Advanced oxidation of methyl-tertiary butyl ether: pilot study findings and full-scale implications

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ABSTRACT

The high solubility and low volatility of methyl-tertiary butyl ether (MTBE) makes it difficult to treat when present at low levels (as in most groundwater supplies) using established technologies such as air stripping and activated carbon. Unlike the established transfer technologies (e.g., air stripping, activated carbon adsorption), advanced oxidation by ultraviolet (UV) light could potentially destroys MTBE and its by-products. As part of this study, extensive pilot and bench scale evaluation was performed to understand the effectiveness of MTBE and its by-products [e.g., tertiary butyl alcohol (TBA) and tertiary butyl formate (TBF)] removal using UV/peroxide in ground and surface waters. The water quality matrix evaluated the impact of MTBE oxidation in the presence of other UV light absorbing compounds (e.g., nitrate) and radical scavengers (e.g., organics). These UV oxidation tests were conducted using both the medium-pressure (MP-UV) and low-pressure, high-output (LP-UV) lamps. Water quality impacts were also summarized using the energy requirement calculations. Based on the information gleaned from pilot testing, authors developed conceptual-level design and operational criteria. Conceptual-level capital and operational costs for full-scale systems were developed and presented.

Key words | advanced oxidation processes, MTBE removal, UV oxidation, UV peroxide

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CONVERSION FACTORS

Units In Paper	Metric Units
1 gallon	3.785 litres
1 foot	0.3048 metres
1 pounds (1b)	0.4535 kilograms
1 gallon per minute (gpm)	3.785 litres per minute
1 gallon per day (gpd)	3.785 litres per day
1 gallon per square feet (gpm/sf)	40.74 litres per square meter
1 square feet (sq ft)	0.0929 square metres
1 part per million (ppm)	1 milligram per litre

INTRODUCTION

Methyl-tertiary butyl ether (MTBE) has been added to gasoline as an octane enhancing replacement for lead and as an oxygenate to lower the ozone and carbon monoxide emission levels. The percentage of MTBE that was added to fuels increased from approximately 3 percent (%) by volume in 1979 (when it was first introduced) to 11–15% in 1998 (USEPA 1998). MTBE was added approximately to 30% of the gasoline sold in United States in 1998 (USEPA 1998). As a result of this widespread usage and its unique physiochemical properties, a portion of this gasoline additive found its

way into the nation's groundwater and surface water supplies and has been reported as a contaminant in some supplies.

The main sources of MTBE contamination of groundwater supplies are leaking underground storage tanks and pipelines, spills and contaminated sites and releases from manufacturing and storage sites. The primary sources of MTBE contamination in urban surface water supplies are releases from gasoline-powered recreation watercrafts and atmospheric deposition through precipitation of industrial or vehicular emissions. MTBE concentrations in the order of 100–200 micrograms per litre (μg L^{-1}) were detected in drinking water wells in areas with leaky underground storage tanks (Gullick & LeChavellier 2000). A national survey conducted by U.S. Geological Survey (USGS) found MTBE to be one of the most predominant organic contaminants, next only to chloroform in urban groundwaters (Squillace et al. 1997).

Regulatory update

The U.S. Environmental Protection Agency (USEPA) has not yet set any drinking water standards for MTBE. However, in 1997, the USEPA Office of Water issued a health advisory on MTBE. This advisory was issued to provide guidance to water suppliers whose source waters had been impacted by MTBE. This advisory recommended keeping the concentrations of MTBE in the range of 20 to 40 μg L^{-1} or less to likely avert unpleasant taste and odor effects (USEPA 1997). The USEPA has included MTBE in its Contaminant Candidate List.

Several states, including Maine, New Jersey, California and New Hampshire have set primary maximum contaminant levels (MCLs) for MTBE. Maine and New Jersey have set MCLs for MTBE of 35 μg L^{-1} and 70 μg L^{-1}, respectively. In December 2000, California and New Hampshire adopted MCLs of 13 μg L^{-1}. The State MCLs are based on protection of human health and not on aesthetic concerns. California also set a secondary MCL of 5 μg L^{-1} based on the organoleptic characteristics of MTBE.

Some recent studies indicated that the beneficial effects of fuel oxygenates are fewer for newer vehicles which use more advanced pollution control equipment. With increasing evidence of MTBE in drinking water supplies, the USEPA recommended complete elimination of MTBE from gasoline fuels by 2004. Several states including California,

New York and Connecticut adopted legislations prohibiting the use of MTBE as a fuel oxygenate. Presently, more studies are being conducted to substitute MTBE with ethanol and other oxygenates to meet the 1990 Clean Air Act Amendments requirements.

LITERATURE REVIEW

Physical and chemical characteristics of MTBE

The effectiveness of MTBE treatment methods is directly related to its physical and chemical characteristics. MTBE is a polar organic compound which has a chemical formula of $CH_3OC(CH_3)_3$. At room temperature, it is a volatile, flammable, colorless liquid with a terpene-like odor (Squillace et al. 1997). The taste and odor thresholds for MTBE in water range from 2.0 μg L^{-1} to 680 μg L^{-1} depending on the individual being tested, level of chlorination, temperature of water, and other factors.

It has been suggested that the treatment of MTBE in drinking water using conventional treatment processes (i.e., air stripping and GAC) poses challenges relative to other organic contaminants, particularly benzene, toluene, ethylbenzene and xylenes (BTEX) compounds, because of its unique physical and chemical properties. A summary of the physical and chemical characteristics of MTBE relative to BTEX compounds is presented in Table 1 (Crittenden et al. 1997; OSTP Report 1997; California MTBE Research Partnership 2000). Comparing the characteristics of MTBE with other BTEX compounds helps to show how the selection of the treatment and remediation technologies may differ if MTBE is present in the water:

- MTBE is about 30 times more soluble than benzene in water. Pure MTBE can reach an equilibrium concentration in water of approximately 5 percent, i.e., 48,000 mg L^{-1}. The relatively low organic carbon partitioning coefficient (K_{OC}) and the high water solubility of MTBE make granular activated carbon (GAC) adsorption less effective for MTBE relative to BTEX compounds.
- Henry's constant for MTBEs is approximately an order of magnitude lower than those of BTEX compounds. Therefore, air stripping of MTBE will tend to be more difficult and more costly relative to those other compounds.

Table 1 | Physical and chemical characteristics of MTBE and BTEX compounds

Physical and chemical properties	MTBE	Benzene	Toluene	Ethyl-benzene	o-Xylene
Molecular weight (gmole^{-1})	88	78	92	106	106
Vapor density at 1 atm and 10°C	3.80	3.36	3.97	4.57	4.57
Specific gravity at 25°C	0.744	0.88	0.8669	0.867	0.8802
Boiling point (°C)	53.6–55.2	80.1	110.6	136.25	144.4
Water solubility(mg L^{-1}) at 25 °C	43,000–54,300	1,730	534.8	161	175
Vapor pressure at 25°C (mm Hg)	245–276	76–95	28.4	9.53	6.6
Henry's constant at 25°C (dimensionless)	0.018	0.23	0.272	0.336	0.212
Log K$_{oc}$	1.091–1.049	1.18–2.16	1.56–2.25	2.94	1.68–1.83
				1.98–3.04	
Log K$_{ow}$	1.20	2.36	2.73	3.24	3.10

Date Sources: OSTP Report 1997; Crittenden *et al.* 1997; California MTBE Research Partnership 2000.

- MTBE is three times more volatile than benzene as indicated by the vapor pressure data. When MTBE is present in the soil as a result of gasoline release, it may separate from the rest of the gasoline compounds, reaching the groundwater faster than the BTEX compounds and dissolving rapidly. Once in the groundwater, MTBE travels at about the same rate as the groundwater since it is much less likely to adsorb to soil or organic carbon.

Overview of treatment technologies

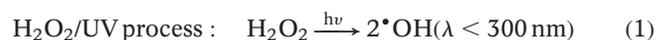MTBE can be removed using one of the following treatment alternatives:

- Advanced oxidation processes (AOPs)
- Air stripping
- Granular activated carbon (GAC) adsorption
- Resin adsorption

Air stripping, GAC and resin adsorption are inefficient in certain cases due to MTBE's relatively low Henry's constant, low organic-carbon partition coefficient and high solubility in water.

AOPs have received an increased interest for MTBE removal due to the limitations of other treatment. AOPs destroy MTBE and other organic contaminants directly in the water through chemical oxidation. The AOPs available for MTBE treatment include: ozone (O$_3$), ultraviolet (UV) photolysis, and their combinations such as O$_3$/peroxide (H$_2$O$_2$) and UV/peroxide. Removal of organic compounds from water by AOPs is primarily accomplished through the reaction of the organic contaminants with the highly reactive hydroxyl radicals (•OH) that can be produced through a variety of mechanisms.

For AOPs, the oxidation of organics can occur by either direct photolysis or reactions with hydroxyl radicals. In direct photolysis, the absorption of UV light by MTBE places it in an electronically excited state, causing it to react with other compounds, and eventually degrade. In contrast, indirect photolysis of MTBE is mediated by hydroxyl radicals that are produced when peroxide is added to the source water either prior to or during UV irradiation. Hydroxyl radicals are produced from the photolytic dissociation of H$_2$O$_2$ in water by UV irradiation (Wagler & Malley 1994). For the UV/peroxide treatment, the degradation of MTBE is primarily due to the oxidation reactions initiated by the highly reactive hydroxyl radicals (Cater *et al.* 2000; Stefan *et al.* 2000):

$$H_2O_2/UV \, process: \quad H_2O_2 \xrightarrow{h\nu} 2\,^{\bullet}OH (\lambda < 300\,nm) \qquad (1)$$

$$^{\bullet}OH + MTBE \longrightarrow Oxidation\ by\text{-}products \qquad (2)$$

The most common sources of UV light are continuous wave low-pressure, high-output mercury vapor lamps (LP-UV) and continuous wave medium-pressure mercury vapor lamps (MP-UV).

UV/peroxide oxidation of MTBE

Wagler & Malley (1994) conducted bench-scale studies to determine the effectiveness of ultraviolet (UV) light, H$_2$O$_2$,

and UV combined with H_2O_2 in removing MTBE from contaminated groundwater in New Hampshire. In general, treatment of a simulated groundwater with pH between 6.5 and 8.0 by UV alone or by H_2O_2 alone produced less than 10% removal of MTBE after 2 hours of exposure. In contrast, the combination of UV and H_2O_2 within the pH range of 5.5 to 10 produced more than 95% removal of MTBE after only 40 minutes of exposure time.

Chang & Young (1999) determined the kinetics of H_2O_2/UV degradation of MTBE by using a re-circulating batch reactor with a low-pressure mercury UV lamp. With a spiked MTBE concentration of $10\,mg\,L^{-1}$, H_2O_2/UV treatment resulted in 99.9% removal. The second order rate constant for the MTBE/•OH reaction under the H_2O_2/UV treatment process was found to be $4.82 \times 10^9\,M^{-1}s^{-1}$. The mean second order rate constant for the reaction of TBF with •OH was found to be $1.19 \times 10^9\,M^{-1}s^{-1}$.

Stefan *et al.* (2000) proposed a detailed reaction mechanism for the degradation of MTBE by UV/peroxide oxidation. According to this mechanism, the primary by-products of MTBE oxidation by •OH are TBF, 2-methoxy-2-methyl propionaldehyde, formaldehyde, acetone, TBA and methyl acetate (Stefan *et al.* 2000). Other intermediates, such as carbonyl compounds (hydroxy-*iso*-butyraldehyde, hydroxyacetone, pyruvaldehyde) and organic acids

(hydroxy-*iso*-butyric, formic, pyruvic, acetic, oxalic) were also detected (Stefan *et al.* 2000).

Cater *et al.* (2000) developed a kinetic model for predicting the electrical energy per order (EE/O) values for MTBE oxidation by UV/peroxide. The EE/O is defined as the number of kilowatt hours of electrical energy required to reduce the concentration of a micropollutant (e.g., MTBE) by one order of magnitude (90%) in one cubic metre of water. The EE/O values for pseudo-first-order degradation of MTBE were found to be between 0.2 and $7.5\,kWh\,m^{-3}\,order^{-1}$ (Cater *et al.* 2000). These EE/O values were found to be a function of the concentrations of MTBE, peroxide and other organics such as BTEX.

MATERIALS AND METHODS

Pilot-scale tests were conducted using LP-UV/peroxide and MP-UV/peroxide treatment systems. Shown in the Table 2 are the test conditions used for evaluating the LP and MP-UV/peroxide processes. The proposed experimental matrix had 14 experiments or trials. Experiment 1 is the baseline experiment with water of ambient quality spiked with $100\,\mu g\,L^{-1}$ of MTBE. In the orthogonal experimental matrix, one condition was changed at a time in subsequent

Table 2 │ MP and LP-UV/peroxide pilot testing experimental matrix

Trial No.	Lamp	MTBE ($\mu g\,L^{-1}$)	MTBE: Peroxide	pH	Nitrate ($mg\,L^{-1}$)	TBA ($\mu g\,L^{-1}$)	Bromide ($mg\,L^{-1}$)
1 Baseline	MP/LP	100	1: 200	Ambient (7.5)	Ambient (20 $mg\,L^{-1}$ as NO_3)	–	Ambient (0.25 $mg\,L^{-1}$)
2	MP/LP	2,900	1: 15	Ambient	Ambient	–	Ambient
3	MP/LP	100	1: 300	Ambient	Ambient	–	Ambient
4	MP/LP	100	1: 50	Ambient	Ambient	–	Ambient
5	MP/LP	100	1: 200	6.5	Ambient	–	Ambient
6	MP/LP	100	1: 200	8.5	Ambient	–	Ambient
7	MP/LP	100	1: 200	Ambient	36	–	Ambient
8	MP/LP	100	1: 200	Ambient	Ambient	200	Ambient
9	MP/LP	100	1: 200	Ambient	Ambient	Ambient	0.5
10	MP/LP	100	1: 200	Ambient	36	200	0.5
11	MP/LP	2,900	1: 15	Ambient	36	200	0.5
12	MP/LP	100	–	Ambient	Ambient	–	Ambient
13	–	100	1: 200	Ambient	Ambient	–	Ambient
14	MP/LP	100	1: 200	Adjusted to Ambient	Half of Ambient	–	Half of Ambient

experiments to isolate the effect. Experiments 1 through 14 were conducted for both LP and MP-UV/peroxide systems.

The goals of the pilot-scale study were to (1) evaluate effects of selected water quality parameters on MTBE removal efficiency by two UV/peroxide systems, (2) identify by-products of MTBE oxidation, and (3) develop design and operating parameters for economic evaluation of potential full-scale facilities treating either surface or groundwater.

The UV/peroxide pilot tests were performed on Santa Monica groundwater and Lake Huron surface water. The average water quality of Santa Monica groundwater and Lake Huron surface water are summarized in Table 3. The pilot tests were conducted at the Ontario Clean Water Agency's surface water treatment plant at Lake Huron in Grand Bend, Ontario, Canada. Approximately, 6,000 gallons of groundwater from Santa Monica was shipped to Grand Bend for pilot testing. The groundwater was sent in a clean tanker truck, in tanker that is normally used for transporting bottled water. At Grand Bend, LP-UV and MP-UV testing was performed employing the reactors that were provided by Trojan Technologies Inc., London, Ontario, Canada. Reagent grade chemicals were used for spiking of MTBE and other compounds to meet the influent water quality conditions. Influent and effluent samples from this testing were sent to a USEPA-certified laboratory for analysis.

Digital images of the UV reactors used for pilot testing are shown in Figure 1. The MP-UV lamp system used in the pilot study had two lamps which were arranged perpendicular to the flow. The MP-UV lamps were rated for 2.8 kiloWatts (kW) power per lamp. The MP-UV lamps were operated at 30% of the full power, i.e., 0.84 kW per lamp.

The reactor volume of the MP-UV is 56 litres (L). The LP-UV system used in the pilot study had three LP-UV lamps arranged parallel to the flow direction. The LP-UV lamps were rated for 0.16 kW per lamp. During pilot testing, the LP-UV lamps were operated at full power. The reactor volume of LP-UV lamps is 38 L.

Both the MP and LP UV reactors were fed Santa Monica and Lake Huron waters from a storage tank of approximately 500-gallon capacity. The feed waters were re-circulated through the UV reactors to achieve the conditions of a completely-stirred tank reactor (as shown in Figure 2). This re-circulation mode of testing simulates a single-pass system through a series of UV reactors, as in full-scale facilities. Batch mode, closed loop re-circulation tests were performed with 900 litres (or 238 gallons) of water per test. The UV/peroxide tests were performed by re-circulating the feed water spiked with MTBE and other constituents (like nitrate in some experiments) at 2,650 litres per minute or 700 gallons per minute (gpm) to yield a retention time of 1 second or less per cycle.

THEORY

The kinetic model describing the rate of oxidation of a micropollutant by UV/peroxide is taken from the work of previous researchers, developed for the monochromatic irradiation at 253.7 nm. The validity of this model is dependent upon the following assumptions and simplifications:

- The decomposition of MTBE is only due to the reaction with H_2O_2 derived hydroxyl radicals. The possible

Table 3 | Santa Monica Groundwater and Lake Huron Surface Water Quality

Parameter	Units	Santa Monica groundwater	Lake Huron surface water
Alkalinity	$mg\,L^{-1}$ as $CaCO_3$	325	82.5
Dissolved organic carbon	$mg\,L^{-1}$	0.45	1.4
Hardness, Total	$mg\,L^{-1}$ as $CaCO_3$	540	95.0
Nitrate as NO_3	$mg\,L^{-1}$	21.5	2.4
pH	Standard Units	8.3	8.3
Total dissolved solids	$mg\,L^{-1}$	750	140
Total organic carbon	$mg\,L^{-1}$	0.52	3.33
Turbidity	NTU	0.14	0.91

Figure 1 | Digital images of the pilot MP-UV and LP-UV lamp systems (Trojan Technologies, Inc.).

reactions between MTBE and other species have been assumed to be negligible.

- The concentration of hydrogen peroxide is assumed to be constant during the course of the reaction.
- The UV absorbance of the water is assumed to be constant during the course of the reaction.

The overall kinetic equation describing the photo-oxidative reactions of MTBE is:

$$\frac{-d[\text{MTBE}]}{dt} = k_{\text{MTBE}}[\text{MTBE}][\cdot\text{OH}]_{\text{SS}}$$

$$= k_{\text{MTBE}}[\text{MTBE}]\frac{2\phi_{\text{H}_2\text{O}_2}N_{0\lambda}F_{\text{S}\lambda}F_{\text{H}_2\text{O}_2\lambda}}{V(k_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2] + \sum k_{\text{s}}[\text{S}])} \quad (3)$$

where: k_{MTBE} is the rate constant for the reaction of MTBE with hydroxyl radicals; [MTBE] is the concentration of MTBE; $[\cdot\text{OH}]_{\text{SS}}$ is the steady state concentration of hydroxyl radicals; $\phi_{\text{H}_2\text{O}_2}$ is the quantum yield for photolysis of peroxide; $N_{0\lambda}$ is the incident photon flux; V is the reactor
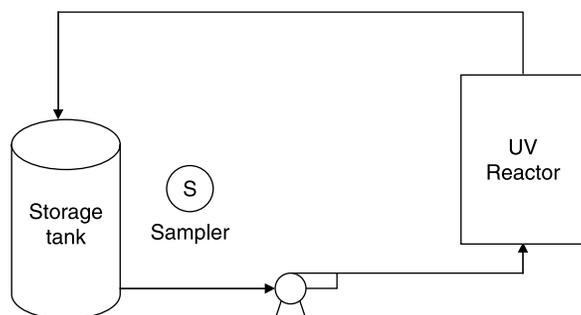
volume and $\sum k_{\text{s}}[\text{S}]$ is the kinetic competition term due to all hydroxyl radical scavengers, and $F_{\text{S}\lambda}$ and $F_{\text{H}_2\text{O}_2\lambda}$ are the fraction of incident light absorbed by the system (i.e., reactor fluid) and the fraction of that absorbed light that is absorbed by hydrogen peroxide respectively. The equations describing $F_{\text{S}\lambda}$ and $F_{\text{H}_2\text{O}_2\lambda}$ are:

$$F_{\text{S}\lambda} = \{1 - 10^{-AL}\} \quad (4)$$

and

$$F_{\text{H}_2\text{O}_2\lambda} = \frac{\varepsilon_\lambda[\text{H}_2\text{O}_2]}{A_\lambda} \quad (5)$$

where, A is the water absorbance at the given wavelength (λ); L is the optical path length of the reactor and ε is molar absorption coefficient for the compound (peroxide).

The overall kinetic equation describing the photolytic and photo-oxidative reaction of MTBE is therefore:

$$-\frac{d[\text{MTBE}]}{dt} = \frac{2k_{\text{MTBE}}\phi_{\text{H}_2\text{O}_2}N_0(1 - 10^{-AL})\varepsilon_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2][\text{MTBE}]}{VA(k_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2] + \sum k_{\text{s}}[\text{S}])} \quad (6)$$

and since

$$\frac{-d[\text{MTBE}]}{dt} = k[\text{MTBE}] \quad (7)$$

describes the pseudo first-order disappearance of MTBE, then:

$$k = \frac{k_{\text{MTBE}}\phi_{\text{H}_2\text{O}_2}N_0(1 - 10^{-AL})\varepsilon_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2]}{VA(k_{\text{H}_2\text{O}_2}[\text{H}_2\text{O}_2] + \sum k_{\text{S}}[\text{S}])}, \text{s}^{-1} \quad (8)$$

Figure 2 | Pilot operation schematic.

and the "water factor" describing the average intensity is:

$$I_{\text{avg}} = \frac{N_0(1 - 10^{-AL})}{\text{Area}*A*L*\text{Ln}(10)} \tag{9}$$

therefore:

$$\frac{k_{\text{MTBE}}}{I_{\text{avg}}} = k'_{\text{MTBE}} = \frac{\text{Ln}(10)\phi_{H_2O_2}\varepsilon_{H_2O_2\lambda}k_{\text{MTBE}}[H_2O_2]}{U_\lambda(k_{H_2O_2}[H_2O_2] + \sum k_s[S])}, \quad \text{cm}^2\text{mJ}^{-1} \tag{10}$$

where,

U_λ is the energy (J) of one Einstein of photons of wavelength λ. $\tag{11}$

The derivation of this fluence (or UV dose) based rate constant parallels the derivation presented by Stefan *et al.* 2000 for direct photolysis applications. This rate constant in units of inverse dose can be determined from Collimated Beam experiments by directly measuring $k(\text{s}^{-1})$ and dividing by the average irradiance (mWcm^{2-1}) in the irradiated sample to arrive at $\text{k}'(\text{cm}^2\text{mJ}^{-1})$. This rate constant can be related to the electrical energy per order (EE/O) parameter for a given reactor by the following (Stefan *et al.* 2000):

$$\text{EE/O} = \frac{P(\text{kW})1000}{Q(\text{gpm})\,60\,\text{Log}(C_0/C)} \tag{12}$$

where, P is the power inputted (kW) from the wall to drive the UV-lamps; Q is the water flow rate (in gallons per minute) through the reactor and C_0 and C are the initial and the final concentrations of the contaminant (e.g., MTBE) under consideration, and from the first order kinetics in the UV reactor:

$$\text{Ln}(C_0/C) = k'D \tag{13}$$

where, D is the UV dose and

$$\text{Log}(C_0/C) = \frac{\text{Ln}(C_0/C)}{\text{Ln}(10)} = \frac{k'D}{\text{Ln}(10)} \tag{14}$$

therefore:

$$\text{EE/O} = \frac{P(\text{kW})1000\,\text{Ln}(10)}{Q(\text{gpm})\,60k'D} = \frac{P(\text{kW})38.38}{Q(\text{gpm})k'D} \tag{15}$$

and since

$$D = I_{\text{avg}}\theta \text{ and } \theta = V_R/Q \tag{16}$$

where, θ is the exposure time and V_R is the reactor volume, then:

$$\text{EE/O} = \frac{0.6396P(\text{kW})}{V_R(\text{gal})k'(\text{cm}^2/\text{mJ})I_{\text{avg}}(\text{mW/cm}^2)} \tag{17}$$

The rate constant k′ was calculated from the pilot data (i.e., EE/O) and the known reactor characteristics (i.e., I_{avg}, V_R, and P). Having calculated the rate constant, the only unknown parameter in the equation for the rate constant is the scavenging term $\sum k_S[S]$. The other parameters (e.g., k_{OH}, $\varepsilon_{H_2O_2}$, λ, $\phi_{H_2O_2}$, A_λ) are either easily measured or are available in the literature. Having thus determined the scavenging capacity of the water, the dependence of the rate constant, k', can be calculated for a range of hydrogen peroxide concentrations. The EE/O can then be calculated for any reactor with these rate constants provided that the average fluence rate and reactor volumes are known. It has to be mentioned that in the case of MP-UV applications the rate constant k' and average fluence rate I_{avg} are wavelength-dependent, through both the fraction of light absorbed by hydrogen peroxide and the molar absorption coefficient $\varepsilon_{H_2O_2}$.

RESULTS AND DISCUSSION

This section presents a summary of the results from MP-UV/peroxide and LP-UV/peroxide systems to treat MTBE in Santa Monica groundwater and Lake Huron surface water. Results presented include the effect of feed water quality (e.g., scavengers), EE/O values, conceptual design/operating conditions and conceptual cost opinions. Results from pilot testing were used in developing the conceptual block diagrams, site layouts and cost opinions.

### Effect of feed water quality on EE/Os

Experiments were conducted to assess the impact of feed water quality on MP and LP-UV/peroxide processes using the following water types:

- Lake Huron and Santa Monica waters spiked with MTBE alone at $1.2\,\mu\text{M}$ and this was defined as the "baseline condition" in the test matrix.

- Lake Huron and Santa Monica waters spiked with MTBE (at 1.2 μM), TBA (at 4.0 μM), nitrate (at 36 mg L^{-1} as N described as nitrate in the rest of the document) and bromide (at 0.5 mg L^{-1}) to simulate "poor water quality condition".

The EE/O (kWh m^{-3} order^{-1}) values measured for MTBE removal from Santa Monica groundwater and Lake Huron surface water are shown in Figure 3. The EE/Os for MTBE removal in Santa Monica water spiked with 1.2 μM (or 100 μg L^{-1}) of MTBE and 200 μM (or 7 mg L^{-1}) of hydrogen peroxide by MP-UV/peroxide and LP-UV/peroxide treatment were respectively 2.20 kWh m^{-3} order^{-1} and 1.44 kWh m^{-3} order^{-1}. In tests conducted with Santa Monica water spiked with MTBE (~1.2 μM), H$_2$O$_2$ (~200 μM), TBA (~4.0 μM), nitrate (~36 mg L^{-1} as N) and bromide (~0.5 mg L^{-1}) to simulate poor quality groundwater, the EE/O values for MP-UV/peroxide and LP-UV/peroxide treatment were 2.58 kWh m^{-3} order^{-1} and 0.96 kWh m^{-3} order^{-1}, respectively. As indicated by the data, the LP-UV/peroxide treatment had lower EE/O values than the MP-UV/peroxide treatment for both the baseline and poor quality water conditions.

As shown in Figure 3, the EE/O values measured for the Lake Huron surface water were lower than those measured for Santa Monica groundwater. Higher EE/O for Santa Monica groundwater can be attributed to the higher carbonate concentration in the water. Carbonate is a known scavenger for the hydroxyl radicals, and being present at elevated levels (scavenging of hydroxyl radical
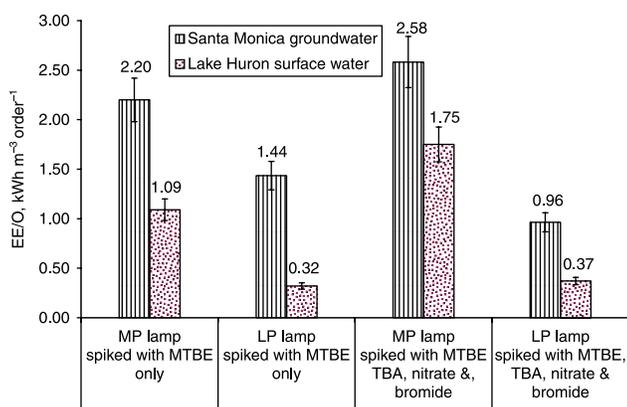
Figure 3 | E/EOs for MP-UV/peroxide and LP-UV/peroxide treatment of Santa Monica and Lake Huron waters.

by the carbonate. Some algae growth was observed in the Santa Monica groundwater that was transported from California and stored at Grand Bend, Ontario (test site). This algae growth may have resulted in an increase in the TOC content and the associated hydroxyl radical scavenging capacity of the water. The lower EE/O values for Lake Huron water is attributed primarily to the lower scavenging capacity of the surface water (no algae) as well as to the lower UV absorption coefficients. The EE/O values measured in this study for MP-UV/peroxide treatment were within the range of EE/Os reported by Cater *et al.* 2000. The earlier studies were performed using batch reactors on Toronto tap water (Cater *et al.* 2000).

Radical scavenging capacities

Experiments were conducted to evaluate effects of bicarbonate, nitrate, TBA, and bromide on MTBE degradation by MP-UV/peroxide and LP-UV/peroxide system. The higher bicarbonate concentrations are known to efficiently scavenge hydroxyl radicals. Carbonate when present at high levels can react with hydroxyl radical (K(•OH/HCO$_3^-$) = 8.5×10^6 M^{-1} s^{-1}; K(•OH/CO$_3^{2-}$) = 3.9×10^8 M^{-1} s^{-1} and thus retard the removal of an organic contaminant through radical pathways. Nitrates in solution may influence the MTBE degradation by two pathways. Nitrates may retard the degradation of MTBE due to their strong UV-absorption in the wavelength region of 190–200 nm where MTBE absorbs or enhance its degradation due to a production of radical species. TBA is a known hydroxyl radical scavenger. Experiments were conducted to evaluate effect of TBA on the MTBE degradation.

The scavenging capacity for Santa Monica water spiked with ~200 μM H$_2$O$_2$ and 1.2 μM MTBE was calculated to be 1.4×10^5 s^{-1}, which is about 3 times the value of 4.72×10^4 s^{-1} that was calculated for ambient Santa Monica water. The effect of peroxide concentration on EE/Os for LP-UV and MP-UV treatment at varying scavenging capacities are shown respectively in Figures 4 and 5. The scavenging capacity for the Lake Huron surface water was calculated as 3.64×10^4 s^{-1} based on a comprehensive water analysis. This value is equal to 77% of that calculated for Santa Monica groundwater (higher carbonate concentration) and, therefore, the LP-UV or MP-UV results

for algae-free Santa Monica water would be similar to those for Lake Huron surface water. It is worthy to note the significant impact on the EE/O of the hydroxyl radical scavenging capacity of the water. The high alkalinity of the Santa Monica water results in a relatively high scavenging capacity of the water. Other natural waters with lower levels of scavenging species will have E/EOs which are correspondingly lower.

An important parameter which determines the efficiency of a photoreactor is its optical pathlength. Essentially, this is the average distance through which a UV photon may travel before it impacts an absorbing surface such as a reactor wall or other absorbing internal surface. For low absorbing waters, the longer the optical pathlength, the greater the opportunity for the photons to be absorbed by the target compound in the water (e.g., H_2O_2). When the pathlength is short much of the electrical energy powering the photoreactor is lost when the photons are absorbed by a surface. For low absorbing waters, the EE/O varies inversely with the optical pathlength of the photoreactor. For highly absorbing waters, the radiation can be absorbed within a distance much shorter than either the physical or average path length. In such cases, the plot of EE/O versus hydrogen peroxide concentration for low/high scavenging waters and pilot/full-scale reactors pathlength reaches a plateau at longer pathlengths. For this reason, large, full-scale photoreactors with longer pathlengths have lower EE/O values than smaller pilot photoreactors. This is especially true for LP-UV lamps whose monochromatic 254 nm emission travels further through the water (i.e., higher UV transmittance) than the shorter polychromatic wavelengths emitted by MP-UV lamps.

Although the pilot reactors used in this study are commercial scale, they are much smaller than those that would be recommended for flows of 1 million gallons day^{-1} or more. Therefore, the EE/O values for full-scale photoreactors were projected to be lower than the EE/Os for pilot reactors (Figures 4 and 5). The EE/O (kWh m^{-3} order^{-1}) can be calculated from the following equation for a batch type reactor stated in the Equation (15). The I_{avg}, V_R, and P are the known characteristics for the given reactor. Hence, based on the pilot information and known information from various full-scale and pilot-scale reactors the EE/Os were calculated and plotted in Figures 4 and 5 for LP-UV/
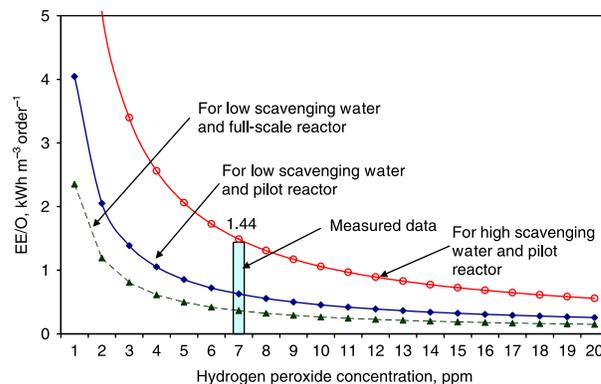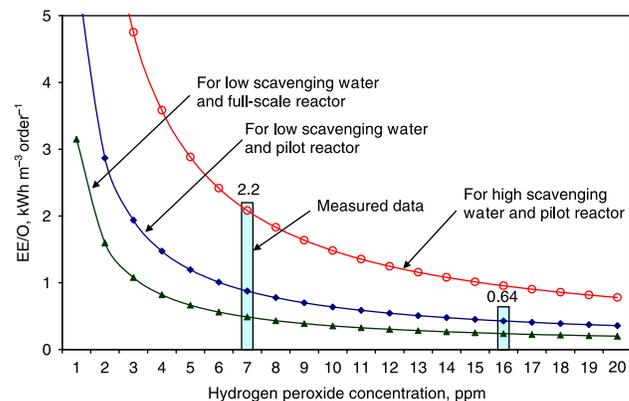

Figure 4 | EE/Os for LP-UV/peroxide treatment of MTBE plotted as a function of initial hydrogen peroxide concentration for low/high scavenging waters and pilot/full-scale reactors.

peroxide and MP-UV/peroxide systems, respectively. These projected E/EO values for full-scale reactors were used as the basis for determining the treatment costs.

Effect of UV lamp on by-products formation

Shown in Figure 6 are the end products after exposure to LP-UV or MP-UV for 2 minutes. These tests were conducted on Santa Monica water spiked with 1.2 μM of MTBE. Higher concentrations of acetone and formaldehyde in waters treated with MP-UV/peroxide indicate possible oxidation of intermediates to these by-products. The data also indicates that for the amount of electrical energy applied in the MP-UV/peroxide process (~ 1.25 kW), which is 3.5 times that of the energy applied in LP-UV/peroxide treatment (~ 0.35 kW), the oxidation pathways may have

Figure 5 | EE/Os for MP-UV/peroxide treatment of MTBE plotted as a function of initial Hydrogen peroxide concentration for low/high scavenging waters and pilot/full-scale reactors.
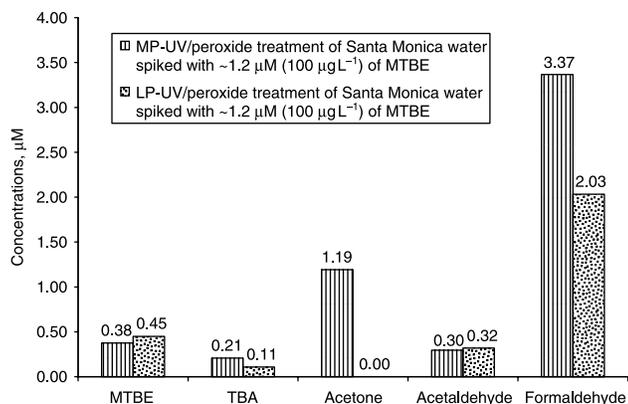
Figure 6 │ End products after ~2 minutes of LP-UV and MP-UV/peroxide treatment.

progressed farther down the reaction pathway (Stefan *et al.* 2000). Polishing treatment with biological activated carbon may be required to remove excess peroxide and end products such as acetone and formaldehyde (AwwaRF Report 2002).

DESIGN CONSIDERATIONS AND TREATMENT COSTS

Process design criteria

The cost for UV/peroxide system was developed for the 1, 3 and 10 mgd systems. Unlike for other AOPs, costs for UV/peroxide treatment were not developed for plant capacities of 0.5 mgd, since there was insufficient information available for systems of this size. The following design criteria were used in developing the UV/peroxide treatment costs for waters with quality comparable to Santa Monica groundwater (with scavenging capacity of $\sim 5 \times 10^4 \, s^{-1}$):

- An EE/O of 0.35 kWh m^{-3} order^{-1} for MTBE removal using MP-UV/peroxide process, with an initial peroxide dose of 15 mg L^{-1}. The EE/O of 0.35 kWh m^{-3} order^{-1} is from Figure 5 for "low scavenging water and full-scale reactor" with hydrogen peroxide dose of 15 mg L^{-1}.
- An EE/O of 0.13 kWh m^{-3} order^{-1} for MTBE removal using LP-UV/peroxide process, with an initial peroxide dose of 15 mg L^{-1}. The EE/O of 0.13 kWh m^{-3} order^{-1} is from Figure 4 for "low scavenging water and full-scale reactor" with hydrogen peroxide dose of 15 mg L^{-1}.

Similar to other AOP technologies, it was assumed that MTBE and its by-products will be further removed by biological GAC treatment. Test data indicated a design loading rate of 2 gpm sf^{-1} and a contact time of 20 minutes is necessary for biological GAC to remove MTBE and its by-products to very low (e.g., non-detect) concentrations. Costs for polishing, biological GAC should be added to the UV/peroxide costs to obtain the total cost for sequential UV/peroxide-biological GAC treatment. Costs were developed for both MP-UV/peroxide and LP-UV/peroxide treatment since the performance data indicated some differences for LP-UV compared to the MP-UV performance.

Process box diagrams and conceptual site layouts

A box diagram of the MP-UV/hydrogen peroxide system is shown in Figure 7. Raw water supply is metered prior to pumping. Booster pumps provide the hydraulic head required for flow through the entire system. Following the pumps, hydrogen peroxide is added to the water at a concentration of 15 mg L^{-1}. Hydrogen peroxide can either
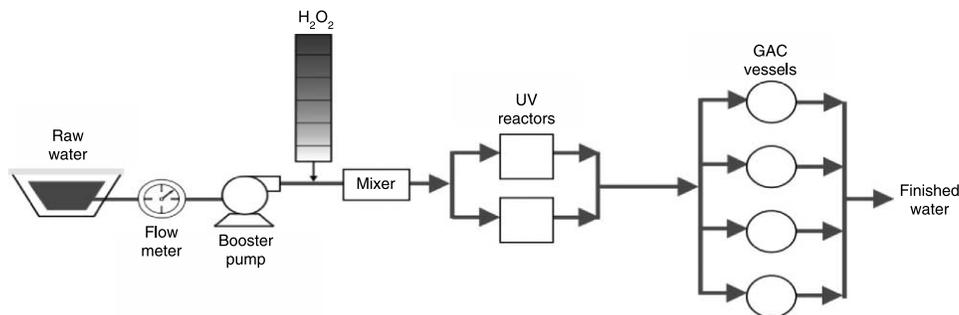

Figure 7 │ Box diagram of MP-UV/peroxide treatment system.

be fed through a venturi-type injector device which facilitates mixing or metered into the process stream and mixed downstream of the injection point via a static or dynamic mixing device. The MTBE contaminated water is then directed through the MP-UV reactors.

The final unit process consists of biologically enhanced GAC polishing to destroy any remaining MTBE and the by-products. Allowing biological growth within the carbon beds enhances the ability of the process to destroy the remaining chemicals and extends the life of the carbon. Pilot testing of GAC resulted in a recommended hydraulic loading of 2 gpm ft^{-2} and a contact time of 20 minutes. The design parameters require multiple pre-manufactured GAC vessels, depending on the flow rate through the system.

Based on the box diagram, potential concept-level site layouts were prepared for 1 mgd (Figure 8) and 10 mgd (Figure 9) treatment systems. Major equipment is shown on the site layout. MTBE contaminated water is pumped from the well pump base and boosted through the booster pump stations. From the booster pumps, the water flows through a mixing device where the hydrogen peroxide is added and mixed. For a 1 mgd system, an 8 feet diameter hydrogen peroxide tank will be required and a 10 feet diameter hydrogen peroxide tank will be required for the 10 mgd system. The process water then flows through a header system and into the UV reactors. The volumes and the number of lamps present in each MP-UV reactor varied with the reactors rated capacity, the assumed EE/O and UV dose. One standby MP-UV reactor train was assumed for all system sizes (0.5 mgd to 10 mgd). The process water is recombined after the UV reactors. Process water would then flow through a distribution header to the GAC vessels. Large pre-manufactured vessels are sold in pairs of 20,000 lb carbon capacity. The size of each vessel is 10 feet in diameter. To meet the hydraulic loading requirement, 4 GAC vessels are required for the 1 mgd system and 40 GAC vessels are required for the 10 mgd system. After determining the number of GAC vessels required to meet the hydraulic loading requirement, the volume of carbon required for each vessel was calculated to meet the required 20 minute contact time. An electrical control room was included to house electrical components and process control equipment.

Technology costs

Shown in Tables 4 and 5 are the costs for MP-UV/peroxide and LP-UV/peroxide treatment, respectively. Every row of the attached cost tables is numbered and the assumptions are described below by row number.

Sizing calculations

(1) Row 1 shows the total number of UV reactor trains, including one redundant train, assumed for each system size.
(2) Number of UV reactor trains in duty at a given time is shown in this row.
(3) One standby UV reactor was assumed for each system.
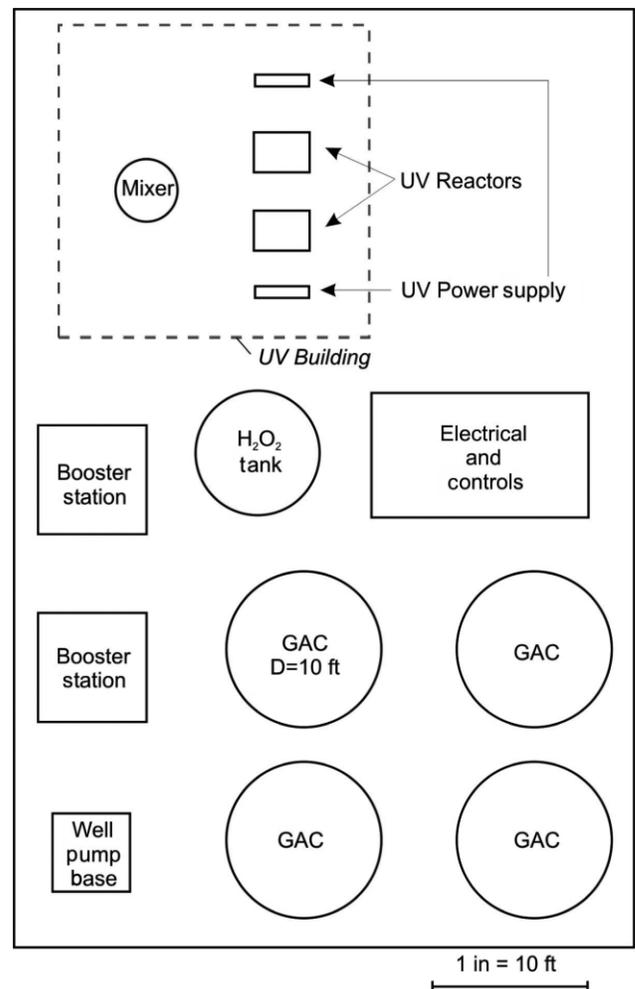(4) One UV transmittance monitor was assumed for each system size.

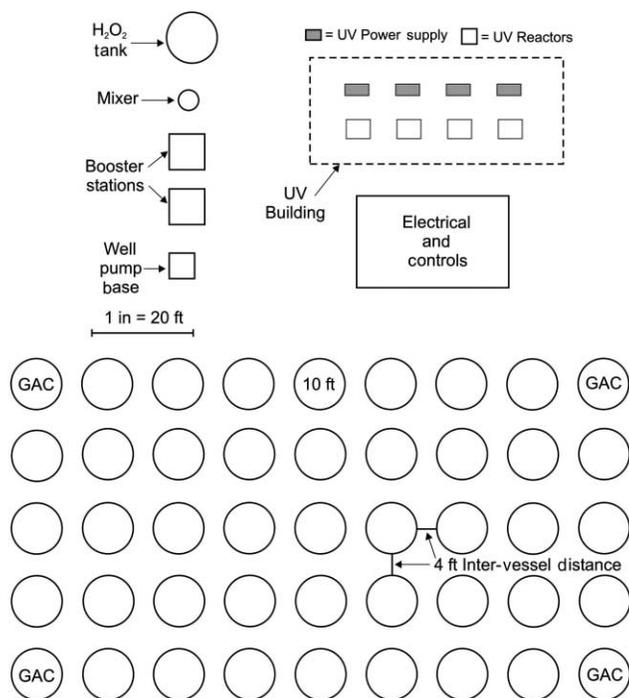**Figure 8** │ Conceptual site layout for 1 mgd MP-UV/peroxide treatment system.

Figure 9 | Conceptual site layout for 10 mgd MP-UV/peroxide treatment system.

(5) Two UV intensity sensors were assumed per reactor.

(6) Two reference UV intensity sensors were assumed per reactor.

(7) Hydrogen peroxide requirements per day were calculated assuming a dose of 15 mg L^{-1} and concentration strength of 35% volume/volume.

(8) UV building sizes were estimated based on reactor sizes and accessory equipment sizes shown in the layout drawings.

Capital cost assumptions

(9) The total cost per UV reactors was obtained by multiplying the number of reactors required (row 1) with the unit cost per reactor. The costs per reactor were obtained from reputed UV manufacturers.

(10) UV manufacturers provided the costs for lamps based on the assumed EE/Os.

(11) The cost for quartz sleeves was also provided the UV manufacturers. Assumed each UV lamp to be provided with a quartz sleeve.

(12) Ballast cost was obtained from manufacturers. Assumed one ballast per two lamps.

(13) One UV transmittance monitor was assumed at unit cost of $15,000. This is also based on vendor quotes.

(14) UV intensity sensor costs were obtained from vendors.

(15) Reference UV intensity sensor costs were also obtained from manufacturers.

(16) Costs for pipes, valves, tees and adapters were estimated based on the amount of piping and valving necessary to install the UV reactors.

(17) Uninterrupted power supply costs were also provided by the manufacturers.

(18) Peroxide storage tank costs were provided by the tank vendors.

(19) Peroxide injection system costs were provided by vendors.

(20) Process cost subtotal consists of the sum of all the above-discussed process costs (rows 9–19).

(21) Process cost multiplier of 2.5 for flow rates equal to or below 1 mgd and 2.0 for flow rates above 1 mgd was used to obtain direct capital cost from process cost. Direct capital cost was obtained by multiplying the process cost (row 20) with the indicated multipliers. The multipliers account for: site work, contractor's overhead and profit, contingencies, engineering and design, mobilization and bonding, legal and administrative, interest during construction, and installation.

(22) Piloting costs were assumed to be $10,000 for flow rates below 1 mgd and $65,000 for flow rates equal to and above 1 mgd. For large systems, the piloting costs were calculated at $65,000 and for small systems it was assumed that limited piloting would be provided for by $10,000.

(23) Permit costs were assumed to be 3% of the process cost subtotal (row 20), with a minimum of $2,500.

(24) Land costs were assumed to be 3% of the process cost subtotal (row 20).

(25) Operator training costs were based on 40 hours of supervisory training at a rate of $45/hour.

(26) The building size for housing was estimated from the footprints (row 8). Costs were developed from the RS Means Building Construction Cost (2002) data for warehouse/office space and equal to $62/sq.ft.

(27) Indirect capital cost subtotal is a sum of all the indirect process costs described in rows 22 through 26.

(28) Total capital cost equals the sum of indirect (row 27) and direct (row 21) capital costs.

Table 4 | Capital, O&M and total costs for MP-UV/peroxide treatment of MTBE

Design flow (mgd)		1	3	10
Design flow (gpm)		695	2,084	6,945
Sizing calculations				
Number of UV reactor trains	(1)	2	2	3
Number of UV reactor trains in duty	(2)	1	1	2
Number of UV reactor trains in standby	(3)	1	1	1
Number of UVT monitors	(4)	1	1	1
Number of UV intensity sensors/reactor	(5)	2	2	2
Number of reference UV intensity sensors/reactor	(6)	1	1	1
Hydrogen peroxide required (gal d^{-1})	(7)	38	114	379
UV building size (ft × ft)	(8)	20 × 20	20 × 20	40 × 20
Capital cost summary				
Process capital cost				
UV reactor cost	(9)	$400,000	$600,000	$900,000
UV lamp cost	(10)	$4,400	$8,800	$17,600
Sleeves cost	(11)	$4,800	$9,600	$14,400
Ballast cost	(12)	$7,200	$14,400	$28,800
UVT monitor cost	(13)	$15,000	$15,000	$15,000
UV intensity sensor cost	(14)	$500	$500	$750
Reference UV intensity sensor cost	(15)	$250	$250	$375
Pipes, valves, tees, couplings, adapters	(16)	$40,000	$50,000	$55,000
Uninterrupted power supply	(17)	$30,000	$40,000	$60,000
Peroxide storage tank	(18)	$36,000	$36,000	$40,000
Peroxide injection system	(19)	$9,000	$9,000	$10,000
Subtotal process cost	(20)	$530,000	$750,000	$1,080,000
Direct capital cost	(21)	$1,325,000	$1,875,000	$2,700,000
Indirect capital cost summary				
Piloting	(22)	$65,000	$65,000	$65,000
Permitting	(23)	$15,900	$22,500	$32,400
Land	(24)	$15,900	$22,500	$32,400
Operator training	(25)	$1,800	$1,800	$1,800
Housing	(26)	$24,800	$24,800	$49,600
Indirect capital cost	(27)	$123,400	$136,600	$181,200
Total capital cost	(28)	$1,448,400	$2,011,600	$2,881,200
Annual O&M summary				
Chemicals (Peroxide)	(29)	$76,048	$228,143	$760,478
Materials (Lamps, sensors, sleeves, ballast replacement)	(30)	$12,193	$24,235	$60,292
Electricity	(31)	$33,360	$100,079	$333,597
Labor	(32)	$36,500	$54,750	$73,000
Total annual O&M cost	(33)	$158,100	$407,208	$1,227,367
For a project period of 20 years with 7% interest				
Amortized total annual cost	(34)	$294,250	$596,298	$1,498,200
Cost/1,000 gallons treated	(35)	$0.81	$0.54	$0.41

Table 5 | Capital, O&M and total costs for LP-UV/peroxide treatment of MTBE

Design flow (mgd)		1	3	10
Design flow (gpm)		695	2,084	6,945
Sizing calculations				
Number of UV reactor trains	(1)	2	5	13
Number of UV reactor trains in duty	(2)	1	4	12
Number of UV reactor trains in standby	(3)	1	1	1
Number of UVT monitors	(4)	1	1	1
Number of UV intensity sensors/reactor	(5)	1	1	1
Number of reference UV intensity sensors/reactor	(6)	1	1	1
Hydrogen peroxide required (gal d^{-1})	(7)	38	114	379
UV building size (ft × ft)	(8)	20 × 20	20 × 20	40 × 20
Capital cost summary				
Process capital cost				
UV reactor cost	(9)	$260,000	$650,000	$1,690,000
UV lamp cost	(10)	$10,800	$43,200	$129,600
Sleeves cost	(11)	$7,200	$18,000	$46,800
Ballast cost	(12)	$10,800	$43,200	$129,600
UVT monitor cost	(13)	$15,000	$15,000	$15,000
UV intensity sensor cost	(14)	$250	$625	$1,625
Reference UV intensity sensor cost	(15)	$250	$625	$1,625
Pipes, valves, tees, couplings, adapters	(16)	$40,000	$50,000	$55,000
Uninterrupted power supply	(17)	$30,000	$40,000	$60,000
Peroxide storage tank	(18)	$36,000	$36,000	$40,000
Peroxide injection system	(19)	$9,000	$9,000	$10,000
Subtotal process cost	(20)	$390,000	$800,000	$1,870,000
Direct capital cost	(21)	$975,000	$2,000,000	$4,675,000
Indirect capital cost summary				
Piloting	(22)	$65,000	$65,000	$65,000
Permitting	(23)	$11,700	$24,000	$56,100
Land	(24)	$11,700	$24,000	$56,100
Operator training	(25)	$1,800	$1,800	$1,800
Housing	(26)	$24,800	$24,800	$49,600
Indirect capital cost	(27)	$115,000	$139,600	$228,600
Total capital cost	(28)	$1,090,000	$2,139,600	$4,903,600
Annual O&M summary				
Chemicals (Peroxide)	(29)	$76,048	$228,143	$760,478
Materials (lamps, sensors, sleeves, ballast replacement)	(30)	$10,869	$42,248	$125,923
Electricity	(31)	$17,253	$51,760	$172,532
Labor	(32)	$36,500	$54,750	$73,000
Total annual O&M Cost	(33)	$96,885	$245,545	$694,082
For a project period of 20 years with 7% interest				
Amortized total annual cost	(34)	$199,345	$446,668	$1,155,020
Cost/1,000 gallons treated	(35)	$0.55	$0.41	$0.32

O&M cost assumptions

(29) Chemical costs for hydrogen peroxide was assumed to be $5.50/gallon.

(30) The material cost was developed assuming once a year replacement for UV lamps and once in five years replacement of sleeves, ballasts, intensity sensors and reference sensors.

(31) Electricity costs were computed based on EE/Os and unit cost of power of $0.08/kWh. The building maintenance power, assumed at 20% of the UV process power, is also included.

(32) Labor costs were estimated using the following assumptions:

   for 0.5 mgd system need 2 hours day^{-1} of operator/ maintenance time,

   for 1.0 mgd system need 4 hours day^{-1} of operator/ maintenance time,

   for 3.0 mgd system need 6 hours day^{-1} of operator/ maintenance time and

   for 10 mgd system need 8 hours day^{-1} of operator/ maintenance time.

   The labor rate was assumed at a typical technician rate of $25/hour.

(33) Annual O&M subtotal consists of the sum of all the O&M costs (rows 29–32).

Total Cost Assumptions

(34) The total capital costs (row 28) were amortized over 20 years at a 7% interest rate and then annual O&M (row 33) was added to derive the amortized total annual cost.

(35) Cost per thousand gallons treated was calculated by dividing the amortized total annual cost (row 34) by the flow rate in thousands of gallons and the days in a year.

SUMMARY

Continuous UV/peroxide pilot tests were conducted using LP and MP lamps on Santa Monica groundwater and Lake Huron surface waters. The EE/O (kWh m^{-3} order^{-1}) values for MTBE removal in Santa Monica water spiked with 1.2 μM (or 100 μg L^{-1}) of MTBE by MP-UV/peroxide and LP-UV/peroxide treatment were respectively 2.2 kWh m^{-3} order^{-1} and 0.7 kWh m^{-3} order^{-1}. In tests conducted with

Santa Monica water spiked with MTBE (~ 1.2 μM), TBA (~ 4.0 μM), nitrate (~ 36 mg L^{-1} as N) and bromide (~ 0.5 mg L^{-1}) to simulate poor quality groundwater, the EE/O values for MP-UV/peroxide and LP-UV/peroxide treatment were 2.58 kWh m^{-3} order^{-1} and 0.96 kWh m^{-3} order^{-1}, respectively. As indicated by the aforementioned results, the LP-UV/peroxide treatment had slightly lower EE/O values than MP-UV/peroxide treatment. In a test conducted with Santa Monica water spiked with 33 μM (or 2,900 μg L^{-1}) MTBE and 480 μM (or 16 ppm) H$_2$O$_2$, an EE/O of 0.64 kWh m^{-3} order^{-1} was measured for MP-UV/peroxide treatment of MTBE. This result illustrates the inverse relationship between EE/O and peroxide concentration within the tested dosage range.

Some algae growth was observed in the Santa Monica water that was stored in a large (3,000 gallon) storage tank at the Lake Huron Water Treatment Plant testing site. This algae growth may have resulted in an increase in TOC content and the associated hydroxyl radical scavenging capacity. The scavenging capacity for Santa Monica water was calculated based on the measured LP-UV/peroxide EE/O (of 1.44 kWh m^{-3} order^{-1}) with ~ 200 μM H$_2$O$_2$ and 1.2 μM MTBE. This scavenging capacity was found to be 1.4×10^5 s^{-1} or 2.5 times the value of 5.57×10^4 s^{-1} that was calculated for the Santa Monica water quality. The EE/O values measured for the Lake Huron surface water were lower than those for Santa Monica groundwater. This is attributed primarily to the lower scavenging capacity (no algae) as well as to the lower UV absorption coefficients for the Lake Huron water. The scavenging capacity of the Lake Huron surface water was calculated to be 4.7×10^4 s^{-1} based on a comprehensive water analysis.

It should be noted that the EE/O varies inversely with the optical pathlength of the photoreactor. Therefore, large, full-scale photoreactors with long pathlengths may result in lower EE/O values than those measured in this study. The EE/O values observed in this study were slightly lower than those reported in the literature for MP-UV/peroxide treatment (Cater *et al.* 2000). The EE/O values reported in the literature were developed using batch reactors and they varied between 0.2 kWh m^{-3} order^{-1} to 7.5 kWh m^{-3} order^{-1} (Cater *et al.* 2000).

The MP-UV/peroxide treatment resulted in higher acetone and formaldehyde generation compared to

LP-UV/peroxide treatment. This indicates that the MP-UV/peroxide treatment progressed farther in the oxidation pathway than the LP-UV/peroxide treatment.

Capital and operations and maintenance (O&M) costs were developed for MP-UV/peroxide and LP-UV/peroxide treatment of MTBE contaminated waters for three system sizes, 1 mgd, 3 mgd and 10 mgd. The cost per 1,000 gallons of treated water for MP-UV/peroxide treatment of MTBE varied from $0.81 (for 1 mgd system) to $0.41 (for 10 mgd system). For LP-UV/peroxide treatment, the costs per 1,000 gallons of treated water varied from $0.55 (for 1 mgd) to $0.32 (for 10 mgd). Polishing treatment with BAC is necessary and would cost an additional $0.20 per 1,000 gallons. For more details on this study consult AwwaRF report (2002).

DISCLAIMER

REFERENCES

AwwaRF 2002 *Removal of MTBE with Advanced Oxidation Processes*. AWWA Research Foundation, Denver, CO, USA.
California MTBE Research Partnership 2000 *Treatment Technologies for Removal of Methyl Tertiary Butyl Ether (MTBE) from Drinking Water: Air stripping, Advanced Oxidation Processes, Granular Activated Carbon, Synthetic Resin Sorbents*, 2nd edition. Center for the Groundwater Restoration and Protection, National Water Research Institute, Fountain Valley, CA.
Cater, S. R., Stefan, M. I., Bolton, J. R. & Safarzadeh-Amiri, A. 2000 UV/H$_2$O$_2$ Treatment of methyl tert-butyl ether in contaminated waters. *Environ. Sci. Technol.* **34**(4), 659–662.
Chang, P. & Young, T. 1999 *Reactivity and By-products of Methyl Tertiary-Butyl Ether Resulting from Water Treatment Processes*. University of California Toxic Substances Research & Teaching Program. University of California, Davis. CA.
Crittenden, J., Hand, D., Perram, D. L. & Marchand, E. G. 1997 *Environmental Technologies Design Option Tools (ETDOT) for the Clean Process Advisory Systems–Adsorption, Aeration and Physical Properties Software*. National Center for Clean Industrial and Treatment Technologies, Michigan Technological University.
Gullick, R. W. & LeChevallier, M. W. 2000 Occurrence of MTBE in drinking water sources. *AWWA J.* **92**(1), 100–113.
OSTP 1997 *Office of Science and Technology Policy Report*. Executive Office of the President. National Science and Technology Council. Committee on Environmental and Natural Resources. Interagency Assessment of Oxygenated Fuels. Washington, D.C., USA.
Squillace, P. J., Pankow, J. F., Korte, N. E. & Zogorski, J. S. 1997 Review of the environmental behavior and fate of methyl tert-butyl ether. *Environ. Toxicol. Chem.* **16**(9), 1836–1844.
Stefan, M. I., Mack, J. & Bolton, J. R. 2000 Degradation pathways during the treatment of methyl tert-butyl ether by the UV/H$_2$O$_2$ process. *J. Environ. Sci. Technol.* **34**(4), 650–658.
USEPA 1997 *Advisory: Consumer Acceptability Advice and Health Effects Analysis on Methyl Tertiary-Butyl Ether (MTBE)*. EPA 822-F-97-008.
USEPA 1998 *MTBE Fact Sheet #3, Use and Distribution of MTBE and Ethanol. EPA 510-F97-016*. Office of Solid Waste and Emergency Response, Washington, D.C.
Wagler, J. L. & Malley, J. P. Jr. 1994 The removal of MTBE from a model groundwater using UV/peroxide oxidation. *J. N. Engl. Water Works Assoc.* **108**, 236–243.