PHOTOCATALYSIS

Bat Sheva Seminar
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Cleaning with (Sun)light
Advanced Oxidation Technologies (AOTs) use powerful oxidising intermediates to oxidise organic pollutants in contaminated air, water and soil. Most of the commercially viable AOTs use uv and/or visible light to generate the hydroxyl radical as the oxidising intermediate. The oxidation reactions are thermodynamically spontaneous ($\Delta G^o < 0$) but are extremely slow in the absence of catalysis. For example:

![Chemical structure of MTBE](image)
Homogeneous AOTs

The UV/O$_3$ process

\[ \text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}^{(1}\text{D}) \]
\[ \text{O}^{(1}\text{D}) + \text{H}_2\text{O} \rightarrow [\text{HO}\cdots\cdot\text{OH}] \rightarrow \text{H}_2\text{O}_2 \]
\[ \text{H}_2\text{O}_2 + h\nu \rightarrow 2 \cdot\text{OH} \]

The VUV water photolysis process

\[ \text{H}_2\text{O} + h\nu \rightarrow \text{H}\cdots + \cdot\text{OH} \quad \Phi = 0.4 \]

The UV/H$_2$O$_2$ process

\[ \text{H}_2\text{O}_2 + h\nu \rightarrow 2 \cdot\text{OH} \quad \Phi = 1.0 \]

UV/vis Fenton’s processes

\[ \text{Fe}^{III}(\text{OH})^{2+} + h\nu \rightarrow \text{Fe}^{2+} + \cdot\text{OH} \quad \Phi \sim 0.5 \]
\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^- \]
Photocatalysis: the only important heterogeneous AOT

The UV/vis TiO$_2$ process

TiO$_2$ + $h\nu$ → $h^+_{vb}$ + e$^{-}_{cb}$

Transit time to surface

= $R^2/\delta D \approx 1 - 10$ ps

e$^{-}_{CB}$ → e$^{-}_{s}$ (as Ti$^{III}_{s}$)

e$^{-}_{s}$ + O$_2$ → O$_2$•$^{-}_{s}$

h$^+_{VB}$ → h$^+_{s}$ (as •OH$_s$)
(Heterogeneous) photocatalysis has come to mean the oxidation by air of noxious or unwanted organic compounds by the action of (sun)light on a particulate semiconductor catalyst (nearly always TiO$_2$), to ‘mineralised’ products. For example:

\[
\begin{align*}
\text{OH} & \\
\text{Cl} & \\
\hline
\end{align*}
\xrightarrow{\text{TiO}_2, \text{hv}} \quad \text{H}_2\text{O}, \text{O}_2
\text{many steps} \quad \rightarrow \quad \text{CO}_2 + \text{H}_2\text{O} + \text{Cl}^-
\]
The hydroxyl radical

\[ \cdot\text{OH} + e^- \rightarrow \text{OH} \quad E_m(\text{SHE}) = +2.27 \text{ V at pH 7} \]

\[ \cdot\text{OH} + \text{O} \rightarrow pK_a = 11.9 \]

*Abstraction of a hydrogen atom* – usually with aliphatic hydrocarbon groups; for example:

\[ \text{CH}_3\text{OH} + \cdot\text{OH} \rightarrow \cdot\text{CH}_2\text{OH} + \text{H}_2\text{O} \]

*Insertion* – usually with unsaturated or aromatic hydrocarbon groups; for example:

\[ \text{CHCl}=-\text{CCl}_2 \text{ (TCE)} + \cdot\text{OH} \rightarrow \cdot\text{CHCl–C(OH)Cl}_2 \]

*Electron transfer* – usually with inorganics; for example:

\[ \text{I}^- + \cdot\text{OH} \rightarrow \cdot\text{I} + \text{OH}^- \]
Crystal structure of TiO$_2$

- Rutile: $E_g = 3.0$ eV
- Anatase: $E_g = 3.2$ eV
Fujishima and Honda

TiO$_2$ band-edge energies and some relevant redox potentials vs. SHE

-1
0
+1
+2
+3

H$_2$/H$_2$O (-0.413)
O$_2$/O$_2^*$ (-0.28)
O$_2$/H$_2$O$_2$ (+0.28)
O$_2$/H$_2$O (+0.83)
H$_2$O$_2$/H$_2$O (+1.35)
O$_3$/H$_2$O (+2.07)
•OH/H$_2$O (+2.27)
Competitive processes on TiO$_2$ particles

Rate of (most) heterogeneous photocatalytic reactions

$$
\Gamma I^\alpha
$$

where $\alpha = 1$ at very low light intensities,

$\alpha$ decreases to $\frac{1}{2}$ at ordinary (higher) light intensities because of $e^-$-$h^+$ recombination

Hence maximum quantum yield for pollutant destruction is only $\sim 0.04 - 0.05$
Laboratory ‘pot’ photocatalytic reactor for water treatment

1000 wt Xe arc lamp
Condenser
IR filter – 10 cm of distilled water cooled externally, cut-off at 1000nm
Mirror - 45° inclined
Fibre optics monitor
Colored glass filter from 300nm and up to 3000 nm
Photocatalytic reactor
Oxygen supply
50 mm Aperture
Stirring bar
Sampling port
Thermocouple
Stirring plate
Water-cooling
MFC
Fixed-bed photocatalytic reactor for air purification
Lab-scale photocatalytic reactor for groundwater remediation

UV lamp or solar radiation

Light pipe

Borehole

Groundwater flow

Catalyst coating

Light scattering device

Chan et al., J. Hydrological Sciences
Photocatalysis is most suitable for end-stage remediation

Time needed to decompose 1 mole of TCE on an irradiated area of 100 cm²

<table>
<thead>
<tr>
<th>Light source</th>
<th>High-pressure Hg lamp</th>
<th>Sunlight</th>
<th>White fluorescent light</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV intensity</td>
<td>~20 mW cm⁻²</td>
<td>&lt;3 mW cm⁻²</td>
<td>~10 μW cm⁻²</td>
</tr>
<tr>
<td>Time</td>
<td>12 days</td>
<td>11 weeks</td>
<td>63 years</td>
</tr>
</tbody>
</table>

1 μW cm⁻² uv light corresponds to ~10¹² photons cm⁻² s⁻¹
Plataforma Solar de Almeria
TiO$_2$ photocatalysis for water purification
Self-cleaning TiO$_2$ surfaces

BUT - UV illumination is in the range of only a few $\mu$W cm$^{-2}$ indoors to a few mW cm$^{-2}$ outdoors

Fujishima et al.
Photocatalytic floor tiles

Fujishima et al. (1999)
Self-cleaning building cladding
Photocatalytic air filter

1. **Prefilter**
2. **Photocatalytic filter**
3. **Fan**
4. **HEPA filter**
5. **UV lamp**

**Airflow Process**
- Air enters the system.
- Prefilter removes large particles.
- UV lamp sterilizes and photocatalytically decomposes malodorous substances into CO₂ and water.
- HEPA filter removes fine particles.
- Clean air is discharged.

**Materials**
- Fabrics, paper, ceramics, etc.
- Absorbent (Active carbon or zeolite)
- TiO₂

**Light Decomposition**
- Light decomposes CO₂ and malodorous substances into water and carbon dioxide.
Disinfection by photocatalysis

Sunada et al. (2003)
Superhydrophilicity

Fujishima et al.
Inter-Particle Electron Transfer

Serpone et al.

$E_g = 2.4 \text{ eV}$

$E_g = 3.2 \text{ eV}$
Bifunctional catalyst for ‘water cleavage’
Other semiconductors

Potential (vs. Standard Hydrogen Electrode)

-0.2 V

GaP, ZrO₂, Si, CdS, KTaO₃, CdSe, SrTiO₃, TiO₂, Nb₂O₅, ZnO, Fe₂O₃, WO₃, SnO₂

H₂/H₂O

O₂/H₂O

Lower edge position of conduction band

Upper edge position of valence band

pH=0
CO$_2$ photoreduction

Halmann et al.
Gabriel Stein (1920–1976)