## Advanced Oxidation Technologies (AOTs)

*Outline*

- Overview and Discussion of Different AOPs
- Derivation of the Concept of “Figures-of-Merit”, Design Parameters
- Applications and Comparison of AOTs

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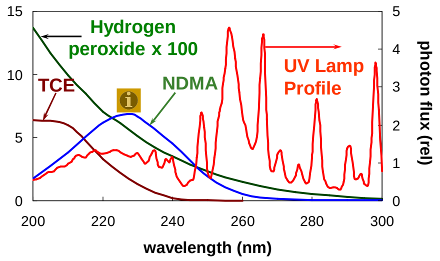
## Advanced Oxidation Technologies (AOTs)

- **Light-driven Homogeneous**
  - **Direct Photolysis**
  - **UV/$H_2O_2$**
  - **UV/$O_3$**
  - **UV/$O_3$/$H_2O_2$**
  - **UV-Vis Fentons**
- **Light-driven Heterogeneous**
  - **UV/$TiO_2$**
- **Dark Homogeneous**
  - **$O_3$/$H_2O_2$**
  - **Fentons**
  - **Electron beams**
  - **High-energy radiation**
  - **Supercritical water oxidation**
  - **Electric discharge**
  - **Sonolysis**

## Light-Driven Homogeneous -
### Direct Photolysis

- **Here the contaminant absorbs UV directly**
- **The molar absorption coefficients must be high (>1000 $M^{-1}$ $cm^{-1}$) at wavelengths where the lamp emission is strong.**
- **Direct Photolysis examples are:**
  - **N-nitrosodimethylamine (NDMA)**
  - **Trichloroethylene (TCE)**
  - **Certain pesticides and herbicides (e.g., atrazine)**

## Pollutant Absorption Spectra



## Light-driven Homogeneous - VUV Direct Photolysis

- **Water absorbs UV below 190 nm.**

$H_2O + h\nu \longrightarrow H\bullet + \bullet OH \quad \Phi = 0.42$

- **Molar absorption coefficients are high, so UV is absorbed within a few $\mu$m.**
- **Advantage of no added chemicals.**
- **Light sources are usually low-pressure Hg lamps (185 nm) or excimer lamps (172 nm).**
- **This process is used in the semiconductor industry to produce ultrapure water.**

## Light-driven Homogeneous – UV/$H_2O_2$

- **Hydrogen peroxide absorbs UV in the 200–300 nm range.**

$H_2O_2 + h\nu \longrightarrow 2\,\bullet OH \quad \Phi = 1.0$

**Molar absorption coefficients are small, so significant levels (>10 ppm) of $H_2O_2$ are required to absorb most of the emitted UV.**

- **Important to have a UV lamp with strong output in the 200–300 nm region.**
- **This process is the most commonly used industrially.**

## Light-Driven Homogeneous – $UV/O_3$

- Ozone ($O_3$) absorbs UV in the 200–300 nm range.

$$O_3 + h\nu \longrightarrow O_2 + O(^1D) \qquad \Phi = 1.0$$

$$O(^1D) + H_2O \longrightarrow [2\ {}^\bullet OH] \longrightarrow H_2O_2$$

- Thus the $UV/O_3$ process is just an expensive way to make hydrogen peroxide, which must then be photolyzed to yield free ·OH radicals.
- Some applications (e.g., the treatment of TNT) require the $UV/O_3$ process.

## Light-Driven Homogeneous – $UV/O_3/H_2O_2$

- As noted before, the UV photolysis of ozone leads to the generation of $H_2O_2$. If $H_2O_2$ is also in the solution, it can act as an enhancer, both from the generation of •OH radicals by photolysis and also by:

$$^\bullet OH + H_2O_2 \longrightarrow {}^\bullet O_2^- + H_2O + H^+$$

$$^\bullet O_2^- + O_3 \longrightarrow {}^\bullet O_3^- + O_2$$

$$^\bullet O_3^- + H^+ \longrightarrow HO_3^\bullet \quad (pK_a = 6.15)$$

$$HO_3^\bullet \longrightarrow {}^\bullet OH + O_2$$

## Light-Driven Homogeneous – UV-Vis Fentons

- $Fe(OH)^{2+}$ and many ferric complexes (e.g., ferrioxalate) absorb in the near UV and up to 500 nm in the visible.
- These reactions generate Fe(II) and in the presence of $H_2O_2$, Fenton reactions occur (pH ~ 3) to generate •OH radicals

$$Fe(OH)^{2+} + h\nu \longrightarrow Fe^{2+} + {}^\bullet OH$$

$$Fe(C_2O_4)_3^{3-} + h\nu \longrightarrow Fe^{2+} + 2.5\ C_2O_4^{2-} + CO_2$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + {}^\bullet OH$$

- Used when pollutant concentrations are high and polluted water absorbs strongly in the 200-300 nm region.

## Light-Driven Heterogeneous –
### UV/TiO$_2$ Process

- Some metal oxide semiconductors can absorb UV and generate hydroxyl radicals on the surface.
- The most efficient and most widely studied substance is the anatase form of TiO$_2$.

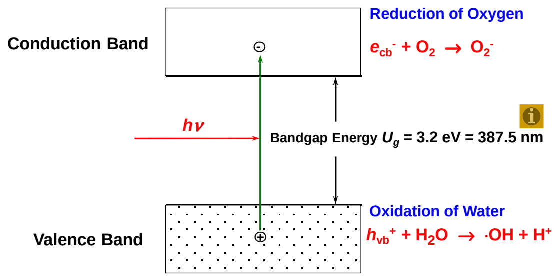
$$TiO_2 + h\nu \longrightarrow e_{cb}^- + h_{vb}^+$$

$$h_{vb}^+ + H_2O \longrightarrow •OH + H^+$$

$$e_{cb}^- + O_2 \longrightarrow •O_2^-$$

- Very popular in academic studies (over 1000 papers), but $\Phi_{OH}$ is only 0.04.
- Very few industrial installations.

## TiO$_2$ Photolysis Mechanism



Conduction Band

**Reduction of Oxygen**

$e_{cb}^- + O_2 \rightarrow O_2^-$

$h\nu$

Bandgap Energy $U_g$ = 3.2 eV = 387.5 nm

Valence Band

**Oxidation of Water**

$h_{vb}^+ + H_2O \rightarrow ·OH + H^+$

## Dark Homogeneous –
### O$_3$/H$_2$O$_2$

- At pH > 7, ozone reacts with H$_2$O$_2$ to generate ·OH radicals:

$$H_2O_2 + H_2O \longrightarrow HO_2^- + H_3O^+$$

$$O_3 + HO_2^- \longrightarrow •OH + •O_2^- + O_2$$

$$•O_2^- + H^+ \longrightarrow HO_2•$$

$$O_3 + •O_2^- \longrightarrow •O_3^- + O_2$$

$$•O_3^- + H^+ \longrightarrow HO_3• \ (pK_a = 6.15)$$

$$HO_3• \longrightarrow •OH + O_2$$

- Overall Reaction:

$$2\,O_3 + H_2O \longrightarrow 2\,•OH + 3\,O_2$$

## Dark Homogeneous –
### Fentons

- **The Fenton Reaction was discovered over 100 years ago and involves reaction of $Fe^{2+}$ with $H_2O_2$ to produce •OH radicals.**

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + \cdot OH$$

- **The reaction rate is optimal around pH ~ 3.**
- **Used only when pollutant concentrations are high, since large amounts of $Fe^{2+}$ and $H_2O_2$ are required.**
- **There is a problem of disposal of the iron sludge.**

## Dark Homogeneous –
### E-Beams and High-energy Radiation

- **Electron beams can be generated with energies 0.1 – 10 keV. These electrons can enter water and generate H• atoms and •OH radicals.**
- **The process is valuable with contaminated waters that absorb UV and visible very strongly.**
- **The same process occurs with high-energy radiation, such as that from radioactive sources (e.g., $\gamma$ rays).**

## Dark Homogeneous –
### Other Processes

- **Electric discharge**
  - **Passage of high-voltage electricity through water generates •OH and other radicals.**
- **Supercritical water oxidation**
  - **Heating contaminated water and oxygen at high pressure can exceed the “critical point”. This results in accelerated oxidation of the organic contaminants.**
- **Sonolysis**
  - **Application of high-energy ultrasound results in “cavitation” in the water. Collapse of these “cavities” results in very high local temperatures and generation of •OH radicals by thermolysis.**

## Concept of Electrical Energy Dose

- **Most AOTs are driven by processes (e.g., UV lamps) that consume electrical energy.**
- **Define *Electrical Energy Dose* (EED) as kWh of electrical energy consumed per m³ of water treated.**

$$\text{EED} = \frac{P \cdot t}{V}$$

**$P$ / kW is the lamp power , $t$ / h is the time of irradiation, $V$ / m³is the total system volume.**

## Figure-of-Merit for AOTs

- **Electrical energy is usually the principal factor in the operating cost of AOT systems.**
- **For low concentrations (<100 mg/L), define *Electrical Energy per Order* ($E_{EO}$) as the electrical energy dose (kWh m$^{-3}$) necessary to reduce the concentration of a pollutant by one order of magnitude.**

## Electrical Energy per Order ($E_{EO}$)

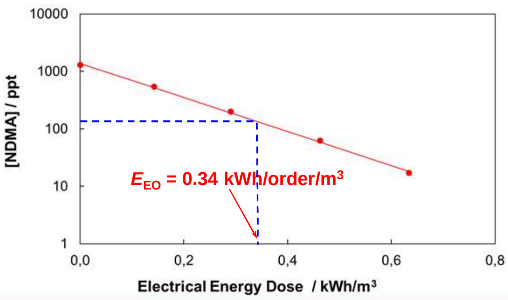
$$E_{EO} = \frac{\text{EED}}{\log(c_i / c_f)}$$

$$\log(c_f) = \log(c_i) - \frac{\text{EED}}{E_{EO}}$$

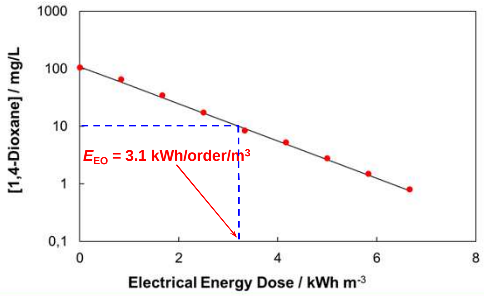
**Thus a plot of log($c_f$) versus EED has a slope of –1/$E_{EO}$.**

**$c_i$,$c_f$ are the initial and final pollutant concentrations**

## Direct Photolysis Treatment of NDMA



## UV/$H_2O_2$ Treatment of 1,4-Dioxane



## $E_{EO}$ Values for Some Pollutants

| Pollutant | •OH rate constant / $10^9$ $M^{-1}$ $s^{-1}$ | Electrical Energy per Order ($E_{EO}$) / kWh/order/$m^3$ |
|---|---|---|
| NDMA (direct photolysis) | --- | 0.15 – 0.3 |
| Benzene and its derivatives | 4 – 7 | 2 – 10 |
| Chlorinated alkenes (e.g., TCE) | 4 – 7 | 1 – 5 |
| 1,4-dioxane | 2.8 | 1 – 3 |
| Atrazine | 2.5 | 1 – 5 |
| MTBE | 1.6 | 0.3 – 1.5 |
| $CHCl_3$ | 0.005 | 10 – 60 |

## Kinetic Scheme

$$H_2O_2 \xrightarrow{h\nu} 2\ {\cdot}OH$$

$${\cdot}OH + M \xrightarrow{k_P} \text{Products}$$

$${\cdot}OH + S_i \xrightarrow{k_{S_i}} \text{Products}$$

Competition between ·OH/ and ·OH/Scavenger ($S_i$)

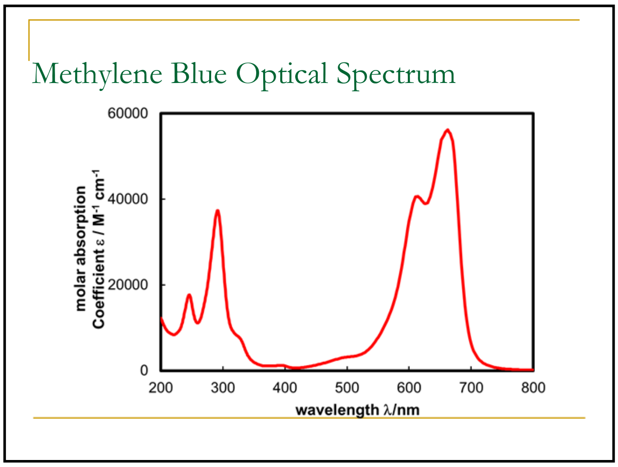
?

## Original paper freely available at

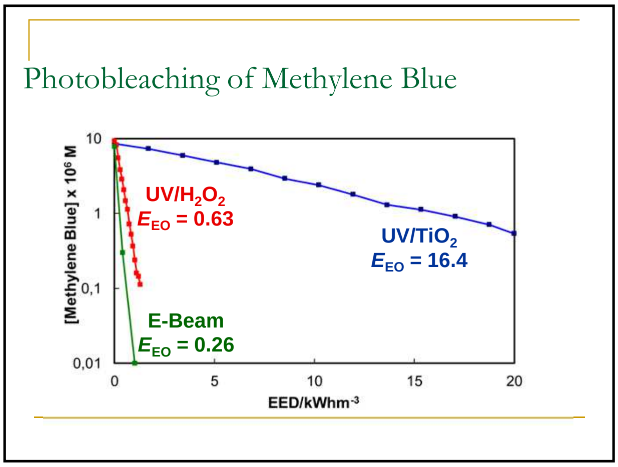
http://iupac.org/publications/pac/73/4/0627/

## Comparison of AOTs

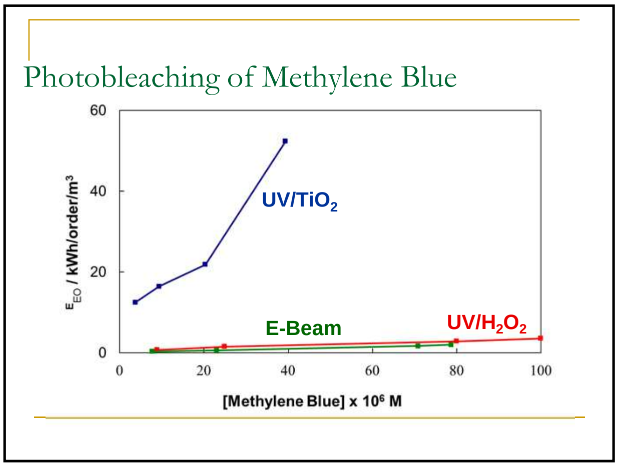
- **Used degradation of methylene blue and phenol to compare the following AOTs**
  - **UV/$TiO_2$**
  - **E-beam**
  - **UV/$H_2O_2$**
- **Bolton, J. R., J. E. Valladares, J. P. Zanin, W. J. Cooper, M. G. Nickelsen, D. C. Kajdi, T. D. Waite and C. N. Kurucz, 1998 "Figures-of-Merit for Advanced Oxidation Technologies: A comparison of homogeneous UV/$H_2O_2$, heterogeneous $TiO_2$ and electron beam processes", *J. Advan. Oxid. Technol.* 3, 174-181.**



## Methylene Blue Optical Spectrum

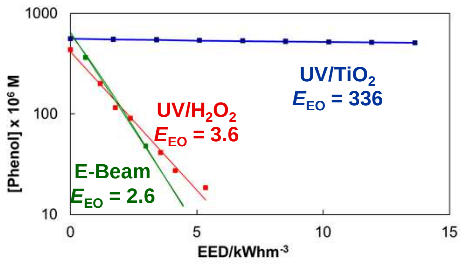


## Photobleaching of Methylene Blue



## Photobleaching of Methylene Blue

## Photodegradation of Phenol

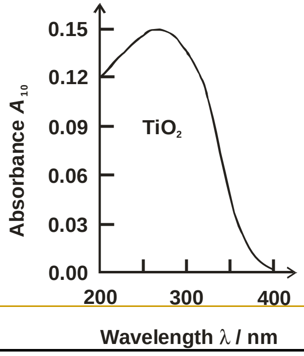


## Hyperlinks >>>>

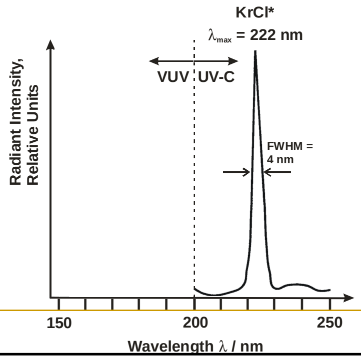
## Lectures 5 and 6

- **Development of Modern Mercury-free Excilamps for Water and Air Treatment and Applications in Photochemical Technology**

## Extinction spectrum (absorption + scattering) of polydispersed $TiO_2$ aqueous solutions, with [P-25 $TiO_2$] = 150 mg $L^{-1}$ and pH ~ 2



## Emission Characteristics of the KrCl* Excilamp Matches the Absorption Maximum of NDMA



## Critical Properties of Water

- Critical temperature
  - $T_c$ = 647.3 K (374.15 °C)
- Critical pressure
  - $p_c$ = 22.12 MPa (221.2 bar, 3028 psi)