CivE 729

Lecture 3
UV-Based Advanced Oxidation Technologies: Chemistry

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Outline

- Photolysis in a collimated beam
- Photolysis of NDMA
- Treatment of MTBE by UV/H_2O_2
- Solar degradation of 1,4-dioxane

N-Nitrosodimethylamine (NDMA)

- Widely distributed in the human environment.
- Found in outdoor air, surface waters, preserved meat, cosmetics, detergents and pesticides.
- Found in groundwater at levels as high as 10 ppb.
- Potent carcinogen and mutagen.
- On USEPA National Priorities List.
- Not currently easily removed.
  - does not air strip
  - does not biodegrade
  - does not adsorb to activated carbon

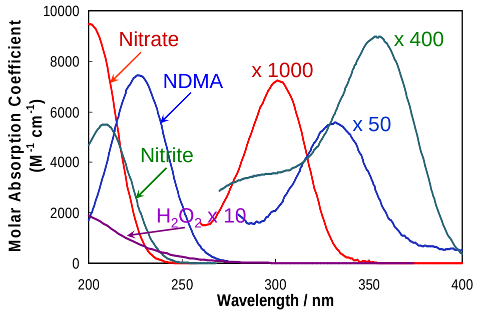
AOT Treatment of NDMA

- UV-based Advanced Oxidation Technologies are very effective in treating NDMA.
  - NDMA undergoes direct photolysis at wavelengths <350 nm.
  - UV/H_2O_2 treatment, which involves generation of •OH radicals, can also be used.
  - High concentrations ratios of H_2O_2 to NDMA are required.
- Stefan, M. I. and J. R. Bolton, 2002. "UV Direct Photolysis of N-Nitrosodimethylamine (NDMA): Kinetic and Product Study.", *Helv. Chim. Acta,* 85, 1416-1426.

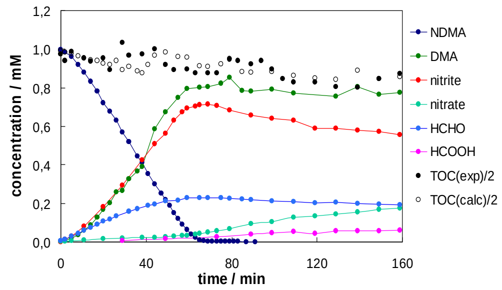
Previous Work

- Several studies on UV direct photolysis of N-nitrosoamines were reported in the 1970-1980 literature, both in aqueous solution and in the gas phase.
- A strong pH dependence was found for the photolysis of NDMA.
- Dimethylamine and nitrite were found as major products.
- No intermediate time profiles, TOC or nitrogen balances were reported.
- Very little work on UV/H_2O_2 treatment of NDMA.

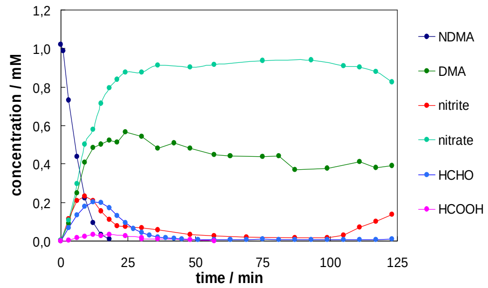
UV Spectra



NDMA Photolysis - pH 7



UV/H_2O_2 Treatment - pH 7



Methyl-*tert*-butyl Ether (MTBE)

- **Fuel oxygenate used as an octane enhancer of reformulated gasoline; largely manufactured in the USA.**
- **High solubility in water; detected in ground and storm water as the second most frequent contaminant (after $CHCl_3$).**
- **Carcinogen in animals; potential human carcinogen.**
- **Not currently regulated as a drinking water contaminant.**
- **Low odor (45 ppb) and taste (39 ppb) detection thresholds.**
- **Drinking water advisory limit of 20 - 40 ppb MTBE, recently issued by USEPA.**
- Cater, S. R., M. I. Stefan, J. R. Bolton and A. Safarzadeh-Amiri, 2000 "UV/H_2O_2 treatment of methyl tert-butyl ether in contaminated waters" Environ. Sci. Technol. 34, 659-662.

MTBE Remediation

- *Traditional Technologies*:
  - *Air-stripping* - can achieve 99% removal of MTBE from water if large air to water ratios are used but is only a mass transfer.
  - *Adsorption on granulated activated carbon* - low affinity; effective at low concentrations, but a high cost of carbon replacement at high concentrations.
  - *Aerobic biodegradation* - difficult to apply to large volumes of MTBE-contaminated water or to ppm-ppb levels.
- *Advanced Oxidation Technologies*:
  - UV/H_2O_2, UV/O_3 and O_3/H_2O_2 processes.

Kinetic Model

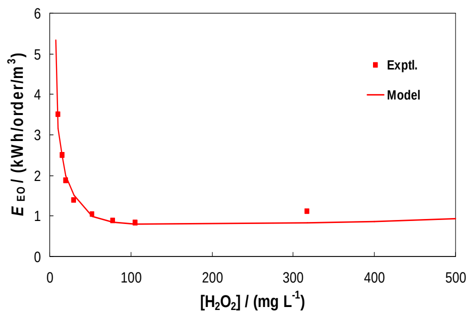
- Assume rate can be estimated from initial conditions.
- Rate of removal of MTBE is

  Rate = $k_2[\bullet OH]_{ss}[MTBE]$
- The steady-state •OH concentration is

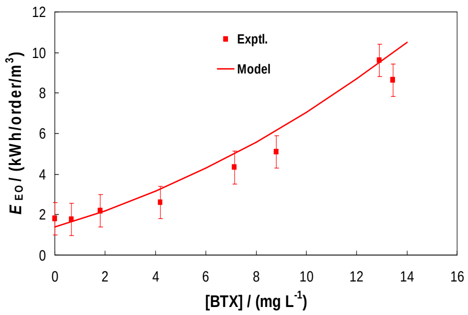
$$[\bullet OH]_{SS} = \frac{G\chi\Phi / V}{k_{MTBE}[MTBE]_o + k_{H_2O_2}[H_2O_2]_o + \sum_i k_{S_i}[S_i]_o}$$

where G is the photon flux output from the UV lamp, χ is the fraction absorbed in the solution, Φ is the quantum yield of generation of •OH radicals from H_2O_2 photolysis and V is the solution volume (L).

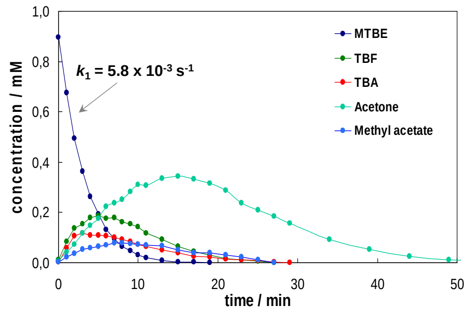
E_{EO} vs. Concentration of H_2O_2



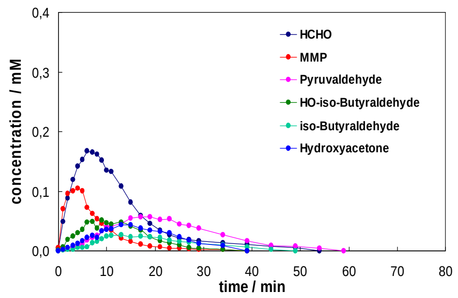
E_{EO} vs. Concentration of BTX



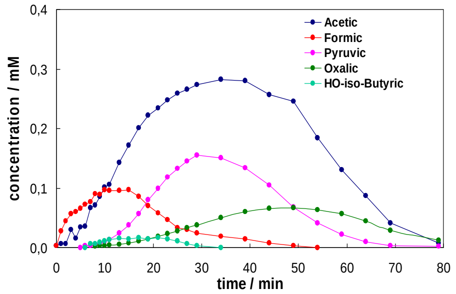
MTBE Degradation (1)



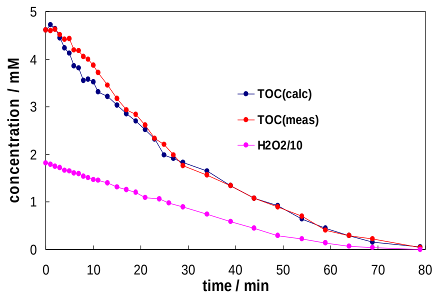
MTBE Degradation (2)



MTBE Degradation (3)



TOC Balance



Homogeneous Solar Photodegradation of Contaminants in Water

- **Based on the UV-Vis Fentons process with ferrioxalate as the absorber**
- **Ferrioxalate absorbs out to 500 nm**
- Bolton, J. R., M. Ravel, S. R. Cater and A. Safarzadeh-Amiri, 1996. “Homogeneous solar photodegradation of contaminants in water”, Proceedings of the ASME International Solar Energy Conference, San Antonio, TX, 31 March - 3 April, 1996, American Society of Mechanical Engineers, United Engineering Center, 345 East 47th St., New York, NY 10017, pp 53-60.

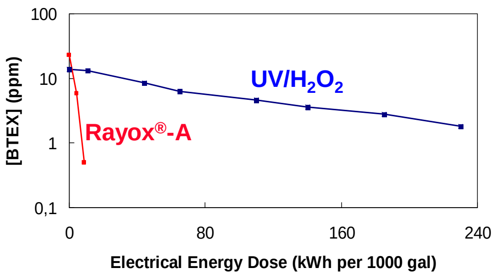
Rayox® -A

- Patented process developed by Calgon Carbon Corporation about 1994
- For Waters of high UV Absorbance, high COD or high pollutant concentration
- Involves addition of ferrioxalate

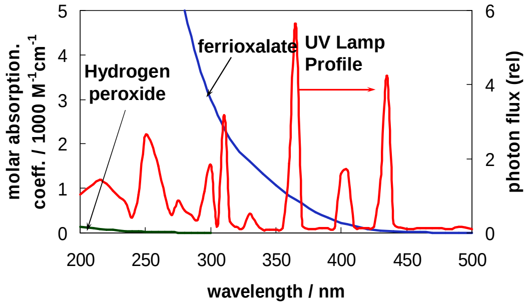
  $Fe(C_2O_4)_3^{2-}$

  which absorbs light over a wide range of wavelengths (including part of the visible) to generate hydroxyl radicals

Treatment of BTEX



Absorption Spectra



Why is Rayox®-A So Efficient?

- Efficient use of lamp output due to absorption of ferrioxalate over the UV and visible range.
- High reactivity of complexed ferrous ion with hydrogen peroxide.
- High quantum yield of Fe(II) formation means a very high quantum yield for generation of hydroxyl radicals.
- Photolysis of Fe(III)-organic intermediate complexes enhances the treatment effectiveness.

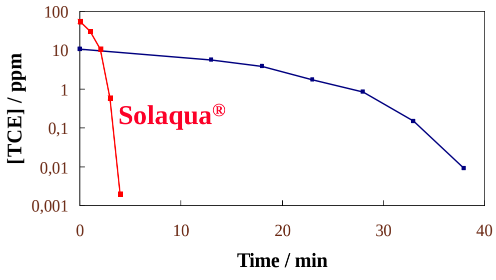
Solar Detoxification

- Most research in solar photocatalytic decontamination has dealt with heterogeneous catalysts, such as titanium dioxide (TiO_2).
- TiO_2 disadvantages include:
  - low quantum yield for ·OH production (ca. 5%)
  - potential for fouling
  - only absorbs 3% of the solar spectrum
  - mass transfer limitation on rates

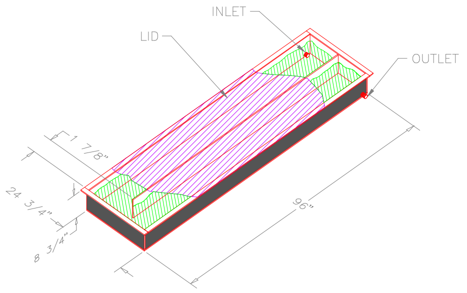
Calgon Carbon's Solaqua® Sunlight Decontamination Process

- homogeneous process
- involves an absorber (ferrioxalate) that absorbs solar radiation out to 500 nm
- the reaction mechanism involves the generation of hydroxyl radicals with a quantum yield of about unity
- 18% of the solar spectrum is absorbed

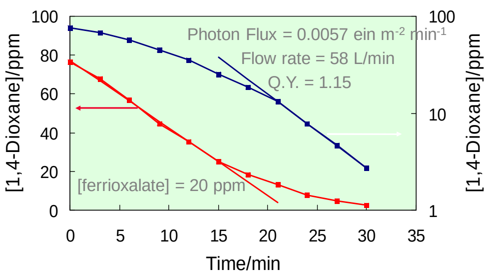
Solaqua® vs. TiO_2



Solar Detoxification Collector

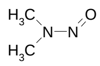


Solaqua® Treatment of 1,4-Dioxane in a Test Solar Reactor

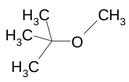


Hyperlinks >>>>

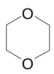
Chemical Structures



N-nitrosodimethylamine (NDMA): $C_2H_6N_2O$
- rocket fuel contaminant
- formation in drinking water: monochloramine is a precursor to NDMA formation during chlorination

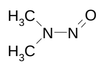


Methyl tert-butyl ether (MTBE): $C_5H_{12}O$



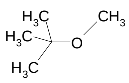
1,4-Dioxane: $C_4H_8O_2$

Chemical Structures > estimation of oxidation and mineralization products

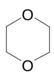


→ CO_2, H_2O, NO_3^-, NO_2^- (NH_4^+)

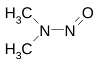
What do you think are the products of mineralization?

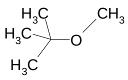


→ CO_2, H_2O

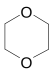


Chemical Structures > estimation of oxidation and mineralization products





Which intermediary oxidation products may be formed?



MTBE → Intermediary Oxidation Products → Mineralization