TREATMENT OF MTBE CONTAMINATED WATER USING UV/CHLORINE ADVANCED OXIDATION PROCESS

By

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Presentation Outline

1. Introduction
2. Research Objective
3. Methodology
4. Result and discussion
5. Conclusion
# Introduction

**Methyl-Tertiary Butyl Ether (MTBE)**

<table>
<thead>
<tr>
<th>Information</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production</td>
<td>▪ 65% of the world MTBE production in volume by China, USA, <strong>Saudi Arabia</strong>, Netherlands and South Korea,</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Uses</td>
<td>▪ 90% used as gasoline additive to raise the oxygen content</td>
</tr>
<tr>
<td></td>
<td>▪ 11-15% by volume blended with gasoline</td>
</tr>
<tr>
<td>Physicochemical</td>
<td>▪ High solubility in water: 50,000 mg/L, 30 times more soluble than Benzene</td>
</tr>
<tr>
<td>properties</td>
<td>▪ Low Koc: difficult to be adsorbed</td>
</tr>
<tr>
<td></td>
<td>▪ Low Henry’s constant (0.02-0.05 at 25°C) – difficult to strip out</td>
</tr>
<tr>
<td></td>
<td>▪ Resistant to microbial decomposition in water</td>
</tr>
</tbody>
</table>

(UNEP, 2005; USEPA; ATSDR; Health Canada 2006; PME)
# Introduction

Information on Methyl-Tertiary Butyl Ether (MTBE)

<table>
<thead>
<tr>
<th>Information</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Environmental sources &amp; fate</td>
<td>▪ Leakage from <strong>Underground Storage Tank</strong>, Spills during transport, &amp; Industrial discharge; common groundwater contaminant in <strong>USA, Canada, &amp; EU countries</strong></td>
</tr>
<tr>
<td>Exposure pathways</td>
<td>▪ Ingestion, inhalation, absorption</td>
</tr>
<tr>
<td>Health effect</td>
<td>▪ Rising health concern, potential carcinogenic risk to human</td>
</tr>
<tr>
<td>Standard for water</td>
<td>▪ <strong>PME G.W: 20µg/L</strong>, USEPA : 20–40µg/L advisory level, WHO &amp; Canadian GV: 15µg/L</td>
</tr>
</tbody>
</table>

(WHO, 2005; USEPA; ATSDR; Health Canada 2006; PME)
### Different treatment methods used for MTBE removal

<table>
<thead>
<tr>
<th>MTBE Removal methods</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption (GAC)</td>
<td>Low affinity to solids/spent adsorbent disposal</td>
</tr>
<tr>
<td>Air Stripping</td>
<td>Expensive, have higher operating costs &amp; water to air contaminant transfer</td>
</tr>
<tr>
<td>Biodegradation</td>
<td>Less efficient, long treatment time, not well developed</td>
</tr>
<tr>
<td>Advanced oxidation processes</td>
<td>A promising technology that completely mineralize the contaminants into H₂O &amp; CO₂</td>
</tr>
</tbody>
</table>

(Levchuk, Bhatnagar et al. 2014)
Different treatment methods used for MTBE removal

- **UV + O₃, H₂O₂, Fenton, TiO₂, Chlorine**
- **OH⁺ + MTBE**
- **TBF, TBA, Acetone**
- **CO₂+H₂O**

(Ray et al., 2006)

Hamid and Ali, 2004
• Chlorine uses and chemistry:
  – chlorine is used as disinf ectant for water and wastewater treatment

  \[ \text{NaOCl} \rightarrow \text{Na}^+ + \text{OCl}^- \]

  \[ \text{OCl}^- + \text{H}^+ \leftrightarrow \text{HOCl} \]

• Chlorine as Oxidant in AOP technology

  \[ \text{HOCl} + \text{UV photons} \rightarrow \cdot \text{OH} + \text{Cl}\cdot \]

  \[ \text{OCl}^- + \text{UV photons} \rightarrow \cdot \text{O}^- + \text{Cl}\cdot \]

  \[ \text{O}^- + \text{H}_2\text{O} \rightarrow \cdot \text{OH} + \text{OH}^- \]

  (Jin et al. 2010)

  Dependence of the ratio HOCl/OCl\(^-\) on pH
  (Feng et al. 2007)
## Different Advanced Oxidation Processes used to remove MTBE in water

<table>
<thead>
<tr>
<th>Methods</th>
<th>Scale of study</th>
<th>MTBE removal (%)</th>
<th>Treatment time</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fenton</td>
<td>Bench scale</td>
<td>99</td>
<td>120 min</td>
<td>Xu et al. 2004</td>
</tr>
<tr>
<td>UV/H2O2,</td>
<td>Bench scale</td>
<td>98</td>
<td>60 min</td>
<td>Hu et al. 2008</td>
</tr>
<tr>
<td>UV/ZnO/H2O2</td>
<td>Bench scale</td>
<td>100</td>
<td>75 min</td>
<td>Eslami &amp; Nasseri, 2008</td>
</tr>
<tr>
<td>UV-vis/TiO2/O2</td>
<td>Bench scale</td>
<td>82</td>
<td>75 min</td>
<td>Eslami et al, 2009</td>
</tr>
<tr>
<td>UV/TiO2</td>
<td>Bench scale</td>
<td>80</td>
<td>60 min</td>
<td>Hu et al. 2008</td>
</tr>
<tr>
<td>UV/TiO2</td>
<td>Bench scale</td>
<td>&gt;95</td>
<td>30 min</td>
<td>Tawabini et al. 2013</td>
</tr>
<tr>
<td>UVC/CNTs</td>
<td>Bench scale</td>
<td>70</td>
<td>30 min</td>
<td>Tawabini et al. 2013</td>
</tr>
<tr>
<td>UV/CNT-TiO2</td>
<td>Bench scale</td>
<td>&gt;60</td>
<td>120 min</td>
<td>Tawabini et al. 2013</td>
</tr>
<tr>
<td>UV/H2O2</td>
<td>Bench scale</td>
<td>&gt;95</td>
<td>20 min</td>
<td>Tawabini et al. 2013</td>
</tr>
<tr>
<td>UV/O3</td>
<td>Bench scale</td>
<td>70-80</td>
<td>30 min</td>
<td>Tawabini et al. 2013</td>
</tr>
<tr>
<td>UV/Chlorine</td>
<td>Bench scale</td>
<td>????</td>
<td>????</td>
<td>Not reported</td>
</tr>
</tbody>
</table>
# UV/Cl₂ AOP Water Treatment

<table>
<thead>
<tr>
<th>Contaminant Type</th>
<th>Removal Efficiency</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylene Blue (MB) and Cyclohexanoic Acid (CHA)</td>
<td>▪ 80-90%</td>
<td>Chan et al, 2012</td>
</tr>
<tr>
<td>Trichloroethylene (TCE)</td>
<td>▪ 2.3 times more efficient than UV/H₂O₂ at pH 5</td>
<td>Wang et al., 2012</td>
</tr>
</tbody>
</table>
| Model Emerging Contaminants: 17-a-Ethinylestradiol, Benzotriazole, Tolytriazole, | ▪ 85-100%  
▪ 30-75% energy reduction  
▪ 30-50% cost saving than UV/H₂O₂                                      | Sichel et al, 2011b              |
| Desethylatrazine, Carbamazepine, Sulfamethoxazole, Diclofenac, Iopamidole        |                                                                                     |                            |
| 2-methylisoborneol                                                              | ▪ 80-90% efficiency at pH 6                                                         | Rosenfeldt et al., 2013    |
Research Motivation and Objectives

- High production and wide use of MTBE, growing Health concern, & regulated
- MTBE is the common ground water pollutants and expensive to treat
- There is need for investigating an alternative treatment technologies to remove MTBE in water
- No work has been reported on the removal of MTBE in water by UV/chlorine AOP

- The main objective of this study was to assess the efficiency of MTBE removal in water using UV/Chlorine AOP
Methodology

• Instruments used
  ➢ NORMAG Photo-reactor
  ➢ Thermo Scientific GC-MS
  ➢ Desktop pH meter
Methods....

![Experimental setup diagram](image)

- **Experimental setup**
  - Reactor /vessel
  - Housed with two types of UV:
    - a) LP UV: $6.5 \times 10^{-3}$ W/cm$^2$, 254 nm
    - b) MP UV: $5.3 \times 10^{-2}$ W/cm$^2$, 200-400 nm
  - UV power unit
  - Circulation pump (Hostaflon®)

- **Experiment procedure**
  1. Adjust pH of the water
  2. Spike MTBE (1ppm)
  3. 10min circulation to homogenize
  4. Treatment types (Chlorine alone, UV alone, UV/chlorine)
  5. Monitoring MTBE residual and byproducts after certain time interval
**Methods….

- **Sample analysis**
  - EPA Method 524.2 protocol was used for MTBE & byproducts analysis

- **Quality control**
  - Ultra pure Deionized Water
  - Instrument calibration ($R^2>0.99$)
  - Replicate experiment
  - Duplicate analysis

- **Data analysis and presentation**
  - MS Excel sheet 2010
  - Graphs, & tables
  - Electrical Energy per Order ($EE_O$)
Result and discussion
Effect of pH on the MTBE degradation with LP & MP UV/Cl₂

Figure 1. Effect of pH on MTBE degradation with LP UV/Cl₂

Figure 2. Effect of pH on MTBE degradation with MP UV/Cl₂
Effect of pH on the MTBE degradation with LP & MP UV/Cl₂

- After 30 min >99% MTBE removal observed regardless of pH
- LP UV is more efficient for both MTBE and its byproducts removal concurrently
- The MTBE degradation could be due to:
  - UV photolysis and/or
  - Oxidation by OH radical and free chlorine
- In UV/Cl₂, OH radical is a major reason for degradation due to higher quantum yield, and less radical scavenging effect by HOCl than H₂O₂ (Rosenfeldt et al., 2013)
- OH radical attack on O-C (71%) and methyl group (29%) (Baus & Brauch, 2007)
Effect of chlorine dose on the MTBE degradation with LP & MP UV/Cl₂

Figure 9a. Effect of Cl₂ doses on MTBE degradation with LP UV/Cl₂

Figure 10a. Effect of Cl₂ doses on MTBE degradation with MP UV/Cl₂
Effect of chlorine dose on the MTBE degradation with LP & MP UV/Cl₂

- At lower Cl₂ dose >99% MTBE remove was achieved for both UV lamps.
- The higher Cl₂ dose might have scavenging effect on the OH radical.
- Other studies reported:
  - 80-90% removal of Methylisobreneol (MIB) by UV/Cl₂ (Rosenfeldt et al., 2013).
  - >95% of MTBE removal by LP & MP UV/H₂O₂ after 20 min, 70-80% by LP&MP UV/O₃ in 30min (Tawabini 2014).
- The differences mainly due to the water quality differences, initial MTBE concentration and the OH radical yied.
MTBE removal in groundwater by UV/Cl$_2$ AOP

- **Optimization criteria:**
  - Higher MTBE removal efficiency
  - Lower concentrations of byproducts
  - Minimum chlorine dose
  - Short treatment time
  - Less electrical energy

- **Optimum condition obtained:**
  - LP UV with 10ppm Cl$_2$ at pH 5, 30 min

- **>99% MTBE removal** in GW was achieved and superior than other AOPs

![MTBE degradation in groundwater with LP UV/Cl$_2$](image)

![TBF concentration](image)

Figure 11a. MTBE degradation in groundwater with LP UV/Cl$_2$

Figure 11b. TBF concentration
## Comparison of MTBE removal efficiency & EE$_O$ of UV/Cl$_2$ & other AOP

<table>
<thead>
<tr>
<th>AOP type</th>
<th>Scale of study</th>
<th>MTBE removal (%)</th>
<th>Treatment time</th>
<th>EEO (kWh/m$^3$)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV/TiO$_2$</td>
<td>Bench scale</td>
<td>&gt;95</td>
<td>30 min</td>
<td>Not reported</td>
<td>Tawabini et al. 2013</td>
</tr>
<tr>
<td>UVC/CNTs</td>
<td>Bench scale</td>
<td>70</td>
<td>30 min</td>
<td>Not reported</td>
<td></td>
</tr>
<tr>
<td>UV/CNT-TiO$_2$</td>
<td>Bench scale</td>
<td>&gt;60</td>
<td>120 min</td>
<td>Not reported</td>
<td></td>
</tr>
<tr>
<td>UV/O$_3$</td>
<td>Bench scale</td>
<td>70-80</td>
<td>30 min</td>
<td>Not reported</td>
<td>Tawabini. 2014</td>
</tr>
<tr>
<td>UV/H$_2$O$_2$</td>
<td>Bench scale</td>
<td>&gt;95</td>
<td>20 min</td>
<td>4.16-5.55</td>
<td></td>
</tr>
<tr>
<td>UV/Cl$_2$</td>
<td>Bench scale</td>
<td>&gt;99</td>
<td>15-30</td>
<td>4.01-6.90</td>
<td>This work</td>
</tr>
</tbody>
</table>

- The MTBE removal obtained by UV/Cl$_2$ is more efficient than other AOPs.
- The EE$_O$ determined for UV/Cl$_2$ is consistent with other studies (Baus & Brauch 200, Tawabini 2014).
- The overall operation cost of UV/Cl$_2$ is cheaper than UV/H$_2$O$_2$ (Rosenfeldt et al., 2013).
Conclusion

- >99% MTBE removal efficiency was achieved using LP UV/Cl₂ in both DI water & groundwater

- Less chemical consumption, short treatment time and relatively low $\text{EE}_O$ was attained
Recommendations

• The following recommendations are proposed:
  – Further study is need on chlorine based chemical oxidation process
  – The chlorine based advanced oxidation process in combination with other oxidant should be investigated
  – The cost estimation for UV/Cl$_2$ in terms of energy and operation needs further investigation at pilot scale
Acknowledgment

• I would like thank
  – Earth Sciences Department for allowing me to conduct this study in the Env’tal lab and different support during the study
  – Center for Environment and Water (CEW)
THANK YOU!