Photochemical AOPs

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Characteristics of Light

✓ **Planck law of radiation**

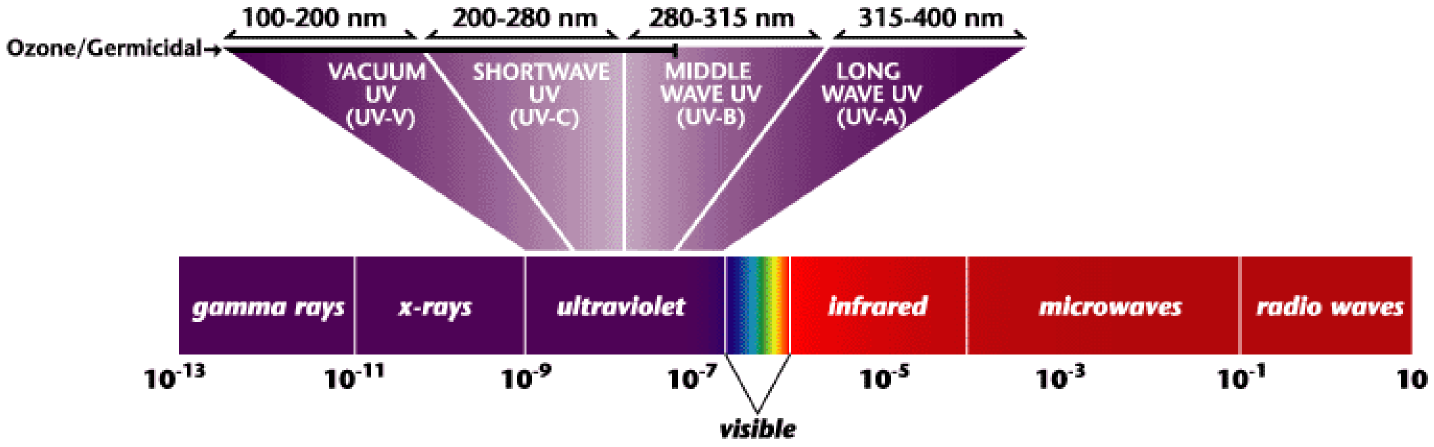
$$u = h\nu = hc/\lambda = hc\bar{\nu}$$

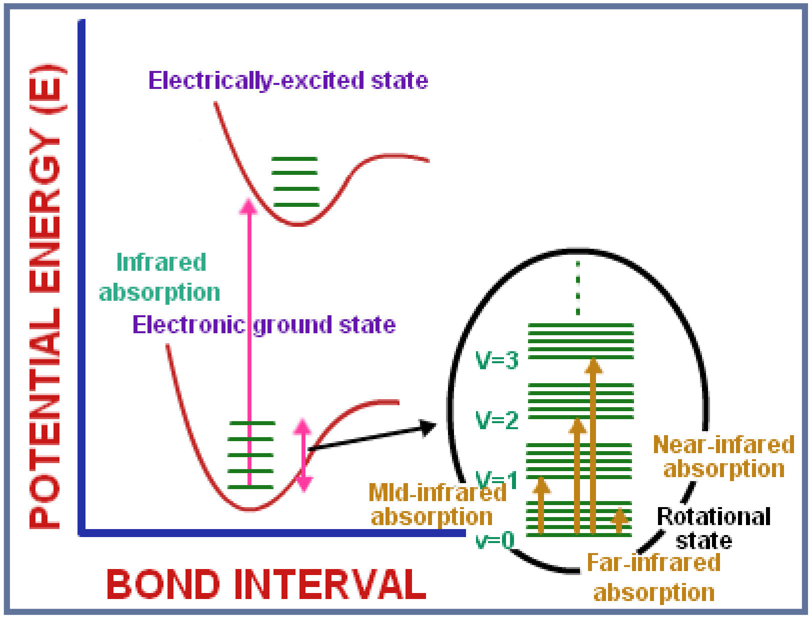
$$U = N_A h\nu = hcN_A/\lambda = hcN_A\bar{\nu}$$

Where u = energy (J) of one photon
v = frequency (s^{-1})
λ = wavelenght (m)
$\bar{\nu}$ = wavenumber (m^{-1})
c = speed of light ($2.9979 x 0^{8}$ ms^{-1})
h = Planck constant ($6.6261 x 10^{-34}$ Js)
N_A = Avogadro number (6.02214×10^{23} mol^{-1})
U = energy per einstein

Characteristics of Light

✓ **Electromagnetic spectrum**





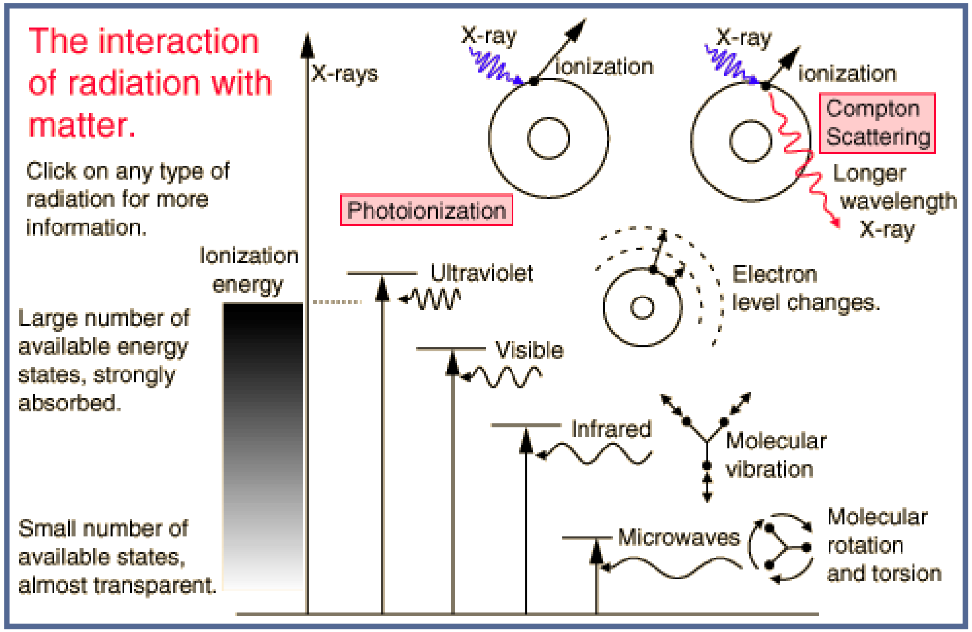


Photo-Excitation and Subsequent Processes

$A + h\nu \rightarrow A^*$
(photo-excitation)

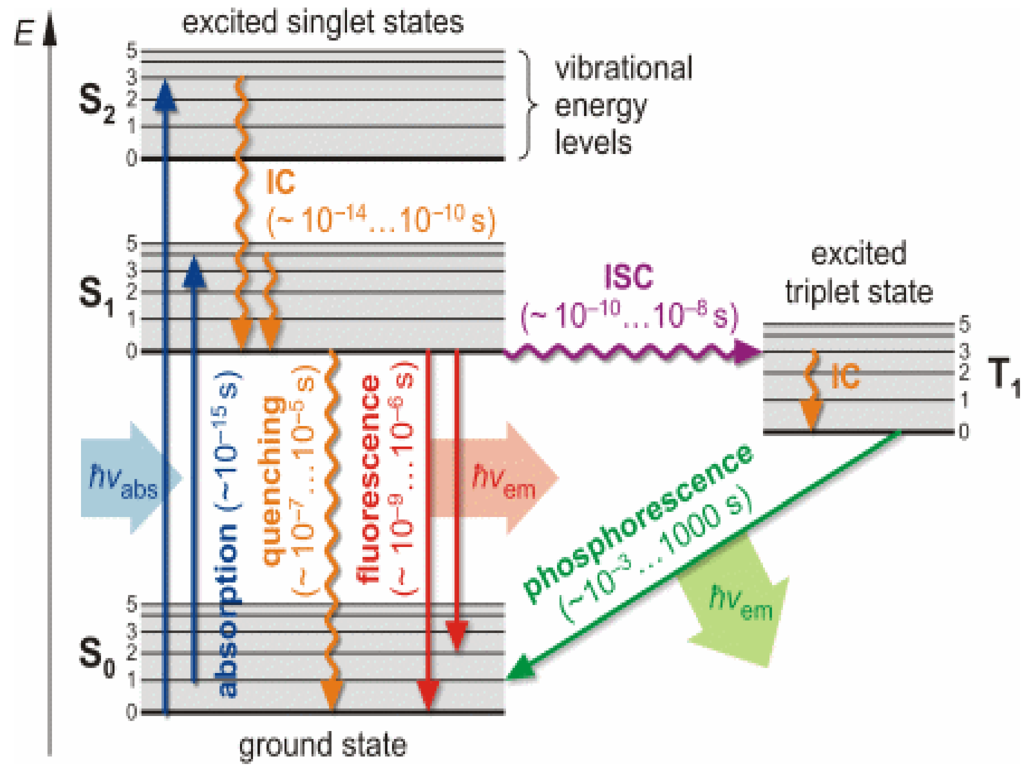
$A^* \rightarrow A + \text{heat}$
(thermal decay)

$A^* \rightarrow A + h\nu'$
(fluorescence)

$A^* \rightarrow A + h\nu''$
(phosphorescence)

$A^* \rightarrow B$
(photochemical reaction)

Fluorescence and Phosphorescence



UV Energy and Bond Dissociation Energy

Radiation energy

Range	Wavelength Range (nm)	Energy Range (kJ/Einstein)
Near Infrared	700 ~1000	120 ~ 171
Visible	400 ~ 700	171 ~ 299
UVA	315 ~ 400	299 ~ 380
UVB	280 ~ 315	380 ~ 427
UVC	200 ~ 280	427 ~ 598
VUV	100 ~ 200	598 ~ 1196

Average Bond Enthalpies (kJ/mol)

Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						

Multiple Bonds

C=C	614	N=N	418	O_2	495
C≡C	839	N≡N	941		
C=N	615			S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

Quantum Yield

√ **Definition**

$$\mathbf{A} + \boldsymbol{h\nu} \rightarrow \mathbf{B}$$

$$\phi_A = \frac{\text{Molecules (mole) of A decomposed per unit volume per unit time}}{\text{Quanta of light (Einstein) absorbed by A per unit volume per unit time}}$$

$$\phi_B = \frac{\text{Molecules (mole) of B formed per unit volume per unit time}}{\text{Quanta of light (Einstein) absorbed by A per unit volume per unit time}}$$

- ϕ_A is not always same as ϕ_B

√ Primary quantum yield: quantum yield for the primary photochemical reaction
√ Overall quantum yield: quantum yield considering the primary photochemical reaction and subsequent thermal reactions

e.g., $A + h\nu \rightarrow B + C$ (primary quantum yield = 0.5)
$A + C \rightarrow B$

Overall quantum yield for the photochemical production of B = 0.5 X 2 =1.0

Kinetics of Photochemical Reactions

✓ Beer-Lambert absorption law

$$I / I_0 = 10^{-\varepsilon b C}$$

ε: molar aborption coefficient (M^{-1} cm^{-1})
b: optical pathlength (cm)
C: molar concentration of photon absorber (M)

✓ Kinetic raw of photochemical reactions

$$A + hv \rightarrow B$$

$$d[A]/dt = \underbrace{I_0(1-10^{-\varepsilon b[A]})}_{\text{Absorbed photon flow by compound, A}} \times \phi$$

Absorbed photon flow by compound, A

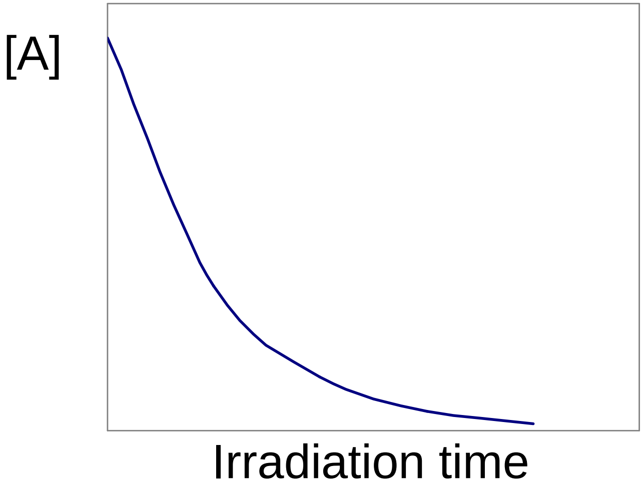
I_0 : incident photon flow (Einstein l^{-1} s^{-1})
ϕ : quantum yield

Kinetics of Photochemical Reactions

At a low concentration ($\varepsilon bc << 0.1$)

$$d[A]/dt = -I_0(1-10^{-\varepsilon b[A]}) \times \phi \approx -2.303\ I_0 \varepsilon b \phi [A]$$

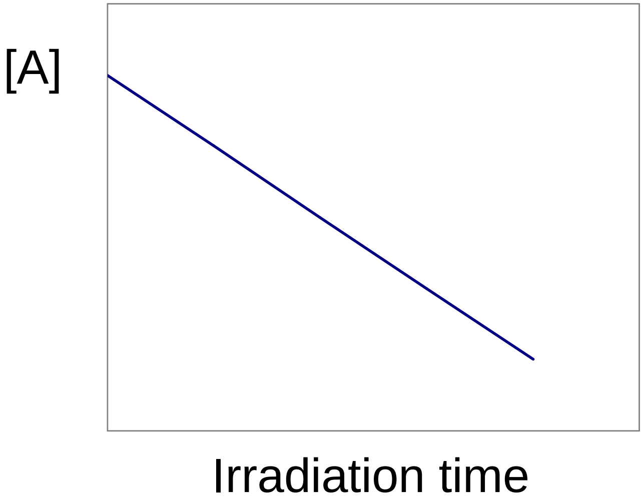
First order kinetics



At a high concentration ($\varepsilon bc >> 1$)

$$d[A]/dt = -I_0(1-10^{-\varepsilon b[A]}) \times \phi \approx -I_0 \phi$$

Zero order kinetics



Photolysis of Pollutants

✓ Direct photolysis

$$T + h\nu \rightarrow P$$

T: Target compound
P: Product

✓ Indirect photolysis

$$A + h\nu \rightarrow R$$
$$R + T \rightarrow P$$

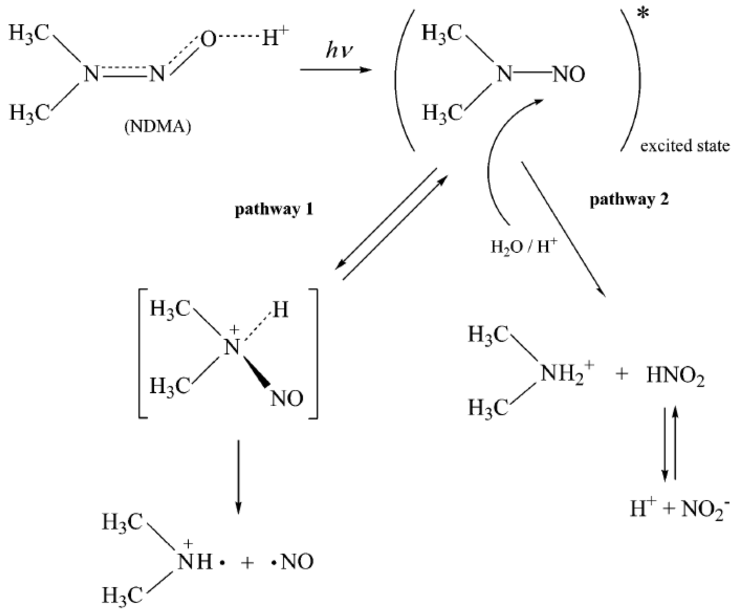
A: Light absorbing compound
R: Reactive compound

✓ Photo-catalysis

$$C + h\nu \rightarrow R$$
$$R + T \rightarrow C + P$$

C: Photo-catalyst

e.g., NDMA photolysis



e.g., UV/H_2O_2 system

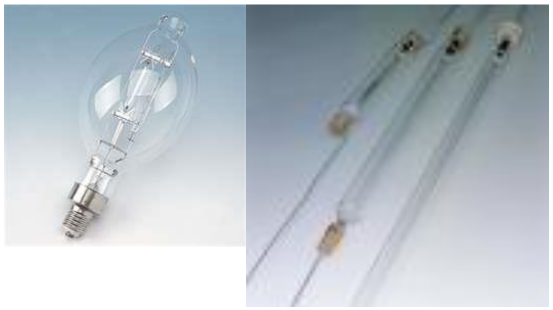
$H_2O_2 + h\nu \rightarrow 2{}^\bullet OH$
Compounds + ${}^\bullet OH \rightarrow$ Products

e.g., TiO_2 photo-catalysis

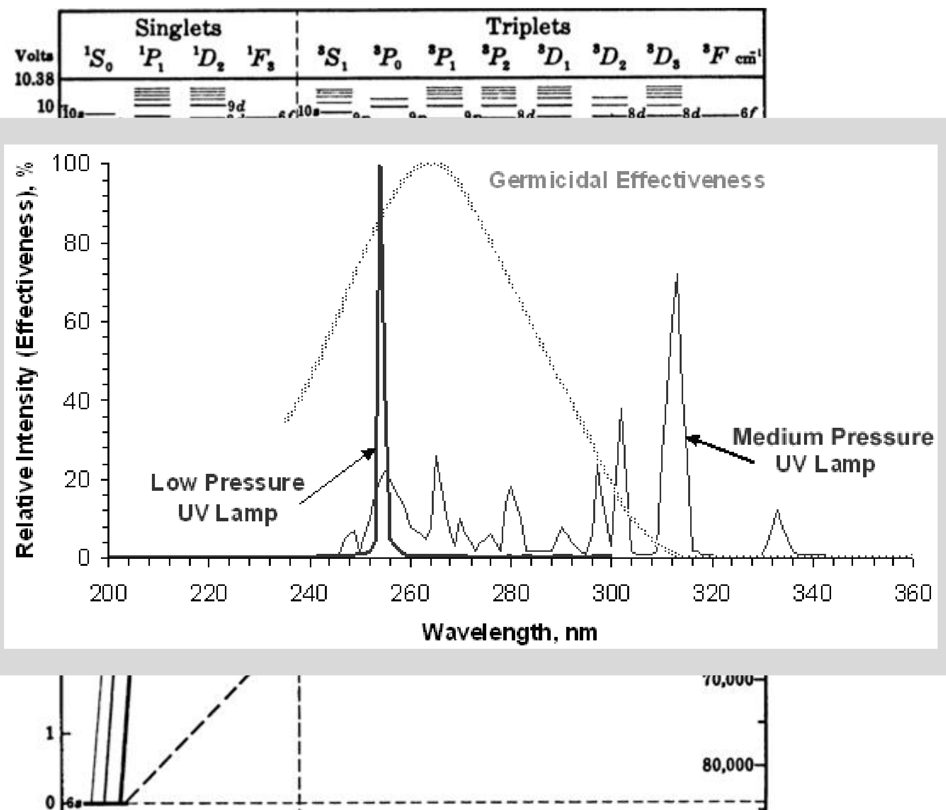
$TiO_2 + h\nu \rightarrow TiO_2(h^+ \;\&\; e^-)$
Compounds + $TiO_2(h^+ \;\&\; e^-) \rightarrow$ Products + TiO_2

UV Lamps

Mercury vapor lamps



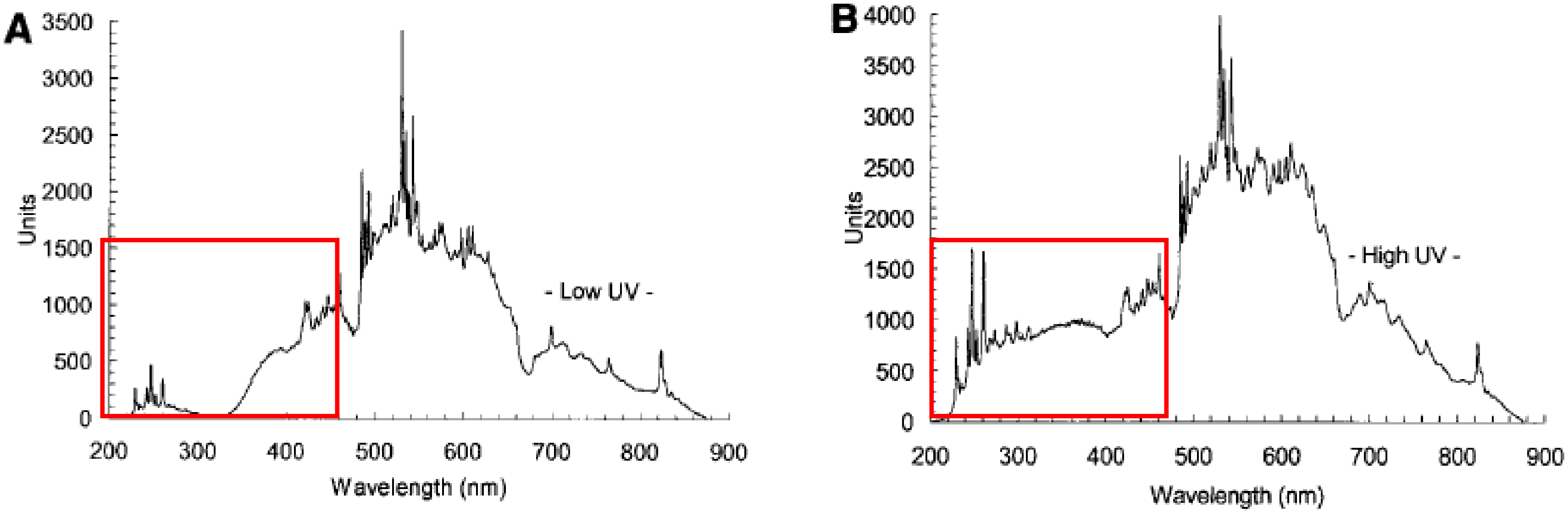
- Low pressure Hg lamps: monochromatic emission at 254 and 185 nm(표준형, 고출력 저압수은 램프)
- Medium and High pressure Hg lamps: polychromatic emission from 200~800 nm(수은 중압, 고압 램프)



Wavelength (nm)	Color
184.5	VUV
253.7	UVC
365.4	UVA
404.7	Violet
435.8	Blue
546.1	Green
578.2	Yellow-orange

UV Lamps

Mercury vapor lamps (medium or high pressure)



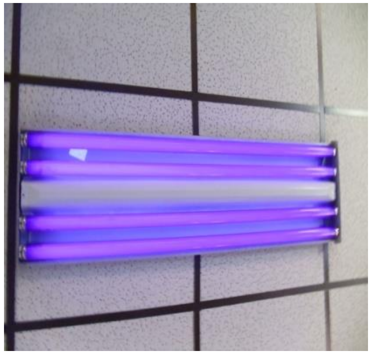
A: Continuous UV lamp

B: Pulsed UV lamp

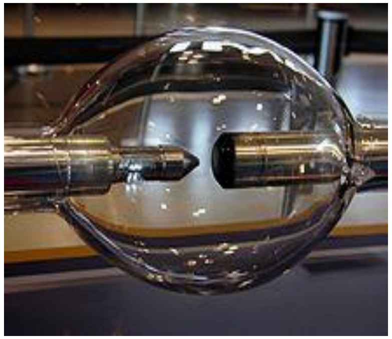
The major difference in emission spectra occurs between 200 and 450 nm.

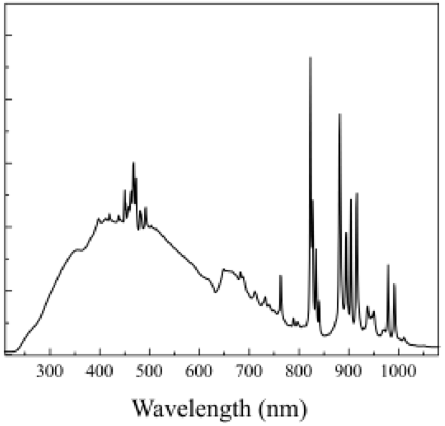
UV Lamps

Black light blue (BLB) lamps



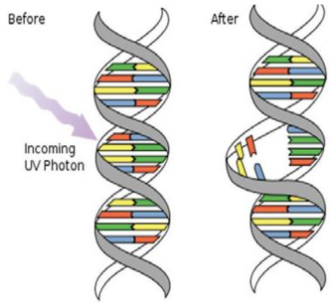
Xenon arc lamps (solar simulator)

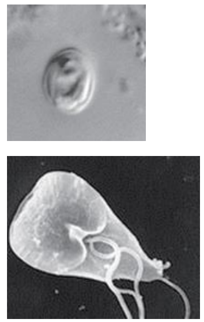




Phosphor	Peak, nm	Width, nm	Philips Suffix.	Osram Suffix.	U.S. Type	Uses
Mixture	450	50	-	/71	-	hyperbilirubinaemia, polymerization
SrP_2O_7, Eu	420	30	/03	/72	-	polymerization
SrB_4O_7, Eu	370	20	/08	/73	("BLB")	forensics, night clubs
SrB_4O_7, Eu	370	20	-	/78	("BL")	insect attraction, polymerization, psoriasis, suntanning
$BaSi_2O_5$, Pb	350	40	/09	/79	"BL"	insect attraction, suntanning lounges
$BaSi_2O_5$, Pb	350	40	/08	-	"BLB"	dermatology, forensics, night clubs
$SrAl_{11}O_{18}$, Ce	340	30	-	-	-	photochemical uses
$MgSrAl_{10}O_{17}$, Ce	310	40	-	-	-	medical applications, polymerization

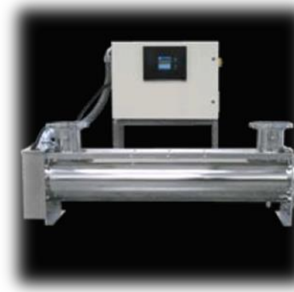
Water Treatment Using Photochemical Reactions





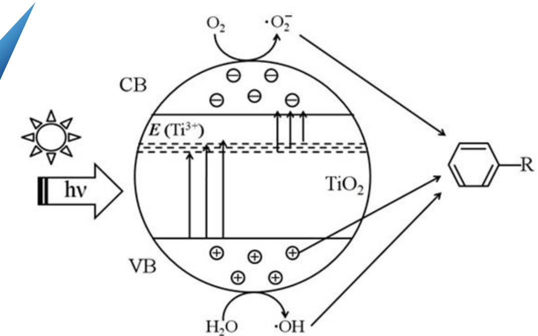
UV Disinfection

Ultrapure Water
Production
(VUV)



Photochemical Reactions

Drinking Water Treatment
(UV/H_2O_2 system)



Wastewater Treatment
(Photo-Fenton, UV/TiO_2???)

The UV/H_2O_2 System

$$H_2O_2 + h\nu \rightarrow 2\,{}^{\bullet}OH$$

Primary quantum yield: 0.5

$$H_2O_2 + h\nu \leftrightarrow [HO^{\bullet} + {}^{\bullet}OH] \rightarrow 2{}^{\bullet}OH$$

Solvent Cage

Subsequent reactions

$${}^{\bullet}OH + H_2O_2 \rightarrow HO_2{}^{\bullet} + H_2O$$

$$2HO_2{}^{\bullet} \rightarrow H_2O_2 + O_2$$

$$2{}^{\bullet}OH \rightarrow H_2O_2$$

The Photo–Fenton System

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + {}^{\bullet}OH + OH^-$$

$63\ M^{-1}s^{-1}$ (fast)

$$Fe(III) + H_2O_2 \rightarrow Fe(II) + HO_2^{\bullet} + H^+$$

$<0.01\ M^{-1}s^{-1}$(slow)

$$Fe(III) + H_2O + h\nu \rightarrow Fe(II) + {}^{\bullet}OH + H^+$$

Photochemical reduction of Fe(III) to Fe(II)

Photochemical Reactions of Ferric Complexes

✓ Ferric-hydroxo complexes

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + \bullet OH + H^+ \qquad (1)$$

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

$$Fe_2(OH)_2^{4+} + h\nu \rightarrow Fe(III) + Fe^{2+} + \bullet OH \qquad (3)$$

The photochemical reaction (2) is dominant due to its high quantum yields (0.1 ~ 0.2) and the high fraction of $Fe(OH)^{2+}$ in weakly acidic conditions

✓ Other ferric complexes

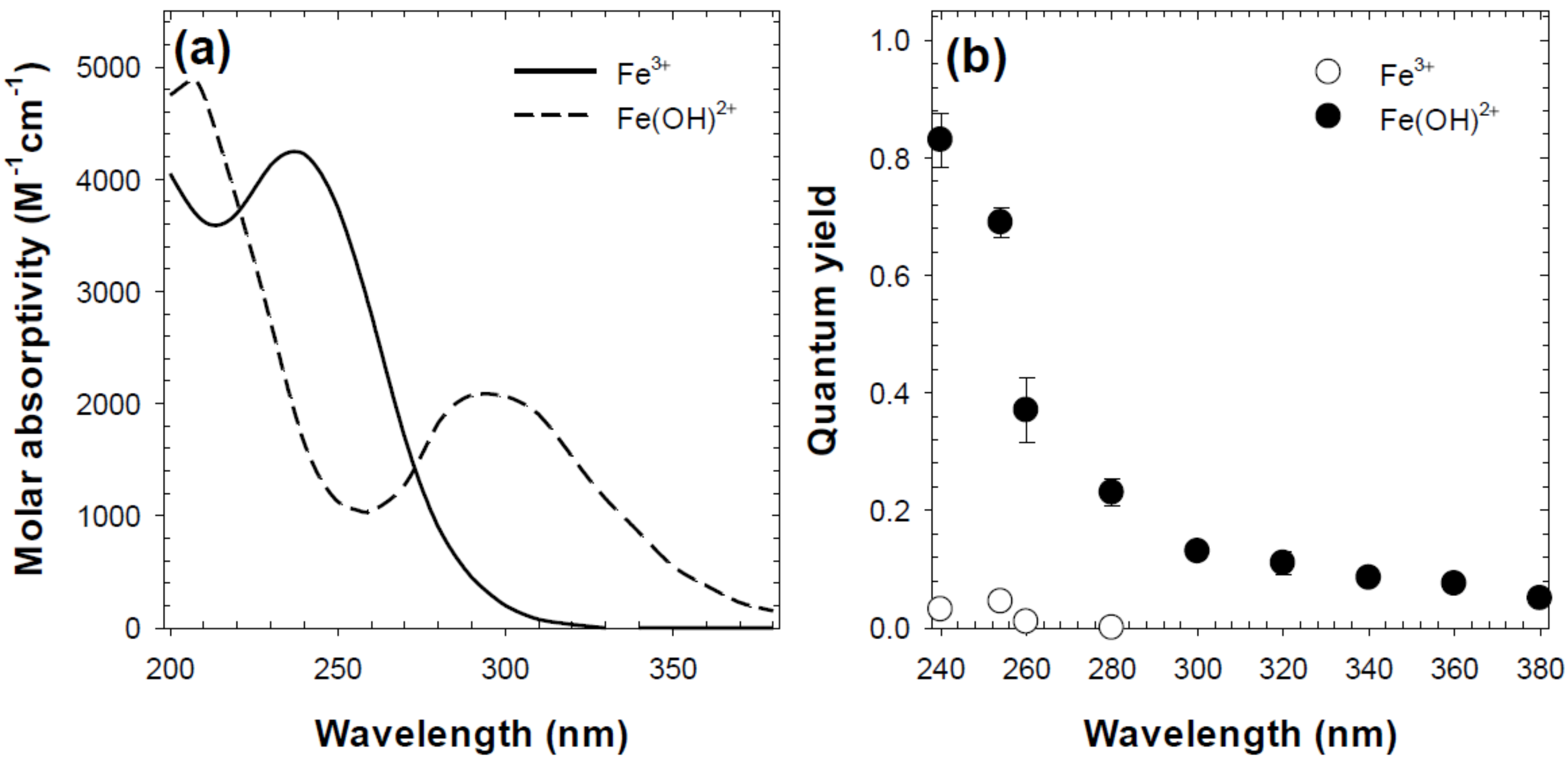
$$\text{General form: } Fe^{3+}(X) + h\nu \rightarrow Fe^{2+} + X\bullet$$

e.g., $Fe(SO_4)^{+} + h\nu \rightarrow Fe^{2+} + SO_4^{-}\bullet$

$Fe(Cl)^{2+} + h\nu \rightarrow Fe^{2+} + Cl\bullet$

$Fe(Ox)_3^{3-} + h\nu \rightarrow Fe^{2+} + 2C_2O_4^{2-} + C_2O_4^{-}\bullet$

Light Absorption and Quantum Yields for Photolysis of Ferric-Hydroxo Complexes



⇑ Molar absorption coefficients (a) and quantum yields for the photochemical reactions (b) of Fe(III)-hydroxo complexes as a function of wavelength

Quantum yields for Photolysis of Several Ferric Complexes

$$Fe^{3+}(X) + h\nu \rightarrow Fe^{2+} + X\bullet \qquad \phi_{Fe2+}$$

Fe(III) complexes	λ (nm)	ε (M^{-1} cm^{-1})	φ
Fe^{3+}	240 ~ 260	2800–4225	0.01–0.06
$Fe(OH)^{2+}$	240 ~ 380	150–1650	0.05–0.8
$Fe_2(OH)_2{}^{4+}$	350	4106	0.007
$Fe(Cl)^{2+}$	347	1600	0.5
$Fe(SO_4)^{+}$	280 ~ 350	576–2043	$(1.51–7.28) \times 10^{-3}$
$Fe(C_2O_4)_3{}^{3-}$	280 ~ 480	0–5550	0.5–0.6 (1.0–1.2)[a]
$Fe(OH)(citrate)^{-}$	365	900	0.28-0.29

[a] Overall quantum yields for the production of Fe(II)

Photo–Ferrioxalate System

✓ Classical Fenton and photo-Fenton system

Classical Fenton

- $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^-$
- Input of high concentration Fe(II)
- Production of large iron sludge

Photofenton

- $Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + \bullet OH$
- Input of low concentration of Fe(II) or Fe(III) (photochemical recycling)
- Reduced iron sludge production

✓ What is the photo-ferrioxalate system?

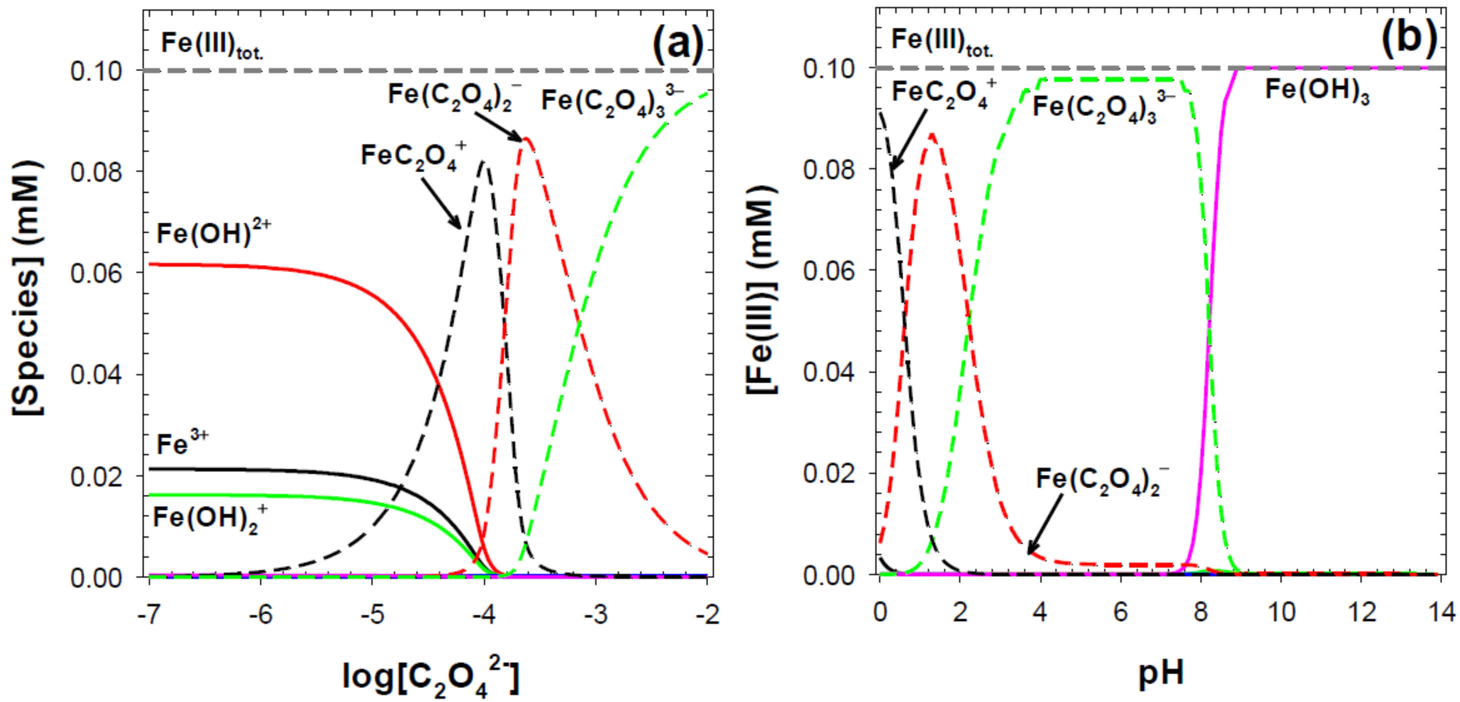
A new photo-fenton system using ferric oxalate complexes, which have better photochemical activity and solubility at neutral pH.

Formation of Ferrioxalates (Fe(III)–Oxalato Complexes)

$$Fe^{3+} + C_2O_4^{2-} \rightleftarrows Fe(C_2O_4)_2^{+} \qquad K_{24} = 2.5 \times 10^9\ M^{-2}$$

$$Fe^{3+} + 2C_2O_4^{2-} \rightleftarrows Fe(C_2O_4)_2^{-} \qquad K_{25} = 1.6 \times 10^{16}\ M^{-2}$$

$$Fe^{3+} + 3C_2O_4^{2-} \rightleftarrows Fe(C_2O_4)_3^{3-} \qquad K_{26} = 6.0 \times 10^{20}\ M^{-3}$$



⇑ Speciation of Fe(III)-oxalato complexes as functions of oxalate concentration (a) and pH (b) ($[Fe(III)]_{tot}$ = 0.1 mM, pH 3 for (a), $[oxalate]_0$ = 3 mM for (b)).

Characteristics of Photo-Ferrioxalate System

High molar absorptivity

High quantum yields for Fe(II) generation

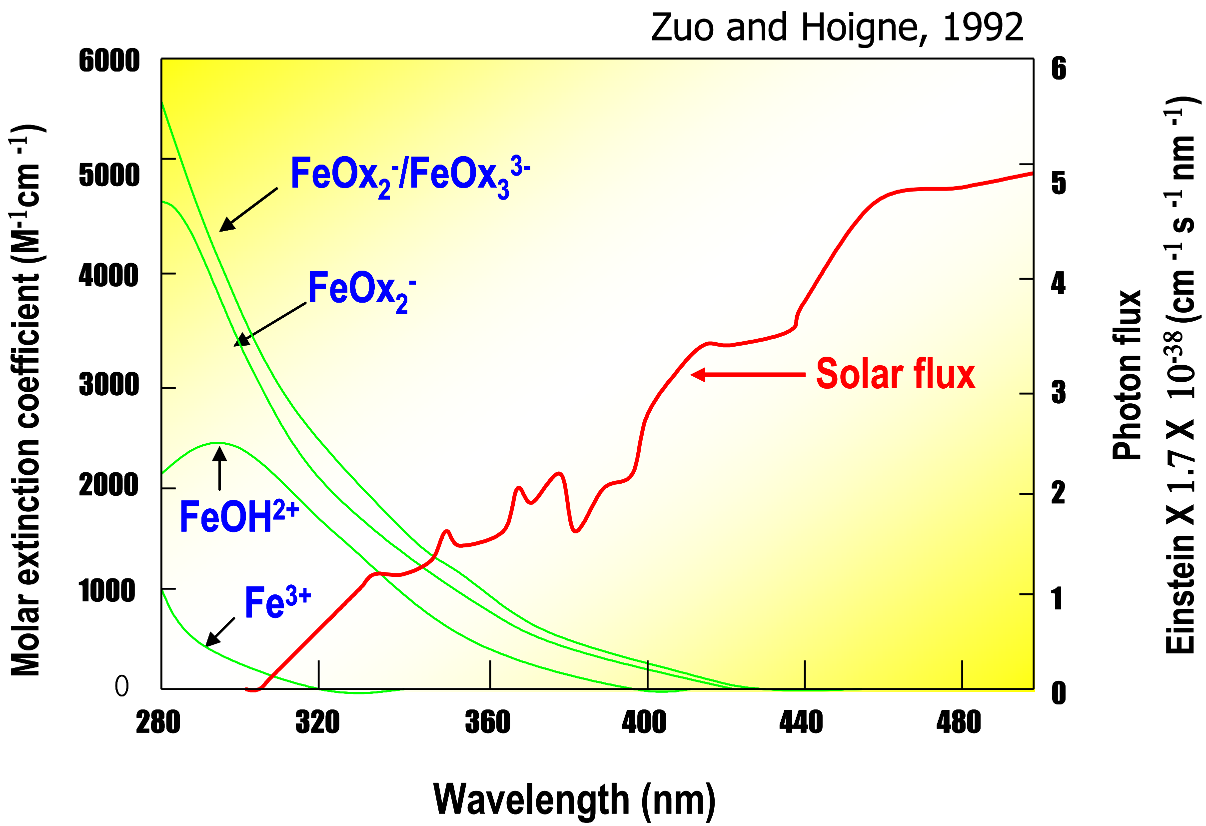
Production of highly reductive radical intermediate (CO_2^{-}•) and H_2O_2

Minimized effects of anions

Available at neutral pH

High Molar Absorptivity

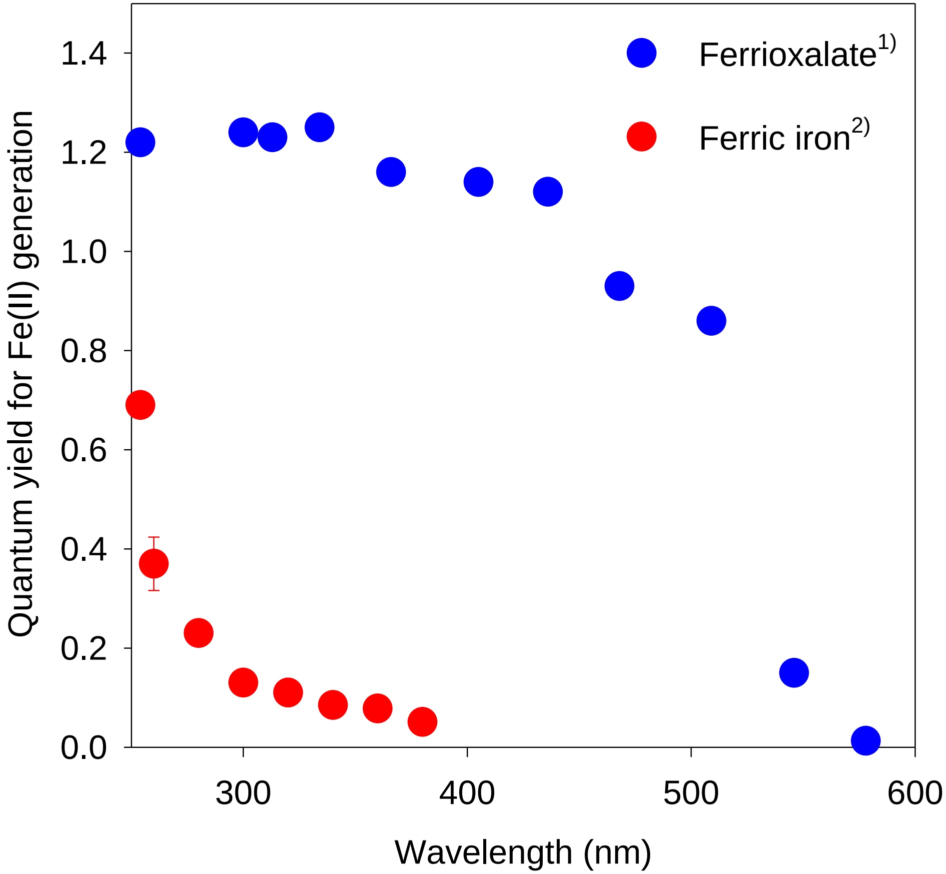
✓ **Light absorption spectrum of ferrioxalate**



- High molar absorptivity and wide light absorption band

High Quantum Yields for Fe(II) Generation

✓ Quantum yields for Fe(II) generation



1) Hatchard and Packer, 1956
2) Lee *et al.*, 2004

Ferric–hydroxo complexes

$Fe^{III}(OH)^{2+} + h\nu \rightarrow Fe^{2+}$

Ferrioxalate

$Fe^{III}(C_2O_4)_3^{3-} + h\nu \rightarrow Fe^{2+} + CO_2^{-}\bullet$

$CO_2^{-}\bullet + Fe(C_2O_4)_3^{3-} \rightarrow Fe^{2+}$

Production of $CO_2{\bullet}^-$ and H_2O_2

✓ Production of highly reductive radical intermediate ($CO_2^{-}\bullet$)

Photolysis of ferrioxalate

$$Fe(C_2O_4)_3^{3-} + h\nu \rightarrow Fe^{2+} + 2C_2O_4^{2-} + C_2O_4^{-}\bullet$$

$$C_2O_4^{-}\bullet \rightarrow CO_2^{-}\bullet + CO_2$$

Redox couples	E^0 (V vs. NHE)
$CO_2/CO_2^{-}\bullet$	- 1.9
e^- (CB) on TiO_2	- 1.5 ~
$N_2H_5^+/NH_3OH^+$	- 1.41
Fe^{2+}/Fe^0	- 0.44

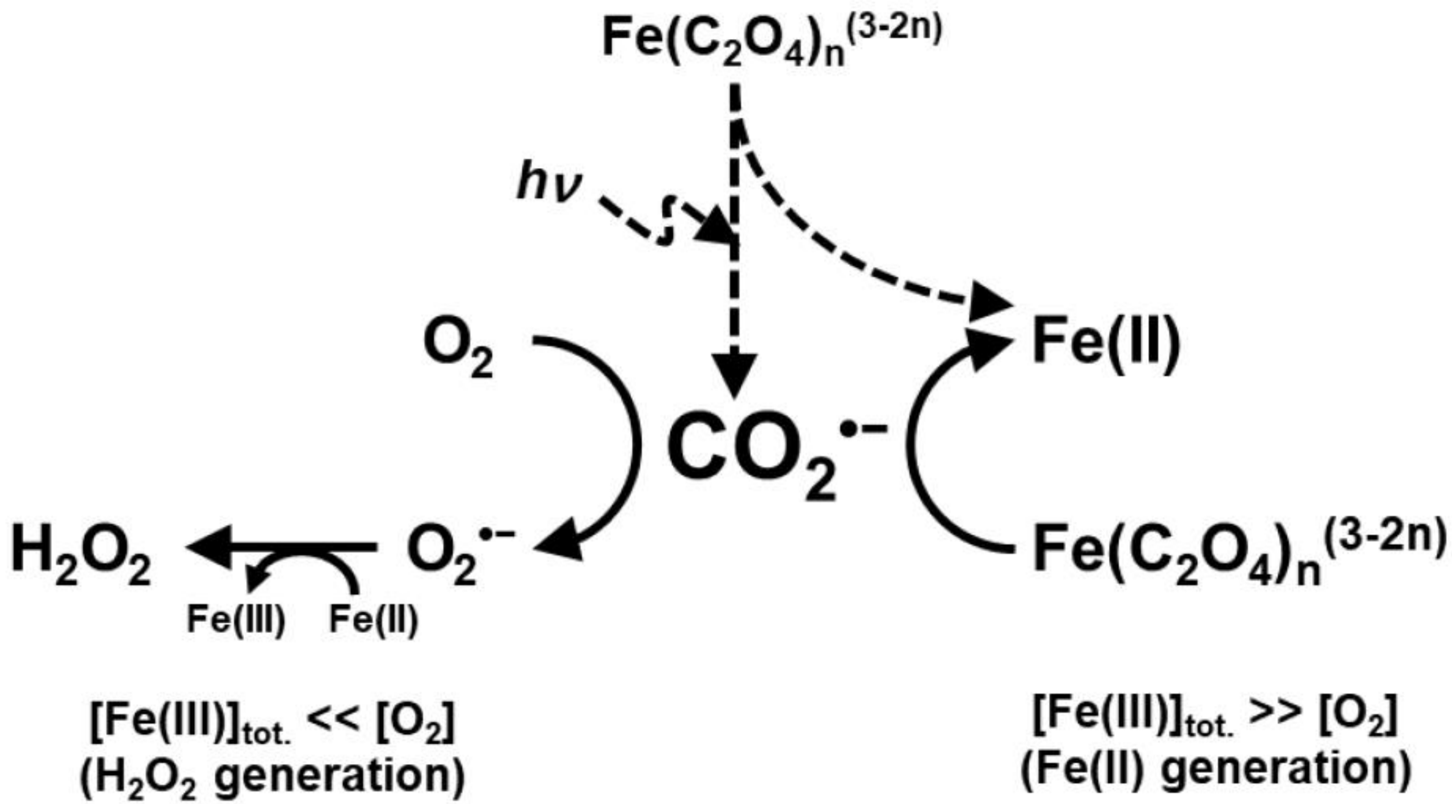
Fe(II) generation

$$CO_2^{-}\bullet + Fe(C_2O_4)_3^{3-} \rightarrow Fe^{2+} + CO_2 + 3C_2O_4^{2-}$$

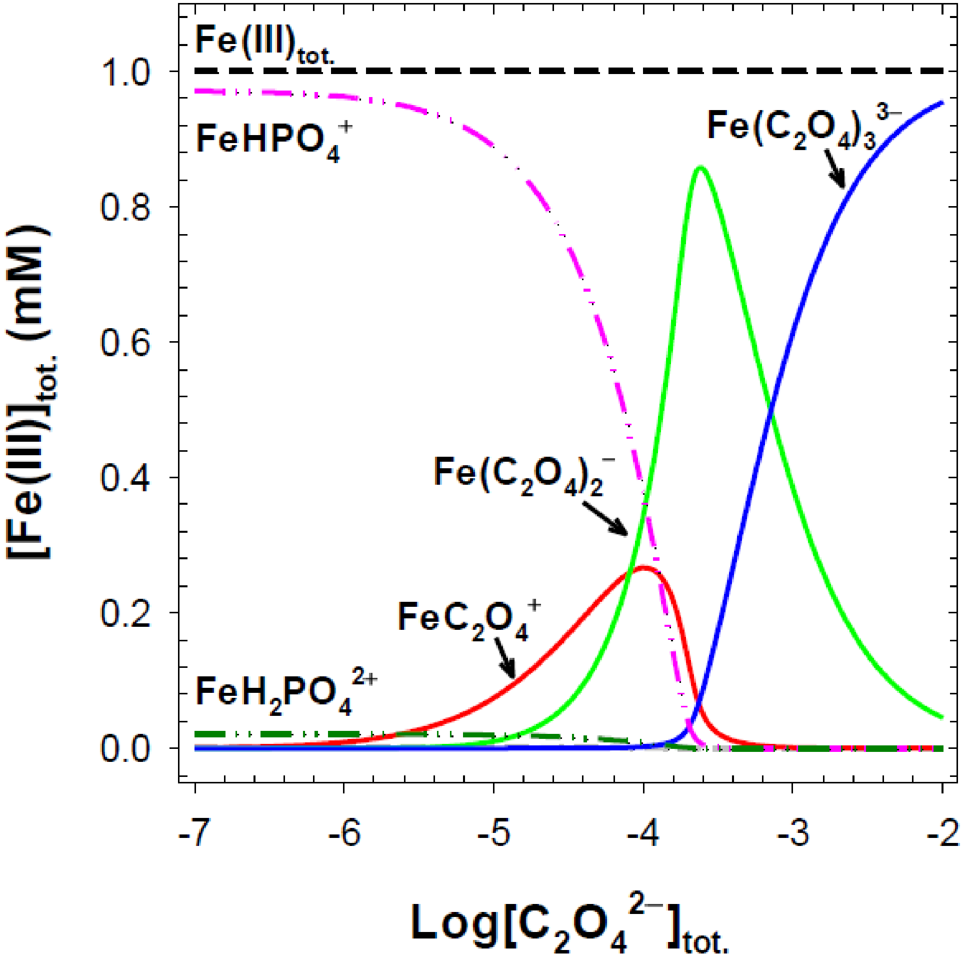
H_2O_2 generation

$$CO_2^{-}\bullet + O_2\ (+\ H^+) \rightarrow O_2^{-}\bullet(HO_2\bullet) + CO_2 \rightarrow\rightarrow H_2O_2$$

Production of $CO_2{\bullet}^-$ and H_2O_2



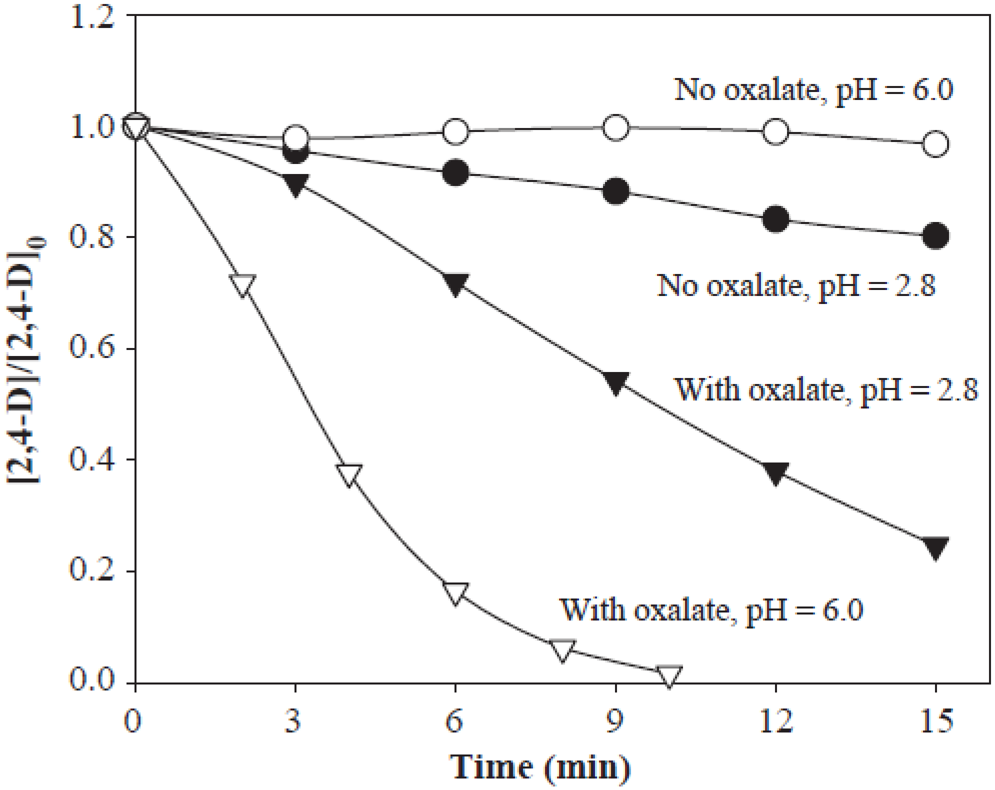
Minimized Effects of Anions

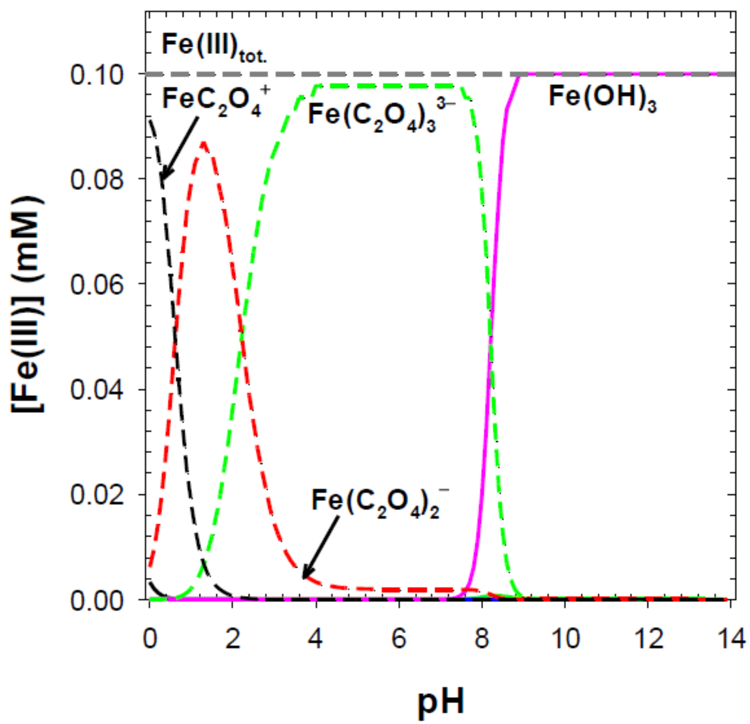


⇐ Speciation of Fe(III) in the presence of phosphate and oxalate; the speciation change from Fe(III)-phosphate to Fe(III)-oxalato complexes as a function of oxalate concentration ($[Fe(III)]_{tot}$. = 0.1 mM, $[Phosphate]_0$ = 1 mM, pH = 3.0)

Available at Neutral pH

Jeong and Yoon, 2005 (Water Res.)

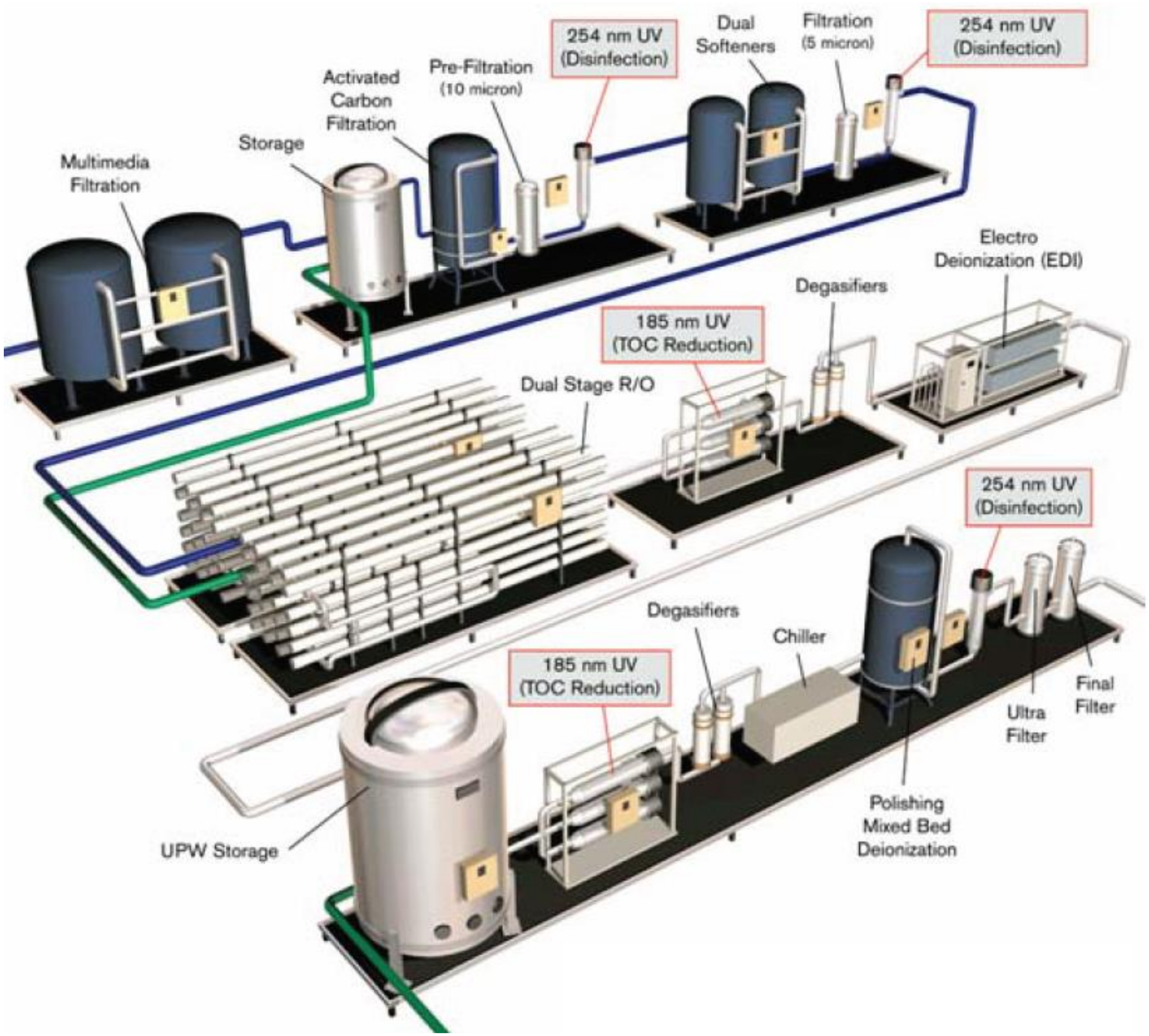




High solubility at neutral pH

⇑ The effect of pH and oxalate on 2,4-D degradation in photo/ferrioxalate system without H_2O_2 addition ($[Fe^{3+}]_0 = 10^{-5}$ M, $[2,4\text{-D}]_0 = 10^{-5}$ M, $[C_2O_4^{2-}]_0 = 0$ or 3×10^{-3} M, O_2 bubbling, $I_0 = 3.47 \times 10^{-6}$ Einstein $l^{-1}\,s^{-1}$).

Vacuum UV (VUV) Technology



(Ultrapure water production process, Aquafine Co.)

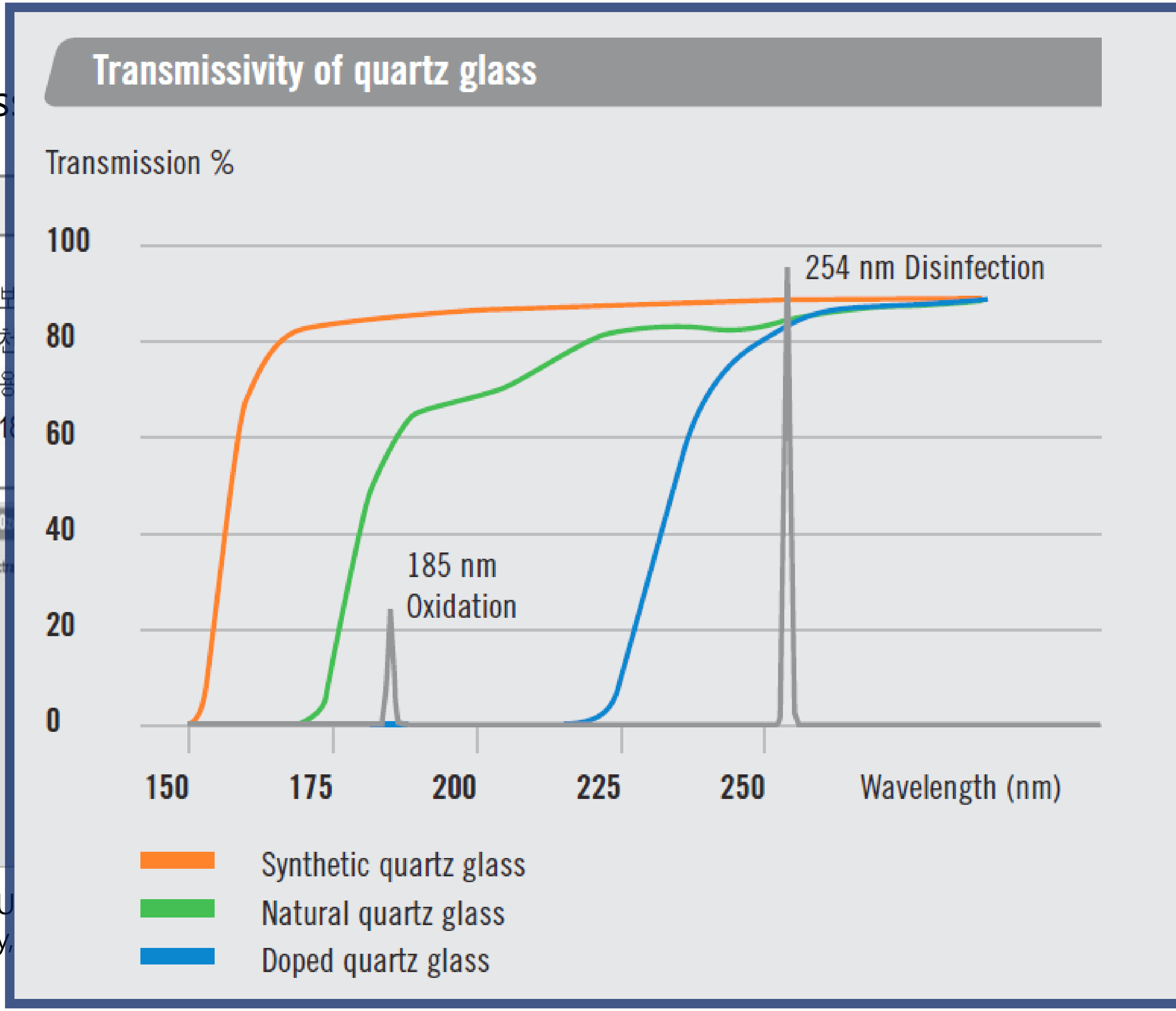
Disinfection
& TOC reduction

VUV Lamps

- UV Emis... tube

구분	
특성	- 보 - 천 옹 - 18
분광 분포	

The total U... % 185 nm energy,



VUV Lamps

Mercury-free Vacuum-(VUV) and UV Excilamps: Lamps of the Future?

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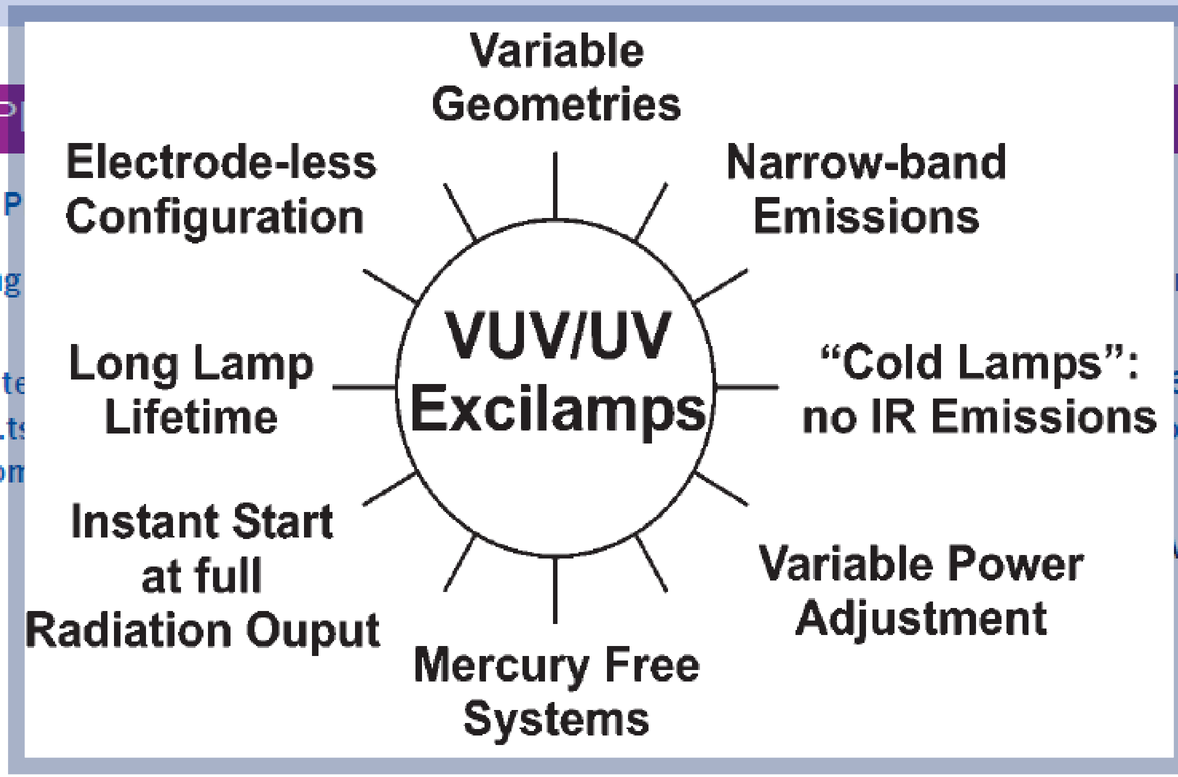

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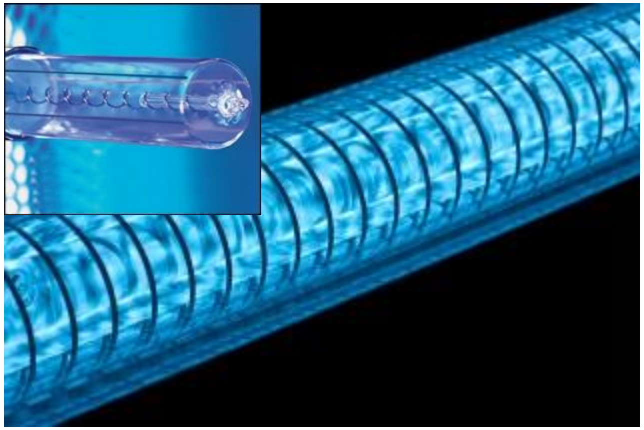
VUV Lamps

Excimer lamps



Excimer	Wavelength	Relative Power mW
Ar_2^*	126 nm	
Kr_2^*	146 nm	
Xe_2^*	172 & 175 nm	
ArF	193 nm	60
KrF	248 nm	100
XeBr	282 nm	
XeCl	308 nm	50
XeF	351 nm	45
KrCl	222 nm	25

- Excimer "excited dimer". Basically, this is a pair of atoms with an excited gas atom which in its ground state is usually unconnected ($Xe + Xe^* = Xe_2^*$ (excimer)).
- Excimers can be formed by noble gases and noble gas/halogen mixtures.
- UV radiation in a very narrow, monochromatic spectral range
- Depending on the gas selected, different narrow-band UV spectrums are emitted, mainly in a single spectral line

Bond Dissociation Energy

Average Bond Enthalpies (kJ/mol)

Single Bonds

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C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						

Multiple Bonds

C=C	614	N=N	418	O_2	495
C≡C	839	N≡N	941		
C=N	615			S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

184.9 nm = 647 kJ/Einstein

253.7 nm = 471 kJ/Einstein

Direct Photolysis by VUV

1. Water (물 분해)

$$H_2O + h\nu\ (<200\ nm) \rightarrow H\bullet + \bullet OH$$

2. Organic compounds (유기물 분해)

$$R\text{-}H + h\nu\ (<200\ nm) \rightarrow H\bullet + \bullet R$$

3. Dissolved oxygen (용존산소 분해)

$$O_2 + h\nu\ (<200\ nm) \rightarrow O\bullet + \bullet O$$

$$O_2 + O\bullet \rightarrow O_3$$

ε_{H2O} = ca. 50 cm^{-1} >> ε_{O2} = 0.9 cm^{-1} (at 1기압)

Water Splitting by VUV

- Primary photochemical processes

$$H_2O + h\nu(< 190\,nm) \rightarrow H^\bullet + HO^\bullet \quad (1)$$

$$H_2O + h\nu(< 190\,nm) \rightarrow H^+ + e^- + HO^\bullet \quad (2)$$

(1): ϕ_{185nm} = 0.33, ϕ_{172nm} = 0.42, ϕ_{148nm} = 0.7, ϕ_{124nm} = 1

(2): $\phi_{175\sim200nm}$ = 0.01 ~0.05

•OH, •H, e-, HO_2•, H_2O_2, H_2

- Secondary reactions

Reaction	k (L mol^{-1} s^{-1})
$e_{aq}^- + H_2O \rightarrow H\cdot + OH^-$	1.9×10^1
$e_{aq}^- + e_{aq}^- \rightarrow H_2 + 2\,OH^-$	$2k = 1.1 \times 10^{10}$
$e_{aq}^- + H\cdot \rightarrow H_2 + OH^-$	2.5×10^{10}
$e_{aq}^- + \cdot OH \rightarrow OH^-$	3.0×10^{10}
$e_{aq}^- + \cdot O^- \rightarrow 2\,OH^-$	2.2×10^{10}
$e_{aq}^- + H^+ \rightarrow H\cdot$	2.3×10^{10}
$e_{aq}^- + H_2O_2 \rightarrow OH^- + \cdot OH$	1.1×10^{10}
$e_{aq}^- + HO_2^- \rightarrow 2\,OH^- + \cdot OH$	3.5×10^9
$e_{aq}^- + O_2 \rightarrow O_2\cdot^-$	1.9×10^{10}
$e_{aq}^- + O_2\cdot^- \rightarrow O_2^{2-}$	1.3×10^{10}
$H\cdot + H_2O \rightarrow H_2 + \cdot OH$	1×10^1
$H\cdot + H\cdot \rightarrow H_2$	$2k = 1.55 \times 10^{10}$
$H\cdot + \cdot OH \rightarrow H_2O$	7.0×10^9
$H\cdot + OH^- \rightarrow e_{aq}^-$	2.2×10^7
$H\cdot + H_2O_2 \rightarrow \cdot OH + H_2O$	9×10^7
$H\cdot + O_2 \rightarrow HO_2\cdot$	2.1×10^{10}
$H\cdot + HO_2\cdot \rightarrow H_2O_2$	$\sim 10^{10}$
$\cdot OH + \cdot OH \rightarrow H_2O_2$	$2k = 1.1 \times 10^{10}$
$\cdot OH + \cdot O^- \rightarrow HO_2^-$	$<2 \times 10^{10}$
$\cdot OH + H_2 \rightarrow H\cdot + H_2O$	4.2×10^7
$\cdot OH + OH^- \rightarrow \cdot O^- + H_2O$	1.3×10^{10}
$\cdot OH + H_2O_2 \rightarrow H_2O + HO_2\cdot \rightleftharpoons O_2\cdot^- + H^+$	2.7×10^7
$\cdot OH + HO_2^- \rightarrow OH^- + HO_2\cdot \rightleftharpoons O_2\cdot^- + H^+$	7.5×10^9
$\cdot OH + H_2O_2^+ \rightarrow H_3O^+ + O_2$	1.2×10^{10}
$\cdot OH + HO_2\cdot \rightarrow H_2O + O_2$	6×10^9
$\cdot OH + O_2\cdot^- \rightarrow OH^- + O_2$	8×10^9

VUV Intensity Attenuation

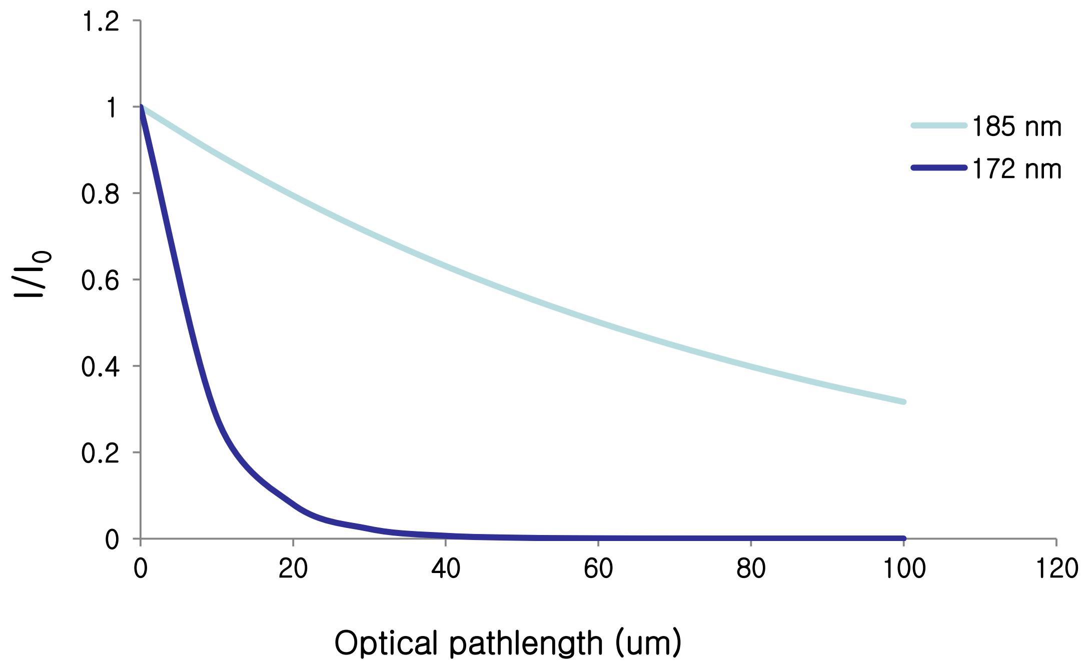
- Beer-Lambert absorption law

$$I / I_0 = 10^{-\varepsilon bC}$$

ε: molar aborption coefficient (M^{-1} cm^{-1})
b: optical pathlength (cm)
C: molar concentration of photon absorber (M)

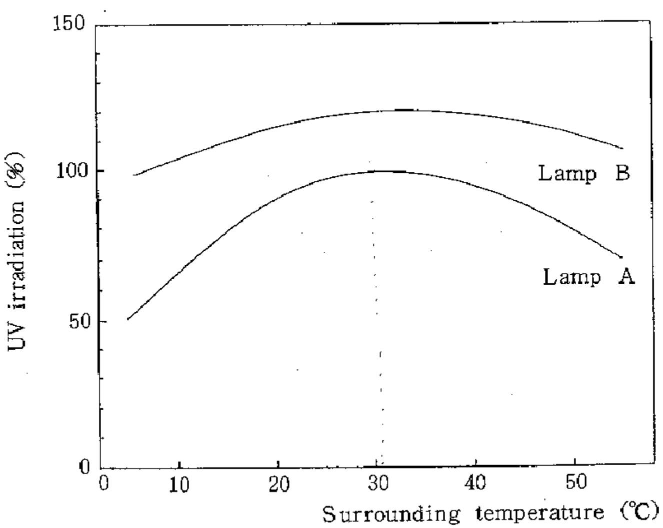
- UV attenuation

Linear absorption coeff. (εC) of water = 50?? cm^{-1} (at 185 nm) and 550 cm^{-1} (at 172 nm)



Affecting Factors

Temperature (온도)



pH (no significant)

Dissolved oxygen (용존산소)

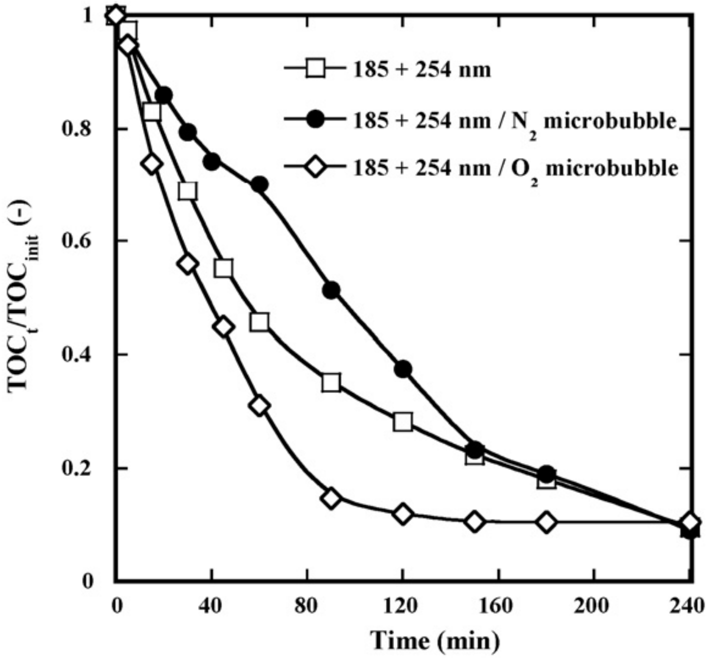
UV shielding substances (용존 혹은 입자성 물질)
(no significant)

Operational conditions of the reactor:
Light intensity, flow rate, volume, etc.

Effect of Dissolved Oxygen

- Mineralization process

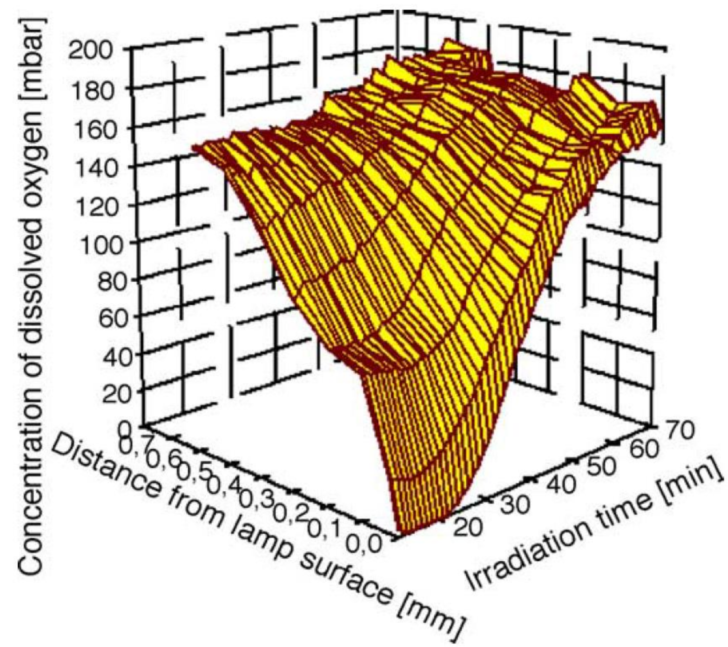
$$^{\bullet}OH + \text{Organic Compounds} \xrightarrow{O_2 \quad O_2} CO_2$$



- Effect on TOC removal

(target compound: methylene blue)

(Tasaki et al., 2009)



- Concentration of dissolved oxygen

(Heit and Braun, 1996)

Effect of Dissolved Oxygen

- Removal of the target compound

$H_2O + h\nu\ (<200\ nm) \rightarrow H\bullet + \bullet OH$

$RH + \bullet OH \rightarrow R\bullet + H_2O$

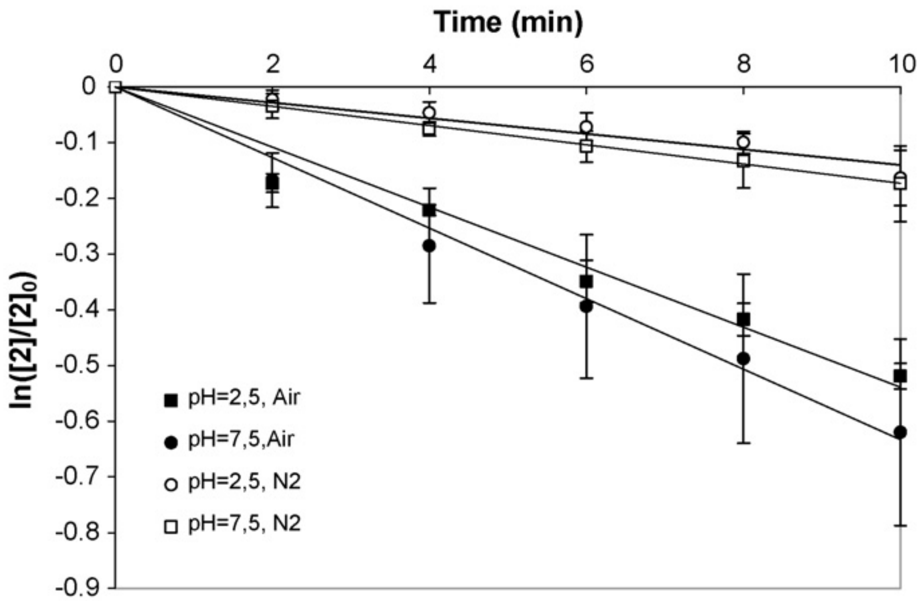
Without oxygen,

$R\bullet + \bullet H \rightarrow RH$

With oxygen,

$O_2 + \bullet H \rightarrow HO_2\bullet$

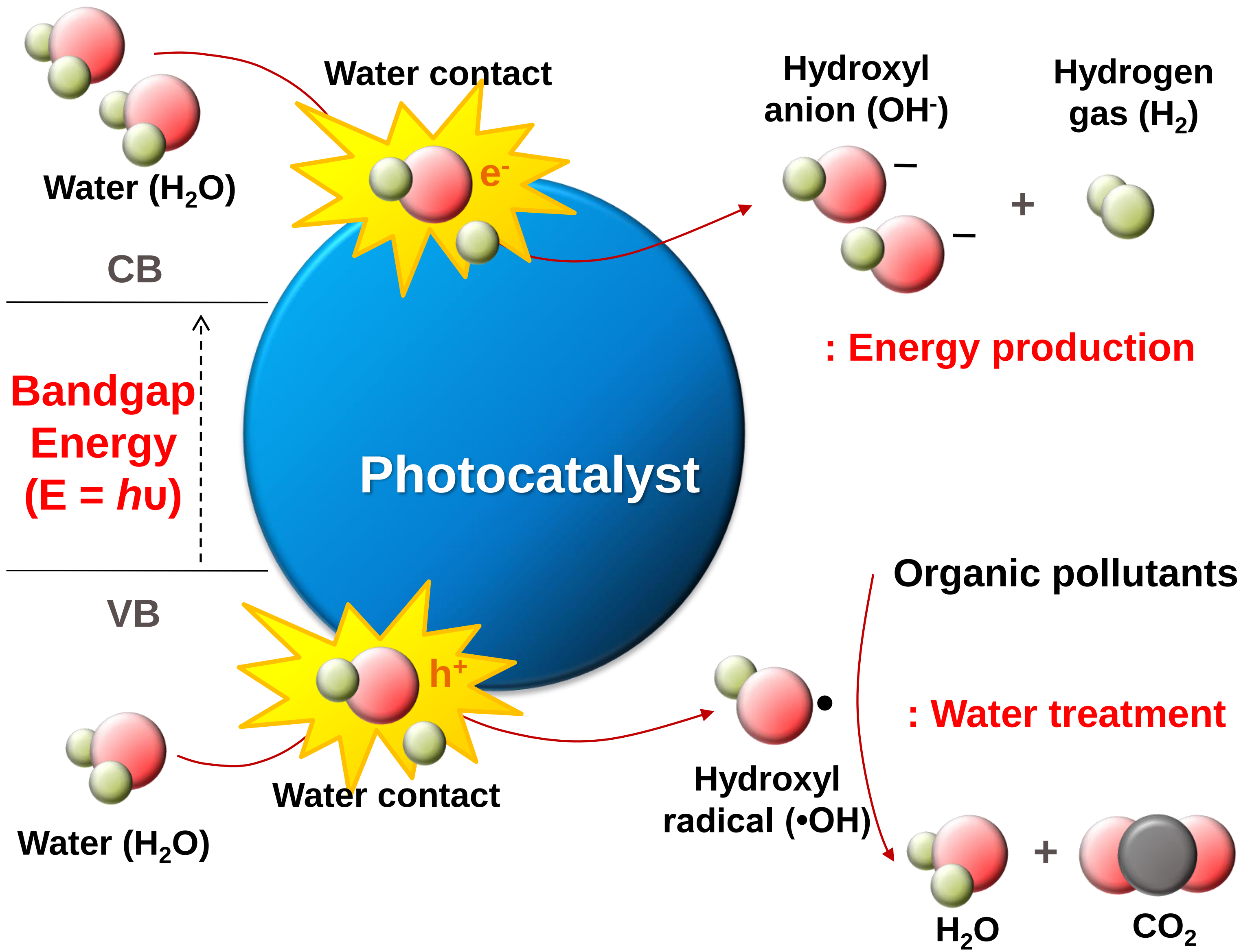
$O_2 + R\bullet \rightarrow ROO\bullet$



Gallic acid degradation by VUV (Quici et al., 2008)

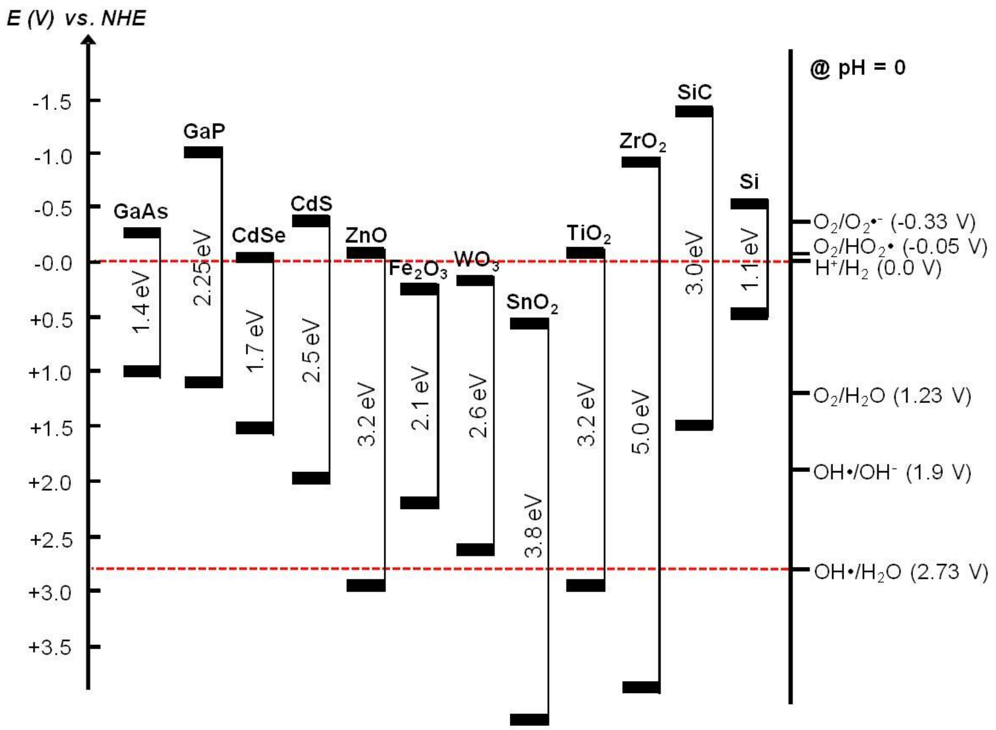
- Dissolved oxygen (DO) also affects the degradation of the target compound.
- DO reacts with $\bullet H$ so that the backward reaction of $R\bullet$ is prevented.

Semiconductor Photocatalysis



TiO_2 Photocatalysis, Why TiO_2?

1. **Band edge levels: Strong oxidation power of h^+ & e^- capture by oxygen**



2. **Excellent (photo)chemical stability**

   anodic photocorrosion:

   $MX + nh^+ \rightarrow M^{n+} + X$

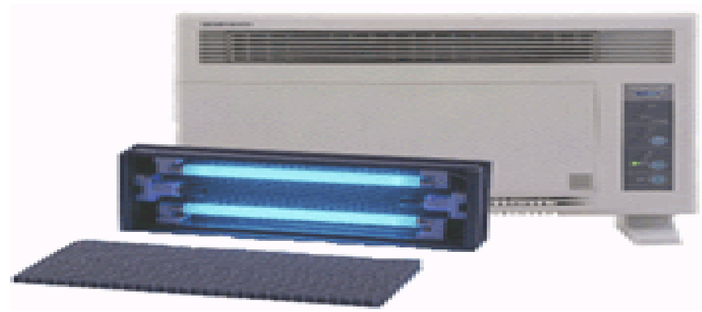
   cathodic photocorrosion:

   $MX + ne^- \rightarrow M + X^{n-}$

3. **Availability: One of top 50 mass-produced chemicals**

Applications of Semiconductor Photocatalysis

Air purification (Trojan Technologies)



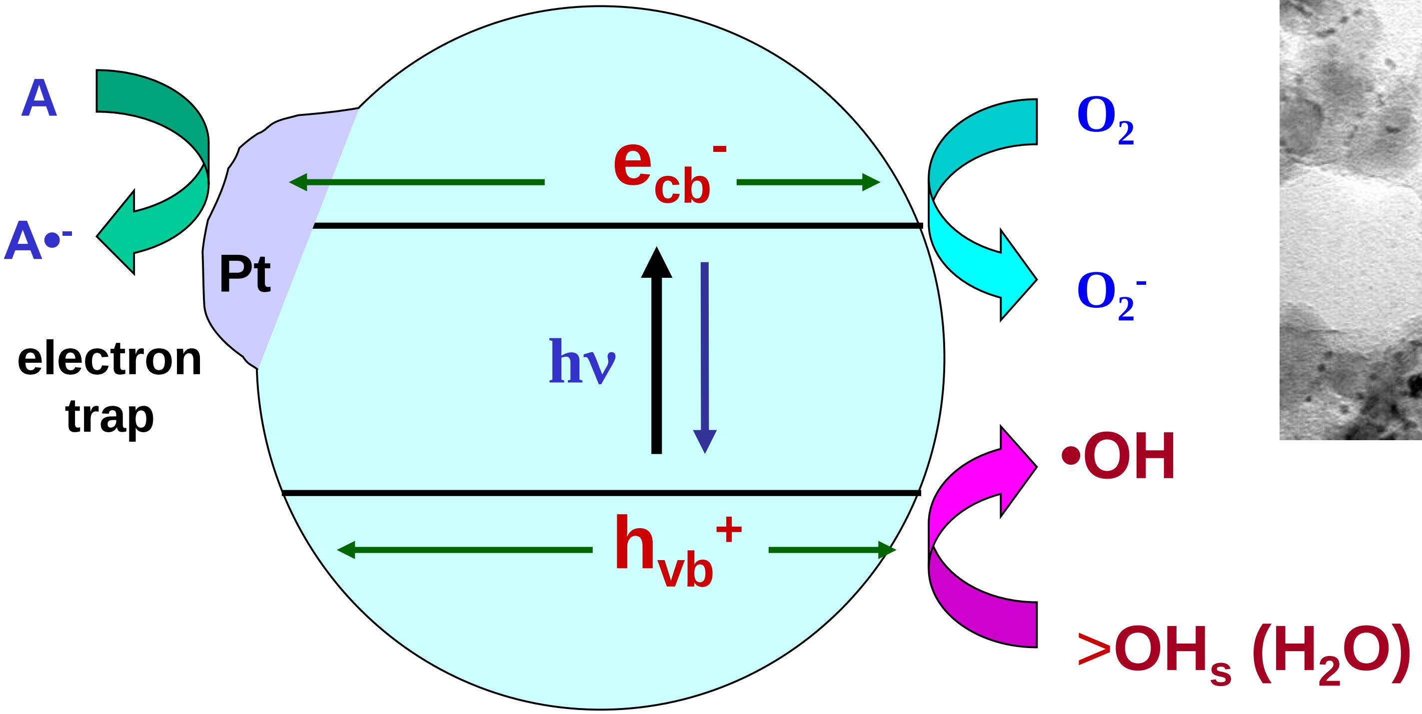
Deordoriser (NHKspring co)

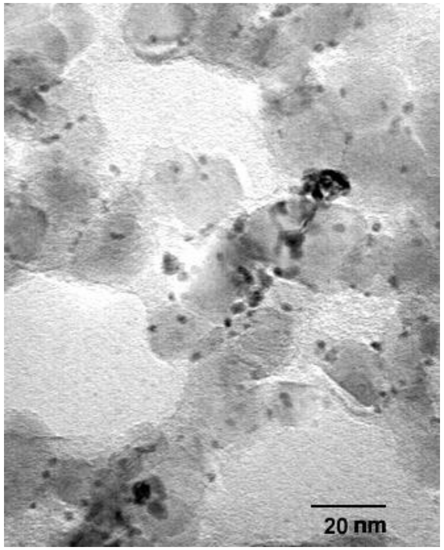
Water purification (Purifics environmental technologies Inc)

Water purification (Photox Bradford)

Source: Prof. W. Choi from POSTECH

Platinized TiO_2



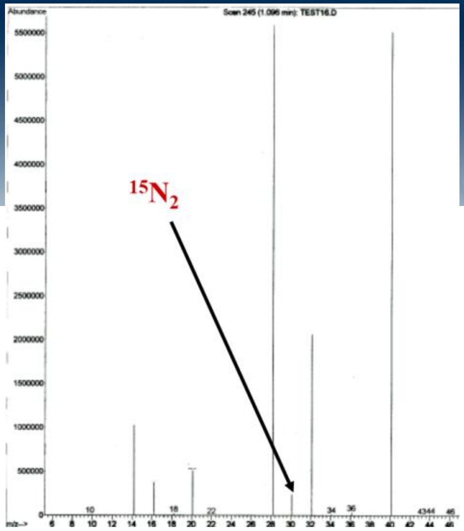


Pt deposits

- Reduce e^-/h^+ pair recombination
- Enhance electron transfer rate

Source: Prof. W. Choi from POSTECH

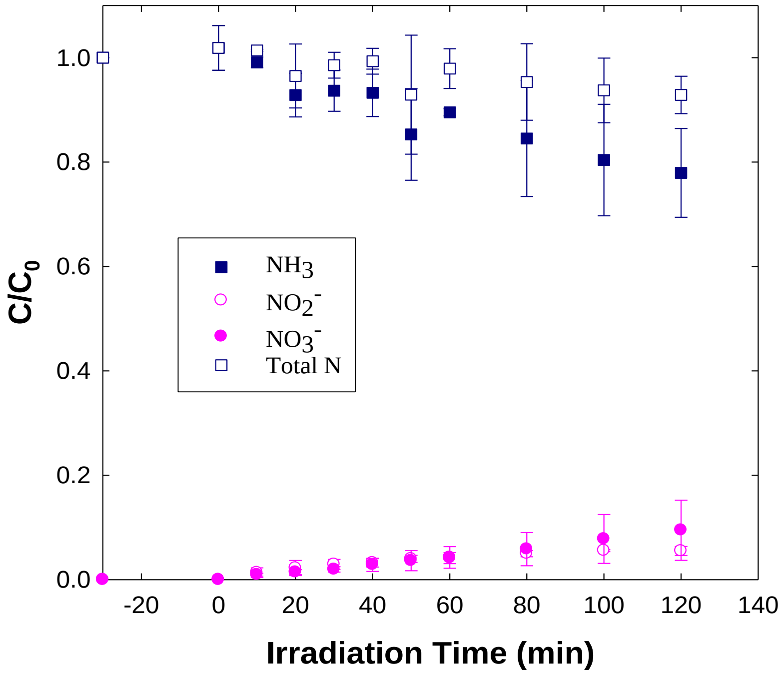
Platinized TiO_2



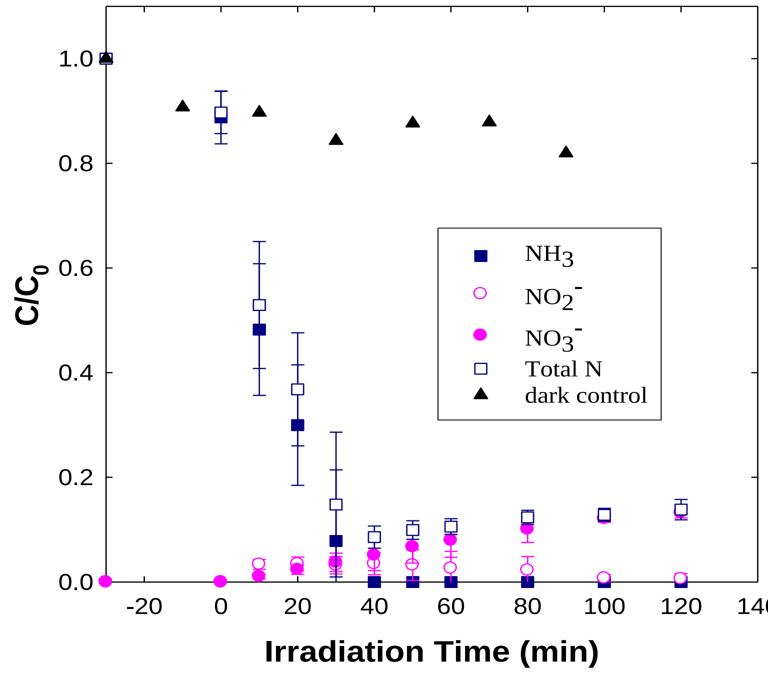
✓ Ammonia oxidation by platinized TiO_2

Platinized TiO_2 does not only accelerate the rate of ammonia oxidation, but also alters the oxidation mechanism (N_2 production).

Pristine TiO_2

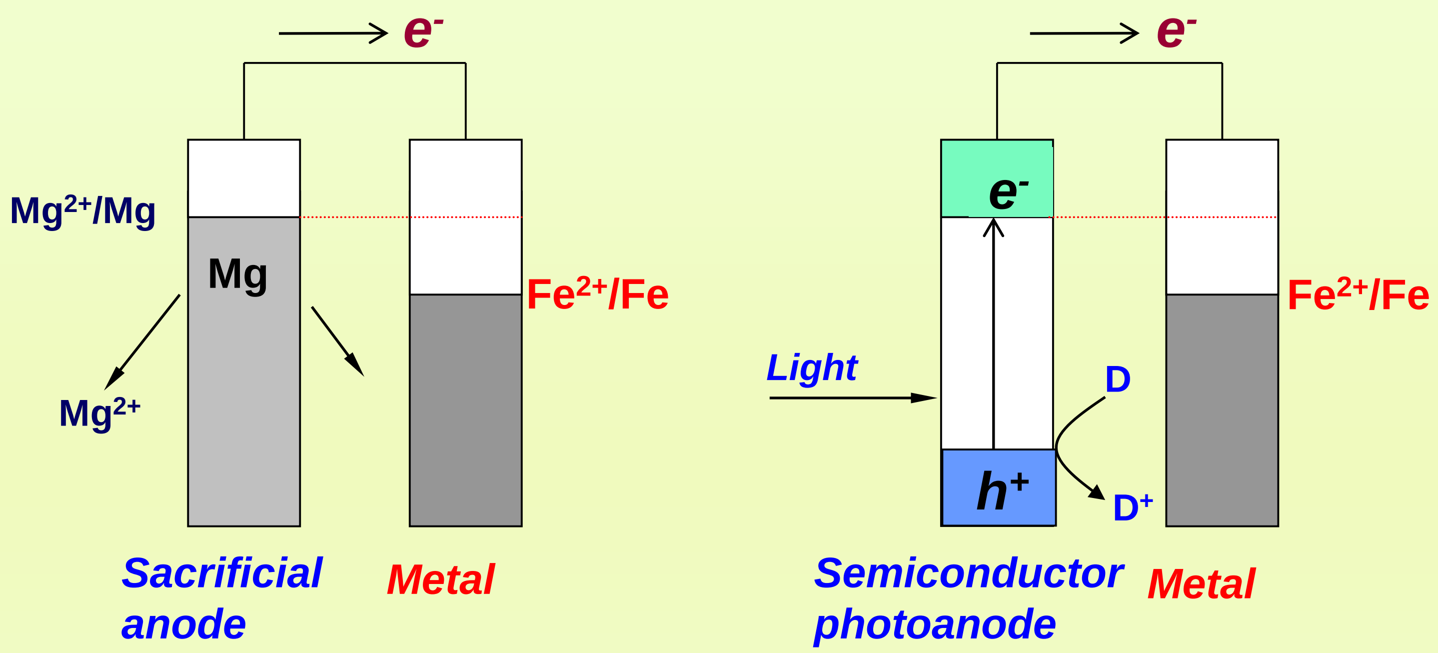


Platinized TiO_2



Source: Prof. W. Choi from POSTECH

Photo-Cathodic Protection of Metals



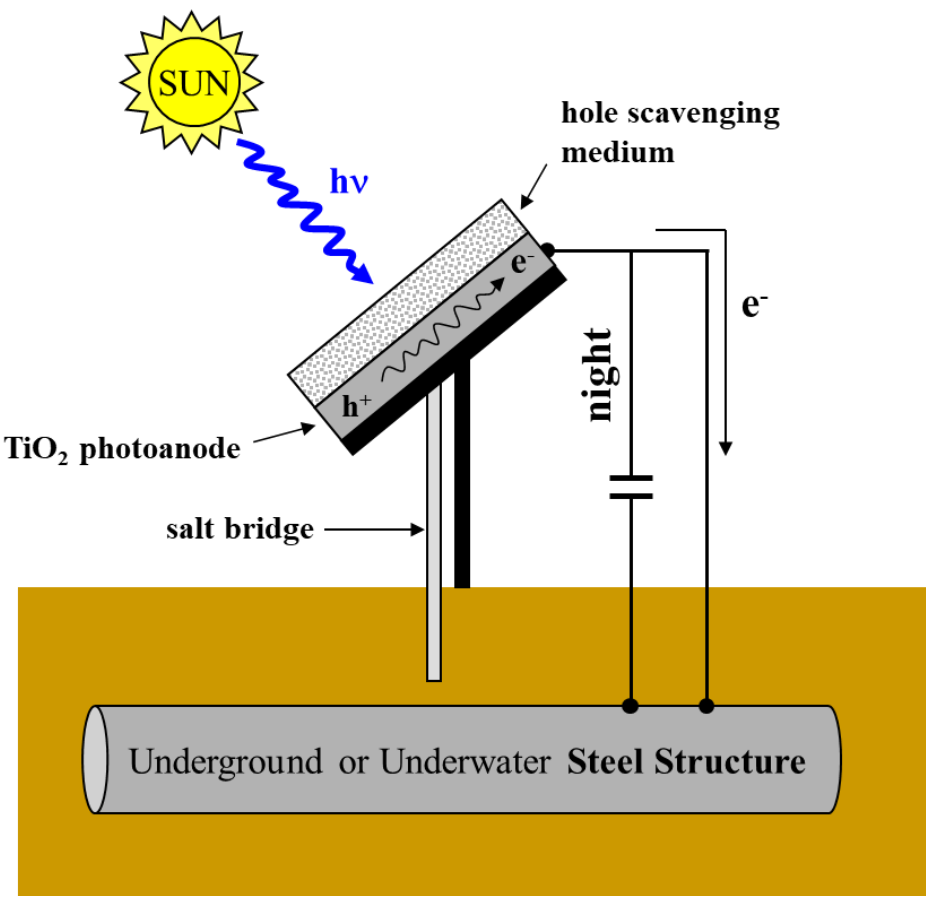
Conventional cathodic protection using a sacrificial anode

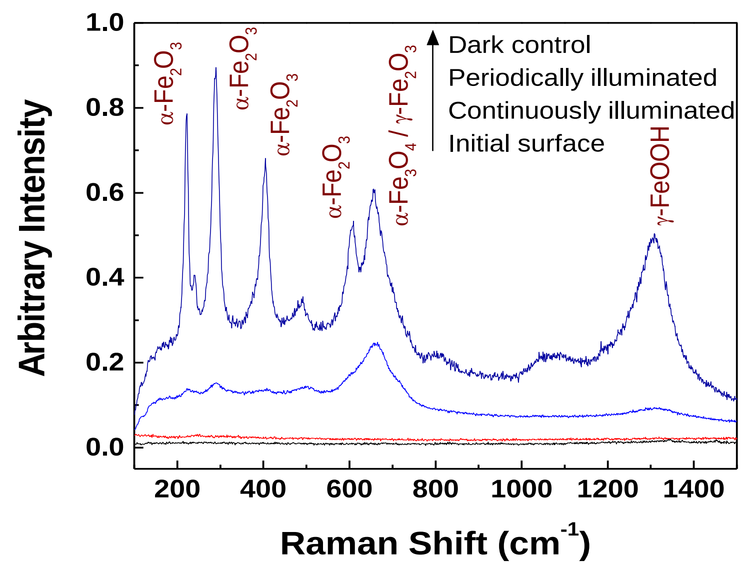
new cathodic protection using a semiconductor photoanode

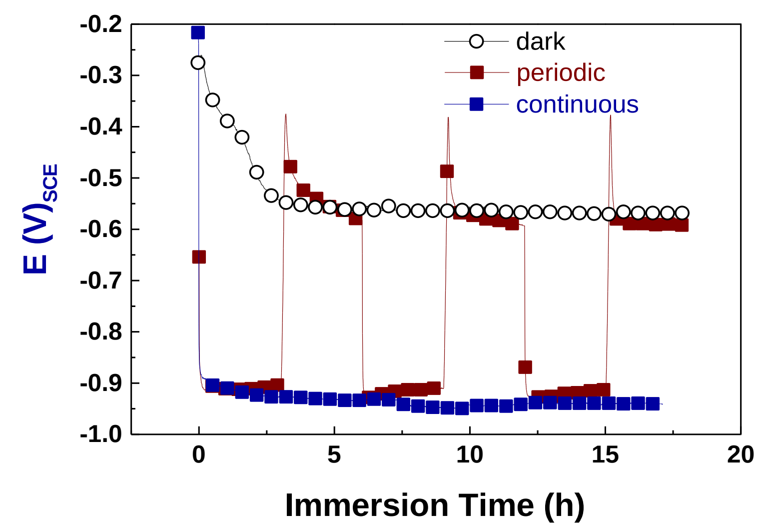
(Park et al., 2001 *Chem. Commun.*, Park et al., 2002, *J. Phys. Chem. B*)

Photo-Cathodic Protection of Metals

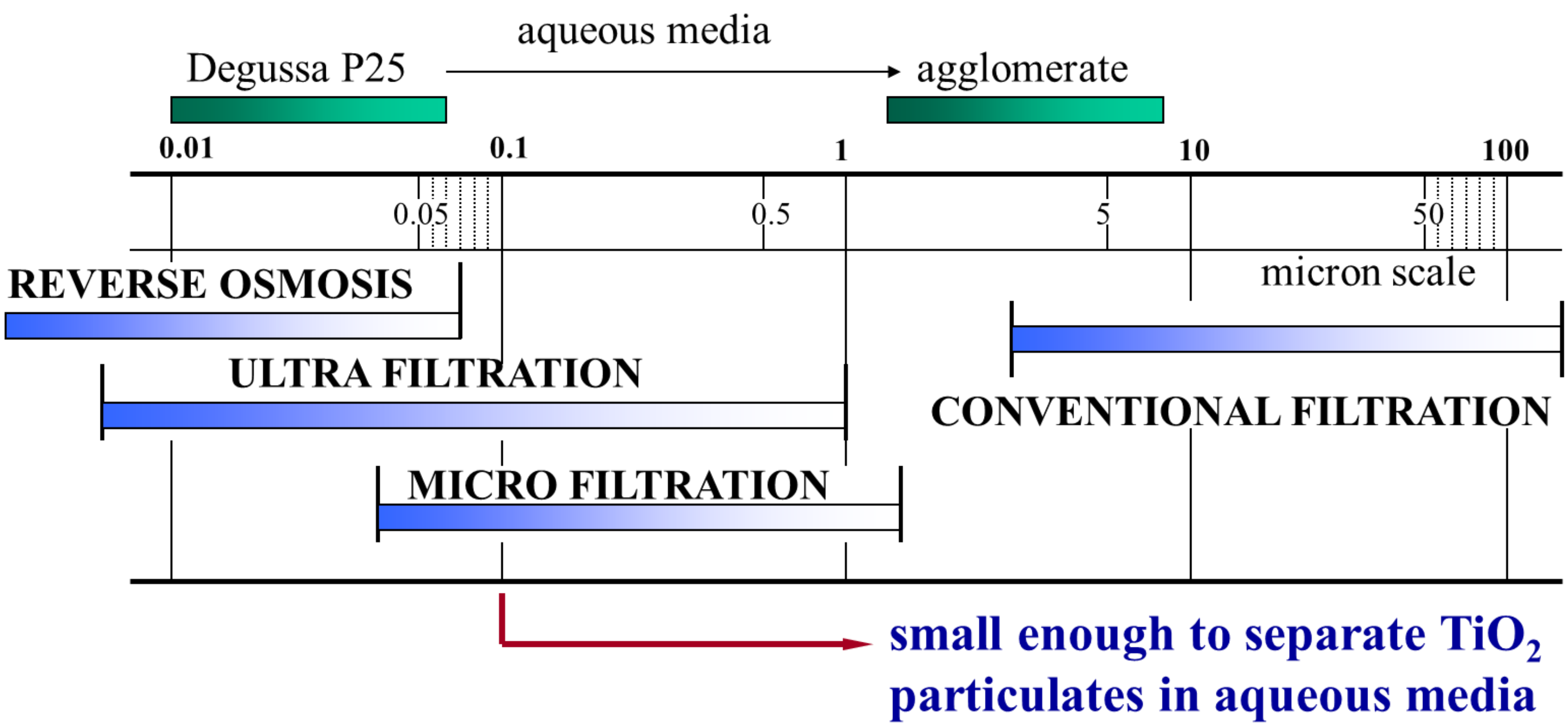
Choi et al.,
US Patent No.
6,559,373 B2 (2003)





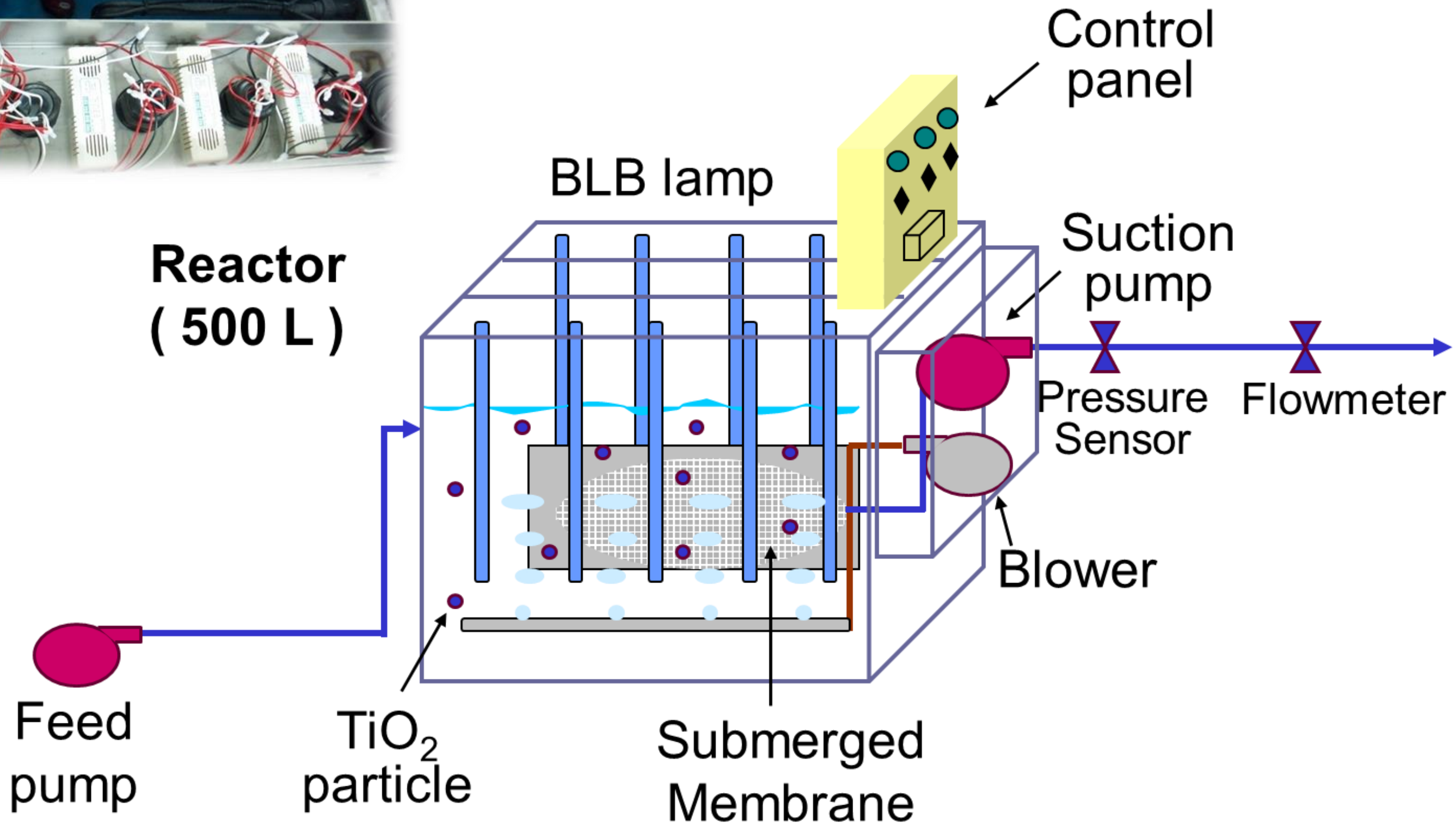


Separation of TiO_2 Particulates



Source: Prof. W. Choi from POSTECH

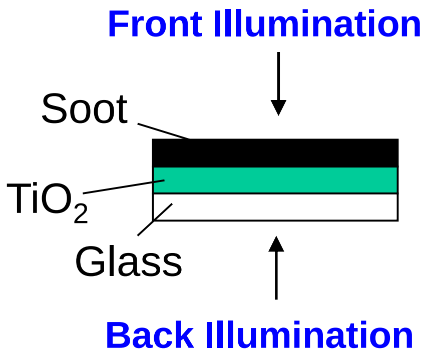
Photocatalytic Membrane System

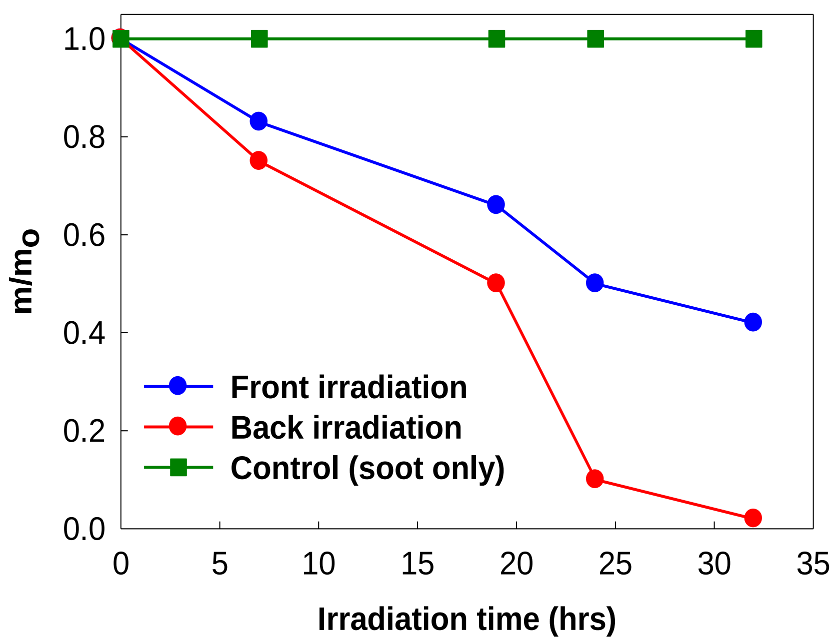


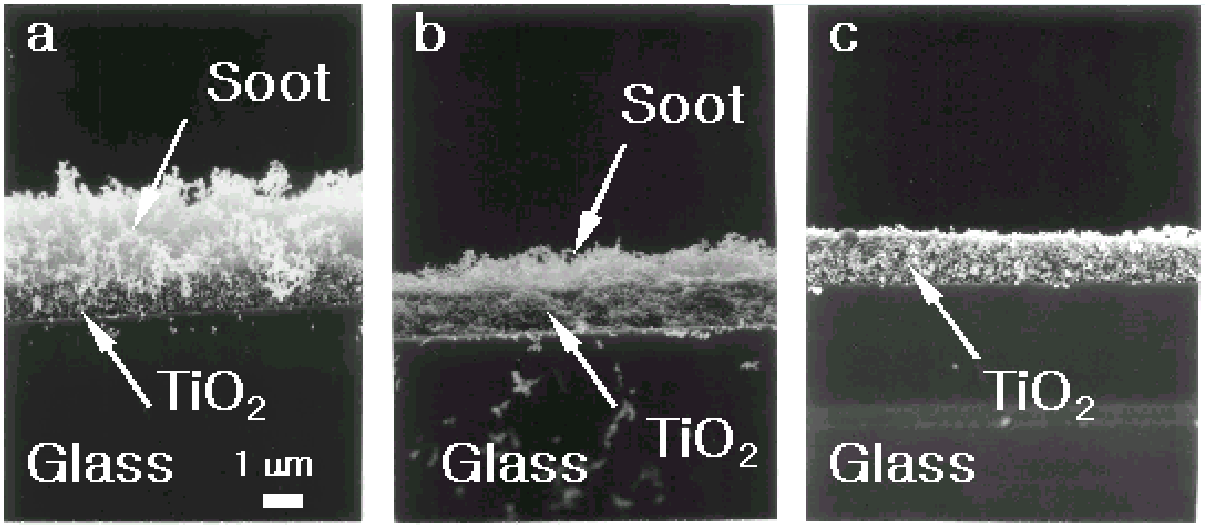
Source: Prof. W. Choi from POSTECH

Migration of •OH from Illuminated TiO_2 Surface

✓ **Photodegradation of soot**



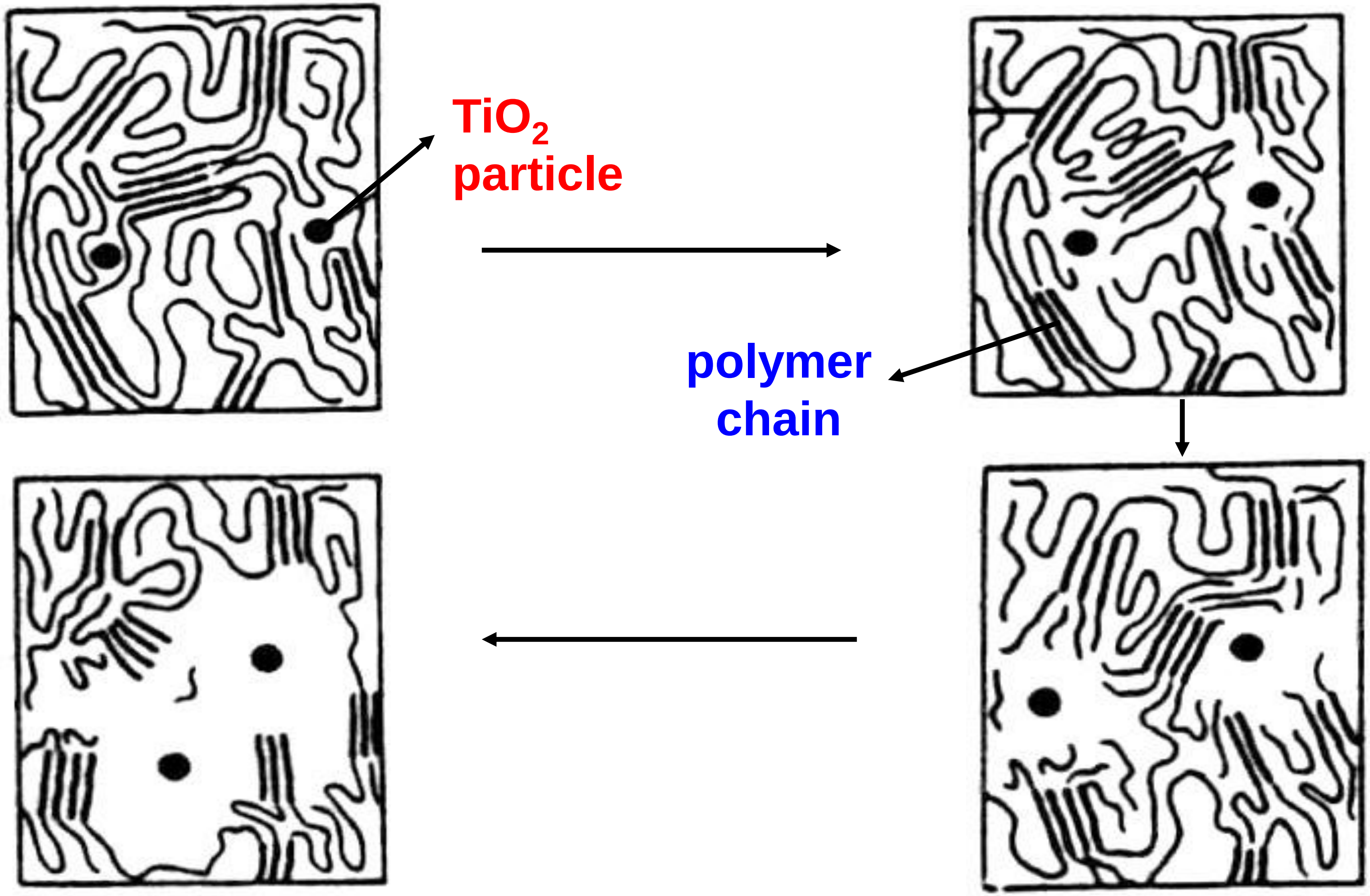




(Lee and Choi, 2002, *J. Phys. Chem. B*)

Migration of •OH from Illuminated TiO_2 Surface

✓ **Photodegradation of polymers**

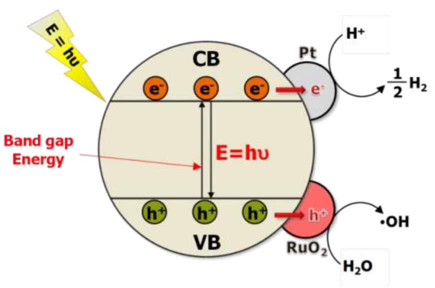


Issues about TiO_2 Photocatalysis

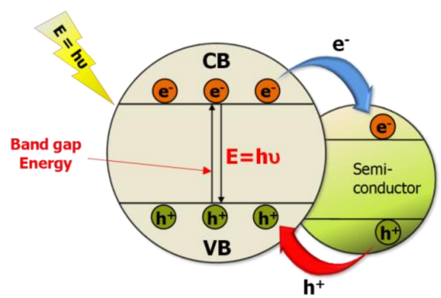
✓ Surface modification

Strategies:

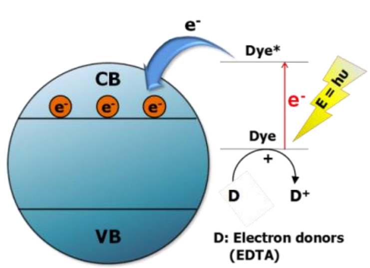
- Prevention of hole-electron recombination
- Visible-light utilization



▲ Metal (or nonmetal) doping

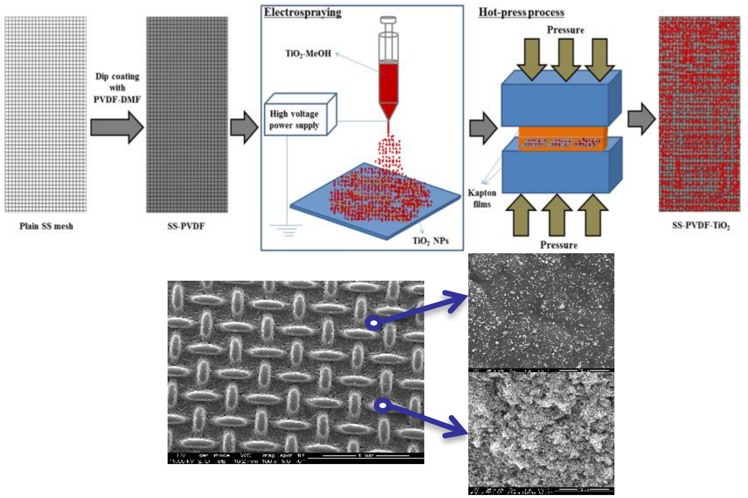


▲ Coupling



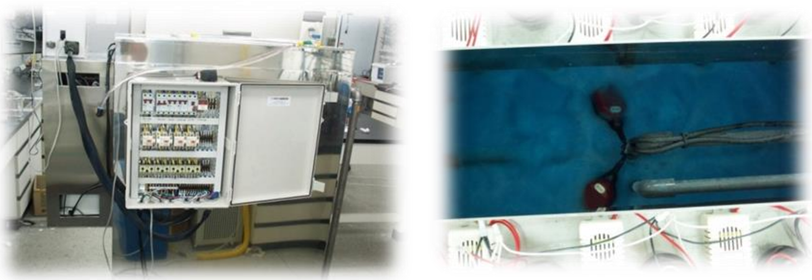
▲ Photosensitization

✓ Separation / Immobilization



▲ TiO_2 coating by electrospraying

Source: Dr. S.W. Hong from KIST

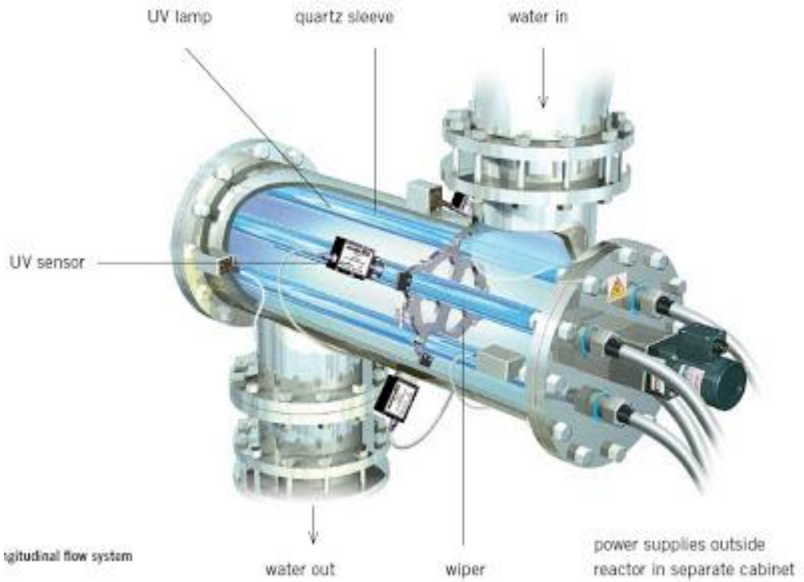


▲ TiO_2 photocatalysis/membrane hybrid system

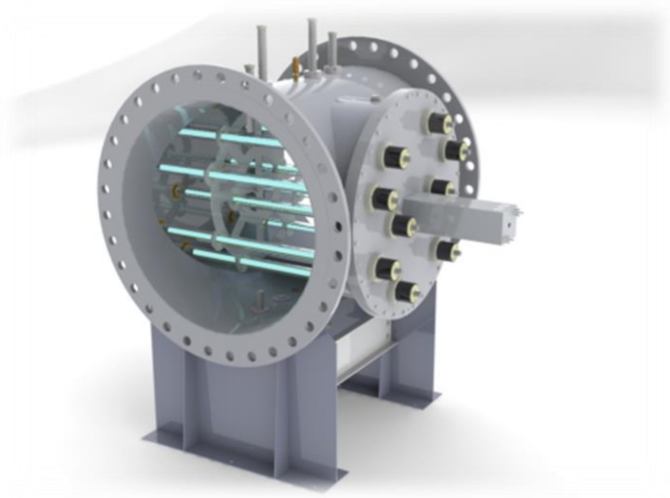
Source: Prof. W. Choi from POSTECH

Photochemical Reactors

Main components:
- UV lamp
- Quartz sleeve
- Wiper for mechanical cleaning of quartz sleeves to protect against fouling
- UV sensor to control UV output
- Power supply



▲ Longitudinal flow system

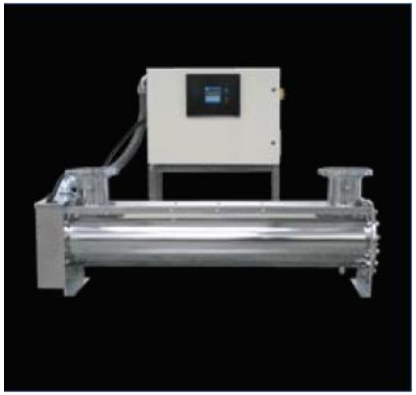


Source: Ozonia Co. (Aquaray® H_2O)

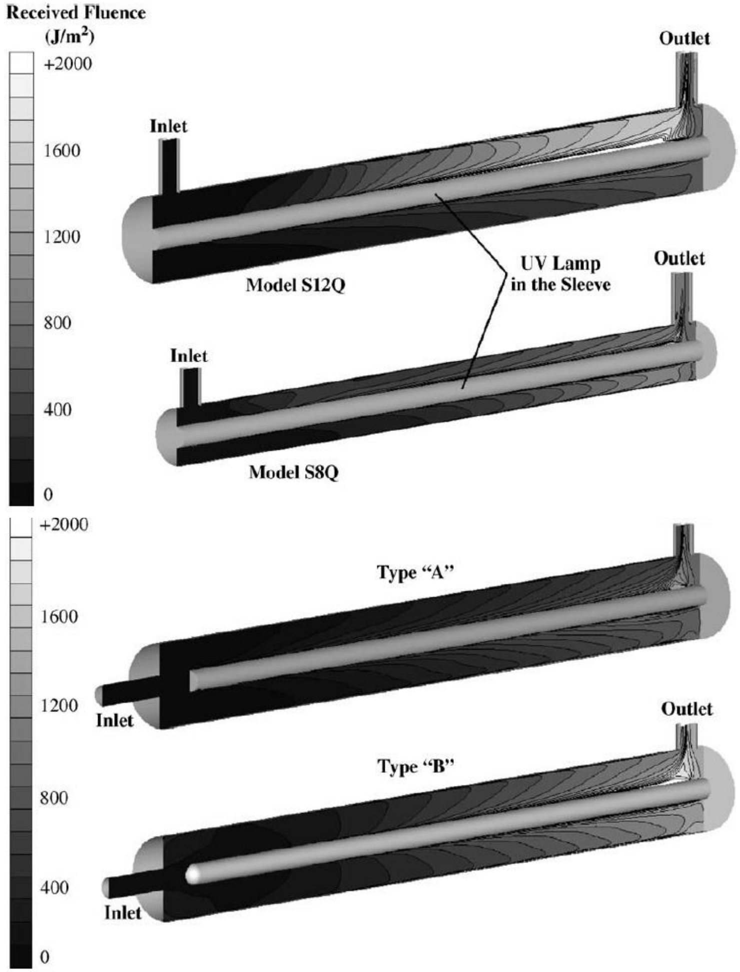
▲ Cross flow system

Photochemical Reactors

(Siemens Co.)

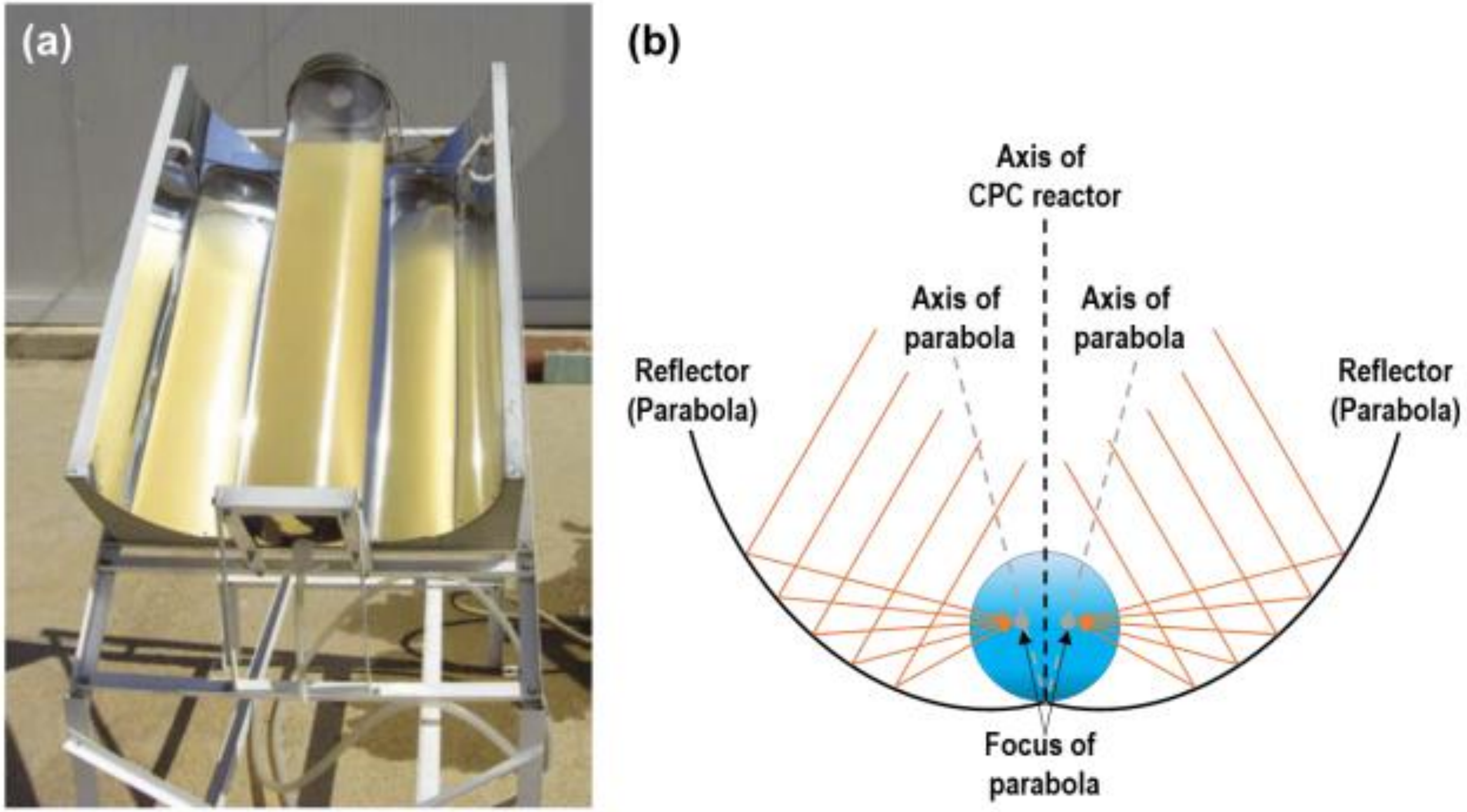


(Aquafine Co.)



Modeling of UV reactor
by Computational Fluid Dynamics (CFD)
(Elyasi et al., 2006)

Photochemical Reactors



⥣ Compound parabolic collectors (CPCs) for sunlight harvesting, a photograph (a) and a cross-sectional diagram (b).

Photochemical Reactors

Figures-of-Merit for Photochemical AOPs

- Electrical energy is usually the principal factor in the operating cost of AOT systems.
- For low pollutant concentrations, we use Electrical Energy per Order (EE/O) as the electrical energy (kWh) necessary to reduce the concentration of a pollutant by one order of magnitude in 1000 L of water.
- For high pollutant concentrations, we use Electrical Energy per Mass (EE/M) as the electrical energy (kWh) necessary to remove 1 kg of pollutant. EE/M can also be based on TOC (1 kg of C).

EE/O or EE/M for Several Photo–Fenton Systems

No.	Light source	Conditions	Target	Energy efficiency (EE/O or EE/M)
1	Medium pressure Hg lamp (λ = 200–600 nm)	[Fe(II)] = 10–40 mg/L, [H_2O_2] = 50–500 mg/L, [Target] = 7–100 mg/L, pH = 3.0	BTX, 1,4-Dioxane, MTBE, TCE, PCE	EE/O = 1.2–2.9 kWh/order/m^3
		[Fe(III)] = 10–40 mg/L, [Oxalic acid]/[Fe(III)] = 3 (molar basis), [H_2O_2] = 50–500 mg/L, [Target] = 7–100 mg/L, pH = 2.8–3.2		EE/O = 0.6–1.8 kWh/order/m^3
2	Low pressure Hg lamp (λ_{max} = 253.7 nm)	[Fe(II)] = 0.5 mM, [H_2O_2] = 10 mM, [Target] = 30.6 mg/L as TOC, pH = 2.8	Synthetic dye wastewater	EE/M = 504.03 kWh/kg TOC
3		[Fe(II)] = 0.5 mM, [H_2O_2] = 5 mM, [Target] = 25 mg/L, pH = 2.8		EE/O = 0.56 kW/order/m^3 EE/M = 750 kWh/kg DOC,
4		[Fe(II)] = 30 mg/L, [H_2O_2] = 3 g/L, [Target] = 2,000 mg/L as COD, pH = 3.0	Olive oil mill wastewater	EE/O = 92.23 kWh/order/m^3
5		[Fe(II)] = 24.1-25.1 mg/L, [H_2O_2] = 133.2-138.8 mg/L, [Target] = 20,000 mg/L	EDTA	EE/O = 10–140 kWh/order/m^3
6		[Fe(II)] = 0.2 mM, [H_2O_2] = 10 mM, [Target] = 64 mg/L, pH = 3.0	Nonylphenol ethoxylate (NP-10)	EE/O = 1.9 kWh/order/m^3 EE/M = 200 kWh/kg TOC,
7	Commercial UV-A lamp (λ_{max} = 360 nm)	[Fe(II)] = 4.6 mg/L, [H_2O_2] = 19 mg/L, [Target] = 10 mg/L, pH = 3.0	Caffeic acid	EE/O = 31.5 kWh/order/m^3 (90% removal)

Examples of EE/O or EE/M Calculation

<Example 1>

We assume that for a hypothetical contaminant with a molecular weight of 100 g/mol

1) 25% of the electrical energy input into a medium pressure UV lamp system produces useful UV photons with an average wavelength of 254 nm.
2) $\phi_{OH} = \chi = 1.0$.
3) One $^{\bullet}OH$ is required to transform and remove one molecule of contaminant.

Calculate EE/M (kWh/kg) value !

Examples of EE/O or EE/M Calculation

<Solution 1>

One Einstein (one mole) of 254 nm photons contains 0.13 kWh of energy according to

$$E = N_A h\nu = N_A hc/\lambda = (6.02\times10^{23})\times(6.6\times10^{-34})\times(3\times10^{8})/(254\times10^{-9})$$
$$= 469 \text{ kJ} = 0.13 \text{ kWh}$$

Considering the energy efficiency, 25%
0.52 kWh of electrical energy produces one Einstein of 254 nm photons.

Since $\phi_{OH} = \chi = 1.0$,
0.52 kWh of electrical energy degrade one mole of the contaminant.

Since the molecular weight of the contaminant is 100 g/mol,
5.2 kWh of electrical energy is required to degrade 1 kg of the contaminant

$\Rightarrow$ EE/M = 5.2 kWh/kg

Examples of EE/O or EE/M Calculation

<Example 2>

2000 L of a wastewater containing 500 mg/L of total organic carbon (TOC) as phenol is treated for 10 hr with an AOP rated at 30 kW to yield an effulent that is 100 mg/L TOC.
Calculate the EE/M value !

<Solution 2>
The mass of TOC removed is 2000 (L) x 0.00040 (kg/L) = 0.8 kg TOC
Thus the EE/M value is (30 x 10)/0.8 = 375 kWh/kg

Examples of EE/O or EE/M Calculation

<Example 3>

A groundwater containing 20 mg/L of trichloroethylene (TCE) flowing at 8.5 m^3/h is treated with an AOP rated at 25 kW. It was found that the effluent concentration of TCE had dropped to 5 ug/L.
Calculate the EE/O value !

<Solution 3>
The orders of removal is $\log(20/0.005) = 3.602$
Thus EE/O value is $25/(8.5 \times 3.602) = 0.82$ kWh/order/m^3