

ADVANCES IN GROUNDWATER TREATMENT TO REMOVE MTBE

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ABSTRACT

We have developed two significant modifications to conventional air-stripping of MTBE from contaminated groundwater. The first modification involves application of thermodynamic principles to improve by at least a factor of three the overall mass transfer efficiency, obtaining very high removal efficiencies, using a combination of higher operating temperatures (40-60 °C) and vacuum pressures (from 0.3 to 0.6 atm) in the system. Higher temperatures and lower operating pressures increase the stripping factor by increasing both Henry's constant and the mass transfer coefficient. These process improvements allow the removal of much less volatile compounds like polyaromatic hydrocarbons (PAHs) and hexachlorobenzene (HCB), or more soluble compounds like methyl tert-butyl ether (MTBE) from contaminated water, increasing the operational range of the stripping unit. Waste heat from an internal combustion engine is used to increase water temperature. The engine supplies the vacuum and uses the gas-phase pollutants as supplementary fuel.

These results have also been applied to removal of these compounds from contaminated groundwater using hollow fiber membranes. Contaminated water is passed through the inside of the fiber, with a vacuum applied to the outside of the membrane. The membrane's hydrophobic properties selectively allow the transfer of organics through the membrane while retaining water inside the fiber, for differential pressures up to 1 MPa (150 psi), based on capillary entry pressure. The hollow fiber membrane construction provides a very high surface area for mass transfer from the water to the gas phase. Much lower volume of gas is generated using this stripping method compared to conventional air-stripping, reducing the size of treatment units. Increased water temperature and high vacuum result in high removal efficiencies, using very compact units for water treatment.

INTRODUCTION

In a recently completed study [1], Keller et al. evaluated several water treatment technologies in terms of their applicability, both technical and economical, to remove MTBE from contaminated water. The study was part of a larger investigation to evaluate the costs and benefits of adding MTBE to gasoline to improve air quality, given the high water treatment costs associated with MTBE contamination [2]. These studies were in turn part of a project funded by the Legislature of the State of California and conducted by the University of California Toxic Substances Research and Teaching Program (UC TSRTP), to provide a scientific recommendation to the Governor of California with respect to the continued use of MTBE [3]. MTBE has risen to prominence in California and other states given the large impact on groundwater resources.

Methyl tertiary butyl ether (MTBE) was first added to gasoline in the late 1970's to replace lead as an anti-knocking agent [4]. To reduce pollutant emissions from motor vehicles in parts of California and other air quality non-attainment areas around the U.S., oil companies developed "oxygenated" gasoline formulations [5], which contain up to 15% MTBE by volume and/or other oxygenates. The 1990 Federal Clean Air Act mandated the incorporation of oxygenates to gasoline in ozone and carbon monoxide non-attainment areas. The State of California followed with the requirement that gasoline sold in the state meet specific requirements, including an oxygen content [6]. MTBE has been the oxygenate of choice due to economic and supply considerations.

Despite federal and state programs to improve handling of gasoline and other fuels in pipelines, underground and above ground storage tanks and other transport modes, gasoline spills and leaks are still relatively common place [7, 8, 9]. In addition, uncombusted gasoline is also spilled from boats and recreational equipment directly to surface waters, which may be water supply reservoirs [2]. The result is that MTBE is the second most frequently detected volatile organic compound in shallow groundwater [10], based on the National Water Quality Assessment program of the USGS. Thousands of Underground Storage Tank (UST) sites have detectable levels of MTBE and in a large number of cases groundwater has been impacted at levels which require treatment [7]. In addition, out of 3,173 drinking water sources tested in California by July 16, 1998, 46 sources had detectable levels of MTBE [11].

There is concern that MTBE can have deleterious health effects [12], and may cause ecological damage. Despite the controversy over the carcinogenicity of MTBE, the main driver for treating contaminated water is the fact that sensitive individuals can detect MTBE in water at very low levels. Based on several taste and odor studies, CAL-DHS proposed on July 24, 1998, a secondary Maximum Contaminant Level (MCL) of 5 ug/L for MTBE [12]. It has now become the secondary drinking water standard for MTBE. It is expected that MTBE contaminated drinking water supplies in California will be required to treat down to the 5 ug/L level. This may in effect become the *de*

facto drinking water standard, since this level is below the concentration that can cause acute or chronic human health effects or ecosystem damages.

The physicochemical properties of MTBE and many of the other oxygenates have increased the magnitude of the problem, when compared to other gasoline constituents. The oxygenates are rather soluble in water, with significantly larger solubility than benzene, toluene, xylenes and other petroleum hydrocarbons (e.g. pentanes, hexanes, etc.). This presents significant issues when considering the fate and transport of these pollutants in the environment and as well as treatment options. Given their high solubility, MTBE and the other oxygenates are quite mobile in the environment. They partition weakly to the organic fraction in soils, sediments and suspended particles, preferentially remaining in the aqueous phase. These compounds are expected to move essentially at the same rate as groundwater flow, with practically no retardation due to sorption. Initial studies indicate that biodegradation in the environment is slow [13, 14, 15], but these results may depend on soil and groundwater conditions. However, the relatively rapid detection of MTBE contamination at many monitoring and water supply sites since its widespread introduction indicates that MTBE is relatively persistent under normal environmental conditions, and natural biodegradation is unlikely to be a major process. Thus, MTBE behaves in many respects like a conservative tracer in the environment.

Given the extent of MTBE contamination, its high mobility in the subsurface and slow natural biodegradation, it is important to take remedial action as soon as possible at sites where MTBE contamination is suspected or known. Once the source has been located, typically a gasoline spill under the leaking underground storage tank, it should be removed via soil vapor extraction immediately to reduce the extent of contamination. In addition, the groundwater plume must be contained via water extraction. The extracted water requires treatment, and as indicated in [1], there are a number of technologies available for this treatment.

The present study presents the results of recent experimental and field work to evaluate innovative approaches to remove MTBE using thermodynamic principles, combined with new water treatment membranes that are specifically applicable for the removal of volatile organic compounds (VOCs) from water. These advances have been combined in a field-scale treatment unit that simultaneously performs soil vapor extraction using an internal combustion engine (ICE) and also treats extracted groundwater using a spray aeration system and a hollow fiber membrane, as part of the Spray Aeration Vapor Extraction (SAVE™) system [16, 17].

AIR STRIPPING MODIFICATIONS

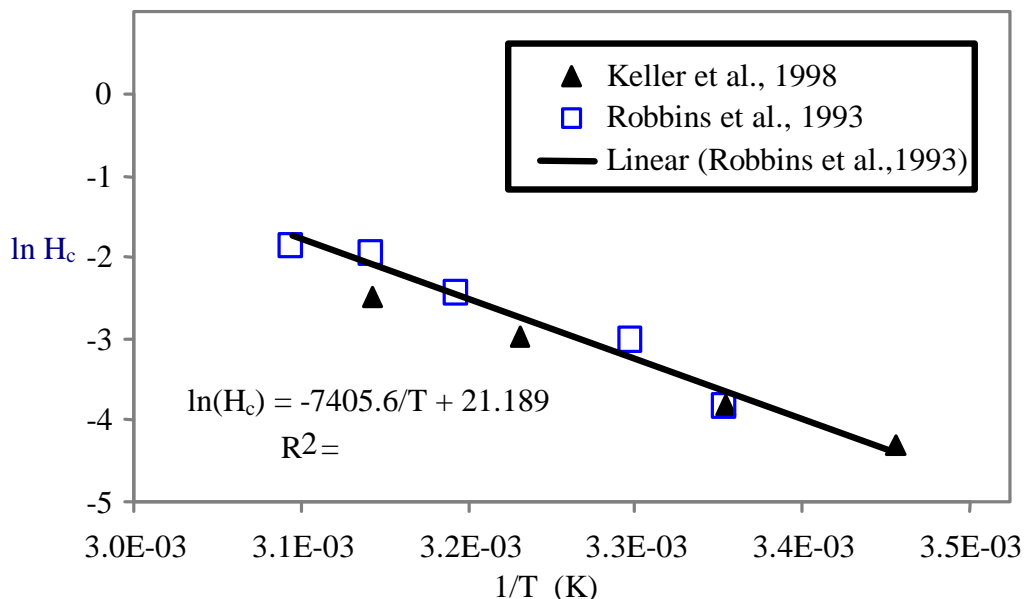
It is well known that increasing the temperature of water to be treated using air stripping will result in increased removal efficiency, because the vapor pressure of the VOC will increase much faster than its solubility, resulting in a much more favorable Henry's constant, H_c , which increases the stripping factor [18]. In addition, reducing the overall pressure of the air stripping unit produces

a similar effect, promoting the flash volatilization of the VOC. However, given the cost of heating the influent water and generating a vacuum, these two well-known improvements to air stripping are rarely applied in environmental applications.

The SAVE system makes use of the excess heat generated by the ICE to preheat the influent water to around 40 °C (104 °F), significantly increasing the Henry's constant. In addition, the vacuum pressure from the engine manifold is used to reduce the overall pressure inside the spray aeration tank. The VOC vapors are then routed directly into the ICE for destruction, along with any VOC vapors from the soil vapor extraction process. Using a catalytic converter and an oxygen sensor feedback loop, the ICE is capable of meeting the most stringent air quality standards in California.

The effect of increasing temperature on MTBE's H_c is presented in Figure 1. The sharp rise in H_c is estimated using the empirical correlation developed by [19], and confirmed experimentally in our laboratories [1]. Given MTBE's high solubility, the experimental error in measuring H_c is significant, and different methods produce considerably different values for this parameter. We have taken the most conservative values for the design of the improved SAVE system as well as for the work with the hollow fiber membranes.

Figure 1. Effect of temperature on MTBE's H_c



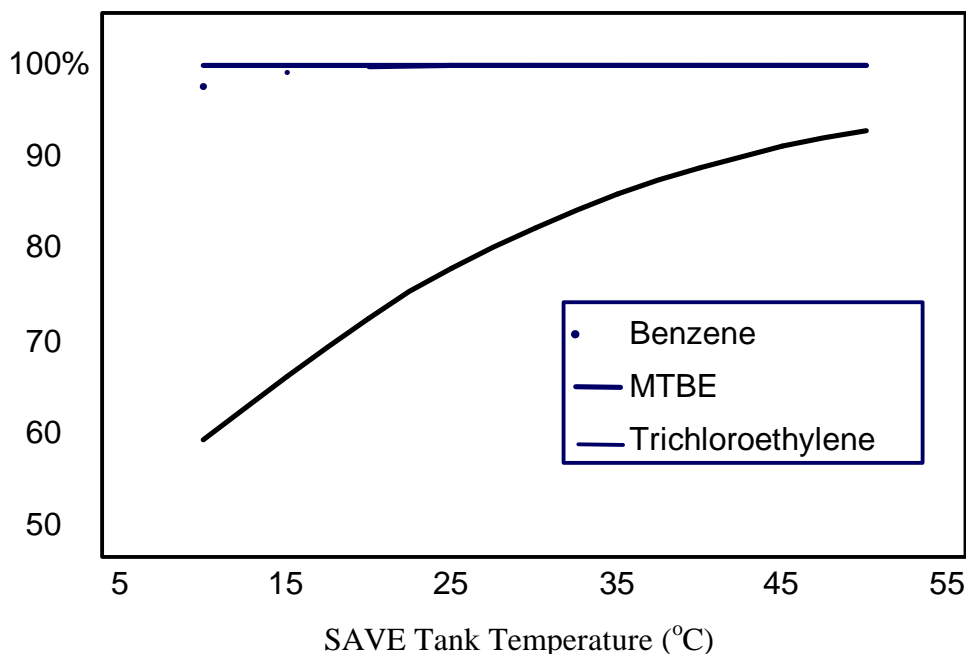
The spray aeration system consists of a sealed vessel into which the preheated influent water is introduced via a spray nozzle. The nozzle produces a fine mist which then contacts the gas phase in the vessel, resulting a large surface area for VOC mass transfer from the liquid to the gas phase. The overall

pressure in the vessel is maintained at around 0.53 atm (15" Hg vacuum). A fraction of the water can be cycled back for additional treatment, resulting in high overall removal efficiencies. Figure 2 presents the results of modeling removal efficiencies using the SAVE system, based on controlled experiments using various influent water concentrations and operating conditions. An overall mass transfer coefficient was determined for the SAVE system following [18]. The studies indicate that temperature has a significantly larger effect on overall removal efficiency than the reduction in the pressure in the vessel. While there is a noticeable improvement in removal by reducing the pressure from atmospheric to 0.5 atm, further reduction in pressure (i.e. higher vacuum pressures) did not significantly improve removal efficiency.

HOLLOW FIBER MEMBRANE

For this study, hydrophobic hollow fiber membranes (HFM) are used. The fiber has an internal diameter of around 50 to 100 μm , and the fiber wall is porous. However, since the fiber is made of hydrophobic polymers (typically olefin based), only VOCs and other non-hydrophilic gases permeate through the membrane. A typical membrane module contains several thousand fibers. HFMs have been successfully used to strip various compounds from water such as volatile organic compounds (VOC), hydrogen sulfide, sulfur dioxide, oxygen, carbon dioxide, bromine, and ammonia using a sweep gas to remove the gases and vapors from the membrane surface, for example [20, 21, 22, 23, 24, 25].

Figure 2. Predicted MTBE removal efficiency in Spray Aeration System



with a partial vacuum on the permeate side [20]. A large concentration gradient

is established between the aqueous phase concentration and the concentration in the gas phase. Uses of pervaporation include the dehydration of alcoholic azeotropes and removal of volatile organic compounds (VOC) from water [25].

HFM is considered in this study to improve the mass transfer rate of MTBE from water to air. Contaminated water is pumped through the lumen side of bundled microporous polypropylene hollow fibers while a vacuum is drawn counter-currently on the outside of the fibers. The hydrophobic membrane allows for efficient transfer of volatile compounds from aqueous to gas phase. While the water is pumped through the hollow fibers, volatile components volatilize and diffuse through the gas-filled pores of the hollow fiber, due to the large concentration gradient. Volatile compounds can then be pulled through by a vacuum, swept away by a sweep gas or reacted with a second solution. Pollutants can be effectively transferred through the gas-filled pores to the gas phase while water does not permeate due to the polymer's hydrophobic nature. Compounds transfer from water to air in response to a concentration gradient maintained by the constant flow of contaminant-free air across the exterior of the fibers. Hollow fibers have a large surface area per unit volume, allowing greater contact between the phases. This provides relatively fast removal of the contaminant. Studies by [20] and [27] showed that mass transfer of volatile organic compounds (VOCs) could be an order of magnitude greater than achievable by packed tower aeration when using HFM with a sweep gas.

There are several advantages of hollow fiber membranes over air-stripping:

- (1) lower air flow rates can be used, requiring smaller vapor-phase treatment units,
- (2) water and air flow rates can be controlled independently to maximize mass transfer because they are separated by the membrane,
- (3) there is no aqueous flow channeling due to the hollow fiber configuration, and
- (4) the air stream will contain little water due to the hydrophobic nature of the membrane.

This allows more efficient treatment of the contaminant in the gas phase [27].

Following the work of [28, 29, 30], an overall mass transfer coefficient for VOC transfer from the water to the gas phase can be obtained for each fiber, as well as for the ensemble of fibers. This can then be used to estimate the removal efficiency of an HFM module of a given length [1]. Figure 3 presents the results of our experimental studies to determine the overall mass transfer coefficient. The figure compares the experimental vs. theoretical removal efficiency of MTBE using a laboratory scale HFM. For the field studies, a much larger HFM module was tested. Based on the laboratory studies, the removal efficiency of the field unit was estimated (Figure 4). As in the case of air stripping, removal efficiency can be significantly improved by increasing the operating temperature.

FIELD TESTS

Based on the results of the laboratory experiments, a field-scale unit was constructed, including an ICE, a spray aeration system and a HFM. The system can be operated such that water is treated in either the spray aeration module or the HFM module, or they can also be operated in series. The unit is fully instrumented to record flowrates, operating pressures and temperatures, engine performance data and other important operating conditions (most of the information can be recorded in the unit's CPU, which can be downloaded directly to a PC or through a cell-phone modem). Sampling ports for water and air streams are available before and after each treatment point.

Figure 3. Theoretical vs. experimental removal efficiency of HFM

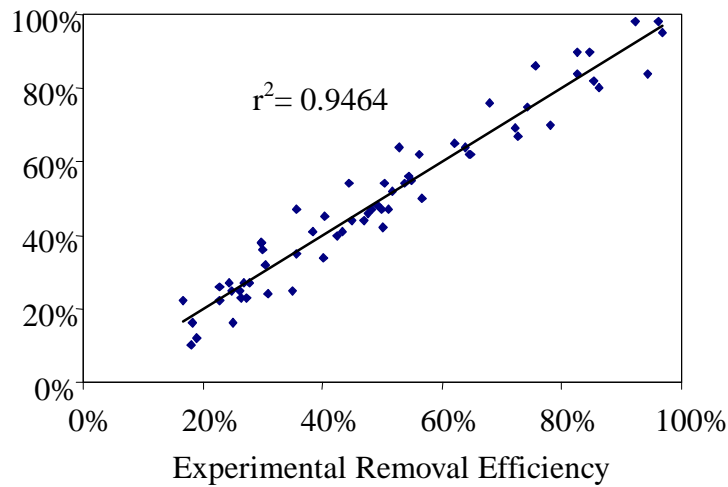
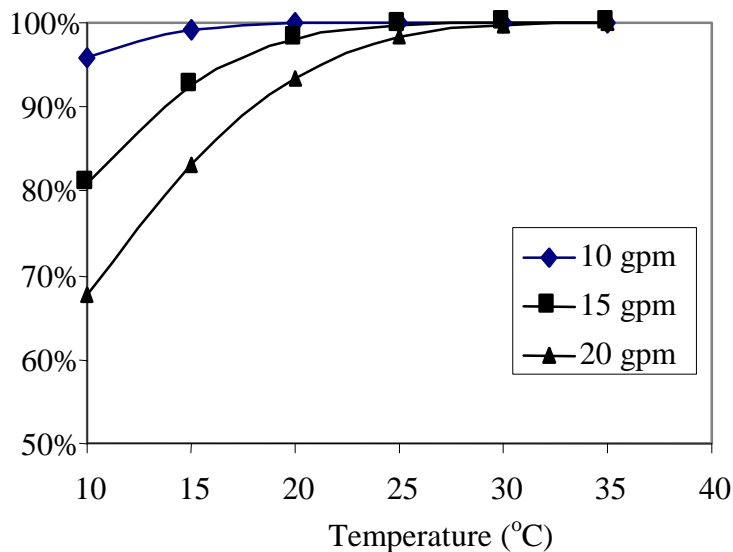


Figure 4. Predicted removal efficiency for field HFM system



The water treatment side is capable of handling flowrates up to 38 L/min (10 gal/min), which is more than sufficient for most individual leaking underground storage tank locations. In the case that the soil vapors do not supply sufficient fuel for the engine, fuel can be supplemented using propane or natural gas. For these tests, propane was used.

The typical influent MTBE concentration ranged from 430 to 2,700 ug/L. It should be noted that either system can handle much higher MTBE concentrations without any significant effect on the operating components. Tests have been done with influent MTBE concentration of up to 31,000 ug/L, with removal efficiencies of 93%. BTEX and other petroleum hydrocarbons were also present at the site and were treated through the same treatment train. One concern at the site is the high level of total dissolved solids (TDS), which ranged from 450 to 520 mg/L. The water was preheated to 39 °C (102 °F), using the waste heat from the ICE as well as an electrical resistance powered by a generator from the ICE.

Table 1 presents the results of the field test at various flowrates. The Spray Aeration system was capable of higher removal efficiency than the HFM module. Their combined removal efficiency achieved the treatment goals at the site. Benzene removal was complete (non-detect in the effluent, although the influent only had 9.5 mg/L). Influent TPH ranged from 56 to 70 ppm, but was not detected in the effluent samples. Since all the H_c of the normal petroleum hydrocarbons are smaller than MTBE's H_c , their removal efficiency is much higher.

The only issue from these field studies was the deposition of Ca and Mg deposits and films, inside the Spray Aeration tank and in the filters before the HFM. Given the short duration of the tests (10 hours in total), it was not possible to study the long-term operational issue. The system is being redesigned to include an acid metering system, to maintain a low pH and thus reduce or eliminate the scaling issue. Other influent water treatment options are under study to resolve this issue. Longer field tests are currently planned for the near future.

Table 1. MTBE removal efficiency during field operation

Water Flowrate (gal/min)	Removal by Spray Aeration (%)	Removal by HFM (%)	Combined Removal (%)
2	88.5%	51%	94.5%
4	80.5%	39.5%	88.0%
8	69.5%	14%	74%

CONCLUSIONS

Using available waste heat and vacuum pressure from an ICE, we have significantly improved the removal efficiency of a spray aeration system and a hollow fiber membrane system, to deal more effectively with MTBE contamination. The unit's design is based on laboratory experiments and tested in the field. Removal efficiencies of 90% or better can be achieved in one pass through the system. Additional removal may be possible by adding more HFM units in series.

High TDS may result in a relatively high rate of filter clean-up. This is not unique to our system, but is a problem when treating many groundwaters using air stripping. Influent pretreatment may be necessary, or the addition of acid to reduce scaling.

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