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TREATMENT OF MTBE CONTAMINATED WATERS USING AIR STRIPPING
AND ADVANCED OXIDATION PROCESSES

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ABSTRACT

The widespread use of the fuel oxygenate methyl tert-butyl ether (MTBE) has led to the contamination of both surface and groundwater supplies. This study evaluates the treatment of MTBE contaminated drinking water using air stripping and advanced oxidation processes (AOPs) on a pilot scale. The treatment efficiency of the air stripper was evaluated at different air/water ratios ranging from 105:1 to 206:1. Although a treatment efficiency of >99% was achieved for each of the air/water ratio studied, the depth of the packing required to achieve this efficiency increased with decreasing air/water ratio. The adsorption studies conducted on MTBE laden off-gas from the air stripper showed that granular activated carbon (GAC) has a higher adsorptive capacity than the carbonaceous polymeric resin. Experiments conducted at different off-gas relative humidity (RH) of 20%, 30% and 50% reveal that the GAC adsorptive capacity decreased with increasing RH, whereas, the RH did not impact the resin adsorptive capacity. Ozone/hydrogen peroxide (O₃/H₂O₂), ozone/UV (O₃/UV), hydrogen peroxide/UV (H₂O₂/UV), and ozone/hydrogen peroxide/UV (O₃/H₂O₂/UV) are the four AOPs evaluated in this study. An increase in the recycle ratio by 100% resulted in a 5% increase in the treatment efficiency. A treatment effectiveness of 98% was achieved with the use of O₃/UV process at an O₃ concentration of 5.8 mg/L. The experimental results have shown that the O₃/H₂O₂ process is a slightly more effective (2 to 3% more) treatment process than the O₃/UV process at the same O₃ concentrations and a H₂O₂:O₃ molar ratio of 1.4:1. Increased treatment efficiencies were observed with increasing H₂O₂:O₃ molar ratios, with the optimum ratio for maximum treatment efficiency being
Non-detectable levels of MTBE were recorded in the O3/H2O2/UV process, at an O3 dosage of 5.8 mg/L and a H2O2:O3 molar ratio of 1.4:1. The O3/H2O2/UV process was more effective than the O3/H2O2 process at lower H2O2:O3 molar ratios and at ratios above 1:1, the difference in the treatment efficiencies was negligible. Tert-butyl formate, tert-butyl alcohol), methyl acetate and acetone were the major oxidation by-products identified in all the AOPS. The conducted cost analyses revealed that air stripping was the most cost effective treatment process compared to the AOPs.
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Chapter 1

INTRODUCTION

1.1 MTBE Background

Methyl tertiary-butyl ether (MTBE) is a polar organic compound, derived from natural gas, which is used as an oxygenate in gasoline to reduce emissions and to increase the octane level. Oxygenated gasoline increases the combustion efficiency of fuel, which in turn reduces carbon monoxide (CO) and hydrocarbon emissions in motor vehicle exhausts. After the phase out of leaded gasoline in 1973, oxygenates were a natural choice for refiners, to replace the octane loss. Ethanol has been used as an oxygenate in gasoline (up to 10% by volume) to enhance octane number. During the 1974 energy crisis, ether-based compounds such as MTBE were added to gasoline to extend the use of gasoline and to boost octane. In the 1980s, some states implemented oxygenated gasoline programs for the reduction of CO emissions during winter (NSTC 1997). The first such winter oxygenate gasoline program was implemented in Denver, Colorado in 1987.

The 1990 amendments to the federal Clean Air Act (CAA) require the use of oxygenates in areas with poor air quality. This was the driving force behind the increased use of oxygenates in the United States. The 1990 CAA amendments required that all gasoline sold in the CO non-attainment areas during winter must contain at least 2.7 weight percent of oxygen. This 2.7% oxygen content has been achieved by the addition of about 15% MTBE (Vance 1998) or about 7.5% ethanol by volume. The amendments also
required the use of federal reformulated gasoline (RFG) in areas with severe ozone (O₃) pollution. The CA requires that RFG contain a minimum average oxygen content of 2% by weight.

The CAA does not specifically mandate the use of any oxygenate, but MTBE has been the oxygenate of choice for most refiners (EPA 1998) because of its favorable blending characteristics and ease of production. MTBE has an octane rating \((\text{R}+\text{M})/2\) of 110, which makes it useful as a gasoline octane booster to replace benzene. MTBE also provides good dilution of undesirable components such as, aromatics, sulfur, olefin and benzene. The relatively low boiling point of MTBE also helps reduce the distillation temperature of gasoline blend, thus helping to meet the distillation temperature requirements. MTBE readily mixes with other gasoline components and can help refiners to easily integrate blending, shipping and production of MTBE into their existing operations.

1.2 Physical and Chemical Characteristics

MTBE is a polar organic compound with a chemical formula \(\text{CH}_3\text{OC(CH}_3\text{)}_3\). At standard temperature and pressure, MTBE is a volatile, flammable, colorless liquid with a terpene-like odor (Squillace et al. 1997). Table 1-1 shows the summary of the physical and chemical characteristics of MTBE relative to BTEX (Benzene, toluene, ethyl-benzene and xylene) compounds. MTBE is highly volatile and tends to occur almost entirely in the vapor phase when released to the atmosphere. MTBE has a relatively short half-life in
surface water of approximately 9 hours (Pankow et al. 1996). Depending on the type of surface water, this half-life can extend from 4 weeks to six months (Howard 1993). Because of the turbulent flow, the half-life of MTBE is lower in streams and rivers and is higher in the case of lakes and reservoirs. MTBE has a high downward mobility in soil because of its low adsorption coefficient and hence can reach the groundwater relatively quickly (Howard 1993). The very high solubility of MTBE further helps in its rapid movement through groundwater. Once MTBE saturation in water occurs, it will float on the surface of water due to its lower density. The very low Henry’s law constant of MTBE indicates its tendency to remain in the water phase and makes it difficult to be removed from water. The taste and odor thresholds for MTBE in water range from 2.5µg/L to 680µg/L, and 2µg/L to 190µg/L, respectively (API 1994; ARCO 1993; Dale et al. 1997; Pirnie 1998; Shen et al. 1997; Young et al. 1996).

1.3 Impact of MTBE on Water Supplies

The primary source of MTBE in groundwater is gasoline releases from leaking underground storage tanks (Davidson and Creek 1999; Johnson et al. 2000). The other ways by which MTBE enters groundwater are from vehicle exhaust emissions, from spillage and evaporation during the manufacture and transport of MTBE and gasoline containing MTBE and from accidental spills or exhaust from boats and personal water crafts (Keller et al. 1998a). The fact that some individuals can detect MTBE in water at very low levels is the main factor for treating contaminated waters to such low levels. It has been identified as the second most common volatile organic compound detected in
wells monitored in urban areas nationwide between 1985 and 1995 (Squillace et al. 1995; Squillace et al. 1996). When accidentally released into the environment, the resistance of MTBE to natural degradation combined with its physical and chemical properties makes it a threat to drinking water supplies. Reports show that MTBE plumes migrate at a rate comparable to groundwater velocities and this mobility of MTBE in water is in part due to its high aqueous solubility and low organic carbon partition coefficient (OSTP 1997).

### 1.4 Toxicity and Health Effects

One of the cancer studies showed that MTBE caused cancer in rats through inhalation exposure at two high dose levels, 3000ppm and 8000ppm (Chun et al. 1992). Another study on mice also showed that MTBE caused cancer at high dose levels of 8000ppm (Burleigh-Flayer et al. 1992). No rigorous or peer-reviewed studies exist indicating a human cancer risk from inhalation or ingestion of MTBE. Extrapolation of data on animal toxicity to data on human health risk is ambiguous and any conclusions that might be drawn from them would be uncertain. The United States Environmental Protection Agency (U.S. EPA) has classified MTBE as a Group C chemical, or a possible human carcinogen. The Office of Environmental Health Hazard Assessment (OEHHA) has set a public health goal of 13µg/L for MTBE in drinking water based on cancer studies in rats and mice (EPA California 1999). However, the levels at which MTBE potentially pose a cancer or non-cancer human health risk are likely far higher than the levels at which humans can detect the taste of MTBE in drinking water. In December 1997, the U.S. EPA’s Office of Water issued a drinking water advisory for MTBE. The advisory
recommends a limit of 20 to 40µg/L for drinking water as the range that is low enough to prevent human health risk. The U.S. EPA has not yet established a maximum contaminant level (MCL) for MTBE.

1.5 Small Water Systems

There are approximately 170,000 public water systems in the United States. EPA classifies these water systems according to the number of people they serve, the source of their water, and whether they serve the same customers year-round or on an occasional basis. A public water system (PWS) is a "system for the provision to the public of water for human consumption through pipes or other constructed conveyances, if such system has at least 15 service connections or regularly serves an average of at least 25 individuals daily at least 60 days out of the year". According to FY2003 data obtained from the Safe Drinking Water Information System (SDWIS) database, there are 161,201 public water systems (PWSs) in operation in the United States.

EPA has defined three types of public water systems:
A community water system (CWS) is "a public water system that serves at least 15 service connections used by year-round residents or regularly serves at least 25 year-round residents". There are 53,363 CWSs serving about 273 million people. A non-community water system (NCWS) is a PWS that is not a CWS. Non-community water systems are divided into non-transient (NTNCWSs) and transient (TNCWSs) systems. A NTNCWS is a PWS that "regularly serves at least 25 of the same persons over 6 months
per year”. Examples of NTNCWSs are schools, factories, office and industrial parks, and major shopping centers. The 19,686 NTNCWSs across the nation serve about 6 million people. A TNCWS is a PWS that "does not regularly serve at least 25 of the same persons over 6 months per year". Examples of TNCWSs are highway rest stops, small restaurants, and recreation areas. The 88,152 TNCWSs serve approximately 23 million people.

EPA also classifies water systems according to the number of people they serve:

- Very Small water systems serve 25-500 people.
- Small water systems serve 501-3,300 people.
- Medium water systems serve 3,301-10,000 people.
- Large water systems serve 10,001-100,000 people.
- Very Large water systems serve 100,001+ people

85 percent of CWS are small or very small, serving 10 percent of those who get their water from a CWS. A system’s water source is a key factor in determining operating characteristics, and source corresponds closely to system size. Larger systems are more likely to use surface water or purchased water as their primary source, whereas most small systems use ground water. Large systems tend to have a higher percentage of industrial, commercial, and agricultural customers, whereas small systems serve primarily residential customers, who, as a group, generally use less water. 93 percent of groundwater systems serving 1,001-3,300 persons and 83 percent of those serving less
than 1,001 persons have a potential source of contamination within 2 miles of their well(s) (EPA 1999). Over 60 percent of small systems also report need in source protection and development, often because their sources are threatened by contamination or supply problems. Systems serving 25-500 persons have many more violations per 1,000 people than do any other size category of systems. Of particular note are MCL violations which, like other types of violations, decrease in frequency with system size. For every one million customers of CWSs serving 500 or fewer people, there are approximately 800 MCL violations and 7,164 total violations. In contrast, for systems serving over 10,000 persons, there are approximately 2 MCL violations and 10 total violations per one million customers (EPA 1999).

The introduction of more stringent regulations would require that the small water systems either upgrade their existing systems or build totally new systems to comply with the standards. It would be expensive for the small systems to provide for the additional equipment of staff required to meet this demand. The complexity further increases as new contaminants are identified in drinking water and new standards are developed. Innovative approach, integrating engineering and economics, and flexibility in terms of technology applications are required to implement the compliance of the standards by the small community systems. The treatment system design should take into consideration the operator ability, capital resources and fluctuations in water quality. The evaluation of the treatment processes and operations on a pilot scale would contribute significantly to the final system design. Most of the water quality problems in small communities can be solved by the implementation of the innovative technologies in individual plants and
units. These individual units can not only be made less expensive, but can also be optimized to reduce the operating costs and maintenance and to increase the robustness.

1.6 Treatment Technologies

MTBE is very persistent under normal environmental conditions and is not very easily biodegradable. Its persistence to biodegradation may be attributed to its stable ether bond and the access to the ether linkage being restricted by the bulky tert-butyl group. The cellular yield of microorganisms utilizing MTBE as the sole organic carbon source has been found to be very low – around 0.2 g cell/g MTBE (Fortin and Deshusses 1999a; Fortin and Deshusses 1999b; Hanson et al. 1999; Salanitro 1995). It has been reported that the low growth rates on MTBE might be due to the formation of certain metabolic intermediates which inhibit cellular growth (Salanitro et al. 1998). The presence of other more easily degradable hydrocarbons may also inhibit MTBE biodegradation (Mo et al. 1997). Although, the presence of other gasoline hydrocarbons have shown to stimulate the co-metabolic biodegradation of MTBE (Hardison et al. 1997; Hyman et al. 1998; Hyman and O'Reilly 1999).

Granular activate carbon (GAC) is a well established and widely used technology for removing organic compounds from water. The relatively low sorption of MTBE results in a fast breakthrough and in turn increases the GAC utilization rate. It has also been reported that GAC is not cost effective for the removal of MTBE, except at low MTBE concentrations (Creek and Davidson 1998; McKinnon and Dyksen 1984). In addition,
since MTBE is only weakly sorbed by GAC, other gasoline constituents such as benzene and toluene in the contaminated groundwater will tend to displace MTBE from GAC (Keller et al. 1998b).

Microporous hollow fiber membranes (HFM) have been successfully used to strip VOCs from water (Sarti et al. 1993; Semmens et al. 1990; Zander et al. 1989; Zhang and Cussler 1985). A recent study on MTBE removal using HFM indicates that high treatment efficiencies are obtained only at very low flow rates of less than 0.5 L/min (Keller and Bierwagen 2001). Also these systems involve high capital costs and there is an issue with scaling and precipitate formation with increased hardness.

1.6.1 Air Stripping

Air stripping technologies are widely used for removing VOCs from drinking water supplies prior to distribution and use of the water for public consumption. Packed tower aeration is the most common air stripping technology for drinking water treatment. Packed tower aeration is a well-understood and proven technology. Although air stripping using a packed tower is a widely used technology for VOCs, its application to MTBE removal from drinking water has been limited.

The effectiveness of an air stripper to remove organic contaminants from water depends upon the volatility of the compound from water and the physical design of the air stripper. Air stripping relies on an equilibrium phase transfer process where the contaminant partitions between the aqueous phase and the air phase. The driving force for
mass transfer between one phase and another derives from the displacement of the system from equilibrium. Equilibrium is the final state toward which the system is moving. The equilibrium partitioning coefficient is called the Henry’s constant which, in dilute solutions, is determined by Raoult’s law using the vapor pressure of the pure compound and its water solubility. In general, the higher the Henry’s constant for a contaminant, the more effective air stripping will be for that contaminant.

Off-gas treatment of the MTBE-contaminated air stream from an air stripping system is often required prior to discharge to the atmosphere. MTBE has been categorized as a hazardous air pollutant (HAP) by the U.S. EPA. In most states, agencies require off-gas treatment in conjunction with an air stripper. Technologies available for the removal of MTBE in the off-gas include: carbon adsorption, thermal and catalytic oxidation, biological treatment, and gas-phase chemical oxidation. The cost of off-gas treatment is generally proportional to the volume of gas (air) being treated. Thus, the higher the air/water ratio in an air stripping system, the higher the costs. Typical volumetric air/water ratios for MTBE removal range from 100 to 200. This results in large gas volumes with very low concentrations of MTBE. Selection of the right off-gas treatment technology for MTBE is a key factor in determining the overall cost of air stripping.

1.6.2 Advanced Oxidation

Environmental regulatory requirements have become more stringent over the past two decades because of increased awareness of the human health and ecological risks associated with environmental contaminants. Conventional treatment technologies, such
as air stripping, carbon adsorption, biological treatment, and chemical oxidation have limitations and may not be cost effective. Air stripping and adsorption simply transfer the contaminants from one phase into another (gas phase in the case of air stripping or solid phase in the case of adsorption). Biological treatment and conventional chemical oxidation have low removal rates for many environmental contaminants.

Advanced oxidation processes (AOPs) provide a promising alternative to conventional treatment technologies. These processes generally involve generation and use of powerful but relatively nonselective transient oxidizing species. AOPs are destructive processes in which the contaminants in water are destroyed through chemical transformation. Oxidation processes involve the exchange of electrons between chemical species. One or more electrons are transferred from an electron donor to an electron acceptor, which has a higher affinity for electrons. In some cases, these electron transfers produce radicals which tend to be highly unstable and highly reactive because one of their electrons is unpaired. AOPs involve the formation of strong oxidants (e.g., hydroxyl radicals) and the reaction of these oxidants with organic contaminants in water. However, the term advanced oxidation processes specifically refers to the processes where the oxidation is caused by hydroxyl radicals (OH\(^*\)). OH\(^*\) has a very high oxidation potential of 2.80V, second only to fluorine and sulfate radicals in a list of strong oxidizing agents. The effectiveness of an AOP, in treating any contaminant, is proportional to its ability to generate hydroxyl radicals.
In water treatment applications, the most commonly used AOPs are those processes which involve the use of ozone (O$_3$), hydrogen peroxide (H$_2$O$_2$) and/or ultraviolet (UV) irradiation. However, the other emerging AOPs include those processes which involve titanium dioxide (TiO$_2$) catalysis, sonolytic cavitation, gamma radiolysis, electron beam (E-beam) irradiation, persulfate and Fenton's reaction. AOPs have been used successfully to treat organic compounds, including MTBE, in drinking water at several places in the United States. Due to the complex chemical and physical processes involved in oxidation reactions, AOPs and their effectiveness in treating organics is not well understood.

1.7 Selection Criteria for Technologies to be studied

The following technologies were selected to be evaluated in this study:

1) Air stripping followed by off-gas adsorption.

2) Advanced oxidation processes
   - Ozone/hydrogen peroxide
   - Ultraviolet irradiation/hydrogen peroxide
   - Ultraviolet irradiation/ozone
   - Ultraviolet irradiation/hydrogen peroxide/ozone

The treatment technologies to be evaluated in this study were selected based on the following criteria - the ability of the process to consistently meet drinking water
standards, simplicity of operation, by-product formation and its impact, robustness of the process, low maintenance and low capital costs.

1.8 Objectives

The overall objective of the proposed study was to evaluate the removal of methyl tertiary butyl ether (MTBE) from drinking water at low concentrations using air stripping followed by off-gas adsorption and AOPs. A comparative feasibility and economic analysis of the different technologies studied has been made. The specific objectives of this study were addressed in two major phases:

Phase I:
Evaluate the combined treatment processes of packed tower air stripping and off-gas adsorption for the removal of MTBE contaminated drinking water on a pilot-scale. This investigation included:

- Building of a pilot scale packed tower air stripper and off-gas adsorber beds to treat up to 20gpm of contaminated water.
- Assessment of the packed tower performance for various air-to-water ratios.
- Determination of the overall mass transfer coefficient.
- Conducting gas phase MTBE isotherms to determine the Freundlich isotherm parameters.
Determination the off-gas MTBE adsorptive capacity of two kinds of commonly used adsorbents, namely, granular activated carbon and a carbonaceous resin.

Study of the impact of relative humidity on the adsorptive capacity of the two adsorbents.

Modeling of the breakthrough behavior of the adsorbents using the pore and surface diffusion model (PSDM).

**Phase II:**

Evaluate the degradation of MTBE in drinking water using various pilot-scale AOPs, namely, ozone/hydrogen peroxide, ultraviolet irradiation/hydrogen peroxide, ultraviolet irradiation/ozone and ultraviolet irradiation/hydrogen peroxide/ozone. This investigation included:

- Designing and fabricating an AOP manifold that served as a basic structure for the various processes studied. This structure was modified slightly for the study of each AOP.
- Evaluation of the impact of various operational parameters (i.e., Flow rate, oxidant concentration) on the degradation of MTBE.
- Identification and quantification of the oxidation byproducts.
- Optimization of operating conditions for each AOP studied and operation of the pilot scale system in a continuous flow mode.
- Provide a comparative analysis of the operational efficiencies and economics of AOP technologies.
1.9 References:


ARCO. (1993). "The Odor and Taste Threshold Studies Performed with Methyl Tertiary-Butyl Ether (MTBE) and Ethyl Tertiary-Butyl Ether (ETBE)." ARCO Chemical Company.


Davidson, J. M., and Creek, D. N. (1999). "Survey of current UST management and operation practices." The California MTBE Research Partnership, Center for...
Groundwater Restoration and Protection, National Water Research Institute, Fountain Valley, CA.


Hyman, M., and O'Reilly, K. "Physiological and enzymatic features of MTBE-degrading bacteria." *Fifth International In Situ and On-Site Bioremediation Symposium*, San Diego, CA, 7-12.


Table 1-1  Physical and Chemical Properties of MTBE and BTEX Compounds

<table>
<thead>
<tr>
<th>Physical and Chemical Properties</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Ethyl-benzene</th>
<th>o-Xylene</th>
<th>MTBE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight [g/mole]</td>
<td>78.11</td>
<td>92.14</td>
<td>106.17</td>
<td>106.17</td>
<td>88.15</td>
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<tr>
<td>Vapor Density @ 1 atm; 10°C</td>
<td>3.36</td>
<td>3.97</td>
<td>4.57</td>
<td>4.57</td>
<td>3.80</td>
</tr>
<tr>
<td>Specific gravity @ 25°C</td>
<td>0.88&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.8669&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.867&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.8802&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.744&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Boiling point [°C]</td>
<td>80.1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>110.6&lt;sup&gt;a&lt;/sup&gt;</td>
<td>136.25&lt;sup&gt;a&lt;/sup&gt;</td>
<td>144.4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>53.6 - 55.2&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Water solubility [mg/L]</td>
<td>1730&lt;sup&gt;a&lt;/sup&gt;</td>
<td>534.8&lt;sup&gt;a&lt;/sup&gt;</td>
<td>161&lt;sup&gt;a&lt;/sup&gt;</td>
<td>175&lt;sup&gt;a&lt;/sup&gt;</td>
<td>43,000 - 54,300 50,000&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Vapor pressure [mm Hg] (@25°C)</td>
<td>76, 95.19&lt;sup&gt;a&lt;/sup&gt;</td>
<td>28.4&lt;sup&gt;a&lt;/sup&gt; 3.79&lt;sup&gt;b&lt;/sup&gt;</td>
<td>9.53&lt;sup&gt;a&lt;/sup&gt; 1.23&lt;sup&gt;b&lt;/sup&gt;</td>
<td>6.6&lt;sup&gt;a&lt;/sup&gt; 0.889&lt;sup&gt;b&lt;/sup&gt;</td>
<td>245 - 276&lt;sup&gt;a&lt;/sup&gt; 3.33&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
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<td>Henry’s Law Constant [-]</td>
<td>0.23&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.272&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.336&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.212&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.018 @ 20°C&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>Log K&lt;sub&gt;OC&lt;/sub&gt;</td>
<td>1.18-1.99</td>
<td>1.56-2.25&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.94 1.98-3.04&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.68-1.83&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.091, 1.035, 1.049&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>Log K&lt;sub&gt;OW&lt;/sub&gt;</td>
<td>2.36&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.73&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.24&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.10&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.20&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>Diffusivity (m²/s) Liquid Gas</td>
<td>9.95 x 10&lt;sup&gt;-10&lt;/sup&gt;</td>
<td>8.87 x 10&lt;sup&gt;-10&lt;/sup&gt;</td>
<td>8.6 x 10&lt;sup&gt;-10&lt;/sup&gt;</td>
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<td>8.45 x 10&lt;sup&gt;-6&lt;/sup&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
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</tbody>
</table>

<sup>a</sup>-(OSTP 1997)
<sup>b</sup>-(Hand and Crittenden 1997)
Chapter 2

TREATMENT OF MTBE BY AIR STRIPPING AND OFF-GAS ADSORPTION

2.1 Abstract

The widespread use of methyl tertiary butyl ether (MTBE) as an oxygenate in gasoline has resulted in the contamination of a large number of ground and surface water sources. Even though air stripping has been proven to be an effective treatment technology for MTBE removal, off-gas treatment is often required in conjunction with it. This study evaluated the combined treatment technologies of air stripping followed by off-gas adsorption, on a pilot scale, for the treatment of MTBE contaminated water. The effect of different air/water ratios on the treatment efficiency of MTBE was studied and the mass transfer coefficient was determined. Air/water ratios of 105:1, 151:1, 177:1, 190:1, 202:1 and 206:1 were used and a treatment efficiency of >99% was achieved for all the runs conducted. The depth of packing required to achieve maximum treatment efficiency decreased with increasing air/water ratio. The impact of relative humidity (RH) on the adsorption of MTBE in the off-gas was evaluated for two adsorbents, namely, granular activated carbon (GAC) and carbonaceous polymeric resin. The breakthrough studies conducted with the MTBE laden off-gas, on the pilot scale adsorber beds, at 20%, 30% and 50% RH indicated that GAC has a higher adsorptive capacity than resin. The adsorptive capacity of GAC decreased with increasing RH, whereas; RH did not impact the resin adsorptive capacity.
2.2 Introduction

Air strippers provide contact between air and water that facilitates volatile materials to move from the water to air. A packed column air stripper consists of a cylindrical column that contains a liquid distribution system above the packing material. The contaminated water is pumped to the top of the tower and is allowed to flow by gravity over the packing material. Air is introduced into the bottom of the tower and it flows countercurrent to the direction of water flow. The packing material is designed to maximize available specific surface area for contact between the contaminated water and the process air, thereby providing the maximum specific surface area possible for volatile contaminants to move from the liquid phase to the gas phase. This results in efficient transfer of volatile contaminants from the water to the air. The contaminant free water leaves the bottom of the tower while the air containing the contaminant exists the top of the tower for further treatment or venting to the atmosphere. Figure 2-1 shows the schematic diagram of a typical air stripper.

At 20°C, MTBE’s Henry’s constant is approximately 0.022. This value is much lower than Henry’s constants for common organic compounds found in groundwater such as TCE, PCE, or benzene. This low Henry’s value constant makes air stripping of MTBE more difficult and more costly than removal of these other compounds. Raising the water temperature will increase the Henry’s constant, however, heating the water would be cost-prohibitive. The packing material is designed to maximize available specific surface area for contact between the contaminated water and the process air, thereby providing
the maximum specific surface area possible for volatile contaminants to move from the liquid phase to the gas phase. Air stripping of VOC contaminated aqueous streams is an effective technology for removing VOCs from water (Nelson et al., 1997; Kavanaugh and Trussel, 1980). Air stripping is often the most promising treatment technology for MTBE contaminated water. It is a proven technology and has been successfully used to remove MTBE from drinking water sources in locations across the US, including full scale installations at La Crosse, Kansas and Rockaway Township, New Jersey (NWRI 2000). The hazardous waste Clean-Up Information (CLU-IN) website, maintained by U.S. EPA, has reported at least two MTBE remediation case studies where GAC adsorption has been replaced by air stripping due to poor GAC performance (Creek and Davidson 1998). The website also lists several other MTBE remediation sites which have successfully used air stripping to treat MTBE. The Site A: Service station, NJ reported a 95% MTBE removal (from an initial concentration of 96µg/L) using air stripping at an air/water ratio of 200:1 to treat 800gpm of contaminated water. The Site B: Service station, FL used an air/water ratio of 210:1 to achieve a 92-98% MTBE removal from an initial concentration of 580 µg/L. Site C: Service station, FL and Site K: Service station, NJ achieved >99.9% removal efficiency when air stripping was combined with catalytic oxidation. Site L: UST Service station, MA had an initial MTBE concentration of 2290 µg/L and they were able to achieve a 97% MTBE removal using air stripping at an air/water ratio of 155:1.

For its higher contaminant removal efficiencies and relative lower costs, air stripping has found wide use in the treatment of MTBE in particular. Side by side with air stripping, granular activated carbon has been used for removing VOCs from the off-gas emitted by
air stripping (Crittenden et al. 1988). Catalytic oxidation of off-gas is restricted to a few systems due to the problems of catalyst deactivation and poisoning (Moretti 2002). Biological treatment is often a slow process and chemical oxidation has the potential of forming more toxic by-products. Off-gas treatment for the removal of MTBE has not been well documented or studied, although experience with other VOCs indicates that adsorption is an effective treatment process (Nelson et al. 1985; Parmele et al. 1979). Vapor phase GAC adsorption is a well-known technology used to remove a wide range of organic compounds from air streams. Removal of organic compounds from air occurs by means of physical adsorption on activated carbon. The air passes through a fixed bed of activated carbon until the capacity of the carbon is nearly exhausted. Gas phase carbon adsorbers are designed as either single-pass or regenerative beds, depending on the mass of chemicals in the feed stream. Adsorption of MTBE from the exhaust air stream (off-gas) is different than that of dry air, since the exhaust air stream usually contains high concentrations of water vapor, which is assumed to be saturated at the temperature of ground water. This study was undertaken to examine the technical feasibility of using a combination of air stripping and gas-phase adsorption to remove MTBE from drinking water.

2.3 Objectives

The main objective of this study was to determine if the combined treatment technologies of packed tower air stripping and gas-phase adsorption can effectively be used to remove MTBE from water supplies. Pilot-plant studies were used to assess the packed tower performance for various air-to-water ratios, determine the overall mass transfer
coefficient. Pilot-plant studies were also used to assess fixed-bed adsorption for the removal of MTBE from the air stripper off-gas using GAC and a carbonaceous polymeric resin. The adsorption studies were used to determine the impact of RH on GAC and resin usage rates and assess the breakthrough behavior using the pore and surface diffusion model (PSDM).

2.4 Materials and Methods

2.4.1 Experimental Setup

Figure 2-2 shows the experimental setup of the pilot scale air stripper and adsorber beds. A packed tower countercurrent flow air stripper was used in this study. The air stripper consisted of cylindrical aluminum sections bolted together to form a tower of 0.6 m internal diameter and a height of 5.7 m. The packing material used in the tower was 2.54 cm (1”) polypropylene Ballast® Saddle™ (Koch-Glitsch Inc., Wichita, KS). The random packed height in the tower was 4.5 m. MTBE was injected into the inlet water, from a Tedlar bag, at a constant rate of 1 mL/min using a peristaltic pump (Masterflex L/S Digital Economy Drive, Cole-Parmer Instrument Co., Vernon Hills, IL). An in-line static mixer (Koflo Model No.: 15-40C-4-12-2, Koflo Corp., Cary, IL) was installed to ensure the complete mixing of MTBE in the water. The contaminated water was pumped to the top of the tower and was allowed to flow by gravity over the packing material. A liquid distributor was provided at the top of the packing to ensure even distribution of inlet water on to the packing. Redistribution rings were located every 0.9 m to provide an even distribution of water through the packed column and minimize wall effects. Fifteen water
sampling ports were provided at equal intervals in the packed column to determine the liquid-phase concentration with packing depth.

Stripping air was drawn into the tower from the bottom, using suction fans connected to the outlet piping. Additional airflow was provided using a low pressure, high volume fan (Fantech FR250, Fantech, Sarasota, FL) connected to the outlet piping. The airflow through the air stripper could be varied from 139 L/s to 221 L/s (2200 gpm to 3500 gpm). The airflow was countercurrent to the water flow. The treated water exited at the bottom of the tower and was discharged into the drain, while the air containing MTBE exited at the top of the tower. A split stream from the main off-gas line was then pumped by a 1 HP Ring compressor (Fuji Electric Co., Tokyo, Japan) through two adsorber beds in parallel, one containing Calgon BPL 6x16 GAC (Calgon, Pittsburgh, PA) and the other containing Ambersorb 600 polymeric resin (Rohm and Haas, Philadelphia, PA). An in-line air heater was used to heat the off-gas before it was passed through the adsorber beds. The adsorbent columns were constructed of 10 cm diameter Plexiglas® pipe and were 30 cm long. The flow through the adsorbent columns was regulated using valves and flow meters (King Instrument Co., Huntington Beach, CA). Air sampling ports provided for sample analysis at the inlet and the outlet of the adsorber beds. Additional ports were provided at the air stripper inlet piping and the main off-gas piping to measure the inlet water MTBE concentration and the total off-gas flow rate, respectively. An Airflow™ PVM100 micromanometer (Airflow Technical Products Inc., Netcong NJ) was inserted through the off-gas port to measure the off-gas flow rate. A Cole-Parmer hygrometer Model 37000-50 (Cole-Parmer Instrument Co., Vernon Hills, IL) was used to
measure the relative humidity (RH) and temperature of the off-gas at the various air sampling ports.

2.4.2 Air sampling procedure

MTBE was extracted from the air stream by use of solid-adsorbent-filled sampling traps in accordance with EPA Method TO-17 procedures (EPA 1997a). Supelco H-Trap (Supelco, Bellefonte, PA) containing the adsorbents Carbopack B™ and Carbosieve S-111™ were used for air sampling. Adequate capacity in terms of breakthrough volume of these adsorbent materials (and trap dimensions) was verified under actual process conditions. One end of the trap was attached to the sampling port by means of a toggle valve and the other end was connected to a 1L stainless steel canister. A pneumatic flow controller with a range of 40 to 80 mL/min was used to regulate the air flow through the trap. Regulation was necessary because the trapping efficiency of the adsorbent materials decreases with increasing flow rate. Prior to sampling the canister was evacuated using a vacuum pump. A digital vacuum gauge, attached to the canister, displayed the pressure within the canister. During sampling, approximately 0.25L of air sample was allowed to pass through the trap and was collected in the canister. The exact volume of sample collected was calculated from the change in pressure of the canister. As the air sample flowed through the trap, MTBE in the sample was adsorbed onto the trap. The concentration of MTBE in the sample was determined from the quantity of MTBE on the trap and the volume of the sample collected. A schematic diagram of the sampling train is presented in Figure 2-3.
2.4.3 Chemicals

MTBE used in this study was 99.99% pure obtained from Supelco (Bellefonte, PA). The internal standard used in this study was 99.99% isopropyl ether (Supelco, Bellefonte, PA).

2.4.4 Experimental Methods

2.4.4.1 Air Stripping

Dechlorinated potable tap water was used in all the experiments conducted. Sufficient GAC was used to remove the free chlorine and the disinfection byproducts. Free chlorine and trihalomethane samples were periodically taken to confirm no breakthrough. The inlet water flow rate to the air stripper was set at 1.07 L/s (17 gpm). A solution of MTBE at a concentration of 9 mg/L was prepared in a 37.85 L (10 gallon) HDPE tank with a floating lid. This solution was then transferred to 10L Tedlar bags (231 series, SKC Inc., Eighty Four, PA), which were used as MTBE feed bags. The purpose of using the Tedlar bags was to minimize the loss of MTBE from the feed solution by volatilization and to reduce fluctuations in the inlet MTBE concentration. The feedbags were connected to the peristaltic pump for injection of MTBE into the inlet water at a constant flow rate of 1 mL/min, through a port located before the in-line static mixer. This produced a 200 µg/L MTBE concentration in the inlet water to the air stripper. As the water flowed through the packing material, air flowed up through the air stripper at a flow rate of 214.5 L/s (3400 gpm), to obtain an air/water ratio of 200:1. The tower was operated for an hour before
water sampling was initialized in order to ensure column flow stability. Water samples were collected at the water inlet port, the ports located along the depth of the tower and at the water outlet. Experiments were also conducted at air/water ratios of 105:1, 151:1, 177:1, 190:1, 202:1 and 206:1 and water samples were collected during all experimental runs.

2.4.4.2 Off-gas Adsorption

The off-gas from the air stripper was saturated with water vapor at a temperature ranging from 14°C to 22°C. Since water vapor can impact adsorbent capacity, it was heated to control the RH. Hence the off-gas was heated to 40°C to reduce the RH before it was passed through the adsorber beds. Three experimental runs were conducted with the same air/water ratio of 200:1 and at different off-gas RH levels of 20%, 30% and 50%. The different RHs at 40°C were obtained by operating the column at different ambient/seasonal conditions. The water and the air flow rates were maintained at 214.5 L/s (3400 gpm) and 1.07 L/s (17 gpm), respectively. The MTBE concentration of the off-gas from the air stripper ranged from 1.2 to 1.9 ppbv. During the three experimental runs, the diameter of the adsorbent columns was 10 cm and the height was fixed at 15 cm for both the adsorbents. The off-gas flow rate through the GAC and the resin columns was maintained at 3.78 L/s (8 cu.ft/min) and 5.19 L/s (11 cu.ft/min), respectively. Air samples were taken at the inlet and outlet of both the adsorber beds at regular intervals throughout each experimental run. Each experimental run was conducted for a period of 21 days.
2.4.5 Analytical Procedure

2.4.5.1 Aqueous MTBE

MTBE water samples were collected from the sampling ports in 40 mL amber volatile organic analysis (VOA) vials in accordance with SW-846 EPA Method 5030 procedures (EPA 1997b). Each 40 mL sample was preserved with 25 mg of ascorbic acid. The samples were analyzed in accordance with procedures outlined in EPA Method 502.2 (EPA 1993). The photo-ionization detector (PID), specified in the method was replaced with a flame ionization detector. The MTBE concentrations were determined by chromatographic separation on a DB-624 Megabore capillary column (J&W Scientific, Folsom, CA) using a HP 5890 Series II gas chromatograph. The chromatographic separation was conducted under temperature programmed conditions starting at 35ºC. The retention time for MTBE was 12.5 minutes.

2.4.5.2 Gas phase MTBE

MTBE samples adsorbed on to the Supelco H-Traps were thermally desorbed by a Tekmar Model 2000 Purge and Trap concentrator (Tekmar Corp., Cincinnati, OH). After the trap was installed in the unit, it was purged with helium for 8 minutes to remove any entrapped moisture. The trap was then heated to 230ºC to release the adsorbed MTBE. The desorbed MTBE was then flushed on to the GC column for analysis. The chromatographic separation was accomplished on a 60 m VOCOL™ capillary column of
3.0μm film thickness, using a Hewlett Packard HP 6890 gas chromatograph equipped with a flame ionization detector. The chromatographic separation was conducted under temperature programmed conditions starting at 35°C, with the injection port and the detector temperatures set at 150°C and 250°C, respectively. The flow rate of the carrier gas (Helium) was set at 5.4 ± 1 mL/min and the GC inlet was operated with a split ratio of 2.5:1. The flame gases air and hydrogen flow rates were set at 400.0 ± 1 mL/min and 35.0 ± 1 mL/min, respectively. A retention time of 7.6 min for MTBE and 8.6 min for isopropyl ether (internal standard) were obtained under these operating conditions. Each trap on which a sample or standard had been loaded was spiked with 100 ng of isopropyl ether. The internal standard technique was used for quantification. Gaseous MTBE and isopropyl ether standards were prepared in 2L static gas dilution bottles. A 9 point calibration curve was constructed by spiking aliquots from the static gas dilution bottles onto clean traps by use of a tee with a regulated flow of Helium at 40 ml/min. The calibration points ranged from 2ng to 1000ng.

2.5 Results and Discussions

2.5.1 Air Stripping

Figure 2-4 shows the concentration profile of the air stripper for all the experimental runs conducted with different air/water ratios. The MTBE concentration at each sampling port normalized over the inlet concentration was plotted as a function of the depth of the port. Figure 2-4 shows a treatment efficiency of >99% was achieved for all the runs, and the
total depth of packing required to achieve the maximal removal decreases with increasing air/water ratio. A depth of 2.6 m was sufficient to achieve maximum treatment efficiency, with an air/water ratio of 206:1; whereas, a depth of 4.2 m was required to achieve the same treatment efficiency with an air/water ratio of 105:1.

2.5.2 $K_{La}$ Determination

The mass transfer coefficient for an air stripper, $K_{La}$, was determined based on four basic equations, which are derived from mass transfer theory (Hand et al. 1999; Kavanaugh and Trussell 1980). In packed tower air stripping, the tower length is defined as the product of the height of a transfer unit and the number of transfer units.

$$L_t = HTU \times NTU$$  \hfill (2-1)

$$HTU = \frac{Q}{A \times K_{La}}$$  \hfill (2-2)

$$NTU = \left[ \frac{R}{R-1} \right] \times \ln \left[ \frac{C_e \times (R-1)+1}{C_e \times R} \right]$$  \hfill (2-3)

$$R = \frac{V_a \times H}{Q}$$  \hfill (2-4)

Where,

$L_t$ = Packing depth (cm)

$HTU$ = Height of a transfer unit (cm)

$NTU$ = Number of transfer units

$K_{La}$ = Overall mass transfer coefficient (cm/s)
a = Specific interfacial area (cm²/cm³)

Q = Water flow rate to the tower (cm³/s)

A = Cross sectional area of the tower (cm²)

R = Stripping factor

V_a = Volumetric air flow rate to the tower (cm³/s)

H = Henry’s law constant (dimensionless)

C_o, C_e = Bulk water-phase MTBE concentration at the inlet and outlet of the tower (µg/L)

The Henry’s law constant was determined based on the estimate of the constant as reported by Paul Sun of Equilon Enterprises, LLC (Sun 1998). The value of K_{La} is based on the MTBE removal due to the packed-height portion of the tower. There is however, some MTBE removal occurring at the top and bottom of the packing, where the contaminated water contacts the air, called the removal due to end effects. Hence, the following expression incorporating the end effects was used to determine K_{La}:

\[
NTU_{measured} = \frac{1}{HTU}(Z) + NTU_{endeffects}
\]  

(2-5)

NTU_{measured} is the NTU value determined from equation (3) at each sample port location at a depth Z, from the top of the packing where C_e is the concentration measured at the sampling port. A plot of NTU_{measured} as a function of depth (Z) was constructed and K_{La} was determined from the slope (1/HTU) of the plot (Ball et al. 1984). Figures 2-5 to 2-10 show the plot of NTU_{measured} versus the depth of the air stripper for each of the experimental runs conducted with different air/water ratios.
The $K_{La}$ values determined for all the runs conducted at the different air/water ratios are listed in Table 2-1. It can be seen from the table that the $K_{La}$ values obtained are almost the same except for one run. This variation might have been due to some analytical or experimental error.

### 2.5.3 Off-gas Adsorption

A plot of the off-gas effluent concentration, normalized over the inlet concentration, as a function of the bed volumes treated was constructed for all the three runs conducted at 20%, 30% and 50% RH. Figures 2-11 and 2-12 show the breakthrough curves for GAC and resin respectively. It can be seen from the Figure 2-11 that there is an impact on the breakthrough behavior of GAC with change in RH of the off-gas. As the RH increased, the adsorptive capacity of GAC decreased and hence the number of bed volumes required to breakthrough also decreased. The resin adsorptive capacity did not change with changing RH. While competitive adsorption between MTBE and water vapor is considered the reason for the reduction in adsorptive capacity of GAC, the resin’s constant capacity even at relatively high humidity levels was attributed to its hydrophobic nature. Hence, it is possible that resin may have a greater capacity for treating an off-gas with RHs higher than 50%.
2.5.4 Water Adsorption Isotherm

Water vapor adsorption isotherms were conducted, for both the adsorbents, to determine their hydrophobicity. Oven dried, weighed samples of adsorbents were equilibrated in an atmosphere of controlled humidity for a period of eight weeks. The required RH was obtained using standard sulfuric acid solutions for which the humidity as a function of solution composition is well known. The uptake of water for each of the adsorbents at each RH was determined. Figure 2-13 shows a plot of the solid phase concentration of water per mg of adsorbent as a function of RH. It can be seen from the figure that resin is more hydrophobic than GAC, having only about 20% of the water uptake of that of GAC, at 90% RH.

2.5.5 Mathematical Modeling

Modeling of the breakthrough curves was performed using the Pore and Surface Diffusion Model (PSDM). The PSDM is a dynamic fixed bed model which requires equilibrium and kinetic parameters and several physical properties of the adsorbate and the adsorbent. From the mass balances on the bulk phase and adsorbent phase, two partial differential equations are obtained for the component. A coupling equation between the bulk phase and the adsorbent phase is obtained by assuming local equilibrium at the exterior of the adsorbent particle. In cases where pore and surface diffusion are present, local equilibrium is assumed along the pore walls. These equations are non-dimensionalized and solved by numerical methods.
The partial differential equations describing the adsorber dynamics in a fixed-bed adsorber are given below. The liquid phase mass balance for component $i$ is given by:

$$\frac{\partial C_i(z,t)}{\partial t} + V \frac{\partial C_i(z,t)}{\partial z} + 3 \frac{k_{fi}(1-\varepsilon)}{\varepsilon R} \left[ C_i(z,t) - C_{pi}(r=R,z,t) \right] = 0$$  \hspace{1cm} (2-6)$$

where $C_i$ = aqueous-phase concentration (mmol/L) of adsorbate $i$ at time $t$ (s) and axial position along the bed $z$ (cm); $C_{pi}$ = adsorbate concentration in adsorbent pores (mmol/L); $V$ = loading rate (cm/s); $k_{fi}$ = film transfer coefficient for adsorbate $i$ (cm/s); $R$ = average adsorbent particle radius (cm); $\varepsilon$ = particle void fraction (porosity). The initial condition for equation (2-6) is:

$$C_i(z,t) = 0 \quad \text{at} \quad 0 \leq z \leq L, t = 0$$  \hspace{1cm} (2-7)$$

where $L$ = bed length (cm). The boundary condition for equation (2-6) is:

$$C_i(z,t) = C_{oi} \quad \text{at} \quad z=0, \quad t > 0$$  \hspace{1cm} (2-8)$$

where $C_{oi}$ = initial concentration of adsorbate (mmol/L). The intraparticle phase mass balance for component $i$ is given by:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \ D_{si} \frac{\partial q_i(r,z,t)}{\partial r} + \frac{r^2 D_{pi}}{\rho_a} \varepsilon_p \frac{\partial}{\partial r} C_{pi}(r,z,t) \right]$$

$$= \frac{\partial}{\partial t} \left[ q_i(r,z,t) + \frac{\varepsilon_p}{\rho_a} C_{pi}(r,z,t) \right]$$  \hspace{1cm} (2-9)$$

where $q_i(r,z,t)$ = solid-phase concentration of adsorbate $i$ (mmol/g); $D_{pi}$ = pore diffusion coefficient for component $i$; $D_{si}$ = surface diffusion coefficient for component $i$; $\varepsilon_p$ = particle void fraction (porosity). The initial condition for equation (2-9) is:
\[ q_i (r,z,t) + \frac{\varepsilon_p}{\rho_a} C_{p,i} (r,z,t) = 0 \quad \text{at} \quad 0 \leq r \leq R, \ t = 0 \] (2-10)

where \( \rho_a = \) apparent adsorbent density (g/cm\(^3\)). The first boundary condition for equation (2-9) is:

\[ \frac{\partial}{\partial r} \left[ q_i (r,z,t) + \frac{\varepsilon_p}{\rho_a} C_{p,i} (r,z,t) \right] = 0 \quad \text{at} \quad r = 0, \ t \geq 0 \] (2-11)

The second boundary condition for equation (2-9) is:

\[ D_{s,i} \rho_a \frac{\partial q_i}{\partial r} (r = R,z,t) + D_{p,i} \varepsilon_p \frac{\partial C_{p,i}}{\partial r} (r = R,z,t) = k_{f,i} \left[ C_i (t) - C_{p,i} (r = R,z,t) \right] \] (2-12)

The equation coupling the aqueous phase concentration of component \( i \) within the adsorbent pores to the adsorbent phase concentration of component \( i \) is given by:

\[ C_{p,i} (r,z,t) = \frac{q_i (r,z,t)}{\sum_{k=l}^{m} q_k (r,z,t)} \left[ \sum_{k=l}^{m} n_k q_k (r,z,t) \right]^{n_i} \] (2-13)

where \( m = \) number of components. The above equation is derived assuming that the adsorption reaction rate is much faster than the mass transfer rate (assumption of local equilibrium).

The resulting system of partial differential equations was converted to a dimensionless form. The dimensionless partial differential equations were then reduced to a system of ordinary differential equations using the orthogonal collocation method. A detailed derivation of the equations and the computer algorithms that were used to solve the
The gas diffusivity, $D_G$, is calculated using the Wilke-Lee modification of the Hirschfelder-Bird-Spotz method (Reid et al. 1987) as shown below:

$$D_G = \frac{D_G \varepsilon_p C_0}{\tau_p \rho_s q_o} \times SPDFR$$

where:

- $C_0$ is the initial inlet concentration (mg/L)
- $D_G$ is the adsorbate gas phase diffusivity (cm$^2$/s)
- $D_s$ is the surface diffusion coefficient (cm$^2$/s)
- $q_o$ is the solid phase concentration in equilibrium with $C_o$ for a single-solute equilibrium (mg/g)
- $\varepsilon_p$ is the void fraction (porosity) of the adsorbent (-)
- $\rho_s$ is the apparent adsorbent density (which includes pore volume) (g/L)
- $\tau_p$ is the adsorbent tortuosity (-).

$SPDFR$ is the surface to pore diffusion flux ratio (-).
\[ D_G = \frac{10^{-4} \left( 1.084 - 0.249 \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} \right) T^{3/2} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{Pr_{AB}^2 f\left(kT/\varepsilon_{AB}\right)} \] 

(2-15)

where \( D_G \) is the gas diffusivity of compound \( B \) in air \((A) (m^2/s)\)

\( T \) is the absolute temperature \((K)\)

\( M_A \) is the molecular weight of \( A \) (air)\((g/mol)\)

\( M_B \) is the molecular weight of \( B \) \((g/mol)\)

\( P \) absolute pressure \((Pa)\)

\( r_{AB} \) is the molecular separation at collision \(=(r_A+r_B)/2\)

\( \varepsilon_{AB} \) is the energy of molecular attraction \(= \sqrt{\varepsilon_A \varepsilon_B} \)

\( k \) is the Boltzmann’s constant

\( f\left(kT/\varepsilon_{AB}\right) \) is the collision function

\( r \) and \( \varepsilon \) can be calculated as follows:

\[ r = 1.18 V_b^{1/3} \] 

(2-16)

\[ \frac{\varepsilon}{k} = 1.21 T_b \] 

(2-17)

where \( V_b \) is the molar volume of liquid at normal boiling point\((m^3/kmol)\)

\( T_b \) is the normal boiling point in Kelvin

The collision function is calculated by:

\[ f\left(kT/\varepsilon_{AB}\right) = 10^a \] 

(2-18)
\[ a = -0.14329 - 0.48343 \times E + 0.109390 \times E^2 + 0.13612 \times E^3 \\
-0.20578 \times E^4 + 0.083899 \times E^5 - 0.011491 \times E^6 \]  \hspace{1cm} (2-19)

where

\[ E = \log \left( \frac{kT}{E_{AB}} \right) \]

The pore diffusion coefficient is related to the adsorbate diffusivity and the intraparticle physical properties as shown in the following equation (Sontheimer, et al, 1988):

\[ D_p = \frac{D}{\tau_p} \]  \hspace{1cm} (2-20)

where: \( D \) is the adsorbate gas or liquid phase diffusivity (\(cm^2/s\))

\( \tau_p \) is the adsorbent tortuosity (-)

\( D_p \) is the pore diffusion coefficient (\(cm^2/s\))

The values of the film transfer coefficient (\(K_f\)) and the Freundlich adsorption isotherm parameter \( K \) were optimized to get the best fit of the experimental data. The three curves predicted by the model for the three runs conducted at 20\%, 30\% and 50\% RH are shown in Figure 2-11 as solid lines. Best agreement between experimental and calculated data was achieved with a \(K_f\) value of 2.1 cm/s and a \(1/n\) value of 0.32 for all three experimental runs and a \(K\) value of 80.0, 60.0 and 19.5 (mg/g)/(mg/L)\(^{1/n}\) for the runs conducted at 20\%, 30\% and 50\% RH, respectively.
When modeling the resin breakthrough curves, the $D_p$ was calculated using the correlation and the values of $K$, $1/n$, $K_f$ and $D_s$ were optimized to get the best fit of the experimental data. The single curve predicted by the model for all the three runs is shown in Figure 2-12 as a solid line. Best agreement between experimental and calculated data was achieved with a $K_f$ value of 0.85 cm/s, a $D_s$ value of $7.03 \times 10^{-15}$ cm$^2$/s, $K$ value of $16 (mg/g)/(mg/L)$, and $1/n$ value of 0.15.

The adsorption isotherm parameters used in the model predictions for both GAC and resin are listed in Table 2-2. In the case of GAC, the difference in the calculated Freundlich $K$ values increases greatly as the RH increases. As stated above, this reduction was due to the effect of water vapor on the carbon’s capacity. The calculated Freundlich $K$ values for the resin studies show no decrease with increasing RH. The hydrophobic nature of the resin prevented the reduction in capacity. This was expected based on the results of the water vapor adsorption isotherms conducted. A similar behavior of carbonaceous resin has been reported in a research (Vandersall et al. 1992) which studied the effect of humidity on the adsorption of organic vapors on carbonaceous adsorbents. Resin was found to have higher hydrophobicity than GAC in the water vapor isotherms conducted. It was reported that the presence of moisture reduces the capacity of both resin and GAC, but this loss of capacity was particularly severe for the less hydrophobic GAC. This study also showed that the decrease in adsorptive capacity (due to the presence of moisture) for high water soluble organic compounds is lower compared to that of low water soluble compounds. This behavior was found to be more pronounced in carbonaceous resin than in GAC. Hence the high water solubility of MTBE might be
the reason for the constant adsorptive capacity of resin even at very high RH levels. Additional research is required to provide further insight into this behavior of the resin.

The analysis of the breakthrough profiles in figures 2-11 and 2-12 and the K values (Freundlich adsorption isotherm parameter) obtained from the model indicate that GAC has a higher adsorptive capacity for MTBE than resin under low humidity conditions. But as the RH increases to 50%, the capacities of both the adsorbents are almost the same. Although raising the temperature of the off-gas would reduce the RH, high air temperatures would in turn reduce the adsorptive capacity. On the other hand, increasing RH to values greater than 50% would cause premature breakthrough resulting in increased regeneration frequencies. Hence a proper balance has to be made between the RH and the temperature of the off-gas in order to optimize the treatment efficiency.

2.6 Conclusions

This study evaluated the combined treatment technologies of air stripping followed by off-gas adsorption for the removal of MTBE contaminated water. Dechlorinated potable tap water was spiked with MTBE and was used in the experiments. The MTBE concentrations studied ranged from 80 µg/L to 250 µg/L. The performance of the air stripper was studied at six different air/water ratios, 105:1, 151:1, 177:1, 190:1, 202:1 and 206:1. A treatment efficiency of > 99% was achieved for each of the test runs conducted. The depth of the packing required to achieve maximum treatment efficiency increased with decreasing air/water ratios. The mass transfer coefficient, $K_{L_a s}$, was determined for
the six air/water ratios studied. The study determined the effectiveness of the two adsorbents, GAC and resin, for the removal of MTBE-laden off-gas from the air stripper was studied. The impact of RH on the breakthrough behavior of the two adsorbents was also studied. GAC had a much higher capacity than resin, but an increase in the RH of the off-gas adversely affected (reduced) the capacity of GAC. RH did not have any noticeable impact on the adsorptive capacity of resin. At the highest value of RH studied (50%), GAC had almost the same capacity as that of resin. So it is likely that the adsorptive capacity of resin would be higher than that of GAC for an off-gas with RH greater than 50%. The modeling of the breakthrough behavior of both the adsorbents was done using the pore and surface diffusion model. The model predictions agree well with the experimental data.
2.7 References:


Determination of Volatile organic Compounds in Ambient Air Using Active Sampling onto Sorbent Tubes, Compendium Method T0-17.


2.8 Notation

The following symbols are used in this paper

\( L_t \) = Packing depth (cm)

\( HTU \) = Height of a transfer unit (cm)

\( NTU \) = Number of transfer units

\( K_L \) = Overall mass transfer coefficient (cm/s)

\( a \) = Specific interfacial area (cm\(^2\)/cm\(^3\))

\( Q \) = Water flow rate to the tower (cm\(^3\)/s)

\( A \) = Cross sectional area of the tower (cm\(^2\))

\( R \) = Stripping factor

\( V_a \) = Volumetric air flow rate to the tower (cm\(^3\)/s)

\( H \) = Henry’s law constant (dimensionless)

\( C_o, C_e \) = Bulk water-phase MTBE concentration at the inlet and outlet of the tower (µg/L)

\( C_{0,i} \) = initial aqueous-phase adsorbate concentration (mmol/L)

\( C_i \) = aqueous-phase concentration of adsorbate i at time t (mmol/L)

\( C_{p,i} \) = adsorbate concentration in adsorbent pores (mmol/L)

\( D_{p,i} \) = pore diffusion coefficient (cm\(^2\)/s)

\( D_{s,i} \) = surface diffusion coefficient (cm\(^2\)/s)

\( K_{f,i} \) = film transfer coefficient (cm/s)

\( L \) = bed length (cm)

\( m \) = number of components

\( q_i \) = adsorbent-phase concentration for solute i (mmol/g)
\( R \) = average adsorbent particle radius (cm)

\( V \) = loading rate (cm/s)

\( \varepsilon_P \) = particle void fraction (porosity)

\( \rho_A \) = apparent adsorbent density (g/cm\(^3\))

\( D_G \) = adsorbate gas phase diffusivity (cm\(^2\)/s)

\( \tau_p \) = adsorbent tortuosity (dimensionless)

\( T \) = absolute temperature (K)

\( M_A \) = molecular weight of A (air)(g/mol)

\( M_B \) = molecular weight of B (g/mol)

\( P \) = absolute pressure (Pa)

\( r_{AB} \) = molecular separation at collision (cm)

\( \varepsilon_{AB} \) = energy of molecular attraction (ergs)

\( k \) = Boltzmann’s constant

Index \( i \) refers to component number \( i \).
Figure 2-1  Schematic diagram of an Air Stripper.
Figure 2-2  Schematic of the pilot scale air stripper and adsorber beds.
Figure 2-3  Setup of the Sampling train used in air sampling.
Figure 2-4  Concentration profile of the air stripper.
Figure 2-5  Plot of NTU\textsubscript{measured} Vs Depth for an air/water ratio of 105:1

![Graph showing NTU measured vs depth for an air/water ratio of 105:1. The regression equation is $y = 0.9898x + 0.1487$, with $R^2 = 0.9711$.]

Figure 2-6  Plot of NTU\textsubscript{measured} Vs Depth for an air/water ratio of 151:1

![Graph showing NTU measured vs depth for an air/water ratio of 151:1. The regression equation is $y = 1.2924x + 0.1759$, with $R^2 = 0.9372$.]
Figure 2-7   Plot of NTU\textsubscript{measured} Vs Depth for an air/water ratio of 177:1

Figure 2-8   Plot of NTU\textsubscript{measured} Vs Depth for an air/water ratio of 190:1
**Figure 2-9**  Plot of NTU$_{measured}$ Vs Depth for an air/water ratio of 202:1

**Figure 2-10**  Plot of NTU$_{measured}$ Vs Depth for an air/water ratio of 206:1
Figure 2-11  Breakthrough behavior of MTBE on GAC at three relative humidity conditions.
Figure 2-12  Breakthrough behavior of MTBE on Resin at three relative humidity conditions.
Figure 2-13  Water Vapor Isotherm.
Table 2-1  \( K_{La} \) values determined for the various experimental runs.

<table>
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<tr>
<th>Air Flow (gpm)</th>
<th>Air Loading Rate (gpm/ft(^2))</th>
<th>Water flow (gpm)</th>
<th>Water Loading Rate (gpm/ft(^2))</th>
<th>Air/water Ratio</th>
<th>( K_{La} ) S(^{-1})</th>
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</thead>
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<tr>
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Table 2-2  Freundlich isotherm parameters - Model predictions.

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<tr>
<th>Adsorbate</th>
<th>Relative Humidity</th>
<th>Model</th>
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<td></td>
<td>%</td>
<td>K (mg/g)/(mg/L)^1/n</td>
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<td>GAC</td>
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</tr>
<tr>
<td>Resin</td>
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<td>16.0</td>
</tr>
<tr>
<td>Resin</td>
<td>30</td>
<td>16.0</td>
</tr>
<tr>
<td>Resin</td>
<td>50</td>
<td>16.0</td>
</tr>
</tbody>
</table>
Chapter 3

OFF-GAS ADSORPTION ISOTHERMS

3.1 Abstract

Methyl tertiary butyl ether (MTBE), a gasoline oxygenate additive, is one of the most common ground water pollutants in the United States. Due to its high water solubility, direct adsorption of MTBE onto granular activated carbon (GAC) is not viable. Air stripping with off-gas treatment is a well established and proven technology for the treatment of MTBE contaminated water. Adsorption isotherms were conducted at 40ºC to evaluate the adsorptive capacity of two adsorbents, GAC and carbonaceous resin, for gas phase MTBE present in the air stream from an air stripping system. The impact of relative humidity (RH), in the off-gas, on the adsorptive capacity of the two adsorbents was also studied. Isotherms were conducted at four different levels of RH, <5%, 20%, 30% and 50%. The results from the isotherms showed that the adsorptive capacity of GAC is, in general, higher than that of resin at all the RHs studied. The adsorption of MTBE onto GAC is hampered by the presence of water, resulting in lower MTBE capacities at higher RH. On the other hand, the adsorptive capacity of resin for MTBE does not seem to be impacted by RH.
3.2 Introduction

Air stripping technologies are widely used for removing halogenated volatile organic compounds (VOC) from drinking water supplies prior to distribution. The contamination of air by the VOCs stripped from the contaminated water has, however, been a public concern. This has led to the enforcement of strict regulations which necessitate development of effective systems for the treatment of air stripping off-gas. It has been reported that air stripping is the most cost effective method for treating MTBE contaminated water (NWRI 2000). Off-gas treatment of the MTBE-contaminated air stream from an air stripping system is often required prior to discharge to the atmosphere. The selection of the appropriate off-gas treatment process is the key factor in determining the overall efficiency of the air stripping technology. The higher the air/water ratio in the air stripping system, the higher the off-gas treatment costs. GAC can effectively remove volatile as well as non-volatile compounds from off-gas streams to undetectable levels before their discharge into the atmosphere (Stenzel and Gupta 1995). The large surface area combined with an extensive microporous structure and the rapid adsorption capability of GAC makes it an effective mechanism for the removal of pollutants from the off-gas streams. The equilibrium capacity of GAC for target compounds is the major factor influencing the design of full scale adsorption columns, and influences its economic feasibility as an effective off-gas treatment.

Off-gas streams produced by air stripping have a very high relative humidity (RH), close to 100%. This would decrease the adsorptive capacity of the adsorbents because the water
molecules adsorb strongly on the active sites and hence would block part of the surface causing premature breakthrough resulting in increased regeneration frequencies. Many studies have reported this pattern (Gregg and Sing 1982; Keener and Gong 1993; Okazaki et al. 1978; Schweiger 1995; Sircar and Myers 1973). On a macroscopic scale, carbon surfaces are considered to be hydrophobic, meaning very little or no adsorption of water is supposed to take place. Despite this, some activated carbons strongly adsorb water and there has been no clear agreement on the reason for this behavior. Several authors have presented experimental results for the adsorption of mixtures containing water on activated carbons (Eissmann and Levan 1993; Freeman and Reucroft 1979; Rudisill et al. 1992; Valenzuela and Myers 1989). Therefore a GAC adsorber bed designed without regard to humidity coexisting with the contaminant in the off-gas would not be able to achieve the desired removal efficiency. The temperature of the off-gas is increased in order to reduce the RH to below 50% (NWRI 2000). A very high increase in the temperature of the off-gas would in turn reduce the adsorptive capacity of the adsorbents.

3.3 Objectives

In this study, adsorption isotherms were conducted to evaluate the adsorptive capacity of two types of adsorbents for gas phase MTBE present in the off-gases from the air stripper treating MTBE contaminated water. This study also evaluated the effect of RH on the adsorptive capacity of the two adsorbents used. Gas phase isotherms were conducted for
both the adsorbents at 40ºC and at the following four different levels of RHs: 50%, 30%, 20% and <5%.

3.4 Experimental Materials and Methods

3.4.1 Adsorbate

The adsorbate used in the study was MTBE (99.9%, Fisher Scientific Co., NJ). Gaseous MTBE standards were prepared in a 10L Tedlar bag. The bag was filled with 6L of clean, dry air and 1mL of pure MTBE in the liquid form was injected into the bag using a syringe through the septum provided in the bag. The filling and the spiking of the bag was conducted at 40ºC. The bag was then equilibrated for at least 4hrs to allow complete vaporization of MTBE.

3.4.2 Adsorbents

The activated carbon used in this study was Calgon’s (Pittsburgh, PA) BPL 6x16 and the carbonaceous resin used in this study was Rohm and Haas’s (Philadelphia, PA) Ambersorb 600. The properties of the adsorbents are listed in Table 3-1. The adsorbents used in this study were dried in an oven at 105ºC for two days and then they were preloaded with the desired RH. To obtain the desired RH, the adsorbents were placed in a tray in a desiccator maintained at a specific humidity. The desired humidity was obtained by adding the required concentration of sulfuric acid (David 2002) at the base of the
desiccator. The adsorbents were allowed to equilibrate at the constant RH for at least 21 days. The adsorbents were weighed regularly and were considered ready for use when the moisture content was stable over a period of time as evidenced by constant weight. This method was adopted for the adsorbents used in the isotherms conducted at 50% RH, 30% RH and 20% RH. For the last set of isotherms conducted at <5% RH, the adsorbents were directly used after being oven dried. This method of preloading of the desired RH on to the adsorbents, prior to conducting the isotherms, was adopted because it would be difficult to control the RH in the Tedlar bags and the moisture might permeate into or outside the bags over time. It would also be difficult to measure the actual RH inside the bags once the isotherm study has been started.

3.4.3 Analytical Procedure

For the isotherms, the adsorbate concentrations were determined by chromatographic separation on a VOCOL™ capillary column of 3.0µm film thickness, using a Hewlett Packard HP 6890 series gas chromatograph equipped with a flame ionization detector. The chromatographic separation was conducted at 100ºC, with the injection port and the detector temperatures set at 150ºC and 250ºC, respectively. The flow rate of the carrier gas (Helium) was set at 5.4 ± 1 mL/min and the GC inlet was operated in the pulsed-splitless mode. The flame gases air and hydrogen flow rates were set at 400.0 ± 1 mL/min and 35.0 ± 1 mL/min, respectively. A retention time of 7.35 min for MTBE was obtained under the conditions used. The GC was calibrated and tuned before the start of each experiment. A seven point calibration was used and the calibration points were 2 ng, 5
ng, 10 ng, 50 ng, 100 ng, 250 ng and 500 ng. The external standard technique was used for quantification. Gaseous MTBE standards were prepared in 2L static gas dilution bottles. Neat MTBE was diluted in methanol and 10µL of the diluted standards were added to each bottle to achieve two stock concentrations, namely, 20 µg/L and 1000 µg/L. Different volumes were then injected to achieve the desired calibration points.

3.4.4 Isotherm Procedure

All the isotherms were conducted using 10L Tedlar bags (231 series, SKC Inc.). The bags were initially checked for any possible leakages by evacuating the air in the bags with a vacuum pump and checking the presence of air over time. Accurately weighed (± 0.1 mg) masses of adsorbents were placed into the bags through the septum fitting. Masses of GAC used ranged from 21.3 to 360.6 mg per bag and that of resin ranged from 20.3 to 301.1 mg per bag. Any air entrapped in the bags while adding the adsorbents was removed by rolling up the bag and sealing the septum cap and the shut-off valve. The bags were then filled with 6L of pure, moisture free air using a precalibrated 6L stainless steel canister (Figure 3-1). 50 mL of the gaseous MTBE from the stock standard, at 123.4 mg/L, was injected into each of the isotherm bags through the septum, using a gas tight syringe with a side-port needle. The filling of the bags with air, the stock standard preparation and the spiking of the MTBE standard were all conducted at 40°C. For each of the isotherms, three blank bags (without any adsorbent) were prepared at the same initial concentration. These procedural blanks were used to determine the quality of MTBE adsorbed on to the walls of the Tedlar bag and also to estimate the overall
accuracy and precision of the spiking and sampling procedures. Procedural triplicates were also prepared, where; one particular adsorbent mass was prepared in triplicate to determine the precision of the isotherm procedure. Two sets of these procedural triplicates were prepared for each adsorbent in a set of isotherm. All the bags were equilibrated in a room at a constant temperature of 40 ± 1°C. The RH in the room was set to the same level as the preloaded RH in the adsorbents. This would ensure that there is no humidity permeating in or out of the bag. The bags were equilibrated for a period of 9 days. The equilibrium period was determined by preparing sample isotherm bags and analyzing the equilibrium concentration over a period of time. The concentrations in the bags were found to remain constant after 9 days of equilibration. Twice a day, each bag was rotated a few times to ensure proper mixing. At the end of 9 days, the equilibrium concentrations in the bags were determined. 500 µL of the air sample from each of the bag was collected in a valved gas-tight syringe (SGE Model V-GT). The syringes were stored at 40°C, along with the bags, prior to sampling. Gas samples collected in the syringes were immediately injected into the GC/FID system for analysis. Since the GC was calibrated at 23°C, a temperature correction was applied to the results based on the GC standard curve.

3.5 Results and Discussion

Isotherms of the gas phase MTBE on GAC and carbonaceous resin were determined at 40 ± 1°C. The initial concentration of the adsorbate (MTBE) used was 1.0 mg/L. Following
the equilibration, the gas phase concentrations $C_e$ were measured and the surface loading $q_e$ was calculated from a mass balance on each isotherm bag.

$$q_e = \frac{(C_o - C_e)V}{m}$$ \hspace{1cm} (3-1)

where, $C_o$ = initial gas-phase concentration of adsorbate, and $m$ = the mass of the adsorbent. The adsorbate volume represented by $V$ was 6050mL. The experimental data were correlated to the Freundlich isotherm equation

$$q_e = K.C_e^{1/n}$$ \hspace{1cm} (3-2)

where, $K$ and $1/n$ are constants for any particular system at constant temperature. The parameter $K$ is related to the capacity of the adsorbent for the adsorbate, and $1/n$ is a function of the strength of adsorption. The logarithmic form of the equation was then used to plot the data. Linear regression of the data points yielded a best-fit line with a slope of $1/n$ and an intercept of log $K$. Figures 3-2 to 3-5 show the isotherm plots for the experiments conducted at <5%, 20%, 30% and 50% RH, respectively. All the regression lines have a $R^2$ value of above 0.98 indicating a very good linear fit. A summary of the $K$ and $1/n$ values obtained for each of the adsorbent at the different levels of RH is shown in Table 3-2.

Analysis of the data in Figures 3-2 to 3-5 reveal that the adsorptive capacity of GAC is higher than that of the resin for all the isotherms conducted. It can be seen from the Table
3-2 that the adsorptive capacity of GAC is adversely impacted (reduced) by increase in relative humidity. The K values for the GAC isotherms conducted at higher RHs are lower than those conducted at lower RHs, indicating that the capacity of GAC is reduced as the RH is increased. As the preloading of the adsorbents is associated with volume filling and blocking of the macropores, a rapid decrease in the available surface area is expected. This would result in a sharp decrease in the adsorption capacity. Competitive adsorption between water vapor and MTBE can be considered as a special case of multi-component adsorption. Adsorption of water vapor onto activated carbon involves primary and secondary adsorptive sites. The primary adsorptive site consists of the surface functional groups such as those that contain oxygen (e.g. carboxylic, lactone and carbonyl groups). These functional groups are capable of forming hydrogen bonds with water vapor. A secondary adsorption site consists of previously adsorbed water molecules. The number of available primary adsorption sites decreases with increasing RH. MTBE is similar to water in that it is a very polar molecule, hence both water and MTBE will compete for the adsorption sites resulting in lower MTBE capacities.

The adsorptive capacity of resin, on the other hand, does not seem to be affected by the change in RH. From Table 3-2 it can be seen that the K values for the resin isotherms are almost the same for all the different RHs. The resin used is a dry, hydrophobic adsorbent. It has a very low water adsorption even at high RHs. Hence all the adsorption sites on the resin are available for MTBE even at very high RH. The difference in the adsorptive capacity of GAC and resin decreases as the RH increases, which is mainly due to the
reduction in the capacity of GAC. This difference would narrow down as the RH increases further, as the capacity of resin is almost constant.

3.6 Conclusions

Adsorption isotherms were conducted to determine the adsorptive capacity of GAC and a carbonaceous resin at 40°C. The adsorptive capacity of GAC was found to be much higher than that of the resin. The effect of RH on the capacity of the adsorbents were studied at four levels of RH, <5%, 20%, 30% and 50%. The capacity of GAC was adversely impacted (reduced) with the increase in RH. This is attributed to the competitive adsorption behavior that takes place between MTBE and water vapor. The adsorptive capacity of resin remains almost a constant at all levels of RH studied. The hydrophobic nature of the resin allows very little water to be adsorbed onto it, and hence does not reduce the adsorptive capacity even at very high levels of RH.
3.7 References


### Table 3-1  Adsorbent Specification (as given by the manufacturer).

**BPL 6x16 Specifications**

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iodine No., mg/g</td>
<td>1050 (Min)</td>
</tr>
<tr>
<td>Butane Activity, weight %</td>
<td>23.3 (Min)</td>
</tr>
<tr>
<td>Ash, weight %</td>
<td>8.0 (Max)</td>
</tr>
<tr>
<td>Moisture (as packed), weight %</td>
<td>2.0 (Max)</td>
</tr>
<tr>
<td>Harness No.</td>
<td>90 (Min)</td>
</tr>
<tr>
<td>Apparent Density, g/cc</td>
<td>0.47 (Min)</td>
</tr>
<tr>
<td><strong>Screen Size</strong>, U.S. Sieve Series, weight %</td>
<td></td>
</tr>
<tr>
<td>On 6 mesh</td>
<td>5.4 (Max)</td>
</tr>
<tr>
<td>Through 16 mesh</td>
<td>5.0 (Max)</td>
</tr>
</tbody>
</table>

**Ambersorb 600 Specifications**

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Size Distribution (U.S. Sieve Series)</td>
<td>20 - 40 mesh</td>
</tr>
<tr>
<td>Mean Particle Diameter, mm</td>
<td>0.65</td>
</tr>
<tr>
<td>BET Surface Area, m$^2$/g</td>
<td>580</td>
</tr>
<tr>
<td>Bulk Density, g/cc</td>
<td>0.54</td>
</tr>
<tr>
<td>Crush Strength, g/bead</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>Pore Size Distribution</td>
<td></td>
</tr>
<tr>
<td>Micropore volume, cc/g</td>
<td>0.22</td>
</tr>
<tr>
<td>Mesopore volume, cc/g</td>
<td>0.17</td>
</tr>
<tr>
<td>Macropore volume, cc/g</td>
<td>0.21</td>
</tr>
<tr>
<td>Water Adsorption (at 81% RH), %</td>
<td>5</td>
</tr>
<tr>
<td>Adsorbate</td>
<td>Relative Humidity</td>
</tr>
<tr>
<td>-----------</td>
<td>-------------------</td>
</tr>
<tr>
<td>GAC</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>GAC</td>
<td>20</td>
</tr>
<tr>
<td>GAC</td>
<td>30</td>
</tr>
<tr>
<td>GAC</td>
<td>50</td>
</tr>
<tr>
<td>Resin</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>Resin</td>
<td>20</td>
</tr>
<tr>
<td>Resin</td>
<td>30</td>
</tr>
<tr>
<td>Resin</td>
<td>50</td>
</tr>
</tbody>
</table>
Figure 3-1  Apparatus used for filling the Tedlar Bag with a constant volume of air.
Figure 3-2  Adsorption Isotherm for GAC and Resin at <5% RH and 40ºC.
Figure 3-3  Adsorption Isotherm for GAC and Resin at 20% RH and 40°C.
Figure 3-4  Adsorption Isotherm for GAC and Resin at 30% RH and 40ºC.
Figure 3-5  Adsorption Isotherm for GAC and Resin at 50% RH and 40°C.
Chapter 4

TREATMENT OF MTBE USING ADVANCED OXIDATION PROCESSES

4.1 ABSTRACT

This chapter is the second phase of this dissertation. The treatment of MTBE contaminated drinking water using advanced oxidation processes (AOPs) has been evaluated in this study. A pilot-scale AOP system was built and used in this study. The four AOPs evaluated in this study are: O₃/H₂O₂, O₃/UV, H₂O₂/UV and O₃/H₂O₂/UV. The impact of different flow parameters, oxidant concentrations and oxidant molar ratios were studied. A treatment effectiveness of 74% was achieved with the use of O₃ alone at a concentration of 5.8 mg/L. The use of UV/O₃ resulted in a considerable increase in the treatment effectiveness (98% at an O₃ dosage of 5.8mg/L) as compared to that of O₃ alone. Experiments showed that the use of H₂O₂/O₃ is a slightly more effective treatment process than UV/O₃ at the same O₃ concentrations. The peroxide to O₃ molar ratio had a great impact of the overall treatment efficiency. Increased treatment efficiencies were observed with increasing H₂O₂:O₃ molar ratios, with the optimum ratio for maximum treatment efficiency being 1:1. Any further increase in the molar ratio decreased the treatment efficiency. Non-detectable levels of MTBE were recorded using an O₃ dosage of 5.8 mg/L and a H₂O₂:O₃ molar ratio of 1.4:1 in the presence of UV radiation. The combined treatment process of UV/O₃/H₂O₂ showed remarkable increase in the effectiveness of MTBE treatment at lower H₂O₂:O₃ molar ratios as compared to the
H₂O₂/O₃ process. At higher molar ratios of 1.4:1 the impact due to the addition of UV was negligible. TBF, TBA, methyl acetate and acetone were identified as the major oxidation by-products in all the processes. None of the processes were able to completely eliminate the by-products in the treated water, at the oxidant dosages and concentration levels evaluated in this study.

4.2 INTRODUCTION

AOPs have been used for the removal of organic chemicals from industrial waste water since the mid-1970s (Prengle 1977). The application of AOPs for drinking water treatment was being evaluated a decade later, in the mid-1980s. Since then many studies have been conducted to evaluate the effectiveness of AOPs in the removal of organic compounds from drinking water (Brunet et al. 1984; Duguet et al. 1985; Glaze et al. 1987; Legrini et al. 1993). MTBE oxidation by AOPs have been reported by several investigators (Barreto et al. 1995; Raupp and Junio 1993; Venkatadri and Peters 1993). It has been shown that MTBE can be completely mineralized through various AOPs such as O₃/H₂O₂ (Leitner et al. 1994; Mitani et al. 2002), H₂O₂/UV (Cater et al. 2000; Chang and Young 2000; Stefan et al. 2000), and TiO₂ photocatalysis (Barreto et al. 1995). At present, there are some full-scale installations of AOPs for the removal of organic contaminants (PCE in Salt Lake City, Utah and NDMA in Canada) from drinking water. However, there are no AOP installations for the removal of MTBE on a full-scale. The design of an AOP system is governed by the influent contaminant concentration, the desired effluent concentration, the flow rate, and water quality parameters. Thus a
complete analysis of the water quality and a thorough pilot scale testing based on the water quality would be essential before a full scale implementation of MTBE treatment.

The removal of MTBE from water can be achieved by the reaction of MTBE with the highly reactive hydroxyl radicals (OH•), which are generated by a variety of mechanisms. OH• are known to react very rapidly with MTBE (K_{OH} = 1.6 to 3.9 \times 10^9 \text{ M}^{-1} \text{s}^{-1}) (Acero et al. 2001; Buxton et al. 1988; Chang and Young 2000) to form oxidation by-products. OH• have one unpaired electron and are non-selective and highly reactive oxidants, only second to elemental fluorine in reactivity (Stanbury 1989). OH• are responsible for the initiation of oxidation reactions by attacking the organic compounds. A hydrogen atom is either abstracted from the organic compound (RH) or added to it. The hydrogen abstraction results in the formation of an organic compound radical (R°):

\[
\text{OH}^- + \text{RH} \rightarrow H_2O + R^\bullet
\]  

(4-1)

The organic radical can further initiate several reactions to form other intermediate organic compounds. Intermediate formation is a common occurrence with AOPs. The intermediates may be even more toxic than the parent compounds, and therefore, the intermediates must be considered during the design process. Given the sufficient time for reaction, OH• are capable of completely mineralizing the parent compound, forming H_2O and CO_2 as the final end products. But this would typically be achieved at a much higher cost. The primary objective of this chapter is to evaluate the use of AOPs for the removal of MTBE from drinking water for small systems. The AOPs to be evaluated in this study
include ozone / hydrogen peroxide (O₃/H₂O₂), ultraviolet irradiation / hydrogen peroxide (UV/H₂O₂), ultraviolet irradiation / ozone (UV/O₃) and ultraviolet irradiation / hydrogen peroxide / ozone (UV/H₂O₂/O₃). The following sections include detailed discussions about the physical and chemical principles behind each AOP, key process and design parameters, the by-product formation and the data from the pilot scale studies.

4.2.1 Ozone / Hydrogen peroxide

When O₃ is introduced into water, it reacts with the hydroxide ions and leads to the formation of one superoxide radical O₂º⁻ and one hydroperoxyl radical HO₂°.

\[ O_3 + OH^- \rightarrow O_2º⁻ + HO_2° \] (4-2)

The hydroperoxyl radical is in an acid-base equilibrium.

\[ HO_2° \leftrightarrow O_2º⁻ + H^+ \] (4-3)

The ozonide radical (O₃°) formed by the reaction between ozone and the superoxide radical (O₂º⁻) decomposes immediately into a hydroxyl radical.

\[ O_3 + O_2º⁻ \rightarrow O_3º⁻ + O_2 \] (4-4)

\[ HO_3° \leftrightarrow O_3º⁻ + H^+ \] (4-5)

\[ HO_3° \rightarrow OH° + O_2 \] (4-6)

This OH° can react with ozone to form HO₄°

\[ OH° + O_3 \rightarrow HO_4° \] (4-7)

\[ HO_4° \rightarrow O_2 + HO_2° \] (4-8)
The decay of the HO$_4^o$ form oxygen and hydroperoxide radical and leads to a chain reaction that can start again (from equation 4-3) forming more hydroxyl radicals. H$_2$O$_2$ is a weak acid and it dissociates to form hydroperoxide (HO$_2^-$) ion in water.

\[
H_2O_2 \leftrightarrow HO_2^- + H^+
\]  \hspace{1cm} (4-9)

\[
HO_2^- + O_3 \rightarrow HO_2^o + O_3^o-
\]  \hspace{1cm} (4-10)

The hydroperoxide ion reacts with O$_3$ to form hydroperoxide radicals (HO$_2^o$), which in turn produces OH$^o$ radicals (Buhler et al. 1984; Staehelin and Hoigne 1982) as shown above (equations 4-3 to 4-8). It can be shown from equations 4-2 through 4-10 that two ozone molecules produce two OH$^o$:

\[
2O_3 + H_2O_2 \rightarrow 2OH^o + 3O_2
\]  \hspace{1cm} (4-11)

The direct oxidation of ethers by O$_3$ is a selective reaction with a slow rate constant – less than 1 M$^{-1}$s$^{-1}$ (Buxton et al. 1988). This is very low when compared to the oxidation by hydroxyl radical oxidants, which is in the range of 1.6 to 3.9 x 10$^9$ M$^{-1}$s$^{-1}$.

O$_3$ is typically produced on-site because it decays very rapidly. Compressed air or pure oxygen is used to generate O$_3$. The generator produces O$_3$ up to 2% by volume when pure oxygen is used and about 0.5 to 1% by volume when compressed air is used. Larger installations typically use liquid oxygen to reduce costs due to drying of the compressed air. Based on the O$_3$ contactors used, a transfer efficiency of about 90-95% can be achieved. H$_2$O$_2$ is typically injected in the aqueous form into the system, depending upon the ratio used. Since O$_3$ is also an effective disinfectant, some O$_3$ residual in the treated water would be beneficial. However, some reports (Gunten and Oliveras 1998; Krasner et al. 1993; Siddiqui and Amy 1993; Song et al. 1997) have indicated that there is a
potential for bromate formation if the influent water has bromide concentrations above 0.1 mg/L. Bromide is oxidized both by molecular ozone and the OH• to form bromate. The source water for small systems under consideration would be typically groundwater and hence they would require minimal disinfection as compared to surface waters used by big water systems. So it may not be necessary to provide the residual O₃ in the treated water. Bromate formation has been shown as a function of H₂O₂ to O₃ molar ratio, and the higher the ratio, the lower is the potential for bromate formation (Liang et al. 1999; Siddiqui et al. 1999).

Karpel Vel et al. (1994) conducted experiments to study the impact of O₃ and combined O₃/H₂O₂ on MTBE and ethyl tert-butyl ether (ETBE). Experiments were conducted in a semi-continuous reactor and the results showed that O₃/H₂O₂ was more effective than using O₃ alone for MTBE treatment. An 80% reduction in MTBE was observed when 3mg of O₃ was used per mg of MTBE, whereas only 1.7mg of O₃ was required to obtain the same reduction in MTBE when used in combination with H₂O₂. A pilot-scale testing (Dyksen et al. 1992), conducted using an in-line application of O₃ and H₂O₂, to evaluate the removal of trichloroethylene (TCE), tetrachloroethylene (PCE) and MTBE showed that the addition of H₂O₂ in conjunction with O₃ significantly improved the removal of MTBE as compared to O₃ alone. Nondetectable levels of MTBE were obtained at an O₃ dosage of 8 mg/L at a H₂O₂ to O₃ ratio of 0.5 and contact times of 3 to 6 minutes. Another pilot-scale study investigated the effectiveness of O₃ and O₃/H₂O₂ (peroxone) processes for MTBE removal showed that the peroxone was more effective than ozone alone (Liang et al. 1999). The use of O₃ at 4 mg/L and H₂O₂ at 1.3 mg/L (a H₂O₂ to O₃
molar ratio of 0.46) resulted in average MTBE removals of approximately 78%. In another study (Liang et al. 2001), a large-scale semi-batch reactor was used to study the removal of MTBE by O₃ and peroxone. Even at high doses of O₃ (10 mg/L), peroxone (at a H₂O₂ to O₃ of 1.0) was more effective than just O₃ alone. Peroxone also oxidized MTBE more rapidly than did O₃ alone under the tested conditions. A recent study (Kavanaugh et al. 2003) conducted to evaluate the removal of MTBE from groundwater by O₃/H₂O₂ process shows that 15 mg/L of applied O₃ and 15 mg/L of H₂O₂ removed approximately 96% of MTBE to a level of 5 µg/L from 130 µg/L. A further increase in the O₃ and H₂O₂ concentrations to 30 mg/L resulted in only a slight improvement in the removal efficiency (97%). Even at that high level of oxidants, it was not possible to achieve a complete mineralization of MTBE.

4.2.2 Ozone / Ultraviolet irradiation

Radiation is a process by which energy is transferred from one location to another. One such form of radiation is ultraviolet light. Ultraviolet light is often used as a disinfectant in water and wastewater treatment. The UV rays lie between the visible violet light (less than 400 nm) and X-ray wavelength (greater than approximately 180 nm). Three types of UV are identified as: long wave, or UV-A, which lies between 315 - 400 nm; medium wave, or UV-B, which lies between 280 - 315 nm; and shortwave, or UV-C, lying below 280 nm. UV radiation has been shown to destroy MTBE through photolysis (Zepp 1988), both direct and indirect. In direct photolysis, the absorption of UV light by MTBE places it in an electronically excited state, causing it to react with other compounds thereby
causing it to degrade. The indirect photolysis of MTBE is carried out by OH•, which are produced when O₃ or H₂O₂ are added. The most common types of UV lamps used are low pressure mercury vapor lamps (LP-UV), medium pressure mercury vapor lamps (MP-UV) and pulsed UV lamps (P-UV). This study was conducted using the LP-UV lamp which emits maximum energy output (98%) at the 254nm wavelength. This is also the ideal wavelength to effectively deactivate microorganisms. The AOP with O₃ and UV radiation is initiated by the photolysis of O₃. H₂O₂ is formed by the photodecomposition of O₃ (Peyton and Glaze 1987).

\[ O_3 + H_2O \xrightarrow{hv} H_2O_2 + O_2 \]  \hspace{1cm} (4-12)

\[ 2O_3 + H_2O_2 \rightarrow 2OH^+ + 3O_2 \]  \hspace{1cm} (4-11)

The O₃ then combines with H₂O₂ to form OH• as mentioned previously. The mechanisms involved in the destruction of MTBE include direct reaction with O₃, direct photolysis by UV irradiation and reaction with OH•. This system contains three components to produce OH• - UV radiation, O₃ and H₂O₂. The two major components of an UV AOP system are the UV dose (the UV radiation per unit volume of water treated) and the concentration of the oxidant used (O₃ or H₂O₂). The O₃/UV process has been applied typically for the treatment of industrial wastewater. They have been used at superfund sites to destroy VOCs and benzidines and at U.S Army ammunition plants to destroy 2,4,6-trinitrotoluene (TNT) and cyclonite (NWRI 2000). In groundwater, they have been used for the treatment of TCE, PCE and pentachlorophenol (PCP). One study (Graham et al. 2004) has reported the use of the O₃/UV process to treat MTBE from surface waters having high turbidity. The use of O₃/UV was more effective than the use of O₃ alone in treating
MTBE at high concentrations of 1200 µg/L. The rate of oxidation using O₃/UV was found to be twice that of O₃ alone.

4.2.3 Hydrogen peroxide / Ultraviolet irradiation

The oxidation of MTBE is achieved through various synergistic oxidation mechanisms that are generated by the H₂O₂/UV process. The direct photolysis of H₂O₂ leads to the formation of OH•. It has been shown in various studies (Baxendale and Wilson 1957; Bielski et al. 1985; Hunt and Taube 1952) that the following reactions occur when H₂O₂ solution is radiated with UV:

\[ H_2O_2 \xrightarrow{hv} 2OH^\circ \quad \varepsilon_{254nm} = 18.6 \text{ M}^{-1}\text{cm}^{-1} \quad (4-13) \]

Also HO₂⁻, which is in acid-base equilibrium with H₂O₂ (equation 4-9) absorbs UV at the wavelength 254nm.

\[ HO_2^- \xrightarrow{hv} OH^\circ + O^- \quad \varepsilon_{254nm} = 240 \text{ M}^{-1}\text{cm}^{-1} \quad (4-14) \]

\[ HO_2^- + O^- \rightarrow O_2^- + OH^- \quad (4-15) \]

\[ H_2O_2 + OH^\circ \rightarrow H_2O + HO_2^- \quad (4-16) \]

\[ HO_2^- + OH^\circ \rightarrow OH^- + HO_2^- \quad (4-17) \]

\[ H_2O_2 + HO_2^- \rightarrow OH^- + H_2O + O_2 \quad (4-18) \]

\[ H_2O_2 + O_2^- \rightarrow OH^\circ + OH^- + O_2 \quad (4-19) \]

The overall quantum yield (Φ) of H₂O₂ in these reactions is unity at the UV wavelength of 254nm and the quantum yield of the primary photolysis reaction of H₂O₂ at 254nm is
0.5. Since the molar extinction coefficient of H₂O₂ at 254nm is rather low, a large amount of H₂O₂ would be required in order to generate sufficient OH• to degrade MTBE (Berglind et al. 1979; Bolton 2001). H₂O₂ does however have a favorable absorption spectrum between 200 and 250 nm, which leads to efficient H₂O₂ photolysis generating more OH• radicals (Pignatello 1992). Therefore a medium pressure mercury lamp with a broad emission spectrum between 200 and 300 nm would be more effective in treating MTBE compared to the LP-UV lamp.

(Wagler and Malley 1994) conducted a bench-scale study to determine the effectiveness of UV and H₂O₂ on the treatment of MTBE contaminated simulated groundwater. They showed that more than 95 percent removal of MTBE was achieved after 40 minutes of exposure time, whereas, only a 10 percent removal was achieved by the use of O₃ alone even after 2 hours of exposure. The study concluded that the OH• formed in the H₂O₂/UV process is the primary oxidant responsible for the removal of MTBE. Methanol, formaldehyde, TBA, and 1,1-dimethylethyl-formate were identified as by-products during this process. Another bench-scale study (Chang and Young 2000), using a recirculating batch reactor with a LP-UV lamp, determined the second order rate constant for the MTBE degradation by OH• in the H₂O₂/UV process to be 3.9 x 10⁹ M⁻¹ s⁻¹. Experiments conducted with an initial MTBE concentration of 10 mg/L and at H₂O₂: MTBE molar ratios ranging from 4:1 to 15:1, achieved >99.9 percent removal of MTBE after 75 minutes of exposure. TBF was identified as the major by-product in this study and it persists even after all the MTBE has been degraded. Stefan et al.,(2000) studied the degradation of MTBE by H₂O₂/UV oxidation in a recirculating batch reactor with a MP-
UV lamp and proposed a detailed degradation pathway. The primary by-products of MTBE oxidation identified from the study include TBF, 2-methoxy-2-methyl propionaldehyde (MMP), formaldehyde, acetone, TBA and methyl acetate. Cater et al., (2000) conducted batch studies using a MP-UV reactor to determine the reaction rate constants for the photooxidation of MTBE by the H₂O₂/UV process. Experiments were conducted at varying initial MTBE concentrations (from 0.08 mg/L to 85 mg/L) and at a constant H₂O₂ concentration of 30 mg/L. It was found that the rate of destruction of MTBE was influenced by the initial concentrations and the rate increased as the concentration of MTBE decreased. At higher concentrations of MTBE, higher concentrations of intermediates were formed which compete effectively with MTBE for the OH• radicals thus reducing the treatment efficiency of MTBE. Kavanaugh et al., (2003) conducted both bench-scale and pilot-scale studies on different water sources spiked with MTBE to determine the treatment effectiveness of the H₂O₂/UV process on MTBE degradation. Studies were conducted with both LP and MP-UV lamps. The bench-scale studies were conducted using a batch reactor and using water with varying levels of dissolved organic carbon (DOC) and alkalinity. Initial MTBE concentration of 200 µg/L and an MTBE to H₂O₂ molar ratio of 1:85 was used. Results indicate that both the LP and the MP-UV lamps were effective in degrading the MTBE. Water samples with high DOC and alkalinity resulted in retarded degradation of MTBE. The MP-UV/H₂O₂ process had higher rate constants for treating waters with high alkalinity as compared to the LP-UV/H₂O₂ process. The opposite trend was found with waters with low alkalinity. It was also found that MP-UV was able to degrade MTBE directly, for all the waters studies, without the addition of any H₂O₂. TBF and TBA were the major by-
products for both the processes (MP and LP), along with acetone and formaldehyde. The pilot-scale studies were conducted in a batch mode, closed loop recirculation to achieve conditions of a completely stirred tank reactor. The water was spiked with 100 µg/L of MTBE and a H₂O₂ to MTBE molar ratio of 200:1 was used. Both LP and MP-UV lamps were used to study the treatment efficiency and the results of these studies were reported as the electrical energy consumed by each process to reduce the concentration of MTBE, in one cubic meter of water, by one order of magnitude – also known as electrical energy per order (E_{EO}). It was shown that the electrical energy expensed in the MP-UV process was about 3.5 times more than the LP-UV process. TBA, acetone, acetaldehyde and formaldehyde were identified as the oxidation by-products. TBF was not detected in the treated water, which the authors have mentioned might have been due to a shortcoming of the analytical method used. There was a significant amount of by-products in the treated water even after 40 minutes of exposure.

4.2.4 Hydrogen Peroxide / Ozone / Ultraviolet irradiation

The oxidation of organics by ozone, hydrogen peroxide, or UV radiation alone is known to have kinetic limitations. UV radiation, when combined with ozone and hydrogen peroxide, produces a highly oxidative environment significantly more destructive than that created with ozone or hydrogen peroxide by themselves or in combination. The oxidant dosage can be significantly reduced in this combination process. This process involves all the mechanisms shown earlier for the production of OH•. The optimum dosage requirements of the oxidants have to be determined to achieve cost efficiency.
4.2.5 Electrical Energy Per Order ($E_{EO}$)

Since most AOPs involve the use of a considerable amount of electrical energy, the cost of electricity is a major component of the total treatment cost. The Electrical Energy Dose (EED) is defined as the electrical energy (kWh) consumed per unit volume of water treated and is determined by the following equation:

$$EED = \frac{1000P}{60Q} \quad (4-20)$$

where $P$ is the electrical power (kW) and $Q$ is the flow in gpm. The Photochemistry Commission of International Union of Pure and Applied Chemistry (IUPAC) has recommended the use of two Figures-of-Merit, the Electrical Energy per Order ($E_{EO}$) and the Electrical Energy per Mass ($E_{EM}$) (Bolton et al. 1996). The $E_{EM}$ is appropriate when the pollutant concentration is high (greater than 1mM), while the $E_{EO}$ is for low pollutant concentrations. The $E_{EO}$ is defined as the electrical energy in kilowatt hours (kWh) required to degrade the contaminant by one order of magnitude in 1 m$^3$ of water. The $E_{EO}$ for a batch reactor is given by:

$$E_{EO} = \frac{EED}{\log(c_i / c_f)} \quad (4-21)$$

where, $c_i$ and $c_f$ are the initial and final concentrations of the contaminant. The $E_{EO}$ for a flow-through reactor is given by:

$$E_{EO} = \frac{P}{Q \log(c_i / c_f)} \quad (4-22)$$

where, $Q$ is the flow rate in m$^3$/h. As the efficiency of a process increases, the $E_{EO}$ value decreases.
4.3 MATERIALS AND METHODS

4.3.1 Experimental Setup

Figure 4-1 shows the schematic of the pilot-scale AOP system used for all the studies conducted in this chapter. The primary system components include a 1” stainless steel (SS) pipe loop system with a 60L cylindrical SS tank (Figure 4-3) which serves as a reaction chamber. De-chlorinated Cincinnati tap water was used for all the studies. The tap water was passed through a carbon filter to remove the residual chlorine and also any trihalomethanes (THM) that may be present in the water. The carbon filtered water was then stored in a 1000 gallon SS tank and a 0.75 HP centrifugal pump (TEEL, Dayton Electric Mfg. Co., Niles, IL) was used to pump this water to the AOP system. All the experiments were conducted at a constant temperature of 20 ± 1°C. The water temperature was controlled using a heater/chiller (depending on the temperature) and a shell and tube heat exchanger. The water from the 1000 gallon tank was pumped through the heat exchanger before it reached the AOP system. The flow through the AOP system and the recirculation ratio within the AOP loop were controlled by a valve located at the outlet of the AOP system. The effluent flow and the recirculation flow were measured by separate flow meters (GPI industrial grade electronic digital meter, Model-U-05609-20, GPI, Inc, Wichita, KS). The temperature of the water within the AOP system was monitored by a temperature gauge (Tel-Tru Model No. 3410-02-74, Tel-Tru Mfg. Co., Rochester, NY). A 2 HP SS centrifugal pump (G&L A, Gould Pumps Co., Seneca Falls, NY) with variable speed control was used as a recirculation pump.
The inlet water was spiked with the required amount of MTBE before it entered the AOP loop. MTBE was injected into the inlet water, from a 10L Tedlar™ bag (Catalog No. 231-08, SKC Inc., Eighty Four, PA), at a constant rate of 2.9 mL/min using a peristaltic pump (Masterflex L/S Easy-Load® II Pump Head and Digital Economy Drive, Cole-Parmer Instrument Co., Vernon Hills, IL). An in-line static mixer was installed downstream to the MTBE injection port to ensure the complete mixing of MTBE in the water. For experiments using H₂O₂, a metering pump (FMI Lab Pump, Model QV-PM6014, Fluid Metering, Inc., Syosset, NY) was used to pump H₂O₂, stored in a 4L chemical feed container, into the AOP loop at a preset flow rate so as to achieve the desired concentration. The flow rate was adjusted using a controller (FMI Stroke Rate Controller, Model V200, Fluid Metering, Inc., Syosset, NY) in order to achieve different feed concentrations. O₃ was generated using a corona discharge O₃ generator (Figure 4-3. Model CD2000, ClearWater Tech, LLC, San Luis Obispo, CA). O₃ is generated by exposing an air stream to a high voltage electrical discharge called corona discharge (CD). Oxygen molecules are split into individual oxygen atoms. Atomic oxygen is very unstable so it combines with other oxygen molecules in the air stream to form ozone. The idea is to produce a constant, controlled spark (corona) across an air gap through which a prepared feed gas is passed. Critical to an efficient, reliable CD ozone generator is drying the feed gas to a dew point of at least -60° F. Moist air will cause nitric acid to form inside the generator which decreases ozone production. The feed air was prepared by a Workhorse-15 (SeQual Technologies, Inc., San Diego, CA) oxygen concentrator (Figure 4-4), which produces 15 standard cubic feet per hour (SCFH) of dry oxygen at 90-95%
purity. Atmospheric air consists of approximately 80% nitrogen and 20% oxygen. The oxygen concentrator uses ambient air as a source of oxygen by separating these two components. It utilizes a pressure swing adsorption system containing zeolite molecular sieves to selectively absorb nitrogen from compressed air. A venturi type differential pressure injector (Figure 4-5, Mazzei Model No. 1078, Mazzei Injector Corp, Bakersfield, CA) was used to inject ozone into the system. The pressure difference between the inlet and outlet ports of the injector creates a vacuum inside the injector body, which initiates the suction of ozone through the suction port. An O$_3$ destruct unit (Figure 4-6, Terminator 25, Ozotech Inc., Yreka, CA), utilizing manganese dioxide / copper oxide catalyst to convert O$_3$ back to oxygen, was attached to the top of the SS reaction chamber to remove any discharge of O$_3$ to the atmosphere. The UV reactor (Figure 4-7, Sanitron Model S50B, Atlantic Ultraviolet Corp., Hauppauge, NY) used in this study utilized a LP-UV lamp (50 watts) housed inside a SS reactor of diameter 10.8 cm and length 128.3 cm. The lamp is positioned at the center of the reactor surrounded by a quartz sleeve with a dual action wiper mechanism for cleaning. A UV detector (Figure 4-8, SUL240, International Light Inc., Newburyport, MA), fixed on the outer surface of the UV reactor, coupled with a radiometer (Figure 4-9, IL1400A, International Light Inc., Newburyport, MA) was used to measure the incident UV radiation.
4.3.2 Materials and Experimental Methods

4.3.2.1 Reagents

MTBE used in this study was 99.99% pure obtained from Supelco (Bellefonte, PA). The internal standard used in this study was 99.99% isopropyl ether (Supelco, Bellefonte, PA). TBA, TBF, acetone, methyl acetate, isopropyl alcohol, benzene and methanol were purchased from Aldrich (Sigma-Aldrich, St. Louis, MO). Sodium thiosulfate and hydrogen peroxide solution (30% H$_2$O$_2$ in water) were supplied by Fisher Scientific (Fisher Scientific, Fairlawn, NJ).

4.3.2.2 Experimental Procedures

Experiments were conducted with de-chlorinated tap water and at a constant temperature of 20 ± 1º C. The inlet MTBE concentration was maintained at a level of 300 µg/L for all the experiments. The AOP system was operated in the flow through mode with recirculation. Two recirculation ratios (2.5:1 and 5:1) were used in this study. The effluent and the recirculation flow rates were 5.7 gpm and 14.2 gpm, respectively, for the recirculation ratio of 2.5:1. For the recirculation ratio of 5:1, the effluent and the recirculation flow rates were 3.3 gpm and 16.5 gpm, respectively. For all the experiments, MTBE was spiked into the inlet water before it entered the recirculation loop and the oxidants (O$_3$ and H$_2$O$_2$) were injected inside the recirculation loop. The concentrations of O$_3$ and H$_2$O$_2$, injected into the system, were determined separately by
shutting off the feed of the other oxidants and MTBE. The mixing of the oxidants or the contaminant (MTBE) would result in the reduction of the oxidant concentration. The measurement of the oxidant concentrations after the experiment is started would give the residual concentration of the oxidant at that point of time. Sampling ports were provided at the inlet, outlet and within the loop of the AOP system. All the experiments were conducted for a period of 2 hours to allow sufficient time for the system to stabilize. It was found from the results of the experiments that the concentration of MTBE and its by-products did not vary significantly beyond the first hour of operation. Samples were collected at the inlet and outlet, at regular time intervals, in 40 mL borosilicate vials provided with caps and disposable Teflon septa. Sampling was done in accordance with SW-846 EPA Method 5030 procedures (EPA 1997b). The excess ozone in the sample was quenched by adding 1 g of sodium thiosulfate to each of the 40 mL vials, to prevent any further reaction of ozone with MTBE and its by-products (Tsugura et al. 1998). The samples were analyzed in accordance with procedures outlined in EPA Method 502.2 (EPA 1993). All the analysis was carried out immediately after sampling.

4.3.2.3 Analytical Methods

Analysis of MTBE as well as the by-products (TBA, TBF, acetone and methyl acetate), and isopropyl alcohol was performed using an Agilent 6890 gas chromatograph (Agilent Technologies, Palo Alto, CA) system with a flame ionization detector (250° C) and a DB-WAX capillary column (J&W Scientific; 60m, 0.325 μm, 0.05 μm film thickness). A purge and trap system utilizing a Tekmar 2016 auto sampler and a Tekmar 3000
concentrator (Teledyne Tekmar, Mason, OH) was used for sample concentration / injection. The temperature was programmed at 40º C for 5 minutes, then to 70º C at a rate of 3º C/min, and to 160º C at 18º C/min and held at 160º C for 4 minutes. Helium was the carrier gas at a flow rate of 24.6 mL/min. The injector port temperature was maintained at 200º C, and the samples were injected in the split injection mode at a split ratio of 10:1. The flame gases air and hydrogen flow rates were set at 400.0 ± 1 mL/min and 35.0 ± 1 mL/min, respectively. A retention time of 4.4, 4.6, 6.4, 6.6, 7.9, 8.8, 9.7, and 10.4 minutes were obtained for isopropyl ether (internal standard), MTBE, acetone, methyl acetate, TBF, TBA, IPA and benzene, respectively, under these operating conditions. Since the addition of salt (1g of Na2S2O3) to the samples would increase the ion content of the aqueous solution (Vickers and George 2002) thereby increasing the recovery of the non-ionic organic species (while purging the sample), the analysis of the standards were also performed after the addition of the same quantity of salt to them. The indigo dye method (Bader and Hoigne 1982) was used to measure the O3 concentration, with absorbance of unreacted dye measured in a spectrophotometer. Hydrogen peroxide was determined by the use of the HACH test kit (Catalog No: 2291700) (Gordon et al. 1992).

4.4 RESULTS AND DISCUSSION

4.4.1 Stability of MTBE in the AOP System

Test runs were conducted by just spiking MTBE in the inlet water, at the two different recirculation ratios to determine if any MTBE was being stripped from the water. The
results indicated that there was no significant loss of MTBE in the water. Control runs conducted with the addition of H$_2$O$_2$ (up to a concentration of 18mg/L), to MTBE showed that no degradation of MTBE occurred in the system in the absence of any UV radiation, even after two hours of operation. No significant increase in the temperature of the treated water was noticed at the flow rates and pressures used in the different experiments conducted.

### 4.4.2 MTBE Removal by LP-UV Alone

Test runs were conducted on the MTBE spiked water, in the presence of monochromatic LP-UV radiation (at a predominant wavelength of 254 nm) showed that there was no significant degradation of MTBE. This shows that LP-UV alone does not degrade MTBE due to the fact that MTBE does not absorb UV radiation at 254 nm. Kavanaugh et al., (2003) have reported MTBE degradation by LP-UV alone on certain waters used in their study. They later concluded that this behavior might be attributed to the production of OH• from UV light interaction with iron and nitrates present in the water. The reactions for the production of OH• from nitrates are shown below (Hoigne and Bader 1976; Zepp 1988):

\[
\begin{align*}
NO_3^- \xrightarrow{h\nu} NO_3^\cdot \rightarrow O(3 P) + NO_2^- & \quad (4-23) \\
NO_2^- \rightarrow NO_2 + O^\circ^- & \quad (4-24) \\
O^\circ^- + H_2O \rightarrow OH^\circ + OH^- & \quad (4-25)
\end{align*}
\]
4.4.3 Effect of Recirculation Ratio on MTBE Degradation

Experiments were conducted at two different recirculation ratios of 2.5:1 and 5:1 to determine their impact on the MTBE treatment efficiency. The \( \text{O}_3 \) and \( \text{H}_2\text{O}_2 \) concentrations were maintained at 3.0 mg/L, each, and the influent MTBE concentration was 300 µg/L for both the experiments. The outlet flow for the experiments conducted at the recirculation ratios of 2.5:1 and 5:1 was 5.3 gpm and 3.1 gpm, respectively. Figure 4-10 shows the effluent concentrations of MTBE and the by-products in the treated water for the two runs. It can be seen that an increase in the treatment efficiency of MTBE is obtained at the higher recirculation ratio. The concentration of the by-products in the treated water is also considerably reduced at the higher recirculation ratio. Thus for a 100% increase in the recirculation ratio, a 5% increase in the treatment efficiency of MTBE is achieved. The concentration of TBF, TBA, acetone and methyl acetate (MA) in the treated water are reduced by 24, 12, 45 and 38%, respectively. It must be noted that the increased recirculation ratio, however, resulted in a 42% decrease in the total output flow of the system. So in determining the total cost involved in the treatment, one must consider if this additional pumping cost would be more economical in improving the treatment efficiency than by considering other means such as increasing the oxidant dosages, etc.
4.4.4 H₂O₂/UV Process

Experiments studying the H₂O₂/UV process were conducted at two initial H₂O₂ concentrations of 4.5 mg/L (0.13mM) and 18 mg/L (0.53mM), in the presence of the LP-UV radiation. This represents a H₂O₂ to MTBE molar ratio of 39:1 and 156:1 for the 4.5 and 18 mg/L of H₂O₂, respectively. The results from the experiments indicate a significant increase in the MTBE degradation as compared to the use of UV alone. A H₂O₂ concentration of 4.5 mg/L gave a 16% removal of MTBE and at 18 mg/L of H₂O₂, a 28% MTBE removal was achieved. However, not all the added H₂O₂ was consumed in the reaction. At least 90% of the H₂O₂ remained in the treated water for both experiments.

The maximum absorption of UV radiation by H₂O₂ occurs at a wavelength of about 200 nm, and it decreases as the wavelength increases (Bolton and Carter 1993). The major drawback to the use of H₂O₂ is its relatively low extinction coefficient. The extinction coefficient (or molar absorptivity) of H₂O₂ at 254 nm is only 19.6 M⁻¹s⁻¹ (Baxendale and Wilson 1957) which is exceptionally low for a primary absorber in a photochemical process. The value of O₃, by comparison, is about 3300 M⁻¹s⁻¹. Most LP-UV lamps have a dominant emission wavelength at about 254 nm. This means in order to generate a sufficient concentration of OH•, with these types of lamps, a prohibitively high dosage of H₂O₂ (Berglind et al. 1979; Bolton 2001) must be added to the medium. The dissociation threshold wavelength of H₂O₂ is 560 nm, meaning that photolytic dissociation of H₂O₂ to OH• can theoretically occur up to this wavelength. But for a molecule to dissociate, it has
to absorb and H$_2$O$_2$ does not absorb significantly above a wavelength of 310 nm. This wavelength is known as the absorption threshold. H$_2$O$_2$ does however have a favorable absorption spectrum between 200 and 250 nm, which leads to efficient H$_2$O$_2$ photolysis generating more OH• radicals (Acero et al. 2001; Pignatello 1992). Therefore a medium pressure mercury lamp that has a strong emission below 250nm would be more effective in treating MTBE compared to the LP-UV lamp used in this study.

H$_2$O$_2$ is a OH• scavenger and so an excess H$_2$O$_2$ can result in a net decrease in the treatment efficiency. However, if H$_2$O$_2$ dose is low, OH• formation will also be low, decreasing the treatment efficiency. Therefore, a balance must be maintained between excess and low levels of H$_2$O$_2$. Although there are no federal or state regulations for residual H$_2$O$_2$ in treated drinking water, it is not desirable to allow an excess level of H$_2$O$_2$ in the treated water due to concerns over biological growth. Residual H$_2$O$_2$ can serve as an oxygen source for microorganisms and can result in the biological re-growth in the distribution system.

4.4.5 MTBE Removal by Ozone Alone

To study the effect of O$_3$ alone on the removal of MTBE from the water, experiments were conducted with three different initial O$_3$ concentrations of 3, 4.5 and 5.8 mg/L. The influent MTBE concentration was maintained at 300 µg/L. Figure 4-11 shows the degradation of MTBE and also the formation of by-products at the three initial O$_3$ concentrations used in this study. A treatment efficiency of 62, 67 and 74% for MTBE
was achieved at O₃ concentrations of 3, 4.5 and 5.8 mg/L, respectively. But the concentration of TBF was very high (225 to 275 µg/L) in the treated water for all the three levels of O₃ concentrations. TBA, acetone and MA were also present in the treated water at lower concentrations, apart from TBF. Researchers (Glaze et al. 1987; Hoigne and Bader 1983a; Hoigne and Bader 1983b) have shown that O₃ decomposes spontaneously during water treatment by a complex mechanism that involves the generation of OH•, as shown in equations 4-4 to 4-8. O₃ can oxidize MTBE directly by molecular O₃ (O₃(aq)) or indirectly through OH• produced during the decomposition of O₃. The direct oxidation with aqueous O₃ is relatively slow \( k_{O₃} = 0.14 \text{M}^{-1}\text{s}^{-1} \) compared to the oxidation by OH• \( k_{OH} = 1.9 \times 10^9 \text{M}^{-1}\text{s}^{-1} \) (Acero et al. 2001). But the concentration of aqueous O₃ is relatively high compared to OH• concentration, which have a half-life in the order of microseconds and therefore can never reach levels above \( 10^{-12} \text{M} \) (Glaze and Kang 1988). It has been shown (Hoigne and Bader 1976) that direct oxidation with molecular O₃ dominates under acidic conditions and OH• oxidation starts to dominate at high pH values. The decomposition of O₃ in water proceeds with the production of OH• at a rate of 1.5 moles of OH• per mole of O₃.

Figure 4-12 shows the results of the experiments presented as histograms with the concentration expressed in µM. It can be seen from the figure that as the O₃ concentration is increased, MTBE degradation is increased also. The concentration of TBF in the treated water increases as more and more of MTBE is being degraded. Upon further increase of O₃, the TBF concentration starts to decrease. As the concentration of TBF increases in the solution, they start to compete with MTBE for the OH• and for aqueous
O₃, thereby reducing the treatment efficiency of MTBE. It should also be noted from the figure that the concentration of acetone, in the treated water, gradually increases with increasing O₃ concentrations. Stefan et al., (2000) have reported that acetone may be formed from the degradation of TBF and TBA, apart from being formed directly from MTBE degradation. Further experiments with increased O₃ concentrations could not be studied due to limitations in the O₃ generation capacity of the generator used in this study.

### 4.4.6 O₃/UV Process

Based on the results obtained from the O₃ alone treatment, discussed above, additional experiments were conducted at the same O₃ concentrations in the presence of LP-UV radiation. All the flow conditions and MTBE inlet concentrations were maintained the same and O₃ concentrations of 3, 4.5 and 5.8 mg/L were used for the different experiments. Figure 4-13 shows the effluent concentrations of MTBE and the by-products for the experiments conducted at different initial O₃ concentrations. Compared to the experiments conducted with O₃ alone, the O₃ and UV combination produced a significant increase in the MTBE treatment efficiencies (24 to 27%). An increase of 44, 40 and 32% in the degradation of MTBE was observed for the experiments with 3, 4.5 and 5.8 mg/L of O₃, respectively. A corresponding decrease of 41, 62 and 84% in TBF concentrations and a decrease of 29, 39 and 63% in TBA concentrations were observed for O₃ concentrations of 3, 4.5 and 5.8 mg/L, respectively. Acetone concentrations in the
treated water increased by about 100% for the 3 and 4.5 mg/L O\textsubscript{3} runs and there was no change in the acetone concentration for the 5.8 mg/L O\textsubscript{3} run.

These enhancements in the treatment efficiencies can be attributed to the supplementary generation of OH\textbullet\ due to the presence of UV radiation or H\textsubscript{2}O\textsubscript{2}. Upon photolysis, O\textsubscript{3} decomposes to form O\textsubscript{2} and oxygen atoms O\textsuperscript{(1)D} (excited state) and O\textsuperscript{(3)P} (ground state) (Bauer et al. 2000; Schriver-Mazzuoli 2001; Smith et al. 2000; Taniguchi et al. 2000). Below 300 nm in the gas phase, the main process is the formation of O\textsuperscript{(1)D} with a quantum yield of $\approx 0.9$.

$$O_3 + h\nu \rightarrow \overset{\lambda<300nm}{\longrightarrow} O^{(1)D} + O_2 \quad (4-26)$$

O\textsuperscript{(1)D} is very reactive with a high heat of formation (Taniguchi et al. 1999) and therefore is unselective and reacts very fast. The O\textsuperscript{(1)D} reacts mainly by insertion into the C-H or the O-H bond (Taube 1957). In the liquid phase, O\textsuperscript{(1)D} reacts with water to form H\textsubscript{2}O\textsubscript{2}.

$$O^{(1)D} + H_2O \rightarrow H_2O_2 \quad (4-27)$$

The H\textsubscript{2}O\textsubscript{2} reacts again with O\textsubscript{3} to form OH\textbullet\ as shown in equations 4-3 to 4-11. So the O\textsubscript{3}/UV process is similar to the H\textsubscript{2}O\textsubscript{2}/O\textsubscript{3} process, where the H\textsubscript{2}O\textsubscript{2} is formed in situ as opposed to being added from an external source in the latter case. This might be true for contaminants that do not absorb UV radiation (as is the case with MTBE). But for substances which absorb UV light, direct photolysis would contribute significantly towards the overall treatment (Glaze et al. 1987).

Figure 4-14 shows the results of the experiments conducted with O\textsubscript{3}/UV process with the effluent concentrations of MTBE and the by-products presented as histograms with the
concentration expresses in µM. It can be seen from the figure that MTBE and TBF degradation increases as the O₃ concentration increases. The formation of OH• in the O₃/UV system is mainly due to the photolysis of O₃ producing H₂O₂, which in turn reacts with O₃ to form OH•. Hence the contribution of the radical pathway, in these systems, is expected to be stronger than in the O₃ alone systems. The addition of UV exerted a positive influence on the degradation of MTBE and its by-products in the O₃/UV process. It has been shown that the quantum yield of direct O₃ photolysis is about 0.5 (Reisz et al. 2003) and the quantum yield of OH• production from the photolyzed O₃ is about 0.1 (Reisz et al. 2003). This is very low compared to the photolysis of H₂O₂, which has a quantum yield of 1.0 (Legrini et al. 1993). Thus the efficiency of OH• generation is very low and despite this fact, the O₃/UV process may be favorable compared to the H₂O₂/UV process because O₃ has a much higher (2 orders of magnitude more) optical absorption coefficient compared to H₂O₂. Also the H₂O₂, which builds in the water due to the photolysis of O₃, reacts with OH• forming HO₂•/O₂• radicals which regenerate OH• when combined with O₃. This kind of regeneration is not present in the case of H₂O₂/UV process. The O₃/UV process is found to be very effective in treating compounds which neither react with O₃ nor absorb UV light (Reisz et al. 2003).

Temperature of the water also plays an important role in the degradation for any contaminant. The temperature of medium usually rises with time for the O₃/UV process. Increase in temperature affects the rate of the chemical reactions and mainly decreases the O₃ solubility. Hence appropriate cooling arrangements have to be made to prevent the increase of temperature. In this study, the temperature of the water did not increase.
during the course of the flow-through experiments. In a study (Beltran et al. 1998a) conducted to determine the effect of the presence of radical scavengers on the \( \text{O}_3/\text{UV} \) process showed that the treatment was inhibited only when the concentration of the carbonate ions were > 50 mM. The carbonate ion concentration in the naturally occurring waters is usually less than 50 mM and so it is not likely to affect the \( \text{O}_3/\text{UV} \) process.

### 4.4.7 \( \text{O}_3/\text{H}_2\text{O}_2 \) Process

As discussed in the previous sections, \( \text{OH}^\bullet \) are produced by the decomposition of \( \text{O}_3 \) in water. So by accelerating this decomposition rate, the \( \text{OH}^\bullet \) production can be increased to a great extent. An increase in the \( \text{OH}^\bullet \) production would result in increased oxidation rates. One of the most common and effective way of increasing the \( \text{O}_3 \) decomposition is by the addition of \( \text{H}_2\text{O}_2 \) to ozonated water. The addition of \( \text{H}_2\text{O}_2 \) results in the net production of 1.0 moles of \( \text{OH}^\bullet \) per mole of \( \text{O}_3 \) used. The dissociation of \( \text{H}_2\text{O}_2 \) in water forms hydroperoxide ion (Equation 4-9), which reacts with \( \text{O}_3 \) resulting in the formation of \( \text{OH}^\bullet \) (Equations 4-10, 4-3 to 4-8) (Forni et al. 1982; Kuo et al. 1997; Staehelin and Hoigne 1982; Staehelin and Hoigne 1985). The \( \text{OH}^\bullet \) can further react with \( \text{O}_3, \text{H}_2\text{O}_2, \) hydroperoxide ion, hydroxyl ion and other species as shown below:

\[
\text{O}_3 + \text{OH}^\circ \rightarrow \text{HO}_2^\circ + \text{O}_2 \quad (4-28)
\]

\[
\text{H}_2\text{O}_2 + \text{OH}^\circ \rightarrow \text{HO}_2^\circ + \text{H}_2\text{O} \quad (4-29)
\]

\[
\text{HO}_2^- + \text{OH}^\circ \rightarrow \text{HO}_2^\circ + \text{OH}^- \quad (4-30)
\]

\[
\text{HO}_2^\circ \leftrightarrow \text{O}_2^\circ^- + \text{H}^+ \quad (4-3)
\]
\[ OH^\circ + OH^- \rightarrow H_2O + O^\circ^- \] (4-31)

\[ O_3 + O_2^\circ^- \rightarrow O_3^\circ^- + O_2 \] (4-4)

\[ O_3^\circ^- + H^+ \rightarrow OH^\circ + O_2 \] (4-32)

\[ O^\circ^- + H_2O \rightarrow OH^\circ + OH^- \] (4-33)

Similar to the Ozonation process, the oxidation of MTBE in the O\textsubscript{3}/H\textsubscript{2}O\textsubscript{2} process occurs both by direct oxidation by aqueous O\textsubscript{3} and indirect oxidation by OH• (Hoigne and Bader 1978). The dual action of O\textsubscript{3} molecules and OH• result in significant enhancement in the rate of degradation of the pollutant (MTBE).

Experiments were conducted at O\textsubscript{3} concentrations of 3, 4.5 and 5.8 mg/L and at a constant H\textsubscript{2}O\textsubscript{2} to O\textsubscript{3} molar ratio of 1.4:1 to study the impact of the O\textsubscript{3}/H\textsubscript{2}O\textsubscript{2} process on the treatment of MTBE. The influent MTBE concentrations was 300 µg/L, the recirculation ratio was 5:1 and samples were collected at the inlet and the outlet of the AOP system at regular intervals for a time period of 2 hours. Figure 4-15 shows the concentration of MTBE and its by-products in the effluent for the experiments conducted at varying O\textsubscript{3} concentrations. It was possible to achieve an MTBE treatment efficiency of >99% with the O\textsubscript{3}/H\textsubscript{2}O\textsubscript{2} process at an O\textsubscript{3} concentration of 5.8 mg/L and a H\textsubscript{2}O\textsubscript{2} to O\textsubscript{3} molar ratio of 1.4:1. As compared to the O\textsubscript{3} alone process, the treatment efficiency increased by 25-30% (for MBE) for the same O\textsubscript{3} concentrations used. A significant reduction in the effluent by-product concentrations was also observed. TBF concentrations were reduced by 40, 69 and 84%, while TBA was reduced by 35, 48 and 75% for experiments conducted with 3, 4.5 and 5.8 m/L of O\textsubscript{3}, respectively. The O\textsubscript{3}/H\textsubscript{2}O\textsubscript{2} process also proved to be more effective than the O\textsubscript{3}/UV process for the destruction of
MTBE. Improvements in the overall treatment efficiency of about 1-3% were observed for MTBE. At the highest level of O₃ concentration used, very little difference was seen between the two processes in terms of treatment efficiency.

The ratio at which the oxidants (O₃ and H₂O₂) are used also plays a major role in the generation of OH• and hence the treatment efficiency. It has been reported (Beltran et al. 1996; Beltran et al. 1994) that the addition of H₂O₂ at high concentrations would inhibit the radical reaction, predominantly by reacting with the OH•. Other studies (Ledakowicz and Gonera 1999; Paillard et al. 1988) have also shown that the rate of degradation of the pollutant decreases with the increase of H₂O₂ concentration beyond an optimum level. Although the exact mechanism for this behavior is still not clear. The theoretical optimum dosage would be at the stoichiometric optimum molar ratio of 0.34 (H₂O₂: O₃).

But in a study (Glaze and Kang 1989) conducted on PCE oxidation by O₃ and H₂O₂, it has been shown that the rate of oxidation increases up to a molar ratio (H₂O₂: O₃) of about 1:1 and then it decreases with further increase in molar ratio. It should be noted that apart from an optimum molar ratio of H₂O₂ and O₃, the oxidant loading based on the contaminant concentration also has to be considered. The optimum molar ratio would also depend on the type of contaminant treated and the water quality parameters. In one study (Beltran et al. 1998b), it has been shown that the optimum molar ratios and concentrations for treating the parent compound (atrazine) were different than those required to treat its by-products.

In order to determine the optimum H₂O₂ to O₃ molar ratio for the treatment of MTBE, in this study, experiments were conducted at different molar ratios. The O₃ concentration
was maintained at a constant level of 4.5 mg/L and H\textsubscript{2}O\textsubscript{2} was added at different concentrations so as to obtain H\textsubscript{2}O\textsubscript{2} to O\textsubscript{3} molar ratios of 0.34:1, 0.50:1, 0.75:1, 1:1 and 1.4:1. The flow conditions, temperature and inlet MTBE concentrations were maintained at the same level as all the previous experiments. The results of these experiments are shown in figure 4-16, where the effluent concentrations of MTBE and the by-products presented as histograms with the concentration expressed in µM. It can be seen from the figure that the overall treatment efficiency of MTBE increases with increasing H\textsubscript{2}O\textsubscript{2} to O\textsubscript{3} molar ratios up to the value of 1:1. On further increasing the molar ratio to 1.4:1, a decrease in the overall treatment efficiency was observed. This may be due to the scavenging of OH• by the increased H\textsubscript{2}O\textsubscript{2} concentration in the feed.

Another factor to be considered in the application of this process is the operating pH. A pH increase is known to favor the formation of OH• due to the higher rate of dissociation of O\textsubscript{3} and H\textsubscript{2}O\textsubscript{2} (Staehelin and Hoigne 1982). The optimal pH range between 7.5-8 has been shown to achieve maximum dissociation (Paillard et al. 1988). This would be the normal pH range for natural waters. Multistage oxidant injection systems have been shown to yield better results in recent studies (Kosaka et al. 2001). The addition of O\textsubscript{3} or H\textsubscript{2}O\textsubscript{2} can be adjusted depending on the remaining pollutant concentration at various locations in the treatment system.
4.4.8  O$_3$/H$_2$O$_2$/UV Process

The O$_3$/H$_2$O$_2$/UV Process is a very powerful process that allows for a rapid and complete mineralization of pollutants. It has been found to be most effective for high concentration effluents (Mokrini et al. 1997). The reaction pathways that lead to the generation of OH$^\cdot$ radicals in this process are the same as that of the other AOPs discussed earlier. This process has not been used much for the drinking water treatment as this is considered to be a very energy consuming process and it would be viable only for treating high concentration effluents. The applicability of this process for the treatment of MTBE contaminated drinking water was evaluated in this study. The experiments conducted earlier for the O$_3$/H$_2$O$_2$ process were repeated again for this process with the addition of UV radiation from a LP-UV lamp. Figure 4-17 shows the results of these experiments. The effluent MTBE and its by-product concentrations for the different experiments are plotted as histograms with the concentration expressed as µM. A comparison of these results with those from the O$_3$/H$_2$O$_2$ experiments (Figure 4-18) shows that there is a considerable increase in the overall treatment efficiency of MTBE with the addition of UV radiation. Another observation that could be made from the comparison is that the increase in the treatment efficiency is more pronounced at the lower oxidant concentrations than at the highest level. At the maximum O$_3$ and H$_2$O$_2$ concentration of 5.8 mg/L, each, the effluent concentration of the by-products was almost the same for both experiments (with and without UV). Although, it should be noted that the O$_3$/H$_2$O$_2$/UV process was the only process, evaluated in this study, which was able to produce effluent with non-detectable levels of MTBE.
Additional experiments were also conducted to study the impact of H₂O₂ to O₃ molar ratios on the treatment efficiency of this process. The same molar ratios that were used in the O₃/H₂O₂ process were used in this study. Figure 4-19 shows a comparison of the results of the two processes plotted as histograms of the effluent concentration of MTBE and its by-products. A similar trend appears for the results of both the treatment processes. The total treatment efficiency increases with increase in the molar ratio up to a ratio 1:1 and a further increase in the ratio results in a decrease in the treatment efficiency. The difference in the treatment efficiencies for experiments conducted with and without the presence of UV radiation is higher at the lower molar ratios and it decreases as the molar ratios approach the optimum ratio of 1:1.

4.5 CONCLUSIONS

The applicability of four AOPs – H₂O₂/UV, O₃/UV, O₃/H₂O₂ and O₃/H₂O₂/UV – for the treatment of MTBE contaminated drinking water was evaluated on a pilot-scale, in this study. Flow-through experiments with partial recirculation were conducted on de-chlorinated tap water spiked with 300 µg/L of MTBE at 20 ºC.

An increase in the recirculation ratio increased the treatment efficiency of MTBE. Experiments conducted at two recirculation ratios of 2.5:1 and 5:1 showed that a 5% increase in the treatment efficiency could be achieved by a 100% increase in the recirculation ratio.
TBF, TBA, acetone and MA were detected and quantified as the primary by-products of MTBE degradation.

Experiments studying the H$_2$O$_2$/UV process demonstrated only a 16% and 28% reduction in MTBE concentration when 4.5 mg/L and 18 mg/L of H$_2$O$_2$ was used with LP-UV, respectively. This reaction condition represents a H$_2$O$_2$: MTBE molar ratio of 39:1 and 156:1 for the 4.5 and 18 mg/L of H$_2$O$_2$, respectively. The low molar extinction coefficient of H$_2$O$_2$ at 254 nm (19.6 M$^{-1}$s$^{-1}$) is the reason for this low treatment efficiency. The use of a MP-UV lamp with a broad emission spectrum or the use of a prohibitively high concentration of H$_2$O$_2$ with the LP-UV lamp would be required to increase the treatment efficiency of this process.

Experiments using O$_3$ alone were able to degrade 62, 67 and 74% of MTBE at O$_3$ concentrations of 3, 4.5 and 5.8 mg/L. But the by-product concentrations were very high in the treated water.

The use of O$_3$ in combination with UV radiation resulted in a dramatic increase in the degradation of MTBE as compared to O$_3$ alone experiments. 90, 96 and 98% MTBE removal was achieved at 3, 4.5 and 5.8 mg/L of O$_3$, respectively. The concentration of the by-products were also lower compared to the O$_3$ alone experiments.

The H$_2$O$_2$/O$_3$ process at a H$_2$O$_2$: O$_3$ molar ratio of 1.4:1 was found to be marginally more effective (1-3%) than the O$_3$/UV process at the same O$_3$ concentrations. Treatment
efficiency of >99.9% was obtained for MTBE at an O$_3$ concentration of 5.8 mg/L and a H$_2$O$_2$: O$_3$ molar ratio of 1.4:1. A complete destruction of the by-products was not achieved even at this high level of oxidant dosage.

The H$_2$O$_2$: O$_3$ molar ratios had a significant impact on the treatment efficiency. Experiments conducted at molar ratios ranging from 0.34:1 to 1.4:1 show that the degradation efficiency increased with increasing molar ratios and a maximum efficiency was obtained at a molar ratio of 1:1. A further increase in molar ratio led to a decrease in the treatment efficiency.

The combined process of O$_3$/H$_2$O$_2$/UV resulted in the maximum treatment efficiency of MTBE of all the AOPs evaluated. Non-detectable levels of MTBE were recorded at an O$_3$ dosage of 5.8 mg/L and a H$_2$O$_2$: O$_3$ molar ratio of 1.4:1. The by-product concentrations recorded at this level were the lowest for all the experiments conducted in this study, with acetone at 16 µg/L, TBF at 36 µg/L, TBA at 4 µg/L and MA at 2 µg/L. The change in H$_2$O$_2$: O$_3$ molar ratios produced similar results as the O$_3$/H$_2$O$_2$ process, with the maximum treatment achieved at the optimum molar ratio of 1:1.

The combined process of O$_3$/H$_2$O$_2$/UV was more efficient than the O$_3$/H$_2$O$_2$ process at lower H$_2$O$_2$: O$_3$ molar ratios. But at the ratio of 1.4:1, there was no significant difference between the two processes.
The electrical energy per order ($E_{EO}$) was calculated for the different processes. The $E_{EO}$ values for the O$_3$/UV, O$_3$/H$_2$O$_2$ and O$_3$/H$_2$O$_2$/UV process, at an O$_3$ concentration of 5.8 mg/L and a H$_2$O$_2$:O$_3$ molar ratio of 1.4:1, are 4.19, 2.46 and 1.70 kWh/m$^3$, respectively. The combined O$_3$/H$_2$O$_2$/UV process has the lowest $E_{EO}$ value, indicating that this process is the most efficient of all the AOPs studied.
4.6 REFERENCES


Figure 4-1  Schematic Diagram of the Pilot-Scale AOP System Used in this Study.
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Figure 4-3  Ozone Generator (Corona Discharge).
Figure 4-4  Oxygen Generator (PSA).
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Figure 4-6  Ozone Destruct Unit (Catalytic type).
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Figure 4-16 Impact of $\text{H}_2\text{O}_2$: $\text{O}_3$ Molar Ratio on the Treatment Efficiency of MTBE in the $\text{O}_3$/H$_2$O$_2$ Process at a Constant Ozone Concentration of 4.5 mg/L shown as histograms.
Figure 4-17 Impact of H₂O₂: O₃ Molar Ratio on the Treatment Efficiency of MTBE in the Combined O₃/H₂O₂/UV Process at a Constant Ozone Concentration of 4.5 mg/L shown as histograms.
Figure 4-18 Impact of Ozone Concentration on the Treatment Efficiency of MTBE in the O₃/H₂O₂ Process at a Constant H₂O₂: O₃ Molar Ratio of 1.4:1 shown as histograms.
Figure 4-19  Comparison of Impact of H₂O₂: O₃ Molar Ratio on the Treatment Efficiency of MTBE for Experiments Conducted with and without the Presence of UV Radiation.
Chapter 5

COMPARATIVE EVALUATION OF THE
DIFFERENT PROCESSES STUDIED

5.1 Abstract

This chapter provides a comparative analysis of the different processes discussed in the previous chapters. A detailed cost analysis of the different processes has also been made. Air stripping has been found to be the most cost effective treatment process (in terms of cost per unit treated) for the removal of MTBE contaminated drinking water at the flow conditions and influent concentrations studied. The AOPs were found to be at least 5 to 6 times more expensive than air stripping. Also air stripping was the only process which did not have any by-products in the treated water. All the AOPs had a considerable amount of by-product concentration in the treated water, which would require further treatment. For the small water systems it would not be necessary to install off-gas treatment for the off-gas from the air stripper, because of the low flows treated. Hence the costs of off-gas treatment units were not considered in the cost analysis. Also the cost for the removal of oxidation by-products from the treated water for the AOP systems was not considered in the cost analysis. The implementation of any of these processes would depend on various factors and would be site specific. There are only a few full scale installations for the treatment of MTBE and hence sufficient data is not available about the reliability and long term performance of the emerging technologies evaluated in this study. The comparison made in this chapter is valid only for the conditions under which
the study was conducted and should not be used in place of a detailed site-specific engineering analysis.

5.2 Air Stripping

The low Henry’s law constant of MTBE makes air stripping more difficult and expensive compared to the other VOCs commonly treated through air stripping. Air stripping has been, however, successfully used to treat MTBE contaminated drinking water and is a well established and proven technology. The performance of an air stripper can be optimized by increasing the contact between the air and water by maximizing the rate of mass transfer from water to air. This would also result in the reduction of the energy costs associated with the operation of the system. A variety of computer models is available to design and optimize the packed tower air stripper (Dzombak et al. 1993; Haarhoff 1988; Hand and Crittenden 1997). There are only a few moving parts (mechanical) in the air stripper which means it requires less maintenance and replacements. Air strippers have a high degree of flexibility, meaning, they are able to handle considerable variations in the inlet flow. They can also handle some degree of fluctuations in the inlet effluent concentrations. The system air flows can be reduced when the influent concentration drops below the design value or can be increased when the concentration increases to meet the treatment goals.

The one major advantage of an air stripper over the other technologies studied is that there are no by-products formed in this process. This would eliminate the necessity for
any additional treatment required to remove the by-products from the treated water. The presence of increased iron, calcium or magnesium in the inlet water, however, may lead to the formation of scales in the air stripper. The packing materials provide a medium for the deposit of scales and it is very difficult to clean these due to their inaccessibility. In very severe cases, a periodic replacement of the packing material may be required. There is also a potential for biological fouling in the air stripper leading to the release of biological solids in the treated water. This could, however, be prevented by disinfection of the inlet water. Short-circuiting within the air stripper may sometimes be caused due to poor air or water distribution and this might lead to decreased treatment efficiencies.

Typically, packed tower air strippers are highly visible since they require tall towers to achieve the required treatment efficiency. Their construction would require heavier foundations and construction permits may be necessary for their installation.

The emission of any organic compound to the atmosphere would require state and municipality permits. The air emissions standards vary from region to region and so it is essential to confirm the local standards before the installation of any new system. MTBE has been classified as a hazardous air pollutant (HAP) under the Clean Air Act. The final Site Remediation NESHAP (National Emission Standards for Hazardous Air Pollutants) - 40 CFR Part 63, has established emissions limitations and work practice standards to control HAP emissions at major sources where remediation technologies and practices are used at the site to clean up contaminated environmental media (e.g., soils, groundwaters, or surface waters). The standards limit the emissions of HAPs from all process vents (air strippers are considered as process vents) at the facility to a level less
than 1.4 kilograms per hour (kg/hr) and 2.8 megagrams per year (Mg/yr), which is approximately 3.0 pounds per hour (lb/hr) and 3.1 tons per year (tpy), respectively.

Table 5-1 shows the mass emissions of MTBE (in lb/hr) that would be produced by an air stripper based on the various influent MTBE concentrations and the flow rates. This table assumes that MTBE is the only HAP/VOC in the air stream. It can be seen from this table that the off-gas treatment would be required only at the highest flow rate scenario and at a very high influent MTBE concentration. For small systems which treat typically about 20 to 60 gpm, it would not be required to provide the additional off-gas treatment. Hence for the cost analysis of the air stripper, the off-gas treatment is not taken into account in this evaluation.

5.3 AOPs

AOPs are destructive processes unlike air stripping where the contaminant is transferred from one phase to another. AOPs destroy MTBE by chemical oxidation induced by the strong oxidants that are generated. The oxidant that is primarily generated in the AOPs is OH•, which is a highly reactive and non-selective oxidant. Each AOP employs a different mechanism for the generation of OH•. AOPs are emerging technologies and there are no full scale installations for the treatment of MTBE. The major concern over the implementation of the AOPs is the formation of potentially toxic by-products. Even though it is possible to eliminate the by-product formation by increasing the oxidant
dosages, or by providing additional secondary treatment, this would result in a steep increase in the treatment costs making it uneconomical.

5.3.1 \( \text{O}_3/\text{H}_2\text{O}_2 \)

The use of \( \text{O}_3 \) and \( \text{H}_2\text{O}_2 \) together has been shown to be more effective than the use of \( \text{O}_3 \) or \( \text{H}_2\text{O}_2 \) alone. The addition of \( \text{H}_2\text{O}_2 \) to \( \text{O}_3 \) reduces the \( \text{O}_3 \) dosage required to obtain similar treatment efficiency. This thus helps in lowering the overall cost of treatment because the cost of \( \text{H}_2\text{O}_2 \) is considerably lower than the cost of producing \( \text{O}_3 \). Although the theoretical yield of OH• in the \( \text{O}_3/\text{H}_2\text{O}_2 \) process is lower than that of the UV/\( \text{H}_2\text{O}_2 \) process, it is less affected by the water quality parameters such as turbidity, etc. After the formation of OH•, however, the interferences are the same for both the processes. The \( \text{O}_3/\text{H}_2\text{O}_2 \) process has been widely tested and applied for a lot of groundwater remediation applications. One major disadvantage of this process is that the use of \( \text{O}_3 \) can result in the formation of bromate, when bromide is present in the source water (Gunten and Hoigne 1994; Krasner et al. 1993; Siddiqui et al. 1999). The bromate formation can be reduced by increasing the \( \text{H}_2\text{O}_2 \) to \( \text{O}_3 \) molar ratios (Song et al. 1997), or by reducing the pH to around 6.5 (Liang et al. 1999). The \( \text{O}_3/\text{H}_2\text{O}_2 \) process also requires an off-gas treatment system for \( \text{O}_3 \) destruction, although \( \text{H}_2\text{O}_2 \) reacts rapidly with most of the \( \text{O}_3 \) and only a very small quantity of \( \text{O}_3 \) is vented. Residual \( \text{H}_2\text{O}_2 \) can promote biological growth by serving as an oxygen source and thus post treatment of excess \( \text{H}_2\text{O}_2 \) maybe required.
5.3.2 \( \text{O}_3/\text{UV} \)

The \( \text{O}_3/\text{UV} \) process is more effective than the use of \( \text{O}_3 \) alone. The \( \text{OH}^\bullet \) generation by the \( \text{O}_3/\text{UV} \) process is more efficient than the \( \text{H}_2\text{O}_2/\text{UV} \) process using LP-UV, due to the fact that the molar extinction coefficient of \( \text{O}_3 \) at 254nm is very high compared to that of \( \text{H}_2\text{O}_2 \). This would mean that a higher concentration of \( \text{H}_2\text{O}_2 \) or the use of a MP-UV lamp would be required to generate the required \( \text{OH}^\bullet \). Although the \( \text{O}_3/\text{UV} \) process is more stoichiometrically efficient in generating \( \text{OH}^\bullet \) than the \( \text{H}_2\text{O}_2/\text{UV} \) or the \( \text{O}_3/\text{H}_2\text{O}_2 \) processes, it is less efficient for generating large quantities of \( \text{OH}^\bullet \) due to the low solubility of \( \text{O}_3 \) in water and potential mass transfer limitations as compared to \( \text{H}_2\text{O}_2 \). Also there is the potential for bromate formation with the use of \( \text{O}_3 \) and off-gas treatment is required for \( \text{O}_3 \) before it is vented into the atmosphere. The UV light penetration is also affected by the turbidity of the source water leading to a reduction in the efficiency. Many compounds like iron and nitrate also absorb UV light thus reducing the process efficiency. Also with the use of UV lamps, there is a potential for contamination of treated water with mercury due to lamp failures. The \( \text{O}_3/\text{UV} \) process has been mostly used for the destruction of high concentration industrial wastes and ordinance wastes. There are currently no systems for the treatment of drinking water. This might be due to the higher treatment costs associated with this process. Both the \( \text{O}_3 \) generation and UV radiation are energy intensive thereby increasing the overall treatment costs.
5.3.3 $\text{H}_2\text{O}_2$/UV

The $\text{H}_2\text{O}_2$/UV process evaluated in this study utilized the LP-UV lamp, which resulted in very low treatment efficiencies. Hence this process is not considered in the cost evaluation conducted in this chapter. The use of MP-UV radiation instead of the LP-UV would, however, make this process more economical and efficient in treating MTBE contaminated water. Since there is no use of $\text{O}_3$, there is no potential for bromate formation and also there are no mass transfer limitations due to the low solubility of $\text{O}_3$. Since $\text{H}_2\text{O}_2$ readily dissolves in water, larger quantity of $\text{OH}\cdot$ are generated in the $\text{H}_2\text{O}_2$/UV process as compared to the $\text{O}_3$/UV process for the same amount of energy spent in the addition of oxidants. The $\text{H}_2\text{O}_2$/UV process has been widely tested and applied for various drinking water applications. There are also full scale systems installed in the US and Canada for the removal of PCE and NDMA, respectively. There are, however, some disadvantages associated with this process. The use of UV lamps has the risk of mercury contamination in the treated water due to lamp failure. The turbidity of source water reduces the treatment efficiency. There is also the potential for the increased formation of disinfection by-products when the high energy MP-UV lamp is used with pre-chlorinated water. Also as discussed earlier, the presence of excess $\text{H}_2\text{O}_2$ in the treated water may result in biological growth.
5.4 Cost Analysis

Cost has a very important role in setting many state and federal pollution control regulations. The extent of this role varies with the type of regulation. The Maximum Achievable Control Technology (MACT) standards regulation explicitly uses cost as the factor in determining how stringent the regulation has to be set. Detailed cost analyses are done by regulators in determining the minimum cost technology used to achieve the goals. A cost evaluation assesses the use of resources ‘spent’ on any treatment technology employed to remove the contaminants from water. The economic technique of cost evaluation is one of the tools available to help choose wisely from a range of alternatives and to design and implement efficient treatment systems. Cost evaluations assess the gains and the costs of carrying out a set of activities. The purpose of the analysis is to identify ways to do the most with the amount of money spent. In other words, it is designed to identify the most efficient approach. This chapter provides a comparative analysis of the different technologies evaluated, for the treatment of MTBE contaminated water, in this study.

Cost analysis is a critical element in the selection process for the right treatment technology. It supports management decisions by quantifying the resource impact of alternative options. A good cost analysis requires an accurate cost measurement data. There are different methods of measuring costs all of which would require a good knowledge of the technology and some cost analysis skills/tools. The primary purpose of cost analysis is to convert the amount of resources (materials, equipment and manpower),
required to implement the project, into dollar values. Any cost analysis begins with the definition of the scope of problem and also the assumptions to be made in the analysis. There are different methods of cost estimation. They are:

- The **engineering approach** (also called the bottom-up approach) is an examination of separate work segments in detail and the compilation of the various detailed estimates into a total. To follow this approach, one must have an extensive knowledge of the system and the activities involved for each item.

- In the **parametric approach**, the cost is related to some of the physical attributes or characteristics like, concentration, flow rate, diameter or length, power consumption, etc. Determining valid relationships between cost and the physical attributes or characteristics is a key to using this method.

- The **analogy approach** uses direct comparison of data from already existing systems to determine the cost of the new system. This process is a judgmental process and requires considerable experience in using this. Also a validation of the direct comparison has to be provided.

The engineering approach has been adopted in this study for the cost estimates. There are three types of costs involved in any treatment technology. They are the capital costs, operation and maintenance (O&M) costs and periodic costs.

- **Capital costs** include all the expenditures that are required to build the system for the treatment/remediation. Capital costs include all labor, equipment, and material
costs, including contractor markups such as overhead and profit, associated with activities such as mobilization/demobilization; monitoring; site work; installation of extraction, containment, or treatment systems; and disposal. Capital costs also include expenditures for professional/technical services that are necessary to support construction of the remedial action.

- **O&M costs** are those costs required to operate and maintain the treatment system throughout its lifetime. These costs are usually estimated on an annual basis. Annual O&M costs include all labor, equipment, and material costs, associated with activities such as monitoring; operating and maintaining treatment systems and disposal. They also include including contractor markups such as overhead and profit and also include expenditures for professional/technical services necessary to support O&M activities.

- **Periodic costs** include those expenditures that might be incurred once every few years, (like equipment replacement/rebuild, etc.) or expenses that occur only once during the O&M period (like the failure of a subsystem requiring the installation of a different system, etc). These costs are neither capital costs nor O&M costs and so it is more realistic to consider them separately.

In certain cases, the remedial action is not considered complete at the end of the construction of the treatment system. It would continue till the remediation goal is achieved and the O&M starts after this goal is achieved and may include prevention or mitigation of the movement of the contaminant into the environment by long term
monitoring of the site. In this evaluation, however, the O&M is assumed to start at the end of construction.

Detailed cost estimates have been completed for all the processes evaluated in this study. However, these estimates are specific to this particular study only and can only be used for comparative purposes. The cost for any new system would be site specific and would depend on a lot of factors including the quantity to be treated, the influent concentration, water quality parameters, etc.

Since the actual air stripper used in this project was an “inherited asset” (was released from a different system that was phased out), it was not possible to calculate the actual value of the air stripper. The capital cost for an air stripper of the same dimensions as the one used in this study was obtained from suppliers. These costs were comparable to the cost of similar sized systems listed in a recent report (NWRI 2000). To estimate the O&M costs for the air stripping system, the energy consumption of the blower and the pump were calculated. Apart from this, analytical costs and labor costs for maintenance and sampling were also taken into account. These cost estimates include the following assumptions for the electrical costs based on an average power cost (summer and winter) of $0.09/kWhr, the labor costs for maintenance and sampling at $40/hr and analytical costs at $200 per sample. The number of samples to be collected was assumed as one sample a week for all the systems. This sampling frequency could be reduced after the first year of operation. Four hours per week of labor was taken into account for maintenance and sampling requirements. The labor and analytical costs were assumed to
be the same for all the systems evaluated. The capital cost for the AOP system was calculated from the actual cost of all the equipment and materials purchased for the system. The piping and electrical works were assumed to be 30 percent of the system cost and installation charges were assumed at 10 percent of the system cost. The contractor profit and overheads and the engineering costs were assumed to be 15 percent, each. Finally a contingency of 20 percent was assumed to account for any possible cost overruns. The equipment was amortized at a discount rate of seven percent over a 30 year period. Amortized annual capital costs and annual O&M costs were combined to determine the total amortized operating cost for each system per 1,000 gallons of treated water.

5.5 Results

Tables 5-2, 5-4, 5-6 and 5-8 provide the details of the total capital costs, total annual costs and the cost for treatment of 1000 gallons of water for the air stripping, \( \text{O}_3/\text{H}_2\text{O}_2 \), \( \text{O}_3/\text{UV} \) and \( \text{O}_3/\text{H}_2\text{O}_2/\text{UV} \) processes, respectively. Appendix A provides the details of all the cost calculations and assumptions made in these calculations. The cost estimate for the \( \text{H}_2\text{O}_2/\text{UV} \) process has not been considered because of the inability of the process to achieve the target effluent MTBE concentration. Tables 5-3, 5-5, 5-7 and 5-9 provide the summary of the annual O&M costs for the air stripping, \( \text{O}_3/\text{H}_2\text{O}_2 \), \( \text{O}_3/\text{UV} \) and \( \text{O}_3/\text{H}_2\text{O}_2/\text{UV} \) processes, respectively. A comparison of the costs of the various processes indicate that, under the conditions evaluated and the assumptions made, air stripping is the most cost effective of all the processes studied with a unit treatment cost of $2.71 per
1000 gallons treated. All the AOPs have a much higher unit treatment cost (5-6 times more) as compared to air stripping. It must also be noted that the treated water from the AOPs still contain oxidation by-products and thus would require further treatment, which would further increase the unit treatment cost.

5.6 Conclusions

The cost analyses conducted in this chapter revealed that air stripping is the most cost effective as compared to the AOPs studied. Air stripping unit treatment cost was $2.71 per 1000 gallons treated. All the AOPs studied have a much higher unit treatment cost (5-6 times more) as compared to air stripping. It is worthwhile to note that the treated water from the AOPs still contain oxidation by-products and thus would require further treatment, which leads to a further increase in the unit treatment cost.
5.7 References


Table 5-1  Off-gas MTBE Emission Rates for different Flow Rate and Influent Concentration Scenarios.

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<td>Co µg/L</td>
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<td>5</td>
<td>0.002</td>
<td>0.006</td>
<td>0.010</td>
<td>0.020</td>
<td>0.039</td>
<td>0.059</td>
</tr>
<tr>
<td>300</td>
<td>5</td>
<td>0.003</td>
<td>0.009</td>
<td>0.015</td>
<td>0.030</td>
<td>0.059</td>
<td>0.089</td>
</tr>
<tr>
<td>400</td>
<td>5</td>
<td>0.004</td>
<td>0.012</td>
<td>0.020</td>
<td>0.040</td>
<td>0.079</td>
<td>0.119</td>
</tr>
<tr>
<td>1000</td>
<td>5</td>
<td>0.010</td>
<td>0.030</td>
<td>0.050</td>
<td>0.100</td>
<td>0.199</td>
<td>0.299</td>
</tr>
<tr>
<td>1500</td>
<td>5</td>
<td>0.015</td>
<td>0.045</td>
<td>0.075</td>
<td>0.150</td>
<td>0.299</td>
<td>0.449</td>
</tr>
<tr>
<td>2000</td>
<td>5</td>
<td>0.020</td>
<td>0.060</td>
<td>0.100</td>
<td>0.200</td>
<td>0.400</td>
<td>0.599</td>
</tr>
</tbody>
</table>
Table 5-2 Summary of the Total Capital, Annual and Unit Treatment Costs for a 20 gpm Packed Tower Air Stripper.

<table>
<thead>
<tr>
<th>ITEM</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air Stripper cost</td>
<td>$20,000</td>
</tr>
<tr>
<td>Piping, fittings and electrical work (30%)</td>
<td>$6,000</td>
</tr>
<tr>
<td>Installation cost (10%)</td>
<td>$2,000</td>
</tr>
<tr>
<td><strong>SUBTOTAL</strong></td>
<td><strong>$28,000</strong></td>
</tr>
<tr>
<td>Contractor Profit &amp; Overheads (15%)</td>
<td>$4,200</td>
</tr>
<tr>
<td><strong>SUBTOTAL</strong></td>
<td><strong>$32,200</strong></td>
</tr>
<tr>
<td>Engineering (15%)</td>
<td>$4,830</td>
</tr>
<tr>
<td><strong>SUBTOTAL</strong></td>
<td><strong>$37,030</strong></td>
</tr>
<tr>
<td>Contingency (20%)</td>
<td>$7,406</td>
</tr>
<tr>
<td><strong>Total Capital</strong></td>
<td><strong>$44,436</strong></td>
</tr>
<tr>
<td>Amortized Annual Capital</td>
<td>$3,581</td>
</tr>
<tr>
<td>Annual O&amp;M Cost</td>
<td>$20,658</td>
</tr>
<tr>
<td><strong>Total Annual Cost</strong></td>
<td><strong>$24,239</strong></td>
</tr>
<tr>
<td>Annual Flow Treated (Gallons)</td>
<td>8935200</td>
</tr>
<tr>
<td>Unit Treatment Cost ($/1000 Gallon)</td>
<td>$2.71</td>
</tr>
</tbody>
</table>
Table 5-3  Summary of the Total Annual O&M Costs for a 20 gpm Packed Tower Air Stripper.

<table>
<thead>
<tr>
<th>ITEM</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Labor/year (4hrs/week @ $40/hr)</td>
<td>$8,320</td>
</tr>
<tr>
<td>Analysis/year (1sample/week @ $200/Sample)</td>
<td>$10,400</td>
</tr>
<tr>
<td>Electrical Cost/year</td>
<td>$1,938</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>$20,658</strong></td>
</tr>
</tbody>
</table>
Table 5-4  Summary of the Total Capital, Annual and Unit Treatment Costs for a 3 gpm O₃/H₂O₂ AOP System.

<table>
<thead>
<tr>
<th>ITEM</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOP System Cost (O₃/H₂O₂)</td>
<td>$15,320</td>
</tr>
<tr>
<td>Piping, fittings and electrical work (30%)</td>
<td>$4,596</td>
</tr>
<tr>
<td>Installation cost (10%)</td>
<td>$1,532</td>
</tr>
<tr>
<td><strong>SUBTOTAL</strong></td>
<td><strong>$21,448</strong></td>
</tr>
<tr>
<td>Contractor Profit &amp; Overheads (15%)</td>
<td>$3,217</td>
</tr>
<tr>
<td><strong>SUBTOTAL</strong></td>
<td><strong>$24,665</strong></td>
</tr>
<tr>
<td>Engineering (15%)</td>
<td>$3,700</td>
</tr>
<tr>
<td><strong>SUBTOTAL</strong></td>
<td><strong>$28,365</strong></td>
</tr>
<tr>
<td>Contingency (20%)</td>
<td>$5,673</td>
</tr>
<tr>
<td><strong>Total Capital</strong></td>
<td><strong>$34,038</strong></td>
</tr>
<tr>
<td>Amortized Annual Capital</td>
<td>$2,743</td>
</tr>
<tr>
<td>Annual O&amp;M Cost</td>
<td>$23,290</td>
</tr>
<tr>
<td><strong>Total Annual Cost</strong></td>
<td><strong>$26,033</strong></td>
</tr>
<tr>
<td>Annual Flow Treated (Gallons)</td>
<td>1629360</td>
</tr>
<tr>
<td>Unit Treatment Cost ($/1000 Gallon)</td>
<td>$15.98</td>
</tr>
</tbody>
</table>
Table 5-5  Summary of the Total Annual O&M Costs for a 3 gpm O$_3$/H$_2$O$_2$ AOP System.

<table>
<thead>
<tr>
<th>ITEM</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Labor/year (4hrs/week @ $40/hr)</td>
<td>$8,320</td>
</tr>
<tr>
<td>Analysis/year (1sample/week @ $200/Sample)</td>
<td>$10,400</td>
</tr>
<tr>
<td>Electrical Cost/year</td>
<td>$4,158</td>
</tr>
<tr>
<td>H$_2$O$_2$ Cost/year</td>
<td>$412</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>$23,290</strong></td>
</tr>
</tbody>
</table>
Table 5-6  Summary of the Total Capital, Annual and Unit Treatment Costs for a 3 gpm O₃/UV AOP System.

<table>
<thead>
<tr>
<th>ITEM</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>AOP System Cost (O₃/UV)</strong></td>
<td>$15,895</td>
</tr>
<tr>
<td>Piping, fittings and electrical work (30%)</td>
<td>$4,769</td>
</tr>
<tr>
<td>Installation cost (10%)</td>
<td>$1,590</td>
</tr>
<tr>
<td><strong>SUBTOTAL</strong></td>
<td>$22,253</td>
</tr>
<tr>
<td>Contractor Profit &amp; Overheads (15%)</td>
<td>$3,338</td>
</tr>
<tr>
<td><strong>SUBTOTAL</strong></td>
<td>$25,591</td>
</tr>
<tr>
<td>Engineering (15%)</td>
<td>$3,839</td>
</tr>
<tr>
<td><strong>SUBTOTAL</strong></td>
<td>$29,430</td>
</tr>
<tr>
<td>Contingency (20%)</td>
<td>$5,886</td>
</tr>
<tr>
<td><strong>Total Capital</strong></td>
<td>$35,316</td>
</tr>
<tr>
<td>Amortized Annual Capital</td>
<td>$2,846</td>
</tr>
<tr>
<td>Annual O&amp;M Cost</td>
<td>$22,983</td>
</tr>
<tr>
<td><strong>Total Annual Cost</strong></td>
<td>$25,829</td>
</tr>
<tr>
<td>Annual Flow Treated (Gallons)</td>
<td>1629360</td>
</tr>
<tr>
<td>Unit Treatment Cost ($/1000 Gallon)</td>
<td>$15.85</td>
</tr>
</tbody>
</table>
Table 5-7  Summary of the Total Annual O&M Costs for a 3 gpm O\textsubscript{3}/UV AOP System.

<table>
<thead>
<tr>
<th>ITEM</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Labor/year (4hrs/week @ $40/hr)</td>
<td>$8,320</td>
</tr>
<tr>
<td>Analysis/year (1 sample/week @ $200/Sample)</td>
<td>$10,400</td>
</tr>
<tr>
<td>Electrical Cost/year</td>
<td>$4,176</td>
</tr>
<tr>
<td>UV Lamp cost/year</td>
<td>$87</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>$22,983</strong></td>
</tr>
</tbody>
</table>
Table 5-8  Summary of the Total Capital, Annual and Unit Treatment Costs for a 3 gpm O$_3$/H$_2$O$_2$/UV AOP System.

<table>
<thead>
<tr>
<th>ITEM</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>AOP System Cost (O$_3$/H$_2$O$_2$/UV)</strong></td>
<td>$17,135</td>
</tr>
<tr>
<td>Piping, fittings and electrical work (30%)</td>
<td>$5,141</td>
</tr>
<tr>
<td>Installation cost (10%)</td>
<td>$1,714</td>
</tr>
<tr>
<td><strong>SUBTOTAL</strong></td>
<td>$23,989</td>
</tr>
<tr>
<td>Contractor Profit &amp; Overheads (15%)</td>
<td>$3,598</td>
</tr>
<tr>
<td><strong>SUBTOTAL</strong></td>
<td>$27,587</td>
</tr>
<tr>
<td>Engineering (15%)</td>
<td>$4,138</td>
</tr>
<tr>
<td><strong>SUBTOTAL</strong></td>
<td>$31,725</td>
</tr>
<tr>
<td>Contingency (20%)</td>
<td>$6,345</td>
</tr>
<tr>
<td><strong>Total Capital</strong></td>
<td>$38,071</td>
</tr>
<tr>
<td>Amortized Annual Capital</td>
<td>$3,068</td>
</tr>
<tr>
<td>Annual O&amp;M Cost</td>
<td>$23,433</td>
</tr>
<tr>
<td><strong>Total Annual Cost</strong></td>
<td>$26,501</td>
</tr>
<tr>
<td>Annual Flow Treated (Gallons)</td>
<td>1629360</td>
</tr>
<tr>
<td>Unit Treatment Cost ($/1000 Gallon)</td>
<td>$16.26</td>
</tr>
</tbody>
</table>
Table 5-9  Summary of the Total Annual O&M Costs for a 3 gpm O$_3$/H$_2$O$_2$/UV AOP System.

<table>
<thead>
<tr>
<th>ITEM</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Labor/year (4hrs/week @ $40/hr)</td>
<td>$8,320</td>
</tr>
<tr>
<td>Analysis/year (1 sample/week @ $200/Sample)</td>
<td>$10,400</td>
</tr>
<tr>
<td>Electrical Cost/year</td>
<td>$4,214</td>
</tr>
<tr>
<td>UV Lamp cost/year</td>
<td>$87</td>
</tr>
<tr>
<td>H$_2$O$_2$ Cost/year</td>
<td>$412</td>
</tr>
<tr>
<td>TOTAL</td>
<td><strong>$23,433</strong></td>
</tr>
</tbody>
</table>
Chapter 6

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

6.1 Conclusions

The treatment of MTBE contaminated drinking water was evaluated using air stripping and advanced oxidation processes on a pilot scale. Experiments were conducted with de-chlorinated tap water spiked with MTBE at a concentration of 300 µg/L.

6.1.1 Air Stripping and Off-gas Adsorption

The performance of the air stripper was studied at six different air/water ratios, 105:1, 151:1, 177:1, 190:1, 202:1 and 206:1. A treatment efficiency of > 99% was achieved for each of the test runs conducted. The depth of the packing required to achieve maximum treatment efficiency increased with decreasing air/water ratios. The effectiveness of GAC and resin in the removal of MTBE from the air stripper off-gas was studied. GAC was found to have a higher adsorptive capacity than that of resin. The increase in the off-gas relative humidity (RH) from 20 to 50% reduced the adsorptive capacity of GAC, which is attributed to the competitive adsorption between MTBE and water vapor. The change in the RH did not impact the resin adsorptive capacity, which is due to the hydrophobic nature of resin that allows very little water to be adsorbed onto it. The modeling of the
breakthrough behavior of both the adsorbents was done using the pore and surface diffusion model. The model predictions agree well with the experimental data.

6.1.2 Advanced Oxidation Processes

Flow-through experiments with partial recirculation were conducted to evaluate the impact of flow parameters, oxidant dosages and oxidant molar ratios on the treatment efficiency of MTBE using the $\text{O}_3/\text{H}_2\text{O}_2$, $\text{O}_3/\text{UV}$, $\text{H}_2\text{O}_2/\text{UV}$ and $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ processes.

An increase in the recirculation ratio increased the treatment efficiency of MTBE. Experiments conducted at two recirculation ratios of 2.5:1 and 5:1 showed that a 5% increase in the treatment efficiency could be achieved by a 100% increase in the recirculation ratio.

TBF, TBA, acetone and MA were detected and quantified as the primary by-products of MTBE degradation.

Experiments studying the $\text{H}_2\text{O}_2/\text{UV}$ process demonstrated a maximum MTBE treatment efficiency of only 28% when 18 mg/L of H2O2 was used with LP-UV. The low molar extinction coefficient of H2O2 at 254 nm ($19.6 \text{ M}^{-1}\text{s}^{-1}$) is the reason for this low treatment efficiency. The use of a MP-UV lamp with a wide range of emission or the use of a prohibitively high concentration of H2O2 with the LP-UV lamp would be required to increase the treatment efficiency of this process.
Experiments using O\textsubscript{3} alone were able to achieve a maximum treatment efficiency of 74\% at an O\textsubscript{3} concentration of 5.8 mg/L and the by-product concentrations in the treated water were very high.

The use of O\textsubscript{3} in combination with UV radiation resulted in a dramatic increase in the degradation of MTBE as compared to O\textsubscript{3} alone experiments. 90, 96 and 98\% MTBE removal was achieved at 3, 4.5 and 5.8 mg/L of O\textsubscript{3}, respectively. The concentration of the by-products were also lower compared to the O\textsubscript{3} alone experiments.

The H\textsubscript{2}O\textsubscript{2}/O\textsubscript{3} process at a H\textsubscript{2}O\textsubscript{2}/O\textsubscript{3} molar ratio of 1.4:1 was found to be marginally more effective (1-3\%) than the O\textsubscript{3}/UV process at the same O\textsubscript{3} concentrations. Treatment efficiency of >99.9\% was obtained for MTBE at an O\textsubscript{3} concentration of 5.8 mg/L and a H\textsubscript{2}O\textsubscript{2}/O\textsubscript{3} molar ratio of 1.4:1. A complete destruction of the by-products was not achieved even at this high level of oxidant dosage.

The H\textsubscript{2}O\textsubscript{2}: O\textsubscript{3} molar ratios had a significant impact on the treatment efficiency. Experiments conducted at molar ratios ranging from 0.34:1 to 1.4:1 show that the degradation efficiency increased with increasing molar ratios and a maximum efficiency was obtained at a molar ratio of 1:1. A further increase in molar ratio led to a decrease in the treatment efficiency.

The combined process of O\textsubscript{3}/H\textsubscript{2}O\textsubscript{2}/UV resulted in the maximum treatment efficiency of MTBE of all the AOPs evaluated. Non-detectable levels of MTBE were recorded at an
O₃ dosage of 5.8 mg/L and a H₂O₂: O₃ molar ratio of 1.4:1. The by-product concentrations recorded at this level were the lowest for all the experiments conducted in this study, with acetone at 16 µg/L, TBF at 36 µg/L, TBA at 4 µg/L and MA at 2 µg/L. The change in H₂O₂: O₃ molar ratios produced similar results as the O₃/H₂O₂ process, with the maximum treatment achieved at the optimum molar ratio of 1:1.

The combined process of O₃/H₂O₂/UV was more efficient than the O₃/H₂O₂ process at lower H₂O₂: O₃ molar ratios. But at the ratio of 1.4:1, there was no significant difference between the two processes.

The electrical energy per order (E_EO) values calculated for the O₃/UV, O₃/H₂O₂ and O₃/H₂O₂/UV process, at an O₃ concentration of 5.8 mg/L and a H₂O₂:O₃ molar ratio of 1.4:1, are 4.19, 2.46 and 1.70 kWh/m³, respectively. The combined O₃/H₂O₂/UV process has the lowest E_EO value, indicating that this process is the most efficient of all the AOPs studied.

6.1.3 Cost Comparison

Air stripping was found to be the most cost effective treatment process evaluated in this study. The air stripping unit treatment cost of $2.71 per 1000 gallons treated was about 5 to 6 times lower than each of the AOP treatment cost. Also the treated water from the AOPs had a considerable amount of oxidation by-products, which would require further treatment.
6.2 Recommendations for Future Work

Based on the conclusions of the present study, further research work can be conducted in the following areas:

1. Low profile air strippers are practical in small water communities. The low profile air strippers occupy a smaller footprint since they are very compact, they are highly mobile, there are no problems due to scaling, require very little maintenance, and do not require heavy foundations. Hence, studies for the removal of MTBE need to be conducted in order to determine the effectiveness of low profile air strippers.

2. AOPs are not well understood because of the large number of complex chemical and physical processes involved. More studies need to be conducted under different water quality parameters such as pH, alkalinity, turbidity, NOM and TOC. For AOPs involving O$_3$, the effect of bromide concentration on the formation of bromate needs to be evaluated.

3. The by-product formation mechanisms and the subsequent removal of these by-products in a cost effective manner need to be determined.

4. The impact of medium pressure UV (MP-UV) lamp on the treatment efficiency and the cost-benefit analysis for the use of MP-UV over LP-UV needs to be evaluated.
The following assumptions were made, for all the processes, to evaluate the total costs and annual O&M costs:

1. The piping, fitting and the electrical costs are assumed to be 30% of the equipment cost.

2. The site work and installation charges are assumed to be 10% of the equipment cost.

3. The contractor overhead and profit is assumed to be 15% of the equipment cost plus piping and electrical plus installation charges.

4. The engineering cost, which includes project management, remedial design and construction management, is assumed to be 15% of the total cost including the contractor overhead and profit.

5. The contingency, which covers unknowns or unanticipated conditions associated with the total cost of the project, is assumed to be at 20% of the overall costs including the overhead and profits and the engineering costs.

6. The amortized annual capital is calculated based on a 30 year period and at a discount rate of 7%. This value is calculated based on the following equation:

\[
x = P \left( \frac{1 - (1 + i)^{-N}}{1 - (1 + i)^{-1}} + i \right)
\]

where

P = The principal borrowed

N = The number of payments

i = The periodic interest rate

x = The amortized annual capital
7. The power cost is assumed to be $0.09/kWhr. This is based on the average power costs for summer and winter which is $0.08/kWhr and $0.10/kWhr, respectively, for Cincinnati, Ohio (obtained from Cinergy/CG&E, Cincinnati, OH).

8. The labor cost is assumed to be $40/hr, since the maintenance and operation of these units would require a skilled labor and also since the operator would be required for only about 4 hours a week.

9. The analytical cost is assumed to be $200/sample.

10. The frequency of sampling is assumed to be one sample per week and the labor hours required for sampling and maintenance is assumed to be 4 hours per week.

Air Stripper

Capital costs for packed tower air stripping systems were determined from the quotes obtained from Carbonair® Environmental Systems, Inc., New Hope, MN and Duall Industries, Owosso, MI. The electrical power requirement for the air stripper was calculated from the actual feed pump and the blower used for the pilot scale unit used, as shown below:

\[
\begin{align*}
\text{Power consumption of the feed pump} & = 0.966 \text{ kW/hr} \\
\text{Power consumption of the blower} & = 1.492 \text{ kW/hr} \\
\text{The total power consumed per hour of operation} & = 2.458 \text{ kWhr} \\
\text{The total power consumption per year} & = 21532.08 \text{ kWhr}
\end{align*}
\]
The total power cost per year (@ $0.09/kWhr) = $1,938

The air stripper was able to operate at a flow rate of 17 gallons per minute (gpm). So the total gallons of water treated per year would be $= 17 \times 60 \times 24 \times 365 = 8,935,200$ gallons.

**Advanced Oxidation Processes**

The capital cost for the different AOP units were calculated from the actual cost of the various components purchased. The break-up of the equipment costs for the different AOPs are shown below:
## O₃/UV System

<table>
<thead>
<tr>
<th>S.No</th>
<th>Component</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SS Reaction Chamber</td>
<td>672.00</td>
</tr>
<tr>
<td>2</td>
<td>Ozone Destruct Unit (Ozotech Inc., Yreka, CA)</td>
<td>251.00</td>
</tr>
<tr>
<td>3</td>
<td>Degas Vent Valve (Armstrong International, Inc., Stuart, FL)</td>
<td>167.00</td>
</tr>
<tr>
<td>4</td>
<td>Ozone Generator (ClearWater Tech, LLC., San Luis Obispo, CA)</td>
<td>1,916.00</td>
</tr>
<tr>
<td>5</td>
<td>Oxygen Concentrator (ClearWater Tech, LLC., San Luis Obispo, CA)</td>
<td>1,496.00</td>
</tr>
<tr>
<td>6</td>
<td>Solenoid Valve (ClearWater Tech, LLC., San Luis Obispo, CA)</td>
<td>105.00</td>
</tr>
<tr>
<td>7</td>
<td>Venturi (Mazzei Injector Corp., Bakersfield, CA)</td>
<td>85.00</td>
</tr>
<tr>
<td>8</td>
<td>Dissolved Ozone Monitor (Analytical Technology, Inc., Collegeville, PA)</td>
<td>2,650.00</td>
</tr>
<tr>
<td>9</td>
<td>UV Reactor (Atlantic UV Corp., Hauppauge, NY)</td>
<td>1,175.00</td>
</tr>
<tr>
<td>10</td>
<td>UV Intensity Meter (Atlantic UV Corp., Hauppauge, NY)</td>
<td>524.00</td>
</tr>
<tr>
<td>11</td>
<td>UV Germicidal Lamp (Atlantic UV Corp., Hauppauge, NY)</td>
<td>116.00</td>
</tr>
<tr>
<td>12</td>
<td>Goulds Pump (NPE)</td>
<td>1,222.40</td>
</tr>
<tr>
<td>13</td>
<td>In-Line Mixer</td>
<td>224.00</td>
</tr>
<tr>
<td>14</td>
<td>Recirculation Flowmeter (3x518.00)</td>
<td>1,036.00</td>
</tr>
<tr>
<td>15</td>
<td>Check Valve (1/4&quot; Compression) (2x35.70)</td>
<td>71.40</td>
</tr>
<tr>
<td>16</td>
<td>Pressure Gage (3x43.59)</td>
<td>130.77</td>
</tr>
<tr>
<td>17</td>
<td>Tel-Tru Thermometer with Recalibrator</td>
<td>36.13</td>
</tr>
<tr>
<td>18</td>
<td>Quick Coupler (1/4&quot; F) (2x23.37)</td>
<td>46.74</td>
</tr>
<tr>
<td>19</td>
<td>Quick Nipple (1/4&quot; M) (8x9.33)</td>
<td>74.64</td>
</tr>
<tr>
<td>20</td>
<td>1” 316 SS Pipe (20’x4.20)</td>
<td>84.00</td>
</tr>
<tr>
<td>21</td>
<td>Check Valve (1” FNPT) (3x91.25)</td>
<td>273.75</td>
</tr>
<tr>
<td>22</td>
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<td><strong>TOTAL EQUIPMENT COST</strong></td>
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O$_3$/H$_2$O$_2$ System

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<th>Component</th>
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<td>1</td>
<td>SS Reaction Chamber</td>
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<td>2</td>
<td>Ozotech Ozone Destruct Unit</td>
<td>251.00</td>
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<td>Armstrong Degas Vent Valve</td>
<td>167.00</td>
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<td>Clearwater Tech Ozone Generator</td>
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<td>Clearwater Tech Oxygen Concentrator</td>
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<td>2,650.00</td>
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<td>10</td>
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<td>11</td>
<td>In-Line Mixer</td>
<td>224.00</td>
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<td>12</td>
<td>Recirculation Flowmeter (2x518.00)</td>
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<td>Chemical Feed Containers</td>
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<tr>
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## O₃/H₂O₂/UV System

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The electrical power requirements for the AOP units were calculated from the actual feed pump, recirculation pump, the O₃ generator, the UV lamp and the H₂O₂ feed pump used for the pilot scale unit used, as shown below:

- Power consumption of the feed pump = 1.127 kW/hr
- Power consumption of the recirculation pump = 3.082 kW/hr

Power consumption of the O₃ system
- O₂ generator = 0.648 kW/hr
- O₃ generator = 0.336 kW/hr
- O₃ destruct unit = 0.033 kW/hr

Power consumption of the UV reactor
- UV lamp = 0.065 kW/hr
- UV monitor = 0.006 kW/hr

Power consumption of the H₂O₂ feed system
- Metering pump = 0.048 kW/hr

The total power consumed per hour of operation for the
- O₃/H₂O₂ process = 5.274 kWhr
- O₃/H₂O₂/UV process = 5.345 kWhr
- O₃/UV process = 5.297 kWhr

The total power consumption per year for the
- O₃/H₂O₂ process = 46,200.24 kWhr
- O₃/H₂O₂/UV process = 46,822.20 kWhr
- O₃/UV process = 46,401.72 kWhr

The total power cost per year (@ $0.09/kWhr) for the
- O₃/H₂O₂ process = $4,158
- O₃/H₂O₂/UV process = $4,214
- O₃/UV process = $4,176

Cost of 30% H₂O₂ (purchased in a 30 gallon barrel) = $16.16/gallon
Consumption of H₂O₂ per hour at the rate of 5.8 mg/L = 11 mL (calculated from the actual consumption during the experiments)
Cost of H₂O₂ per hour = $0.047/hr
Annual cost of H₂O₂ = $412

The AOP system was able to operate at a flow rate of 3.1 gallons per minute (gpm). So the total gallons of water treated per year would be
= 3.1 x 60 x 24 x 365
= 1,629,360 gallons.