01 Jan 2000

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Recommended Citation

J. Sutherland et al., "Chemical Oxidation of MTBE under O2-Rich and O2-Limited Environments Coupled with Biological Degradation of Oxidation Byproducts," *Environmental and Pipeline Engineering 2000*, pp. 174 - 180, American Society of Civil Engineers, Jan 2000.
The definitive version is available at https://doi.org/10.1061/40507(282)20

Chemical Oxidation of MTBE under O_2-Rich and O_2-Limited Environments Coupled with Biological Degradation of Oxidation Byproducts

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Abstract

The H_2O_2/UV advanced oxidation process (AOP) was investigated to determine byproduct formation under different experimental conditions (pH, alkalinity, and H_2O_2/UV dose). A key factor in the efficiency of the AOP was the dissolved oxygen concentration. Gas chromatography/mass spectrometry (GC/MS) analysis was used to identify byproducts resulting from oxidation under oxygen-rich and oxygen-limited conditions. Resultant oxidation byproducts were analyzed for their susceptibility to biological degradation. Biodegradation rate constants were determined and modeled for the primary byproducts of the advanced oxidation process. Inhibition resulting from the presence of multiple byproducts in a biological system was investigated as well. Effects of process parameters such as pH, alkalinity, and residual H_2O_2 concentrations were also determined.

Introduction

MTBE has been used in gasoline since the late 1970s as an octane-enhancing replacement for lead. The 1990 amendments to the Clean Air Act mandated a weight percentage of oxygen in gasoline to reduce carbon monoxide emissions. MTBE is the most widely used compound to meet this requirement. It can constitute up to 15% (by volume) of oxygenated fuel (USEPA, 1998). Between 1984 and 1994, the annual increase in production of MTBE was an average of 26% (Kirschner, 1995). The production of MTBE was estimated to be eight billion-kg in 1995, and in 1997 the Oxygenated Fuels Association estimated that 70% of all gasoline in the United States contained the compound (Eweis, 1998).

MTBE is a possible human carcinogen that has the ability to move through the subsurface and into groundwater systems. MTBE is more volatile (V_p=245-251 mm Hg)[1], more soluble (43,000-54,300 mg/L), and more mobile (log K_{ow}=0.94-1.30) than BTEX compounds, which have been of greatest concern in the past. MTBE is considered to be recalcitrant to biological degradation and is difficult to remove from groundwater using conventional processes. The hydrophilic nature of MTBE makes carbon adsorption inefficient. The Henry's constant is also relatively low for MTBE (K_h=0.00058-0.003 atm

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m^3 mol^{-1}) (Squillace et al., 1997) making air stripping inefficient due to the large air-water ratios required.

Advanced oxidation treatment (AOT) remains as a viable alternative and has been successfully used to degrade MTBE into simpler compounds (Wagler and Malley, Jr., 1994) supporting the possibility of an Integrated Chemical/Biological (ICB) process to remove MTBE from groundwater. The use of AOTs implies the use of hydroxyl radicals in initiating degradation reactions. Specifically for the degradation of MTBE, processes such as sonolysis/O_3 (Kang and Hoffman,1998), peroxone (O_3/ H_2O_2) (Sun et al., 1999), and H_2O_2/UV (Stefan et al., 2000) have been used to generate the necessary hydroxyl radicals.

Stefan et al. (2000) emphasized the importance of oxygen on the byproduct pathways for MTBE by a H_2O_2/UV process. Additionally, they describe pathway mechanisms that features carbon-centered radicals. However, their investigation dealt with a non-constant dissolved oxygen concentration. Building on a similar hypothesis, experiments presented here targeted constant dissolved oxygen concentrations.

Materials and Methods

Chemical Methods

A 4.0-liter Pyrex photoreactor was used to carry out UV/H_2O_2 chemical oxidation. The reactor was fitted with a quartz sleeve, leaving 3.6 liters for the reaction volume. A 460-watt medium pressure lamp was placed in the sleeve. The lamp is broad spectrum and emits radiation from the ultraviolet (UV) to the infrared (IR). The reactor was kept at 20(±2)°C with distilled water externally recycled from a cooling bath and fed through heat exchanger coils (Tygon tubing wrapped around the outside of the reactor) and an annular space in the quartz sleeve.

The availability of oxygen in the reactor liquid was maintained by first filling the headspace with either oxygen or nitrogen. Then the headspace gas was internally sparged and recirculated into the liquid with a peristaltic pump. The headspace occupied 0.2 liters of the reactor.

A 10 mM phosphate buffer was used to hold the pH at either 6 or 8. The reactor was spiked with an initial MTBE concentration of 300 mg/L. The initial hydrogen peroxide concentration was 200 mg/L and held between 200 and 100 mg/L for the duration of an experiment. Subsequent experiments discussed in this paper used initial concentrations of 25 and 100 for MTBE and H_2O_2, respectively.

Qualitative analysis of the byproducts was conducted with gas chromatography/mass spectrometry (GC/MS). A GC/FID was used to determine byproduct concentrations and a TOC analyzer was used to determine the dissolved organic carbon concentrations. Hydrogen peroxide was measured with Hach Model HYP-1 thiosulfate titration method.

Biological Degradation

Susceptibility of oxidation byproducts to biodegradation was determined using a native culture (volatile suspended solids (VSS) concentration = 3,950 ± 470 mg/L) from the return activated sludge (RAS) of the Bissell Point Publicly Owned Treatment Works

(POTW) in St. Louis, MO. An enhanced culture from the RAS was used in kinetic, inhibition, and residual peroxide experiments. The enhanced culture was maintained in an aerated batch reactor at room temperature, with a mean cell residence time of 100-120 days. It was fed a combination of acetone, methyl acetate, and nutrient solution and had an average VSS of 750 mg/L over the duration of the project.

Preliminary experiments were performed in 22-mL vials sealed with crimp top Teflon lined septa. Various concentrations of native culture were used for each test at liquid volumes of 11 mL. The compounds analyzed were added to the vials producing final concentrations of 30-40 mg/L. Vials were then incubated at room temperature on an orbital shaker table. Studies to estimate kinetic constants, inhibition parameters, and residual H_2O_2 effects were performed in 255-mL bottles capped with MiniNert valves. The bottles were filled with 200 mL of enriched microbial solution from the batch reactor and spiked with the compound to be analyzed producing liquid concentrations of 1-40 mg/L. Bottles were incubated at room temperature on an orbital shaker table.

Compound concentrations were monitored over time using headspace analysis on a HP Series II 5890 gas chromatograph (GC) equipped with a flame ionization detector and 30m, 0.45mm, 2.5μm DB-VRX capillary column. Once the compound concentration went below detectable limits, the solution was spiked with the same compound at the same concentration and monitored again until the compound concentration was undetectable. At the end of each test, the final temperature, pH, and solids concentration were determined.

Results and Discussion

Oxygen-rich versus oxygen-limited conditions - Dissolved oxygen proved to be a significant factor in the process of converting MTBE into biodegradable byproducts. The major byproducts under oxygen-rich conditions were TBF, TBA, methyl acetate, acetone, and formic acid. The same major byproducts were found under oxygen-limited conditions. However, the formation of more than 50 other byproducts (some of which were polymers) decreased their presence.

It is hypothesized that carbon-centered radicals are being formed under both oxygen-rich and oxygen-limited conditions. Under oxygen-rich conditions there is an ample source of oxygen for reactions with the carbon-centered radicals. The byproduct pathways tend to be driven toward lower molecular weight compounds like methyl acetate, acetone and formic acid. With less oxygen to interact with under the nitrogen-sparge, the carbon-centered radicals appear to be forming a variety of polymerized compounds with each other. The formation of these polymers caused wastage of hydrogen peroxide. The hydroxyl radicals react with the polymers leaving less to react with MTBE or TBF. Therefore, additional hydrogen peroxide and reaction time was needed beyond that used under oxygenated conditions.

Typical data for MTBE and TBF degradation are presented in Table 1. This data shows times required to reach non-detectable concentrations of both compounds in relation to the dissolved oxygen concentration. TBF is similar to MTBE in that it is recalcitrant (which will be discussed later in this article) and, thus, a target for chemical oxidation. It was decided that the oxidation process should continue until TBF has reached non-detectable concentrations as well. As Table 1a shows for the nitrogen-sparge

condition, MTBE and TBF were not detectable after 24 minutes and 56 minutes, respectively. Similarly, Table 1b shows that under an oxygen-sparge, MTBE and TBF reached non-detectable concentrations in 14 minutes and 26 minutes, respectively. This was significantly less time than with a nitrogen-sparge, even with a higher initial MTBE concentration for the oxygen-sparged system.

Subsequent experiments were performed taking into account dissolved oxygen as a key parameter for efficient MTBE oxidation. Table 2 shows typical results from these experiments. Despite the detectable concentrations of TBF, this particular end product would potentially be ready for biodegradation. Notwithstanding the differences in the initial concentrations of MTBE and H_2O_2 (listed in the Table 2 caption) from the previous experiments, the major byproducts are the same.

Table 1a. Removal of MTBE and TBF with nitrogen sparge versus time

	Time (minutes)												
Compound	**0**	**2**	**8**	**14**	**18**	**24**	**26**	**36**	**44**	**48**	**54**	**56**	**60**
[MTBE] (mg/L)	178.9 ± 10.1	73.5 ± 10.4	21.9 ± 1.0	5.7 ± 8.1	5.0 ± 1.0	1.7 ± 0.1	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]
[TBF] (mg/L)	ND[1]	9.1 ± 1.2	31.2 ± 1.2	33.8 ± 1.9	27.5 ± 1.2	21.0 ± 0.1	22.6 ± 1.4	11.7 ± 0.9	8.0 ± 0.3	5.3 ± 0.4	2.2 ± 0.2	2.4 ± 0.5	ND[1]

Table 1b. Removal of MTBE and TBF with oxygen sparge versus time

	Time (minutes)								
Compound	**0**	**2**	**6**	**14**	**18**	**24**	**26**	**36**	**40**
[MTBE] (mg/L)	252.0 ± 0.8	131.1 ± 9.3	37.4 ± 1.2	3.4 ± 0.1	ND[1]	ND[1]	ND[1]	ND[1]	ND[1]
[TBF] (mg/L)	12.9 ± 0.2	61.8 ± 2.8	67.7 ± 1.2	43.3 ± 2.0	28.3 ± 1.8	12.6 ± 0.2	8.4 ± 1.0	ND[1]	ND[1]

[1]ND, non-detectable

Table 2. Concentration of MTBE and its oxidation byproducts using the procedure described in Materials and Methods with an O_2 sparge, $[H_2O_2]_o$=100 mg/L, $[MTBE]_o$=25 mg/L

	Time (minutes)							
Compound	**0**	**0.5**	**1**	**1.5**	**2**	**3**	**4**	**5**
[MTBE] (mg/L)	24.8 ± 0.2	8.7 ± 0.2	4.4 ± 0.006	2.1 ± 0.1	1.3 ± 0.04	ND[1]	ND[1]	ND[1]
[TBF] (mg/L)	ND[1]	8.8 ± 0.2	8.0 ± 0.2	6.1 ± 0.1	6.0 ± 0.5	4.1 ± 0.7	2.2 ± 0.05	1.2 ± 0.1
[TBA] (mg/L)	ND[1]	3.7 ± 1.7	4.6 ± 2.1	2.8 ± 0.7	2.9 ± 0.4	2.1 ± 1.8	1.0 ± 1.0	1.4 ± 1.3
[MA] (mg/L)	ND[1]	ND[1]	ND[1]	1.2 ± 0.05	ND[1]	2.2 ± 0.5	2.4 ± 0.6	1.0 ± 0.9
[Acetone] (mg/L)	2.3 ± 1	1.3 ± 0.2	2.3 ± 0.3	2.8 ± 0.3	4.1 ± 0.5	4.2 ± 0.9	4.7 ± 0.5	4.4 ± 0.3
[FA] (mg/L)	ND[1]	1.2 ± 0.3	10.6 ± 0.5	11.3 ± 0.8	11.6 ± 0.8	6.5 ± 0.9	4.2 ± 0.2	2.5 ± 0.1

[1]ND, non-detectable

Byproduct Biodegradation - Preliminary biodegradation studies using native cultures (initial compound concentrations = 30 mg/L) showed that acetone and methyl acetate were completely degraded in 9 days, while MTBE, TBA, and TBF showed no signs of degradation after 7 days. Further degradation tests were performed with the enhanced culture after 60- and 150-days of enrichment. Degradation data was analyzed using a zero order model (Table 3) and a utilization model from Monod kinetics (not shown).

Compound degradation, when multiple carbon sources were present, was evaluated using the 150-day enriched culture. Acetone was incubated with different combinations of methyl acetate, formic acid, MTBE, and TBA. Acetone was removed below detectable limits for all experimental combinations, however, the rate was slower than the rates observed for acetone degradation when it was the sole carbon source. In all cases, methyl acetate was immediately degraded at rates similar to those observed when it was the sole carbon source (Table 4). When acetone and methyl acetate were present together, methyl acetate was preferentially degraded, followed by acetone. Acetone degradation showed a similar lag when formic acid was present.

Table 3 Results of biodegradation tests performed at similar initial conditions

	Parameter	Native Culture[1]	60-Day Enriched Culture[2]	150-Day Enriched Culture[2]
Acetone	zero order removal rate ($mg/L\ min^{-1}$)	0.0019	0.0711	0.0197
	VSS (mg/L)	825 ± 80	920 ± 40	750 ± 30
Methyl Acetate	zero order removal rate ($mg/L\ min^{-1}$)	0.0034	0.3729	0.2675
	VSS (mg/L)	590 ± 180	630 ± 10	420 ± 20

[1]Performed in 22-mL vials with 11 mL of solution
[2]Performed in 255-mL bottles with 200 mL of solution

Table 4 Results of biodegradation tests when multiple compounds were present (initial compound concentration = 15 mg/L)

Compounds In Reactor[1]	Zero Order Removal Rate for Acetone (mg/L min^{-1})	Zero Order Removal Rate for Methyl Acetate (mg/L min^{-1})
A	0.0854	
MA		0.250
A-MA	0.0119	0.161
A-FA	0.00949	
MA-FA		0.160
A-MA-FA	0.0141	0.153
A-MA-FA-TBA-MTBE	0.0171	0.503

[1]A, acetone; MA, methyl acetate; FA, formic acid; TBA, *tertiary*-butyl alcohol

The effect of H_2O_2 on the degradation of a combination of acetone, methyl acetate, and formic acid by the 150-day enriched culture was examined at initial peroxide concentrations of 11.7-304.2 mg/L. H_2O_2 appeared to enhance degradation at lower concentrations while significantly slowing it at higher concentrations. At H_2O_2 = 30.4 mg/L, 15 mg/L of methyl acetate and acetone were removed to non-detectable levels in 35 and 900 minutes respectively as compared to 86 and 962 minutes when H_2O_2 = 0 mg/L. However, at H_2O_2 = 304 mg/L it took over 70 minutes for methyl acetate to reach non-detectable levels and over 2,100 minutes for acetone.

Conclusions

Dissolved oxygen has proven to be a significant factor in the oxidation of MTBE by an H_2O_2/UV system. Fewer and more oxidized byproducts resulted from oxygen-rich conditions. However, under oxygen-limited conditions, there was a random formation of polymers and other byproducts that caused wastage of oxidant and energy.

Acetone and methyl acetate are biodegradable at rapid rates while MTBE, TBA, and TBF appear to be recalcitrant to the enriched culture. When multiple carbon sources in the form of acetone, methyl acetate, formic acid, MTBE, and TBA were present, the enriched culture selectively degraded methyl acetate first followed by acetone. There was a slight lag before acetone began degrading in each experiment when other biodegradable carbon sources were present. Hydrogen peroxide appeared to increase the removal rate at low concentrations indicating that chemical oxidation may be occurring. At higher concentrations the rate of biodegradation significantly decreased indicating a possible toxic affect.

An Integrated Chemical/Biological (ICB) process to remove MTBE from groundwater appears feasible based on the results of this research. H_2O_2/UV oxidation under oxygen-rich conditions produces biologically favorable byproducts in a relatively short time. Those products are in turn biodegradable at relatively rapid rates. Combining the two technologies produces a remediation process that has the potential to significantly reduce the cost of treating MTBE contaminated groundwater.

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