Remediation of MTBE-contaminated groundwater by integrated circulation wells and advanced oxidation technologies
Bassam Tawabini and Mohammed Makkawi

ABSTRACT
The proximity of shallow groundwater systems to sources of contamination usually exposes them to severe environmental threats. Hazardous pollutants that leak from gas stations, landfills, and industrial facilities may eventually reach the underneath shallow groundwater aquifers, posing risks to human health and the environment. Cleaning contaminated groundwater sources has always been a challenge to the local authorities. This is even more challenging when dealing with difficult pollutants such as methyl tertiary butyl ether (MTBE) due its high solubility in water, poor biodegradability, and poor adsorption onto solids. This study aims to assess the efficiency of a pilot groundwater remediation system to treat a shallow aquifer contaminated with MTBE. The in-house designed and fabricated pilot system combines the technology of circulation wells and UV-based advanced oxidation technology for the breakdown and removal of MTBE from water. An ultraviolet/hydrogen peroxide (UV/H$_2$O$_2$) process was used in this study to remove MTBE from water. The concentration of MTBE was reduced from approximately 1,400 $\mu$g/L to as low as 34 $\mu$g/L within 30 minutes, with a treatment efficiency of about 98%. The study also assesses the effects of the UV intensity and the treatment time needed to remove the target pollutant.

Key words | advanced oxidation, circulation wells, groundwater, MTBE, treatment

INTRODUCTION
Gasoline additives, called oxygenates, are chemicals added to gasoline to improve its combustion efficiency and reduce carbon monoxide (CO) emissions. Despite stiff opposition to its use (Mehlman 2006), methyl tertiary butyl ether (MTBE) became a popular oxygenate when lead was banned as an anti-knock agent. However, as a result of its high water solubility, it soon became one of the commonly detected groundwater pollutants. Human exposure to MTBE has been linked to ill-health symptoms such as headache, dizziness and nausea (Hernando et al. 2003). Chronic exposure of MTBE at toxic level is carcinogenic in rats and mice, and mutagenic in vitro of the same mammals (Mennear 1997). The growing concern about its polluting nature accounts for its gradual phase out in the USA, Japan and Europe (McCarthy & Tiemann 2006). However, it is still much in use in the Middle East and Asia, with Saudi Arabia and China as the leading producer and consumer respectively (Halim & Mohammad 2007).

Unlike most other water contaminants, the treatment of MTBE in water is very challenging due its very high solubility in water, associated biodegradation challenges, and poor adsorption onto solids (Eweis et al. 1997; Tawabini 2014). Removal of MTBE in water is being intensely researched (Keller & Bierwagen 2001; Sutherland et al. 2004; Hu et al. 2008; Innocenti et al. 2014) with resultant regular introduction of new and modified technological designs (Levchuk et al. 2014). Air stripping, adsorption, advanced oxidation processes (AOPs), biological methods are the commonly
researched approaches for the design of every new MTBE (and other organic pollutants) treatment technology.

Air stripping is an established method for the treatment of volatile organics from groundwater. One of the advantages of this method is lower water chemistry interference. That is, the efficiency of air stripping is not affected by water quality such as chemical oxygen demand (COD), salinity, total dissolved solids (TDS), pH and so on (Sutherland et al. 2004). However, very high flow rates are required to achieve effectiveness and economic efficiency. For a very high air/water ratio of about 105–206:1, a treatment efficiency of over 99% of MTBE was reported (Ramakrishnan et al. 2004). Hence, the application of air stripping for MTBE treatment is limited by its low Henry’s constant, leading to a very high air-water ratio. Furthermore, MTBE removed from groundwater is released into the air (Levchuk et al. 2014), leading to air pollution. This is in addition to fouling and carbonate scaling of air stripping towers (Sutherland et al. 2004). Removal efficiencies of over 90% were reported for varying MTBE concentrations in different case studies cited by Deeb and his group in the application of air stripping for the treatment of drinking water (Deeb et al. 2006).

The biological method is a cost-effective and environmentally-friendly approach for most environmental pollutants. However, bioremediation of MTBE remains a grey area with numerous controversies. Generally, MTBE is highly stable to microbial attack (Deeb et al. 2000; Fayolle et al. 2001; Levchuk et al. 2014). This stability is coupled with the fact that microbes find carbon sources from PAHs and other hydrocarbons more readily than MTBE. Nonetheless, there are numerous reports on the aerobic degradation of MTBE (Deeb et al. 2000; Rosell et al. 2006; Rosell et al. 2010). On the other hand, only very few anoxic MTBE degradation studies are documented (Waul et al. 2009), while Schmidt and his team concluded that fuel oxygenates biodegrade much slower than hydrocarbons (Schmidt et al. 2004). Bioremediation on a field scale is generally slow (Müller et al. 2007) due to a number of environmental factors. A field demonstration of bio-stimulation involving the release of dissolved oxygen into an anoxic underground MTBE plume demonstrated a sharp decrease of MTBE concentration to about 10 μg/L (Wilson et al. 2000). Recently, a report (van Afferden et al. 2011) from another field treatment of contaminated groundwater near Leuna Refinery, Germany showed that biotreatment of MTBE and other volatiles on a field scale is promising, with a removal efficiency of about 70%.

AOPs utilize hydroxyl radicals (OH•) to degrade organic contaminants in water to carbon dioxide and water. The production of OH radicals is achieved in different ways that typify the different methods/processes of AOPs. Commonly researched AOPs include the use of photocatalysts (like TiO2), ozone, UV, H2O2 and their combinations. Combining these methods, such as UV/TiO2, O3/H2O2, O3/UV, UV/H2O2, have been shown to improve their efficiencies and often times economies due to enhanced production of OH radicals and synergistic effects where the drawback of one is compensated for by the advantage of the other (Mitani et al. 2002; Gogate & Pandit 2004). AOPs involving ozone (e.g. O3/H2O2, O3/UV) may produce hazardous bromate during the degradation of MTBE if the water contains a high level of bromide ions (Shih et al. 2005). On the other hand, when UV is combined with H2O2 for pollutant treatment, the UV provides better disinfection than ozone and irradiates peroxide to release OH radicals, which decompose organic pollutants without producing harmful bromate (Vilhunen et al. 2011). Hu and his team demonstrated that MTBE photo-degradation during the first 60 min in UV/H2O2 and UV/TiO2 systems achieved 98% and 80% degradation, respectively. (Hu et al. 2008). In another study, Sutherland and his group reported that advanced oxidation provided the lowest treatment costs for MTBE-contaminated waters compared to air stripping and GAC (Sutherland et al. 2004).

A groundwater circulation well (GCW) is a type of Pump and Treat (P&T) system and is assembled in one complete in-situ setup. This technology is used to clean up hydrocarbon-contaminated groundwater efficiently. GCW systems are designed to create in-situ vertical groundwater circulation cells by drawing groundwater from an aquifer through one screened section of a multi-screened well and discharging it through another screened section (Johnson & Simon 2007). The contaminants can be mobilized effectively and moved up to be treated. GCW could utilize a combination of different remediation technologies such as aeration, adsorption by activated carbon (AC) or air stripping.

Groundwater qualities vary around the world. The uniqueness of groundwater sources in each location makes...
the search for optimum conditions of contaminant treatment seemingly endless. For UV-based AOPs, the concentration of initial MTBE, dosage of H2O2 used and effects of total organic carbon (TOC), TDS and pH values are the commonly assessed parameters. Salari and his team (Salari et al. 2005) further modeled the effects of irradiation time in addition to these parameters at the optimized condition using an artificial neural network approach. Most, if not all, available reports on MTBE treatment by UV/H2O2 are of bench-scale research. Available field reports of MTBE treatment applied other methods such as bioremediation, air-stripping (Cater et al. 2000; Deeb et al. 2006) and in-situ chemical oxidation (ISCO) including Fenton process (Krembs et al. 2010; Innocenti et al. 2014). There is therefore a need to evaluate the performance and efficiency of UV/H2O2 systems in the field.

In this study, the main objective was to demonstrate the treatment efficiency of GCW combined with UV/H2O2 technologies for the removal of MTBE as a groundwater pollutant. The effects of UV intensity and H2O2 dosages, in addition to irradiation time, on the removal efficiency of MTBE from contaminated groundwater were also investigated in the field.

MATERIALS AND METHODS

Site location

The field test was conducted in an open desert location in the Ghunan Area, Dammam (Figure 1). Ghunan is situated in Eastern Province, Saudi Arabia. Its geographical coordinates are 26°8′0″ North, 49°34′0″ East. There are no residential areas within more than 20 km, but there are nearby hazardous waste landfills. At the site, two sets of wells were drilled; one for remediation and one for monitoring. The water level was measured and the groundwater flow direction was determined using tracer analysis from the initial well to the remediation well.

Geologic investigations

The aquifer system in the study area lies in the Arabian Platform. On the basis of hydraulic properties of various units of the aquifer system, the lithologic succession can be divided into aquifers and intervening aquitards. They are, from bottom to top, Umm Er Radhuma (UER) aquifer, the Rus aquitard, the Dammam aquifer and the Neogene aquifer. Except for local facies variations, limestone, dolomitic limestones and dolomites represent the aquifers while shales, marls and anhydrites represent the aquitards (Abderrahman et al. 1995; Edgell 1997; Lloyd 1997). The aquifers in the study area, being a carbonate aquifer system, are characterized by karsts (Al-Saafin et al. 1990).

The electric resistivity imaging (ERI) method was used to delineate the depth to the water table. The fluid content and degree of water saturation in the porous medium can be interpolated to approximately define shallow saturated zones. The method involves measuring the electrical resistivity of subsurface materials, which provides information on the different geological layers, structures and the associated occurrence of groundwater (Muchingami et al. 2012). In this study, the apparent resistivity section (Figure 2) elucidates that the low resistivity layer of 5.5 ohm.m is around 15–16 m below the ground surface (green color). This low resistivity layer represents the groundwater upper boundary (water table). Using ERI results as a guide, one remediation well and six monitoring wells were drilled to a depth of 20 m, where the water table was encountered at 16 m below the ground surface.

Site hydrogeology

After the wells’ completion, geologic samples were collected and hydraulic heads were measured to define both the general geology and hydraulic gradient in the site, respectively. White marl and weathered limestone dominate the geology of the shallow aquifer. However, loose silty sand represents the unsaturated zone. The aquifer is Neogene in age and it is unconfined, shallow, and semi-heterogeneous. The hydraulic gradient, which fairly reflects the general slope of the area’s topography, shows a value of 0.0003 with a SE-NE trend. Slug tests were conducted to estimate the hydraulic conductivities (K) using the Hvorslev procedure (Hvorslev 1951). Two hydraulic conductivities were estimated following slug test procedures. Values of K range from 9.3 × 10^{-6} m/s to 5.0 × 10^{-6} m/s. Generally, the values indicate low heterogeneity. The observed high hydraulic conductivity values supports a previous observation that indicated the karstic
nature of the aquifer (Freeze & Cherry 1979). This implies that the aquifer could be vulnerable to contamination.

**Groundwater characteristics**

In order to evaluate the physico-chemical characteristics of the groundwater aquifer at the study site, samples were taken to the laboratory to be tested for various parameters. Average results of the laboratory tests are presented in Table 1. The high levels of turbidity and suspended solids will affect the efficiency of the UV lamps and need to be removed prior to degradation by the UV/H\textsubscript{2}O\textsubscript{2} process. Moreover, the high levels of cations ($\text{Ca}^{2+}, \text{Mg}^{2+}, \text{Na}^{+}$) and anions ($\text{SO}_4^{2-}, \text{Cl}^{-}, \text{NO}_3^{-}$) of the water will also impact the efficiency of the treatment process due to the scavenging effect via consuming some of the hydroxyl radicals needed to degrade the target pollutant (i.e. MTBE). (Tawabini et al. 2009).

**Installation of circulation wells**

The circulation well used in this study consists of a well with upper and lower circulation mechanisms. The upper setup is composed of injection outlets that recharge the aquifer with treated water from the remediation system. The lower part of the well is screened at a depth of 17 m to intercept the contaminated groundwater. A submersible pump is installed in the screen to reinforce the pumping effect. The pumping rate was estimated to be between 2.6 and 7.9 gallons per
minute based on a mathematical simulation approach (Iwalewa & Makkawi 2014). During the system's operation, polluted water is pumped from the aquifer and sent to the system for treatment. The treated water is, then, returned back to the remediation well through the upper injection outlets. Considering a proper pumping rate, this action stimulates the movement of water without disturbing the aquifer or distributing the contaminant in its environment.

The pilot UV-based treatment unit (photoreactor)

In this study, the pilot UV/peroxide treatment unit used for the field test (Figure 3) was designed and fabricated locally at KFUPM. The eight-chamber UV unit is equipped with a Variable Frequency Driven (VFD) water submersible pump with a capacity of 1.5 liters per second at 20 m head away. Amalgam straight UV lamps (Part No. UVI 300 4C P 19/2000) were purchased from UV-Technik, Germany. The UVI-type lamps are doped with a special amalgam to reduce the internal pressure of the mercury vapor. Amalgam lamps give more than twice the power per unit of length produced by a conventional low pressure mercury lamp. UVI lamps emit radiation mainly at a wavelength of 253.7 nm. The UV lamp arc dimension is 1,000 mm in length and 19 mm in diameter. The total power for each lamp is 100 W and the intensity is 670 μW/cm². The eight UVI lamps were in-housed in cylindrical chambers of 1,060 mm length × 130 mm diameter. The UV chamber was plasma-cut and machined to accommodate the UV lamps. A stainless steel 500 mm length × 300 mm diameter (top) and 15 mm diameter (bottom) cyclone was used as a pretreatment step to reduce turbidity. A 500 mm length × 150 mm AC column was included in the system as a post-treatment unit whenever needed. However, in this phase of the study, no AC materials were packed in the column.

The treatment unit is also equipped with a stainless steel dust-proof (IP 66) control panel that consists of starters, sight glasses and sensors for certain parameters such as pH and temperature. The unit is powered by a 7.6 kW-capacity power generator. Fluid circulation within the system is regulated by a flow control containing ball valves and a flow measuring device for monitoring the flow. A 500-L tank for storage and recirculation of treated water was provided at the site. The MTBE-contaminated water is pumped into the UV reactors, and is circulated through the UV chambers over a certain period of time (30 minutes). The effluent water is recirculated back into the aquifer after being circulated through the treatment unit for 120 min.

A dosage of 200 mg/L of hydrogen peroxide (H₂O₂) was added to the water to reach a ratio of 1:200 of MTBE/H₂O₂. The MTBE-contaminated water was then pumped through the UV/H₂O₂ unit and circulated for 2 hours with a sequence of two lamps illumination after every 30 minutes. This UV illumination sequence was tested to reduce the energy consumed by the UV lamps and to check the impact of pulse illumination. In each day of the pilot testing phase, the water tank was filled from the remediation well with MTBE-contaminated water. The turbidity level was reduced by the cyclone from 47.5 FTU to as low as 3.2 FTU. This pretreatment step greatly enhances the action of the UV lamps by generating hydroxyl radicals needed for the degradation of the target contaminant.

Initially, a water sample was taken to determine the initial concentration of MTBE before treatment. Then the treatment unit was turned on and the water circulated through the photoreactor for 30 minutes, and samples

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.15</td>
</tr>
<tr>
<td>Conductivity, mS/cm</td>
<td>7,330</td>
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<tr>
<td>Dissolved oxygen, mg/L</td>
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<tr>
<td>Turbidity, FTU</td>
<td>47.5</td>
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<tr>
<td>Total alkalinity, mg/L</td>
<td>67.8</td>
</tr>
<tr>
<td>Total hardness, mg/L</td>
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</tr>
<tr>
<td>Total suspended solids (TSS), mg/L</td>
<td>98.5</td>
</tr>
<tr>
<td>Total dissolved solids (TDS), mg/L</td>
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</tr>
<tr>
<td>Sulphate, mg/L</td>
<td>1.60 × 10³</td>
</tr>
<tr>
<td>Chloride, mg/L</td>
<td>1,990</td>
</tr>
<tr>
<td>Bromide, mg/L</td>
<td>6.35</td>
</tr>
<tr>
<td>Nitrate, mg/L</td>
<td>12.2</td>
</tr>
<tr>
<td>Sodium, mg/L</td>
<td>1.09 × 10³</td>
</tr>
<tr>
<td>Calcium, mg/L</td>
<td>573</td>
</tr>
<tr>
<td>Magnesium, mg/L</td>
<td>145</td>
</tr>
<tr>
<td>Potassium, mg/L</td>
<td>52.1</td>
</tr>
<tr>
<td>Total organic carbon (TOC), mg/L</td>
<td>8.49</td>
</tr>
</tbody>
</table>
were taken at 0, 10, 20 and 30 minutes. After completing the cycle, the water was pumped back to the water tank and a second cycle of treatment started while increasing the number of UV lamps to four. Again samples were taken at 0, 10, 20 and 30 minutes to determine the residual of MTBE. The process was repeated for a 3rd and 4th cycle with six and eight UV lamps respectively. After the 2-hr treatment, the treated water in the tank was re-injected back into the aquifer. The pilot testing was again repeated on the second and third day to assess the removal efficiency.

Chemical analysis

Fifty (50) mL of water samples were collected in an amber-color glass and transferred to the laboratory for immediate analysis of MTBE and its degradation by-products (acetone, tert-butyl alcohol (TBA) and tert-butyl formate (TBF) using gas chromatography mass spectrometry (GC/MS) and as per USEPA Method 5030C (USEPA 2003). A purge and trap (Teledyne Teckmar, USA) sample introduction system followed by gas chromatography (Thermo Scientific Trace GC Ultra, USA) was coupled with an ISQ mass spectrometer. 5 ml of the sample was introduced into the P&T and allowed to purge to 11 min at a stable temperature of 40 °C and 40 mL/min flow. While the purging temperature was set at 140 °C, the desorb temperature was 200 °C with 300 mL/min flow and for 2 min to ensure desorption of the volatiles. After desorption, the unit is baked at a very high temperature of 270 °C for 3 minutes and then deionized water is run as a blank sample before analyzing the next sample to prevent carry-over of volatiles. The GC/MS conditions used for MTBE and its by products were described by Tawabini (2014). All sampling and analyses were performed in replicates. Chemicals used were purchased from Sigma-Aldrich.

RESULTS AND DISCUSSION

Removal of MTBE

Table 2 shows that high removal efficiency of MTBE was attained using the UV/H₂O₂ photoreactor. The results reveal that removal efficiency ranges from 71.5% when using two UV lamps to as high as 91.6% when using eight UV lamps in the first day of the pilot testing. There is a noticeable increase in the removal efficiency as the number of UV lamps increases from two to four lamps or more. However, the increase is not consistent, probably...
due to the different initial concentration of MTBE and the consumption of hydrogen peroxide (H₂O₂). The results, in general, clearly indicate that the pilot GCW-AOP treatment unit has achieved a removal efficiency of more than 90% within a short period of time compared to other classical treatment methods (Deeb et al. 2006; Krembs et al. 2010; Innocenti et al. 2014).

**Effects of UV intensity on MTBE removal efficiency**

As shown in Figure 4, the removal efficiency of MTBE using the UV/H₂O₂ process was very high. The MTBE level was reduced from 1,356 μg/L to around 405 μg/L in less than 30 minutes. In fact, removal was very high in the first 10 minutes, which indicates a powerful degradation of MTBE using only two UV lamps with 100 ppm H₂O₂. Despite the fact that treatment continues with more UV lamps, the increased removal efficiency rate was due probably to the consumption of hydrogen peroxide (H₂O₂). This result is better than the 70% reported from field bio-remediation treatments (van Afferden et al. 2011) and comparable to results (98%) from a batch experiment using AOP (specifically, UV/H₂O₂) (Hu et al. 2008). Even though increasing the number of UV lamps increases removal efficiency, using six UV lamps is almost as efficient as using eight UV lamps, with about 95% MTBE removal efficiency.

**Effect of treatment time**

Figure 4 also shows the effect of exposure or irradiation time on MTBE removal using a combined circulation well and UV/H₂O₂ process. The 30-minute cycles of treatment using two, four, six and eight UV lamps are presented for the three consecutive days of pilot testing. It is clear that in the first 30-minute cycle using two UV lamps and 200 ppm H₂O₂, the MTBE level was reduced from

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**Table 2** | Overall % of MTBE removal at the end of each day

<table>
<thead>
<tr>
<th>No. of lamps used</th>
<th>Day 1 Cᵢ –</th>
<th>Day 2 Cᵢ –</th>
<th>Day 3 Cᵢ –</th>
<th>No. of replicate samples</th>
<th>Overall mean (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1,356</td>
<td>311</td>
<td>157</td>
<td>3</td>
<td>75.2</td>
</tr>
<tr>
<td>4</td>
<td>92.3</td>
<td>89.4</td>
<td>67.9</td>
<td>3</td>
<td>83.2</td>
</tr>
<tr>
<td>6</td>
<td>84.1</td>
<td>97.2</td>
<td>83.0</td>
<td>3</td>
<td>88.1</td>
</tr>
<tr>
<td>8</td>
<td>91.6</td>
<td>98.6</td>
<td>79.1</td>
<td>3</td>
<td>89.8</td>
</tr>
</tbody>
</table>

Cᵢ – initial concentration of MTBE in μg/L.

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**Figure 4** | Removal of MTBE using 200 mg/L H₂O₂ and different UV lamps over 2 hrs for 3 days.

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1,356 μg/L to around 375 μg/L on day 1. No additional removal was achieved after the first 10 minutes. This could be due to the low intensity with using only two UV lamps. The treated effluent from the unit was discharged into the water tank, which caused the concentration of MTBE in the tank to dilute to around 993 μg/L, and the second 30-minute cycle started with four UV lamps. Using four UV lamps reduces the concentration of MTBE from 993 μg/L to 77 μg/L to as low as 87 μg/L in 30 minutes. Similarly, in the third 30-minute cycle using six UV lamps, the MTBE level was reduced from 483 μg/L to as low as 87 μg/L in 30 minutes. In the fourth 30-minute cycle, the MTBE level was reduced to around only 26 μg/L. The overall reduction of the MTBE level in the 2 hour treatment time reached more than 98%. This result is consistent with the result reported by Salari et al. (Salari et al. 2005).

CONCLUSION

The study demonstrated a novel method for the removal of MTBE from contaminated groundwater using circulation well technology combined with UV-based advanced oxidation technology. The study also showed that the concentration of MTBE was reduced from 1,400 μg/L to as low as 34 μg/L within 30 minutes, with treatment efficiency of about 98%.

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