# Treatment of MTBE Contaminated Water using UV/Chlorine Advanced Oxidation Process

By

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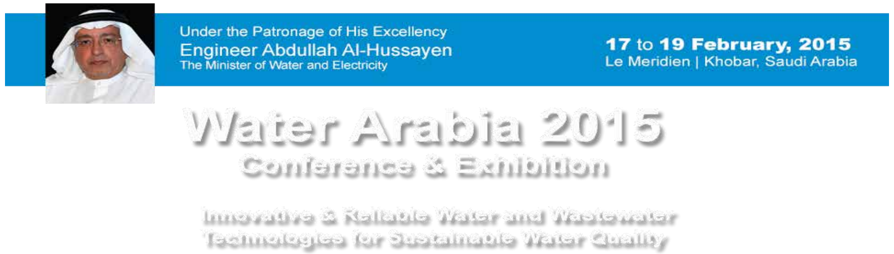
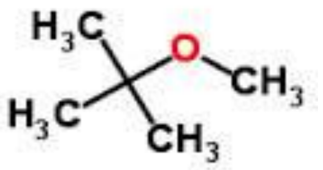


# Presentation Outline

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

# Introduction

## Methyl-Tertiary Butyl Ether (MTBE)




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



(WHO, 2005; USEPA; ATSDR; Health Canada 2006; PME)

# Introduction

## Information on Methyl-Tertiary Butyl Ether (MTBE)

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

(WHO, 2005; USEPA; ATSDR; Health Canada 2006; PME)

# Different treatment methods used for MTBE removal

| MTBE Removal methods | Comment |
|---|---|
| Adsorption (GAC) | Low affinity to solids/spent adsorbent disposal |
| Air Stripping | Expensive , have higher operating costs<br>& water to air contaminant transfer |
| Biodegradation | Less efficient, long treatment time, not well developed |
| Advanced oxidation processes | A promising technology that completely mineralize the contaminants into $H_2O$ & $CO_2$ |

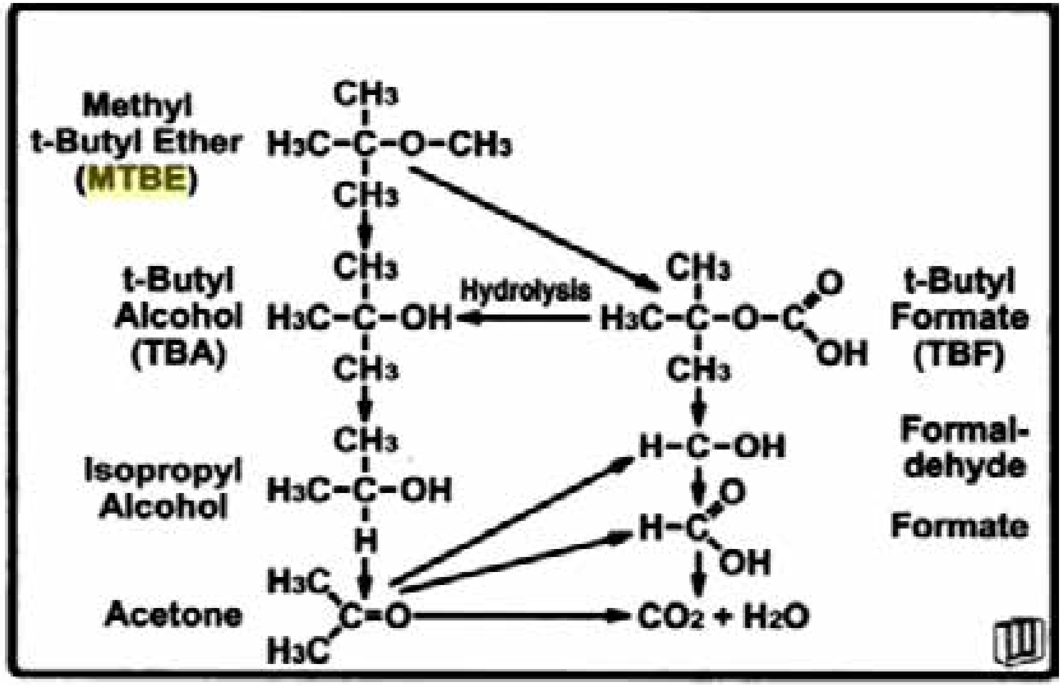
**(Levchuk, Bhatnagar et al. 2014)**

Hamid and Ali, 2004

# Different treatment methods used for MTBE removal

UV + $O_3$, $H_2O_2$, Fenton, $TiO_2$, **Chlorine** → $OH^{\bullet}$ + MTBE → TBF, TBA, Acetone → $CO_2$+$H_2O$

(Ray et al., 2006)




Hamid and Ali, 2004

- **Chlorine uses and chemistry:**
  - chlorine is used as **disinfectant for water and wastewater treatment**

$$NaOCl \leftrightarrow Na^+ + OCl^-$$

$$OCl^- + H^+ \leftrightarrow HOCl$$

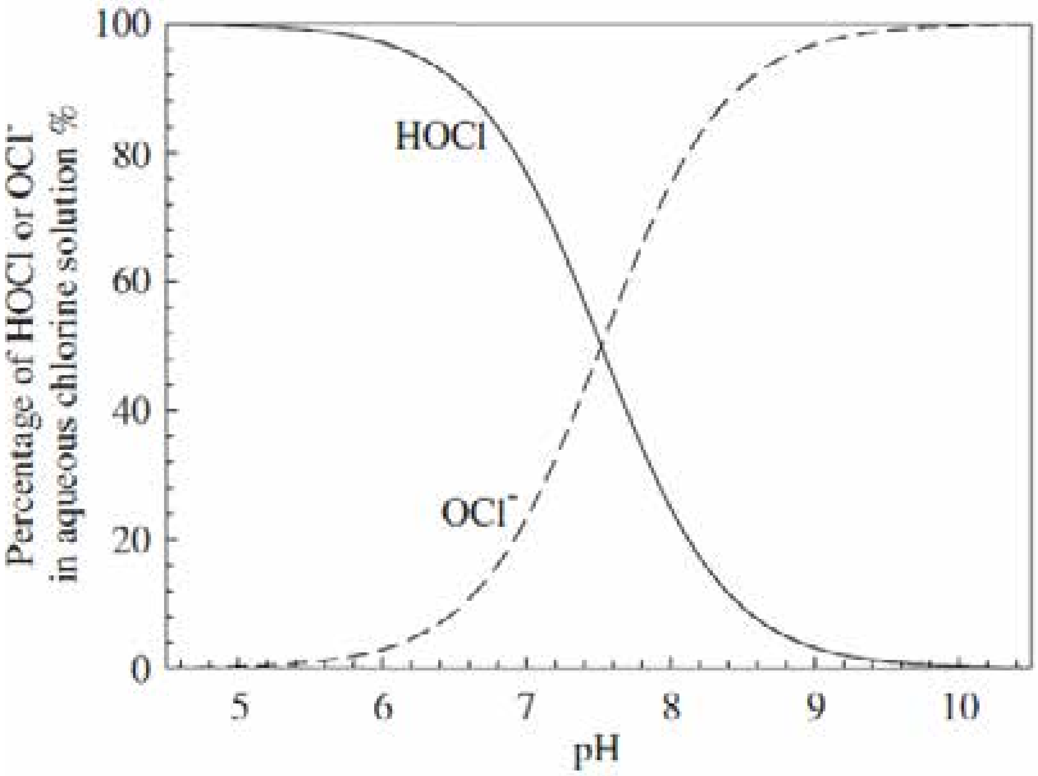
- **Chlorine as Oxidant in AOP technology**

$$HOCl + \text{UV photons} \rightarrow {}^{\bullet}OH + Cl^{\bullet}$$

$$OCl^- + \text{UV photons} \rightarrow {}^{\bullet}O^- + Cl^{\bullet}$$

$$O^- + H_2O \rightarrow {}^{\bullet}OH + OH^-$$

(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

| Methods | Scale of study | MTBE removal (%) | Treatment time | References |
|---|---|---|---|---|
| **Fenton** | Bench scale | 99 | **120 min** | Xu et al. 2004 |
| **UV/H2O2,** | Bench scale | 98 | **60 min** | Hu et al. 2008 |
| **UV/ZnO/$H_2O_2$** | Bench scale | 100 | **75 min** | Eslami & Nasseri, 2008 |
| **UV-vis/TiO2/O2** | Bench scale | 82 | **75 min** | Eslami et al, 2009 |
| **UV/TiO2** | Bench scale | 80 | **60 min** | Hu et al. 2008 |
| **UV/TiO2** | Bench scale | >95 | 30 min | Tawabini et al. 2013 |
| **UVC/CNTs** | Bench scale | 70 | 30 min | |
| **UV/CNT-TiO2** | Bench scale | >60 | **120 min** | |
| **UV/H2O2** | Bench scale | >95 | **20 min** | Tawabini. 2014 |
| **UV/O3** | Bench scale | 70-80 | **30 min** | |
| **UV/Chlorine** | **Bench scale** | **????** | **????** | **Not reported** |

# $UV/Cl_2$ AOP water treatment

| Contaminant type | Removal efficiency | Reference |
|---|---|---|
| Methylene Blue (MB) and Cyclohexanoic Acid (CHA) | ▪ 80-90% | Chan et al, 2012 |
| Trichloroethylene (TCE) | ▪ 2.3 times more efficient than $UV/H_2O_2$ at pH 5 | Wang et al., 2012 |
| Model Emerging Contaminants:<br>17-a-Ethinylestradiol, Benzotriazole, Tolylriazole, Desethylatrazine, Carbamazepine, Sulfamethoxazole, Diclofenac,Iopamidole | ▪ 85-100%<br>▪ 30-75% energy reduction<br>▪ 30-50% cost saving than UV/H2O2 | Sichel et al, 2011b |
| 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

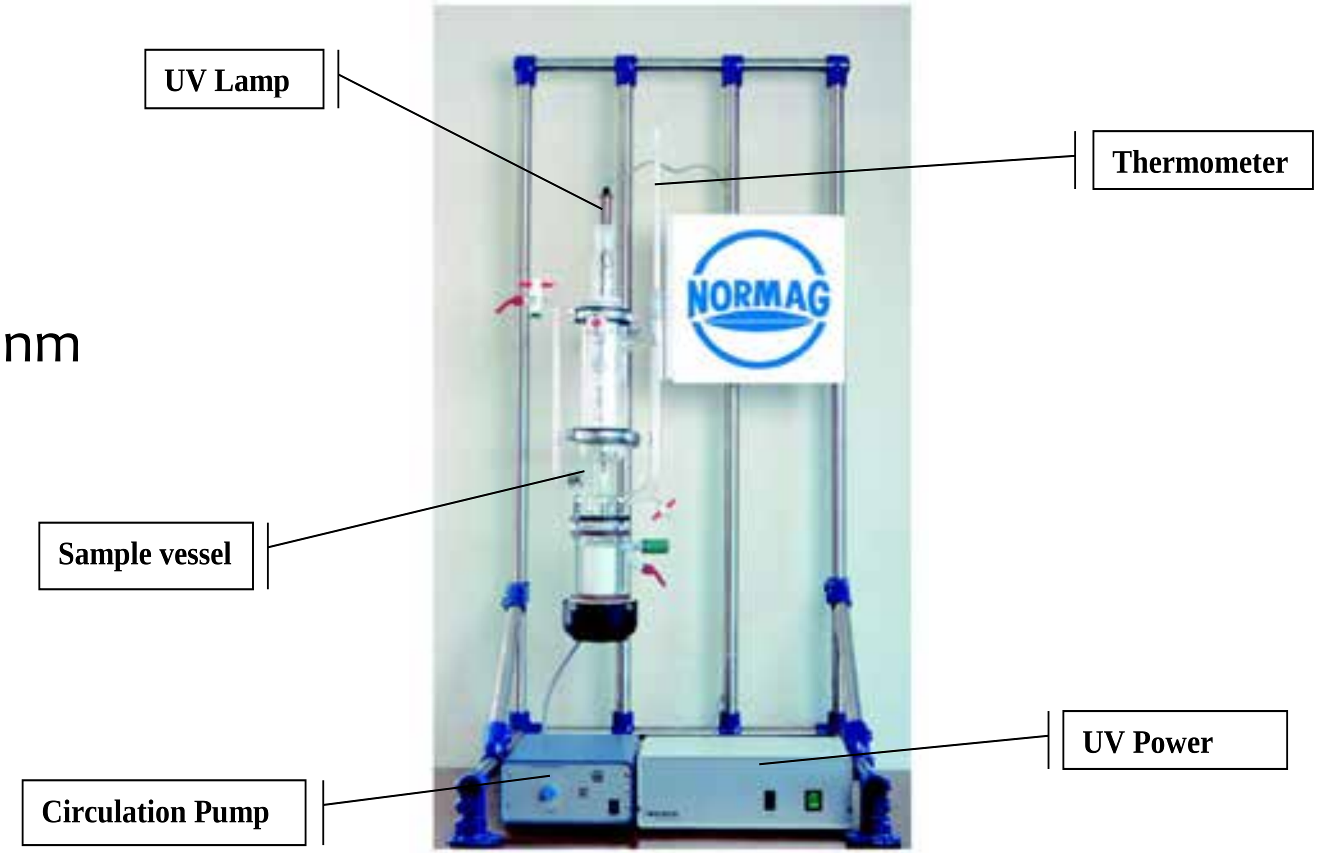
- **Instruments used**
  - NORMAG Photo-reactor
  - Thermo Scientific GC-MS
  - Desktop pH meter

Thermo GC/MS with HS/P&T

# Methods….

## ❖ Experimental setup

- ✓ Reactor /vessel
- ✓ Housed with two types of UV:
  - a) LP UV: $6.5 \times 10^{-3}$ W/cm², 254 nm
  - b) MP UV: $5.3 \times 10^{-2}$ W/cm², 200-400 nm
- ✓ UV power unit
- ✓ Circulation pump (Hostaflon®)



NORMAG Photo-reactor

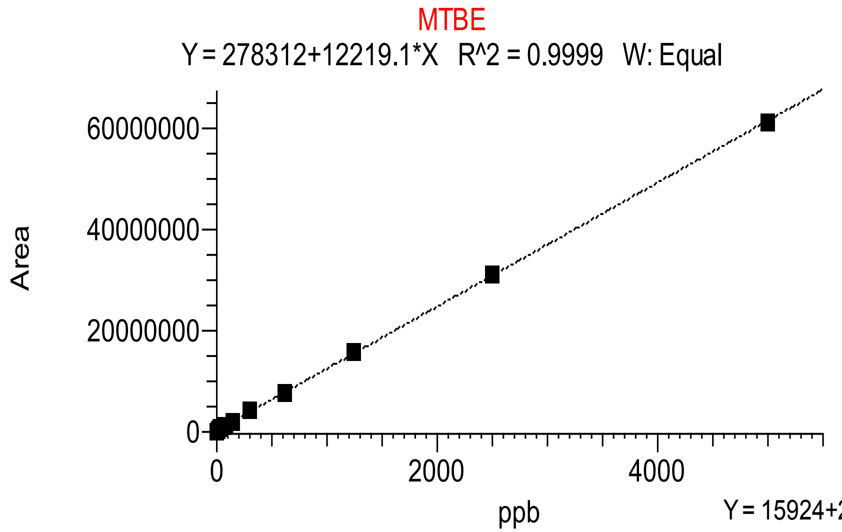
## ❖ Experiment procedure

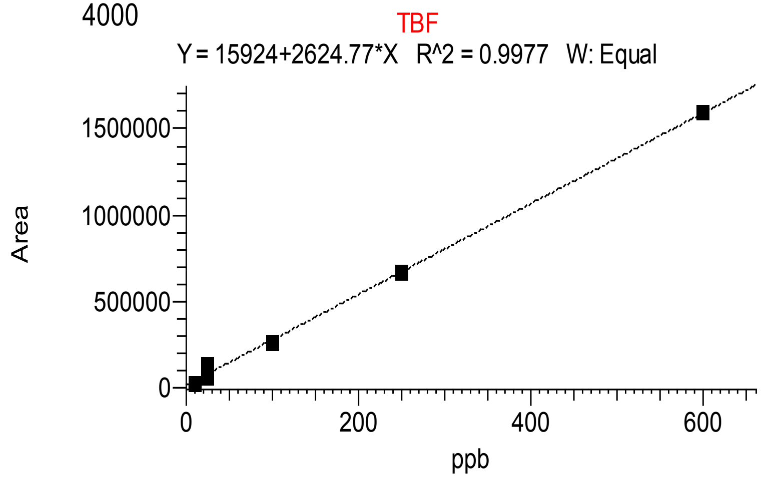
1. Adjust pH of the water
2. Spike MTBE (1ppm)
3. 10min circulation to homogenize
4. Treatment types (Chlorine alone, UV alone, UV/chlorine)
5. Monitoring MTBE residual and byproducts after certain time interval

# 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/$Cl_2$

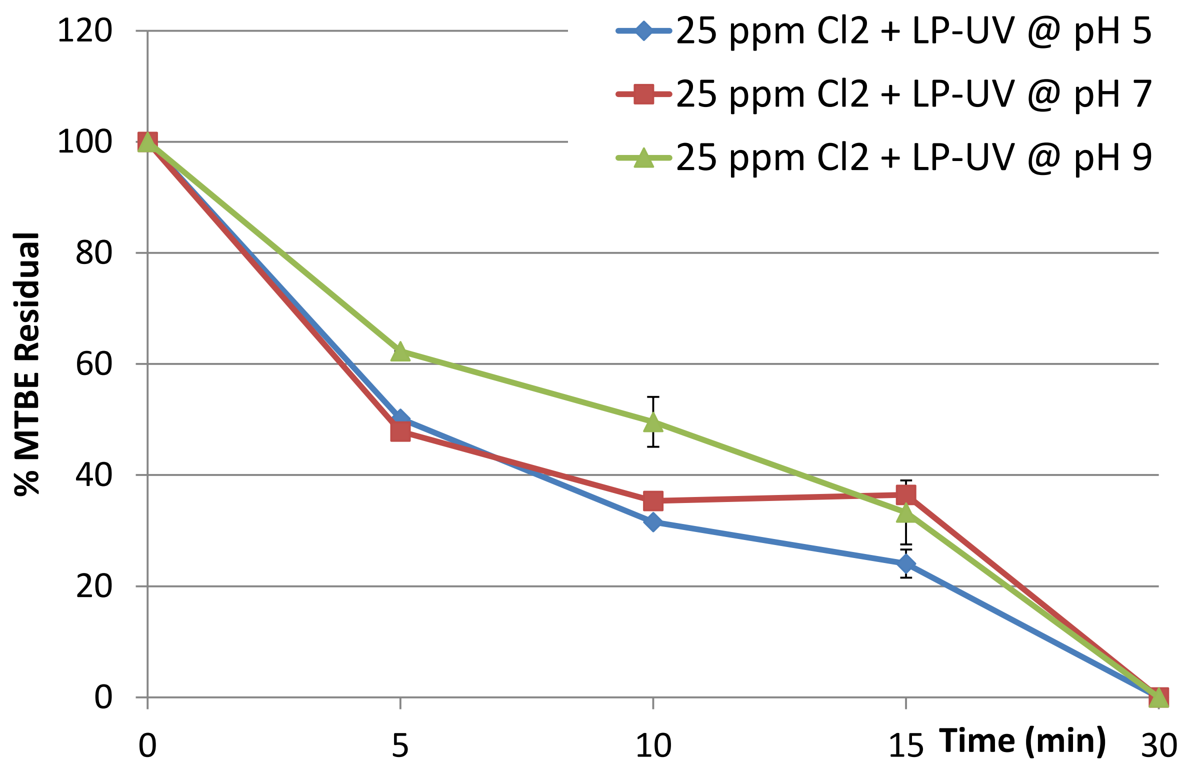



Figure 1. . Effect of pH 0n MTBE degradation with LP UV/Cl2

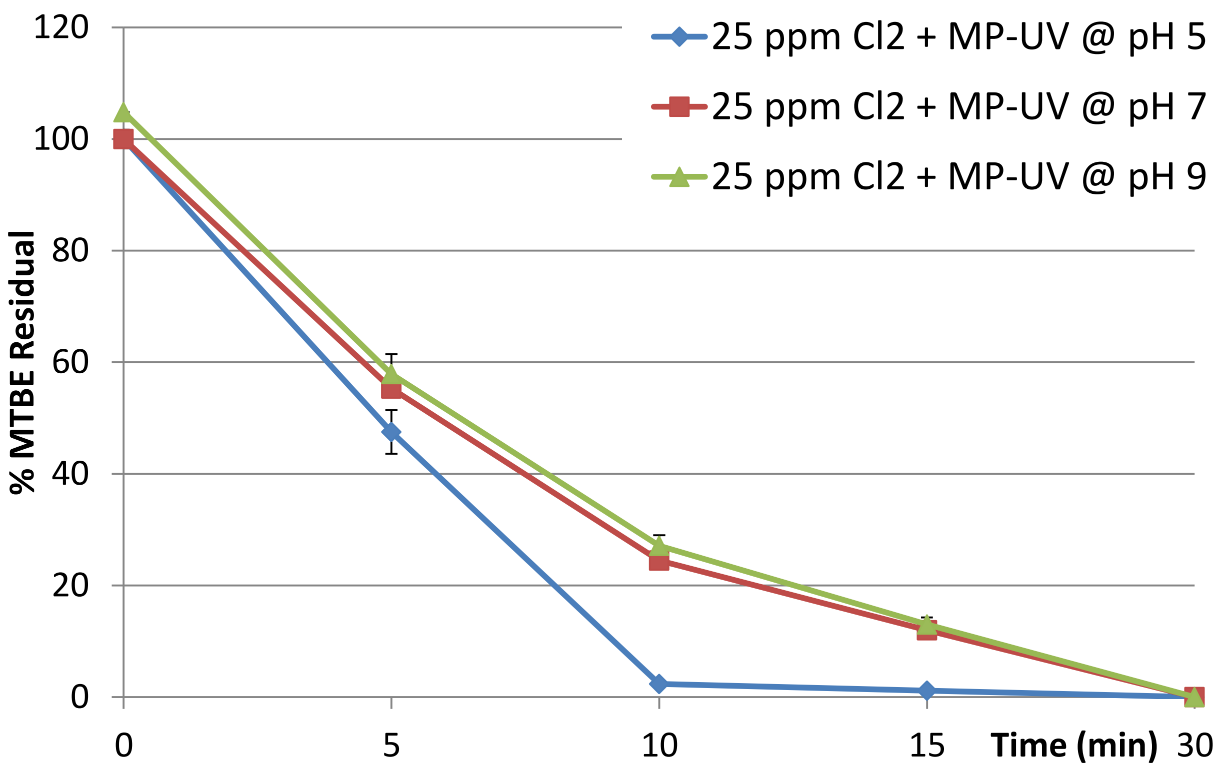



Figure 2. Effect of pH 0n MTBE degradation with MP UV/Cl2

# Effect of pH on the MTBE degradation with LP & MP UV/$Cl_2$

- 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/$Cl_2$, OH radical is a major reason for degradation due to higher quantum yield, and less radical scavenging effect by HOCl than $H_2O_2$ (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/$Cl_2$

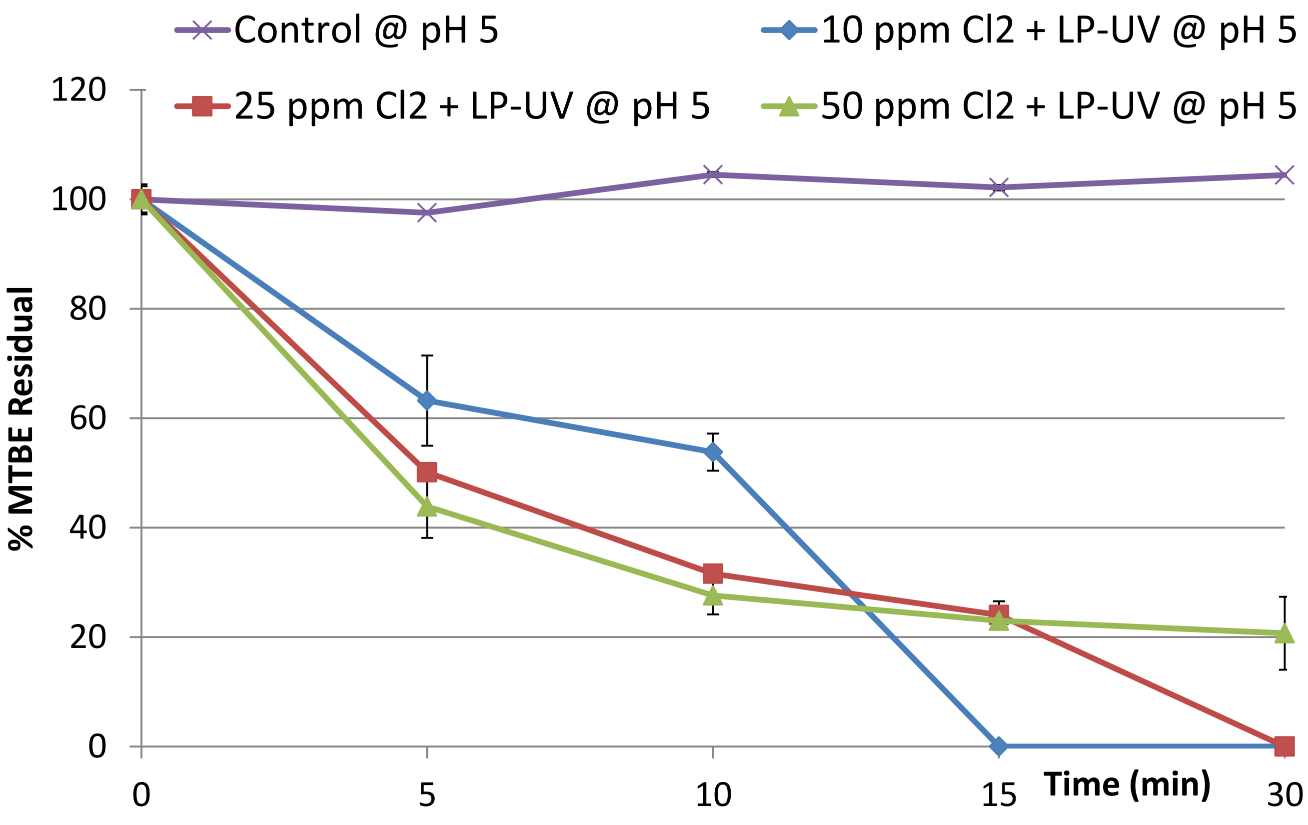



**Figure 9a. Effect of Cl2 doses 0n MTBE degradation with LP UV/Cl2**

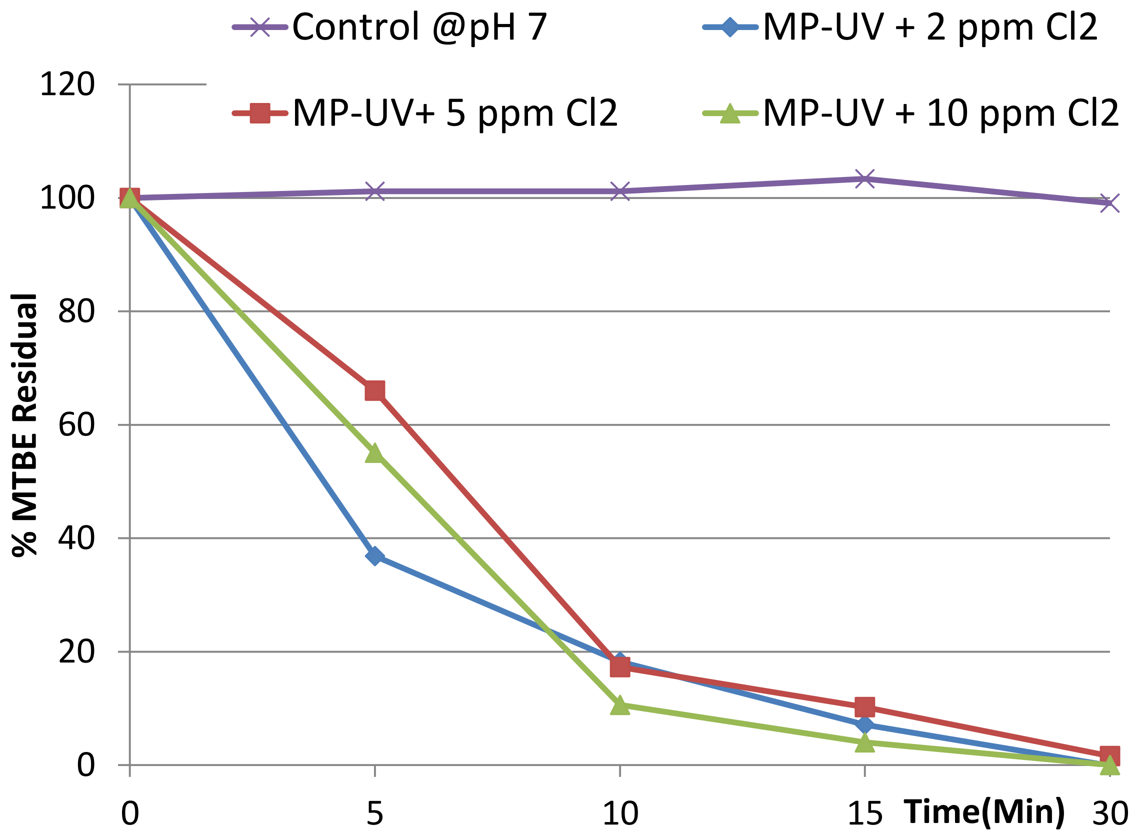



**Figure 10a. Effect of Cl2 doses 0n MTBE degradation with MP UV/Cl2**

# Effect of chlorine dose on the MTBE degradation with LP & MP UV/$Cl_2$

- At lower $Cl_2$ dose >99% MTBE remove was achieved for both UV lamps
- The higher $Cl_2$ dose might have scavenging effect on the OH radical
- Other studies reported :
  - 80-90% removal of Methylisobreneol (MIB) by **UV/$Cl_2$** (Rosenfeldt et al., 2013)
  - >95% of MTBE removal by **LP &MP UV/$H_2O_2$** after 20 min, 70-80% by **LP&MP UV/$O_3$** 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

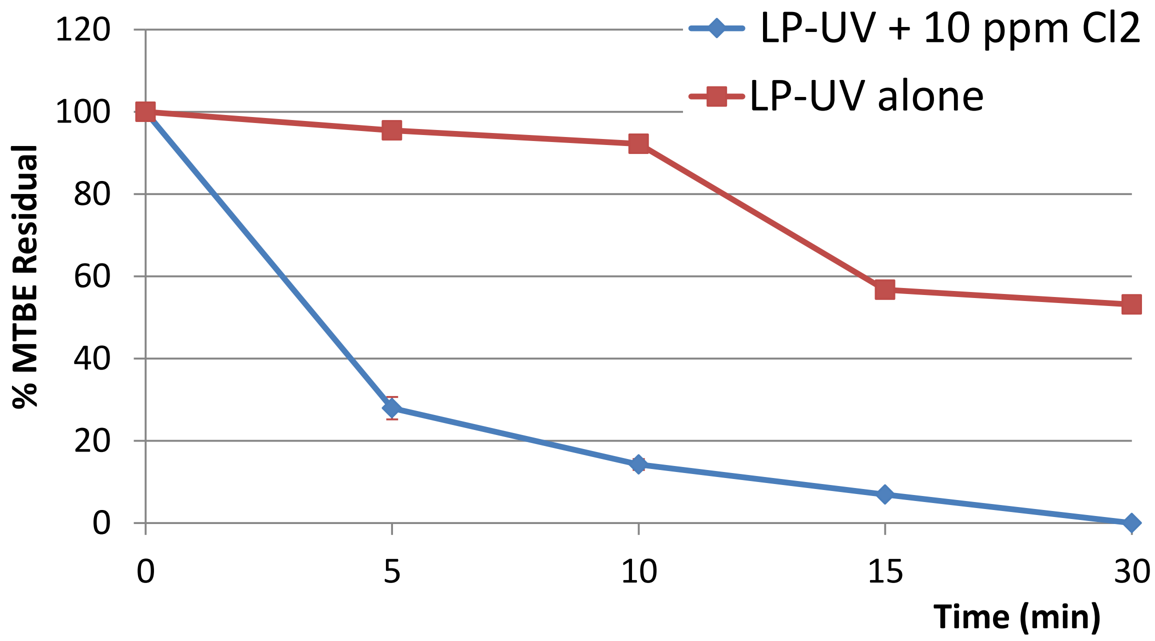



**Figure 11a. MTBE degradation in groundwater with LP UV/Cl2**

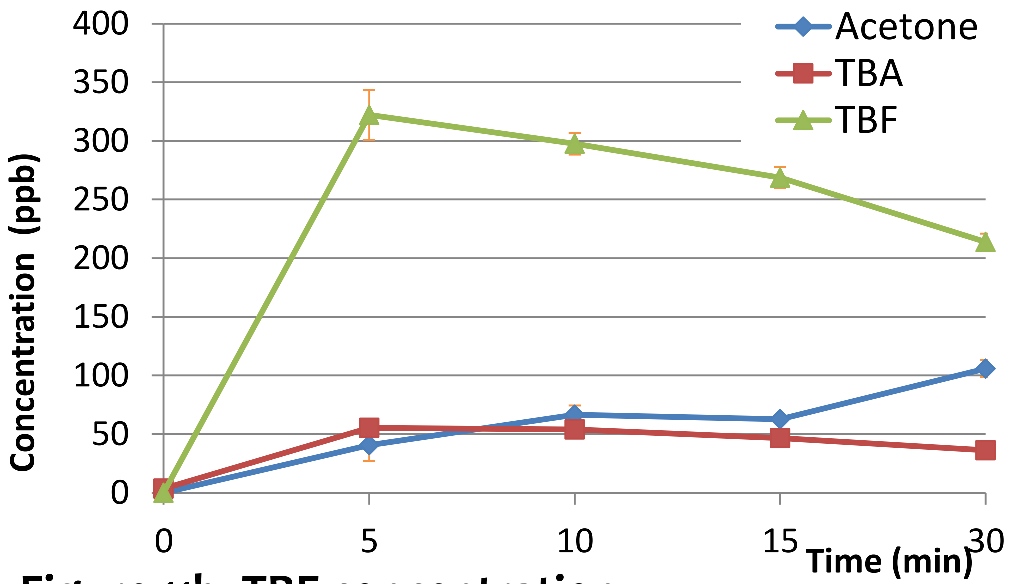



**Figure 11b. TBF concentration**

# Comparison of MTBE removal efficiency & $EE_O$ of $UV/Cl_2$ & other AOP

| AOP type | Scale of study | MTBE removal (%) | Treatment time | EEO (kWh/m3) | References |
|---|---|---|---|---|---|
| **UV/TiO2** | Bench scale | >95 | 30 min | Not reported | Tawabini et al. 2013 |
| **UVC/CNTs** | Bench scale | 70 | 30 min | Not reported | |
| **UV/CNT-TiO2** | Bench scale | >60 | 120 min | Not reported | |
| **UV/O3** | Bench scale | 70-80 | 30 min | Not reported | Tawabini. 2014 |
| **UV/H2O2** | Bench scale | >95 | 20 min | **4.16-5.55** | |
| **$UV/Cl_2$** | **Bench scale** | **>99** | **15-30** | **4.01-6.90** | **This work** |

- 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 $UV/H_2O_2$ (Rosenfeldt et al., 2013)

# Conclusion

- >99% MTBE removal efficiency was achieved using LP UV/$Cl_2$ in both DI water & groundwater

- Less chemical consumption, short treatment time and relatively low $EE_O$ 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!