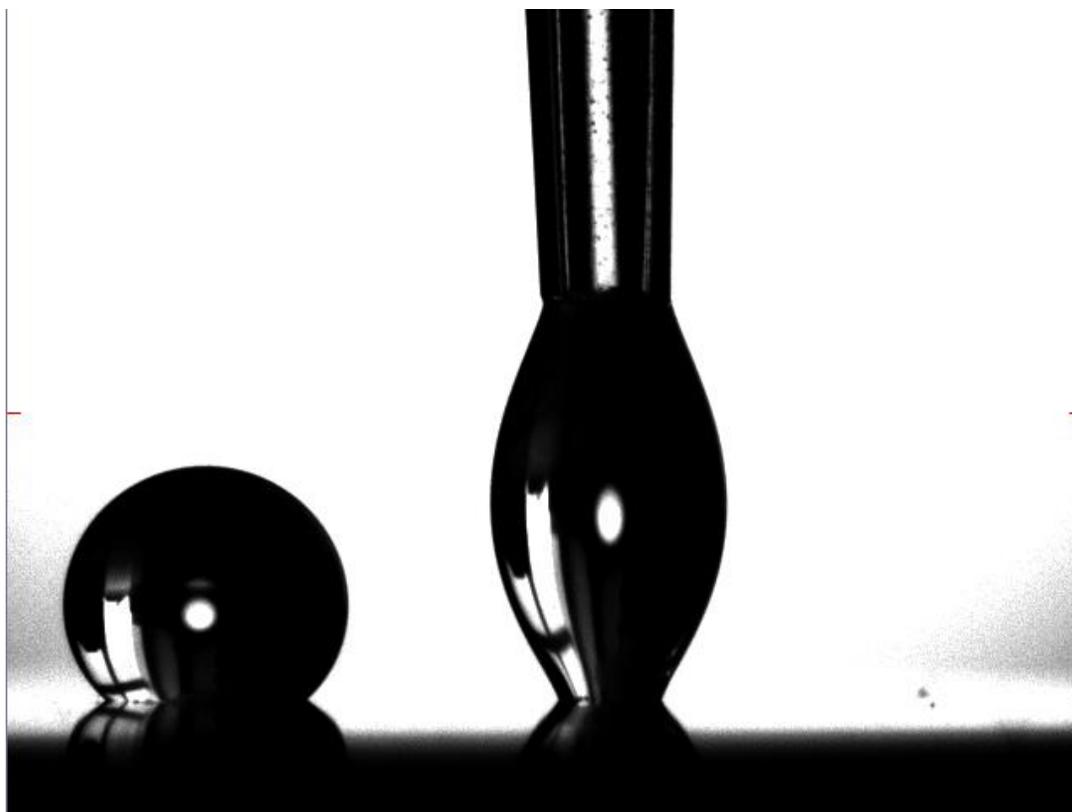


Figure 17: A silanated filter where the water clings to the dropper instead of the surface

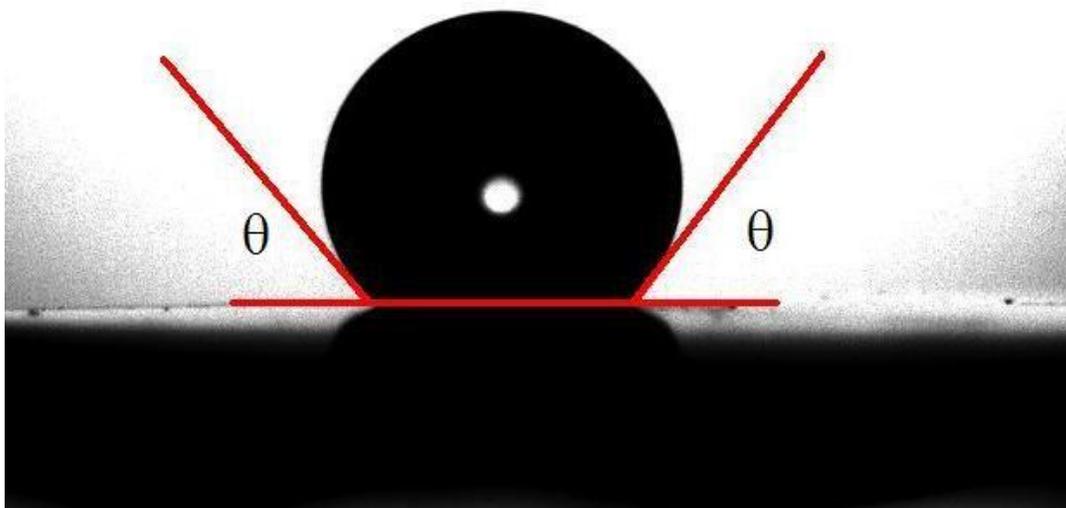


Figure 18: The contact angle is the average of both angles of the drop to the surface

Experiment 2: Permeability of Hydrogen Peroxide

After 24 hours of mixing on a shaker table, the filter was found to be broken. Two possible reasons as to why the filter had broken were explored: the high concentration of the hydrogen peroxide and the speed of the shaker table. The experiment was run again with lower concentrations of hydrogen peroxide while mixing less vigorously on the shaker table, which resulted in another broken filter. A third test was conducted without mixing, and the filter survived the test. Since the filter could not last even on the lowest mixing speed, it was concluded that the shaker table could not be used for future experiments. Although the filter was designed to withstand high pressures, it was meant to be used for vacuum filtration where it would be supported against a firm surface.

Measuring the concentration of hydrogen peroxide showed that after three days, the amount of hydrogen peroxide that had passed through the filter would be negligible. Fenton's Reagent uses up the hydrogen peroxide at a very fast rate, which would not allow the hydrogen peroxide enough time to pass through the filter.

Experiment 3: Separation of 1200ppm MTBE from Water (no mixing)

Only three samples were collected in Experiment 3, including samples of the starting solutions. While it was determined that the concentration of MTBE in one liquid tank decreased as the concentration in the other increased, the resolution provided by the three samples was not great enough to perform an in-depth analysis.

Experiment 4: Separation of 600ppm MTBE from Water (no mixing)

Experiment 4 attempted to establish whether MTBE passed through the silanated filter without mixing. The results from the experiment are shown in Figure 19 and Table 4.

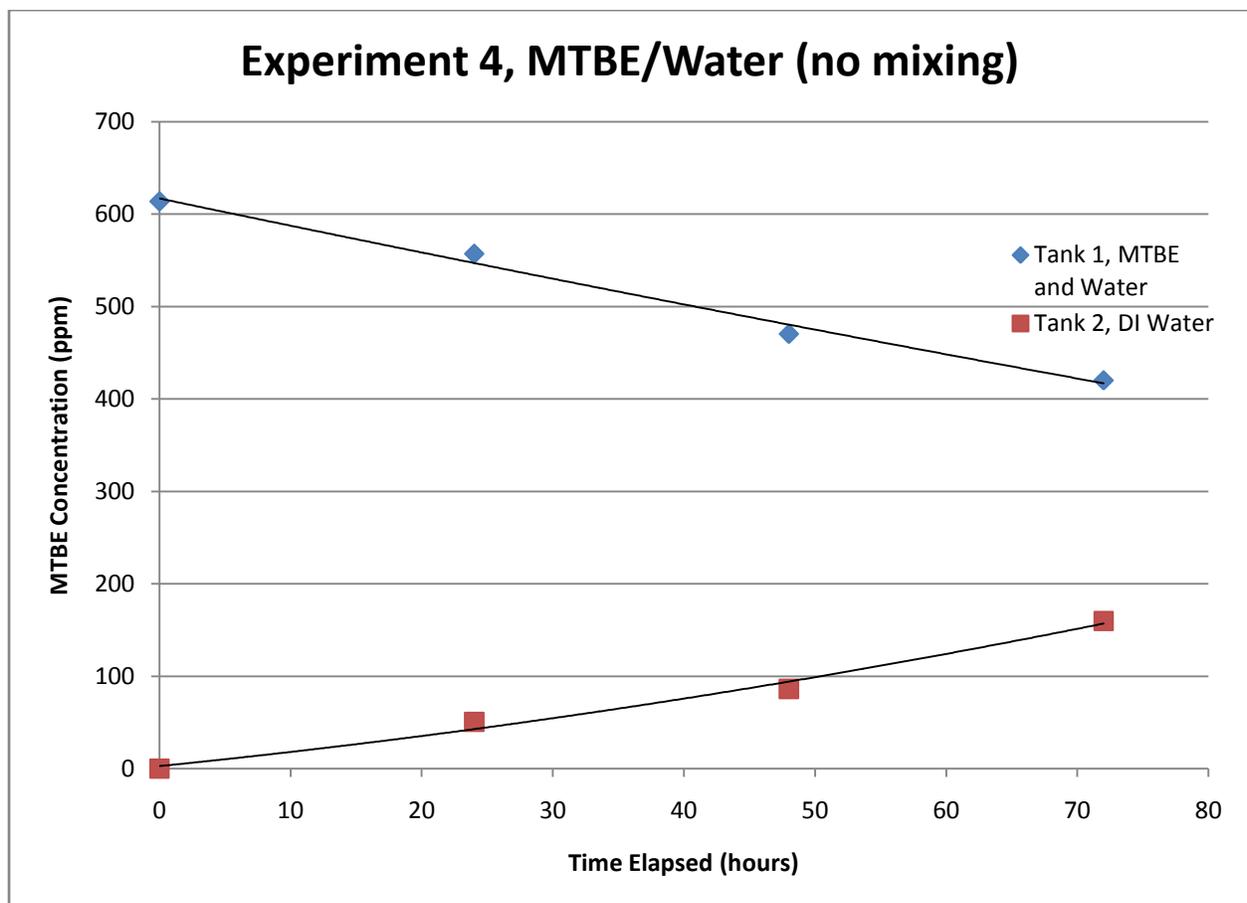


Figure 19: Experiment 4, MTBE and Water without Mixing

Table 4: Experiment 4, MTBE and Water without Mixing

Time Elapsed (hours)	Tank 1 MTBE Concentration (ppm)	Tank 2 MTBE Concentration (ppm)
0	613.6	0
24	557	50.6
48	470.4	86.2
72	420.2	159.6

As illustrated in Table 4, the concentration of MTBE in the first liquid tank decreased about 190ppm over a period of 4 days. At the same time, the concentration of MTBE on the tank originally filled with pure water increased about 160ppm. While the expected pattern of decreasing the concentration in one tank and increasing in the other was observed, the results showed that more MTBE was gained in one tank than was lost in the other. This was due to both the lack of mixing, which did not allow for accurate MTBE concentration readings, and the fact that MTBE was lost to the environment during each sampling. The various sources of error are discussed in the “Sources of Error” section of the report. The filter was found to be broken after the fourth day, and further sampling was impossible. The linear change in concentration was expected due to the large concentration gradient across the membrane, since the sampling time was low due to a broken filter after 4 days.

Experiment 5: Separation of MTBE from Water (no mixing)

The results from experiment 5 were similar to those of experiment 4. However, the transport properties were observed over a period of ten days. There was a period of linear decrease in MTBE concentration in tank 1, after which the concentration began to asymptotically decrease to a value of 250ppm. The MTBE concentration on the water side increased linearly for the duration of the experiment. These results are shown in Figure 20.

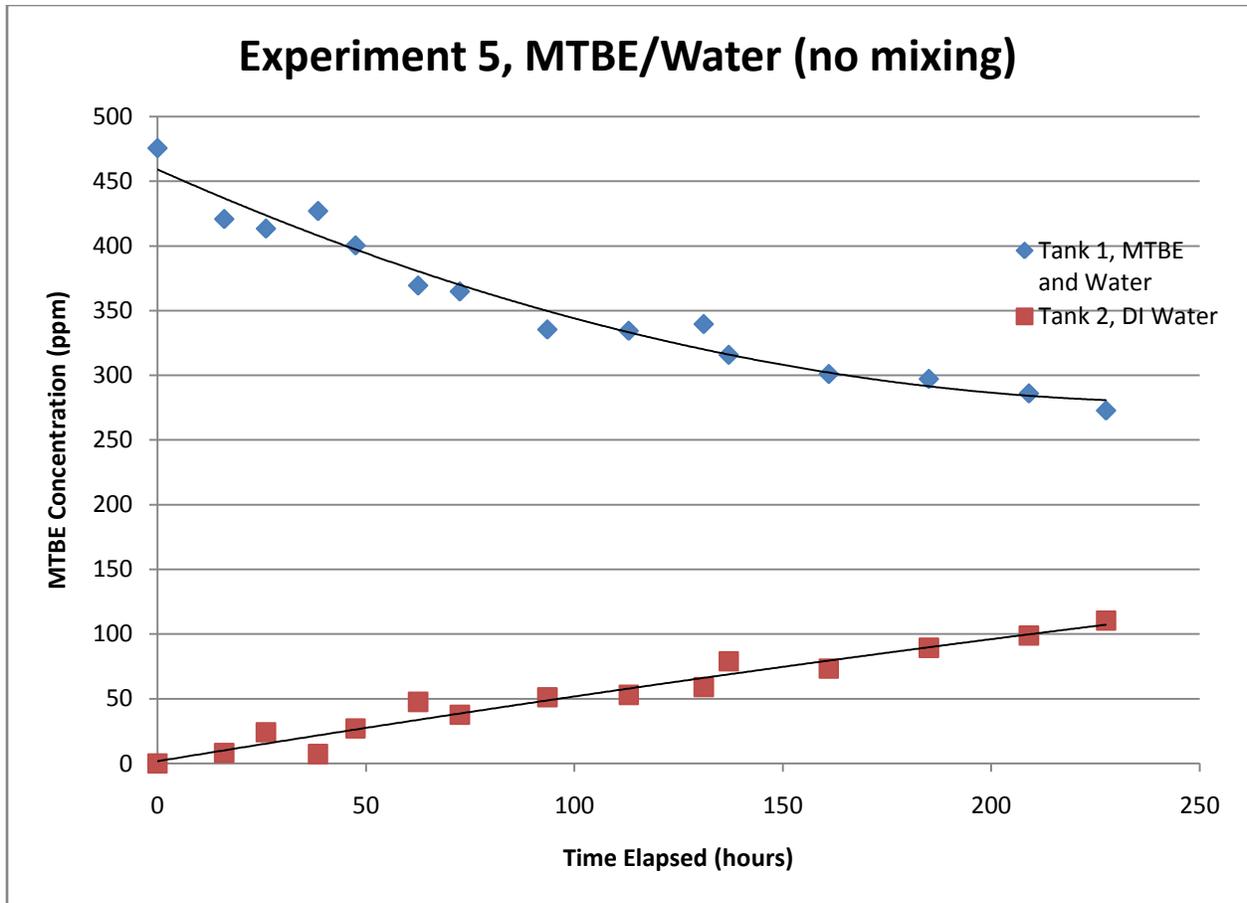


Figure 20: Experiment 5, MTBE and Water without Mixing

The linear decrease in MTBE concentration at the start of the experiment was attributed to the large concentration gradient across the filter. The concentration gradient was sufficiently large to not impede the transport of MTBE across the filter, allowing maximum transport based on the rate of volatilization and condensation of MTBE. However, as the concentration gradient decreased, it became the limiting factor for the rate of transport across the membrane.

The linear increase in MTBE concentration on the water side was a result of a lack of mixing. The MTBE that was transferred across the membrane most likely diffused slowly through the water in the connections and into the bottle where samples were being taken. If the liquid in the bottles were well-mixed, the graph would most likely show a nonlinear increase in concentration.

Experiment 6: Separation of MTBE from Water (with mixing)

Experiment 5 was conducted to determine the effect of mixing on the transport of MTBE. Over a period of five days, the concentration of MTBE in one tank decreased almost linearly while the concentration in the other tank increased with decreasing rate. This result is shown in Figure 21.

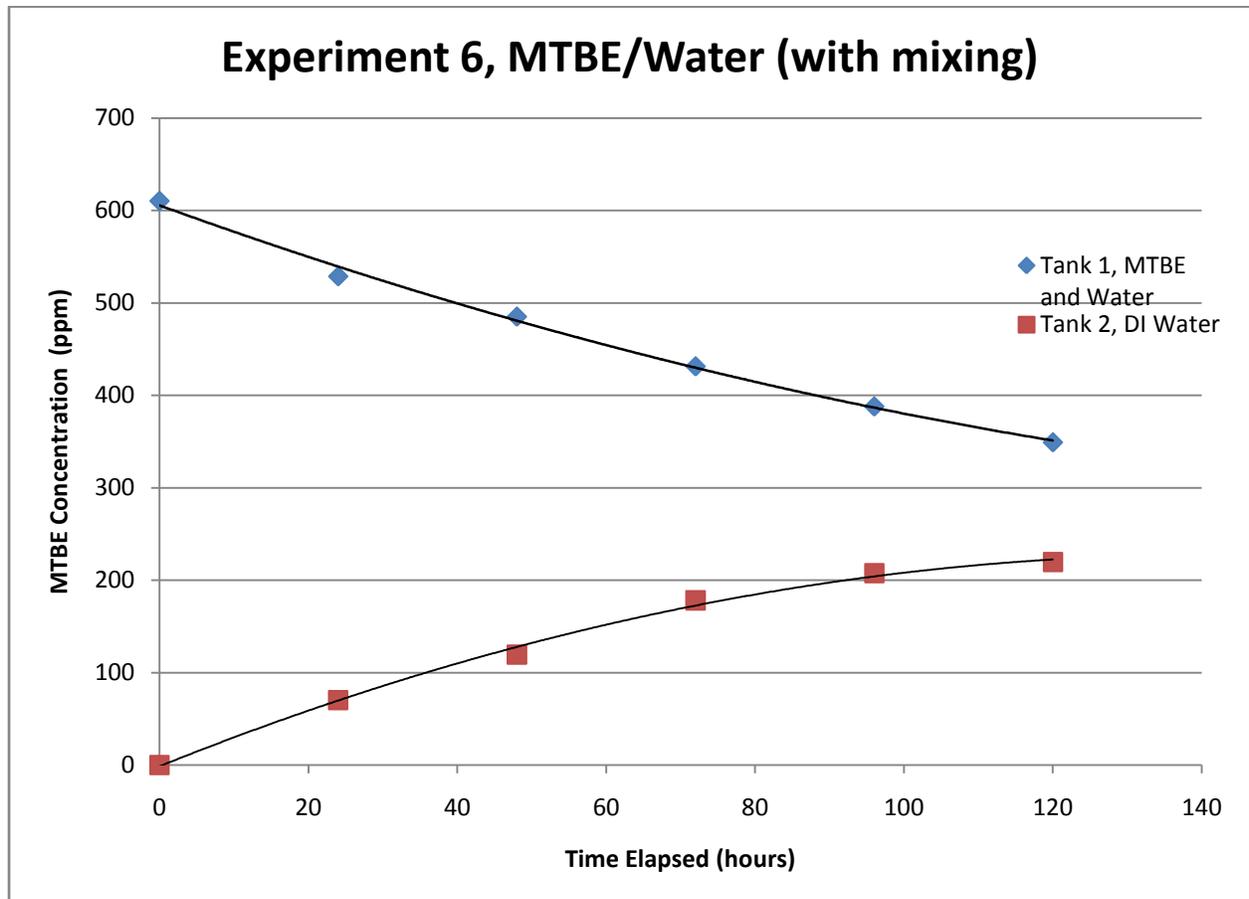


Figure 21: Experiment 6, MTBE and Water with Mixing

To mix the liquids, the separation unit was placed on two magnetic stirrers on a lab bench. The stirrers were left running for the five-day duration of the experiment. This heat from the stirrers, coupled with the heat from the sunlight coming through the nearby window, caused the temperature of the liquids to increase. This caused more of the MTBE to move to the gas phase in the space above the liquid, which means more MTBE was lost each time a sample was

collected. Some MTBE also condensed on the cool surface of the bottle around the cap, further reducing the actual concentration of MTBE in the liquid. Prolonging the experiment by one more day would most likely have shown the MTBE transport rate decreasing, and beginning to asymptotically approach 300ppm. However, the filter cracked before the next sample was collected. The experiment was run multiple times, but a period of five days was the longest time the filter was able to survive.

During the first two days of the experiment, the concentration of MTBE in the water side increased linearly, which was expected since the concentration of the MTBE side decreased linearly. However, as the total MTBE on the water side increased, the rate began to decrease and followed a nonlinear pattern. At the same time, the concentration on the MTBE side decreased linearly the entire time instead of leveling off. This behavior was attributed to the greater amount of MTBE loss due to the increase in temperature. Where the curve should have been leveling off, the greater MTBE loss to the environment caused lower concentration readings, making the first line almost linear while making the second nonlinear.

Due to the constant movement of the magnetic stirring rods against the bottom of the bottles, small pieces of plastic were shaved off and floated in the liquids. With a longer run time, it would not be feasible to use magnetic stirrers for mixing since the bottles would become damaged further.

When comparing the results of this experiment to the experimental runs without mixing, it was concluded that mixing did not have an effect on the rate of MTBE transport across the membrane. The transport was most likely limited by the rate of volatilization and condensation of MTBE and not by the size of the concentration gradient across the membrane, at least during the start of the experiment. More testing on this theory was not conducted, because better mixing resulted in breaking the filter. However, given infinite time and no reaction to degrade the MTBE, the concentration of MTBE in both bottles would be expected to asymptotically approach the value of half the initial concentration.

Experiment 7: Fenton's Oxidation

Once it was determined that MTBE passes through the silanated membrane while water, hydrogen peroxide and Fenton's reagent did not, an experiment was conducted with Fenton's reagent in the second bottle. The expected results were that the MTBE would pass through the filter where the Fenton's reagent would degrade it, thus allowing a large concentration gradient to remain across the filter. Given infinite time, the concentration of MTBE in the first bottle should decrease to zero, leaving pure water behind. The results from the experiment are displayed in graphical form in Figure 22.

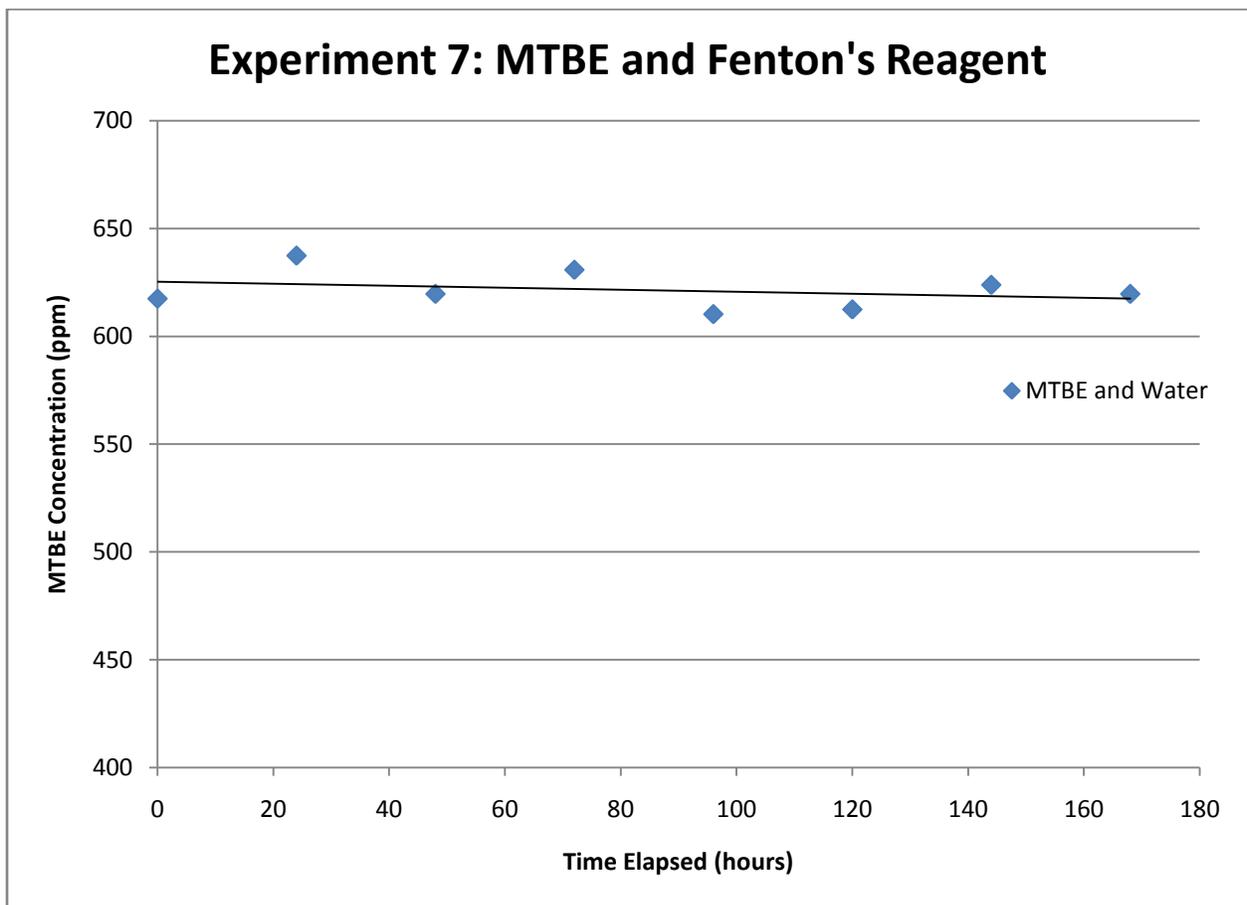


Figure 22: MTBE and Fenton's Reagent

The data from experiment 7 shows that the concentration of MTBE did not change after 7 days of testing, even when the liquids were mixed after day four. The chemical oxygen demand of the Fenton's reagent could not be measured since it would react with the COD chemicals and automatically show the maximum concentration of the vial. However, preliminary testing showed that the Fenton's reagent did not pass through the filter and did not affect the COD readings of the other liquid.

During the testing, it was observed that the bottle containing Fenton's reagent changed from an orange-brown, opaque liquid on day zero to a yellowish, clear liquid with large amounts of brown precipitate at the bottom of the bottle. When the separation unit was disassembled, the filter was covered in a brown sludge. Even when the filter was cleaned with water, a brown residue remained, as shown in Figure 23.

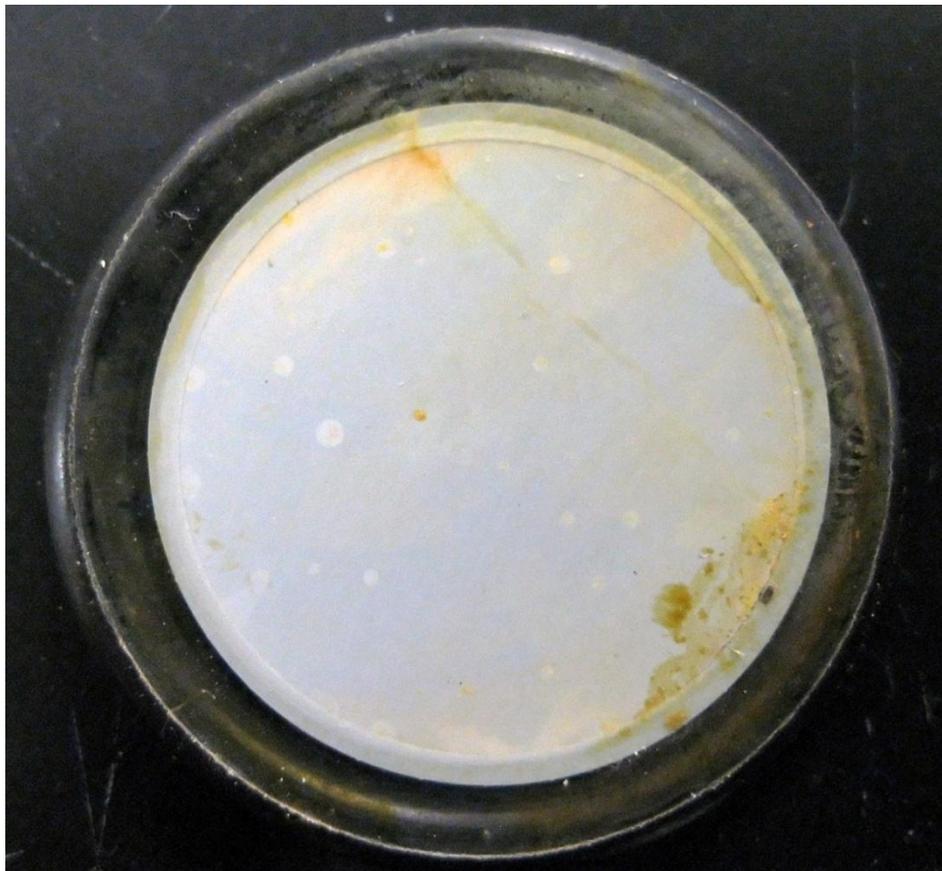


Figure 23: A Silanated Filter, After Exposure to Fenton's Reagent

When the pH of Fenton's reagent is too basic, iron precipitates out of solution. This precipitate coated everything in the separation unit, including the filter. The pores clogged, and MTBE was not able to pass through. Additional experiments with Fenton's reagent varied the amount of hydrogen peroxide and iron sulfate used, but the results remained the same. To eliminate the precipitate that clogged the pores of the membrane, the pH of the solution must be adjusted.

Additional Observations

During the experimentation process, it was observed that some chemicals had an effect on the epoxy being used to hold the separation unit together. After several days of exposure to MTBE or hydrogen peroxide, the typically clear epoxy attaching the tube connectors to the bottles became brown. For longer exposure times, especially to Fenton's reagent, the epoxy broke down completely and the connectors detached from the bottles. Therefore, chemical reactions may have been taking place with the epoxy that contributed to some of the unexpected results obtained from the experiments.

Conclusions and Recommendations

The surface chemistry of anodized aluminum oxide membranes was successfully modified from hydrophilic to hydrophobic using liquid immersion with octadecyltrichlorosilane. Although vapor deposition is ideal since it creates self-assembled monolayers on a surface, it was concluded that it was ineffective with this silane due to its high boiling point.

Methyl *tert*-butyl ether successfully permeated the hydrophobic, porous filter. The transport time was on the order of days as opposed to hours, which implies that very large surface areas would be necessary for commercial purposes. Mixing the liquids with magnetic stirrers did not improve transfer times. It was concluded that, at least for the first few days of filtration, the MTBE permeation rate was limited by the rate of volatilization and condensation of MTBE as opposed to the concentration gradient across the membrane.

The results for the effectiveness of advanced oxidation processes in the separation of MTBE from water were inconclusive. Precipitate from Fenton's reagent clogged the pores of the membrane, impeding the permeation of MTBE through the filter. Further tests should be conducted where the pH of Fenton's reagent is varied to reduce or eliminate the iron precipitate that is formed.

The filters used in this study were extremely fragile and could not withstand any significant amount of stress. When coupled with the high price of each filter, it is difficult to create a cost-effective method of using them to separate MTBE from water on a large scale. One recommendation for future projects is to explore the possibility of reinforcing the filter by depositing metals on the nanoporous structure, or thickening the membrane by replicating its honeycomb structure. The former can be accomplished by the electrodeposition of metals, while the latter involves creating nanowire arrays on the anodized aluminum surface with chemical reactions (Skinner & Washburn, 2006). Strengthening the membranes would allow larger filter sizes to be used, which may improve transfer times. It may also allow for better mixing of the system without cracking the filters.

Each time a sample was collected from the separation unit, the caps on the bottles were opened and the liquids were exposed to the environment. This caused the MTBE in the gas phase to

escape the bottle, reducing the overall MTBE concentration. For future experiments, a better sampling method should be devised in which MTBE vapor is not allowed to escape.

Finally, an alternative should be found to the epoxy that was used to hold parts of the separation unit together. The ideal situation would eliminate altogether the need for epoxy, and would consist of a unit with highly chemically resistant materials.

Sources of Error

Many sources of error were introduced over the course of the project. These errors originated from a number of sources, primarily from experimental measurements and procedures.

Experimental measurement errors could have come from numerous areas. These include simple measurements of chemicals via graduated cylinders or weight scales. The micropipettes, which were used many times during experimentation, may have lost their calibration and introduced error. Also, due to the need to recalibrate the UV spectrometer upon every use, there was a consistent error in the absorbance measurements which affected the concentration values.

Other sources of error include the volatility of MTBE and the volume of the sample being used for chemical oxygen demand (COD) tests. The volatility was a significant source of error because MTBE readily vaporizes, and there was a loss of MTBE into the environment every time the bottles were opened to collect a sample. Small variations in the sample volumes used in COD tests may have produced large inconsistencies when absorbances were measured.

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Appendices

Appendix 1: Raw Data

Table 5: Experimental Results, MTBE and Water, Raw Data

600ppm EXP 4			
Day	MTBE/Water Abs.	Water Abs.	COD Vial Range
0	0.3162	0.0094	-
1	0.2879	0.0347	100-4500
2	0.2446	0.0525	100-4500
3	0.2195	0.0892	100-4500
4	? (.3266)	? (.1902)	20-900
5	0.2168	0.1435	100-4500

600ppm EXP 5			
Day	MTBE/Water Abs.	Water Abs.	COD Vial Range
0	0.3212	0.016	-
1	0.2804	0.0511	20-900
2	0.2586	0.0757	20-900
3	0.2317	0.105	20-900
4	0.21	0.1197	20-900
5	0.1906	0.1257	20-900

600ppm EXP 6			
Day	MTBE/Water Abs.	Water Abs.	COD Vial Range
0	0.2538	0.016	-
1	0.2264	0.02	20-900
1	0.2227	0.028	20-900
2	0.2295	0.0196	20-900
2	0.2162	0.0295	20-900
3	0.2007	0.0398	20-900
3	0.1984	0.0348	20-900

4	0.1837	0.0416	20-900
5	0.1832	0.0425	20-900
6	0.1858	0.0455	20-900
7	0.1739	0.0555	20-900
8	0.1665	0.0526	20-900
9	0.1646	0.0607	20-900
10	0.159	0.0654	20-900
11	0.1524	0.0712	20-900

Table 6: Experimental Results, MTBE and Fenton's Reagent, Raw Data

MTBE/Fenton EXP		
Time Elapsed	MTBE Side Abs.	COD Vial Range
0	0.3247	20-900
24	0.3347	20-900
48	0.3258	20-900
72	0.3314	20-900
96	0.3211	20-900
120	0.3222	20-900
144	0.3279	20-900
168	0.3258	20-900

Appendix 2: Low-Range Chemical Oxygen Demand Testing Procedure

(Taken from the guidelines posted in the Wastewater Treatment Laboratory at Worcester Polytechnic Institute)

The Micro-COD Test Method accu-Test Low Range Twist-Cap Vials Laboratory

Procedure (5-150 mg/L COD) is as follows:

1. Preheat COD heater block to 150°C.
2. Remove the cap from a COD twist cap vial.
3. Carefully add 2.5 mL of sample down the side of the vial such that it forms a layer on top of the reagents.
4. Replace the twist cap.
5. Thoroughly mix the contents of the sealed vial by shaking.
6. Process standards and blanks exactly as the samples.
7. Place the twist-cap vial in a COD heater block capable of maintaining 150°C (+/- 2°C) for 2 hours.
8. Remove the vial from the heater block and allow to cool.
9. Allow any suspended precipitate to settle and wipe the outside of the vial clean with Kimwipes.
10. Set the wavelength of the spectrophotometer to 600 nm, and, using a procedural blank, zero the absorbance reading.
11. Read the absorbance of each standard and sample on the spectrophotometer.
12. Prepare a graphic calibration curve by plotting the absorbance of the standards versus their known concentrations. Compare the absorbances of the samples to the graphic calibration curve to determine COD concentrations.

Appendix 3: Cobalt-Ultraviolet Spectrophotometry Method

(Taken from Slack, 2004)

The following is an outline of the procedure used to measure hydrogen peroxide concentration:

1. Partially fill a 25-mL volumetric flask with saturated NaHCO_3 solution (prepared by dissolving 25 g of analytic-grade sodium bicarbonate in 250 mL of E-pure water).
2. Add 1.03 mL of cobalt stock solution (1000 mg/L).
3. Select a test sample volume based on estimated H_2O_2 concentration – a sample volume of 1mL was used for these experiments.
4. Add the test sample to the flask.
5. Fill the flask to the 25mL mark with additional NaHCO_3 solution.
6. Let stand at room temperature for 15 minutes for full color development. Analyze sample promptly.
7. Measure the absorbance at selected wavelength (320 nm was selected for these experiments).
8. Use a calibration curve to determine the concentration of H_2O_2 in the test sample.