Advanced Oxidation Process

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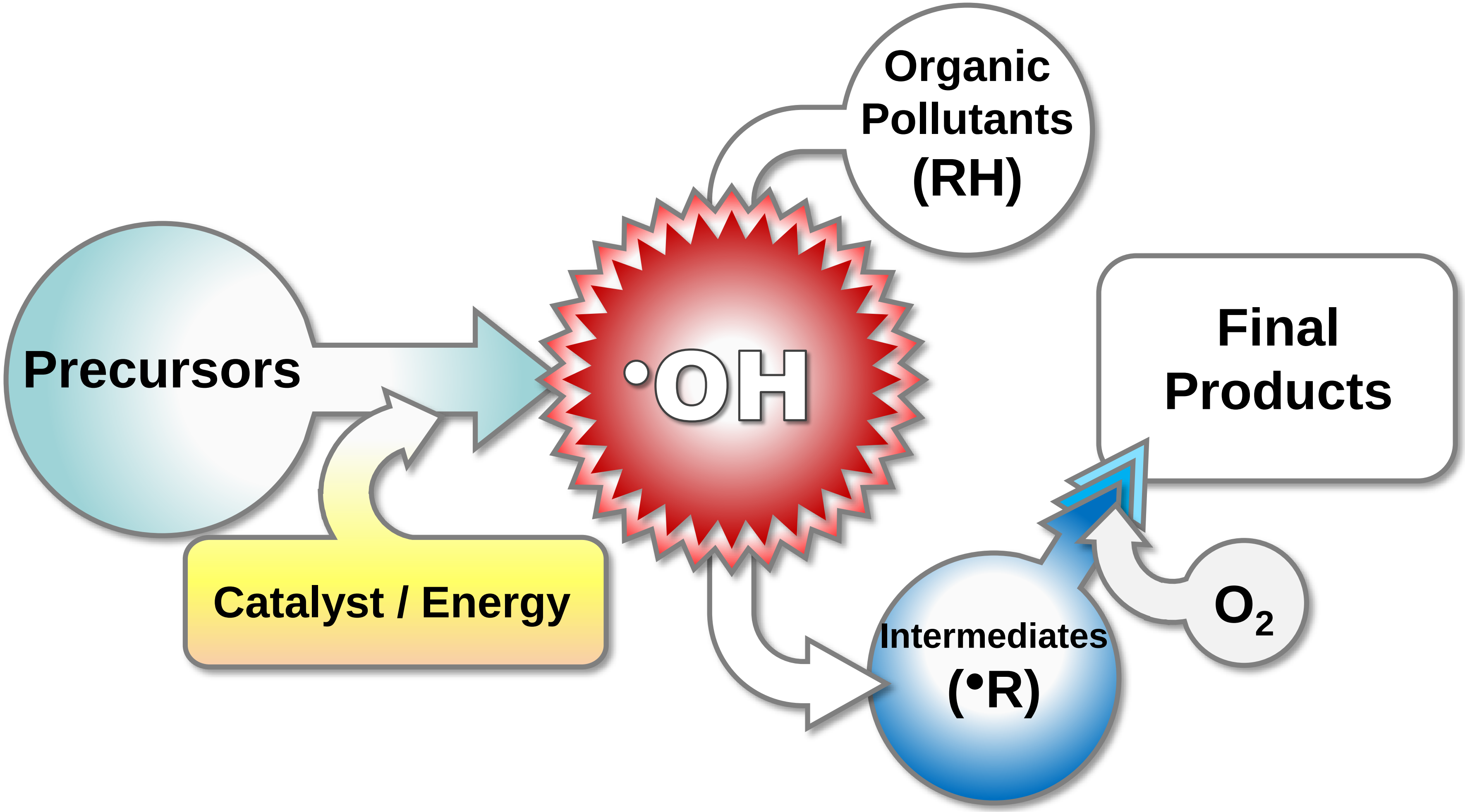
OUTLINE

1. Advanced Oxidation Process
2. Ozonation
3. Fenton Process
4. Photochemical Process

1. Advanced Oxidation Process

What is “Advanced Oxidation Process” ?

AOP (or AOT): Water treatment process (or technology) utilizing hydroxyl radical (•OH), a nonselective oxidizing radical species



Oxidants for water treatment

Standard Redox Potential (V_{NHE})

$^{\bullet}$OH (E^0($^{\bullet}$OH/OH^-) = +2.8 V_{NHE}; 1e red.)

O_3 (E^0(O_3/O_2) = +2.08 V_{NHE}; 2e red.)

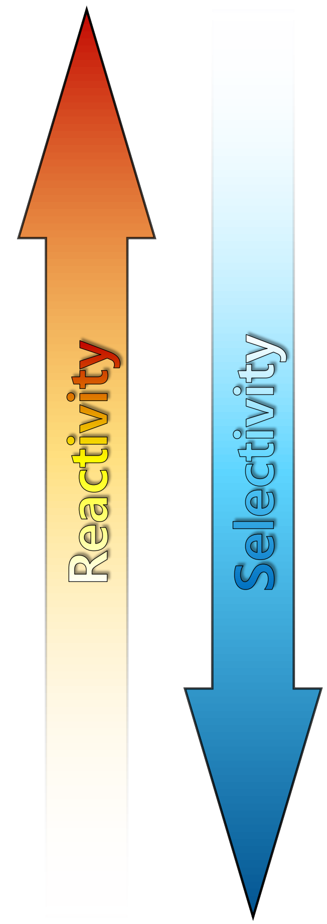
H_2O_2 (E^0(H_2O_2/2H_2O) = +1.776 V_{NHE}; 2e red.)

Fe(VI) (E^0(Fe(VI)/Fe(III)) = +2.20 – 0.7 V_{NHE}; 3e red.)

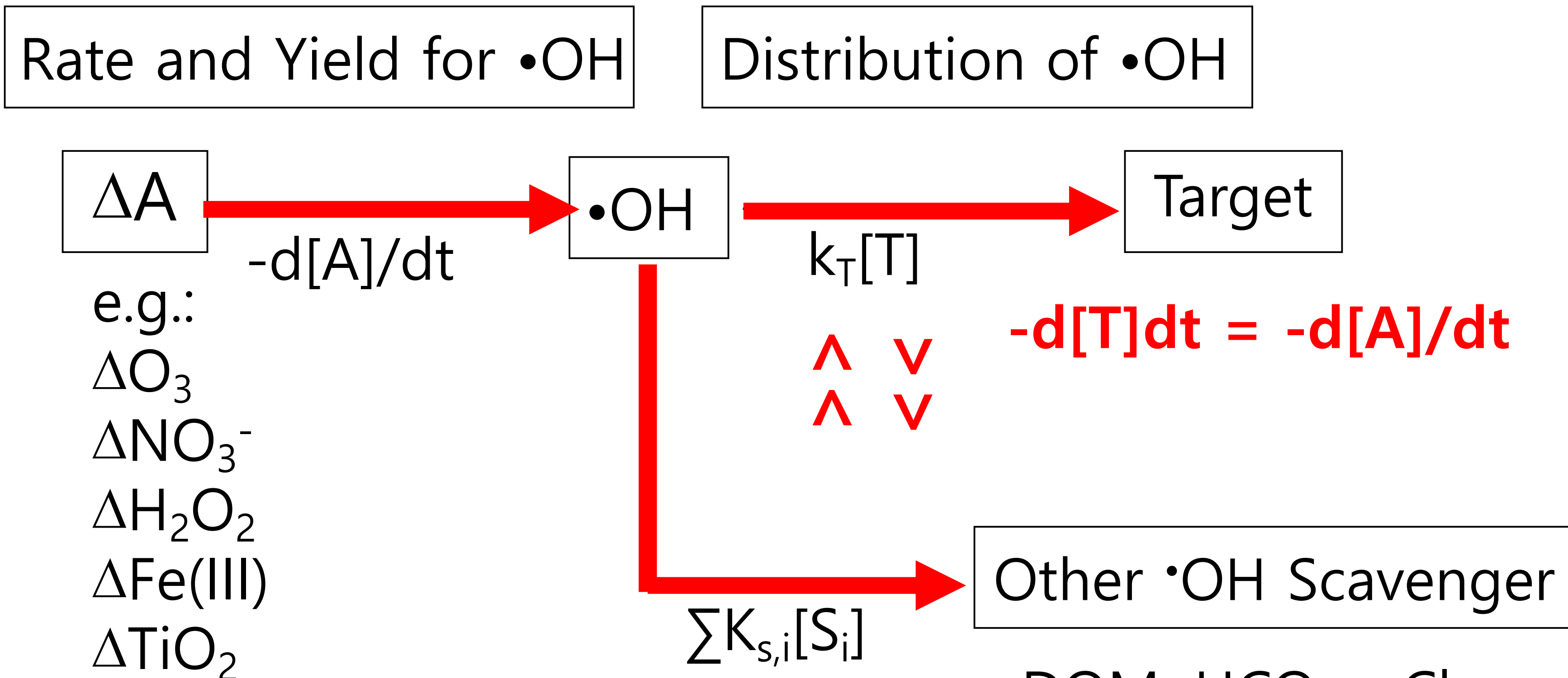
Cl_2 (E^0(Cl_2/2Cl^-)+1.48 – 0.84 V_{NHE}; 2e red.)

ClO_2 (E^0(ClO_2/ClO_2^-) = +1.04 V_{NHE}; 1e red.)

O_2 (E^0(O_2/2H_2O) = +0.695 V_{NHE}: 2e red.)



Key Parameters in AOP



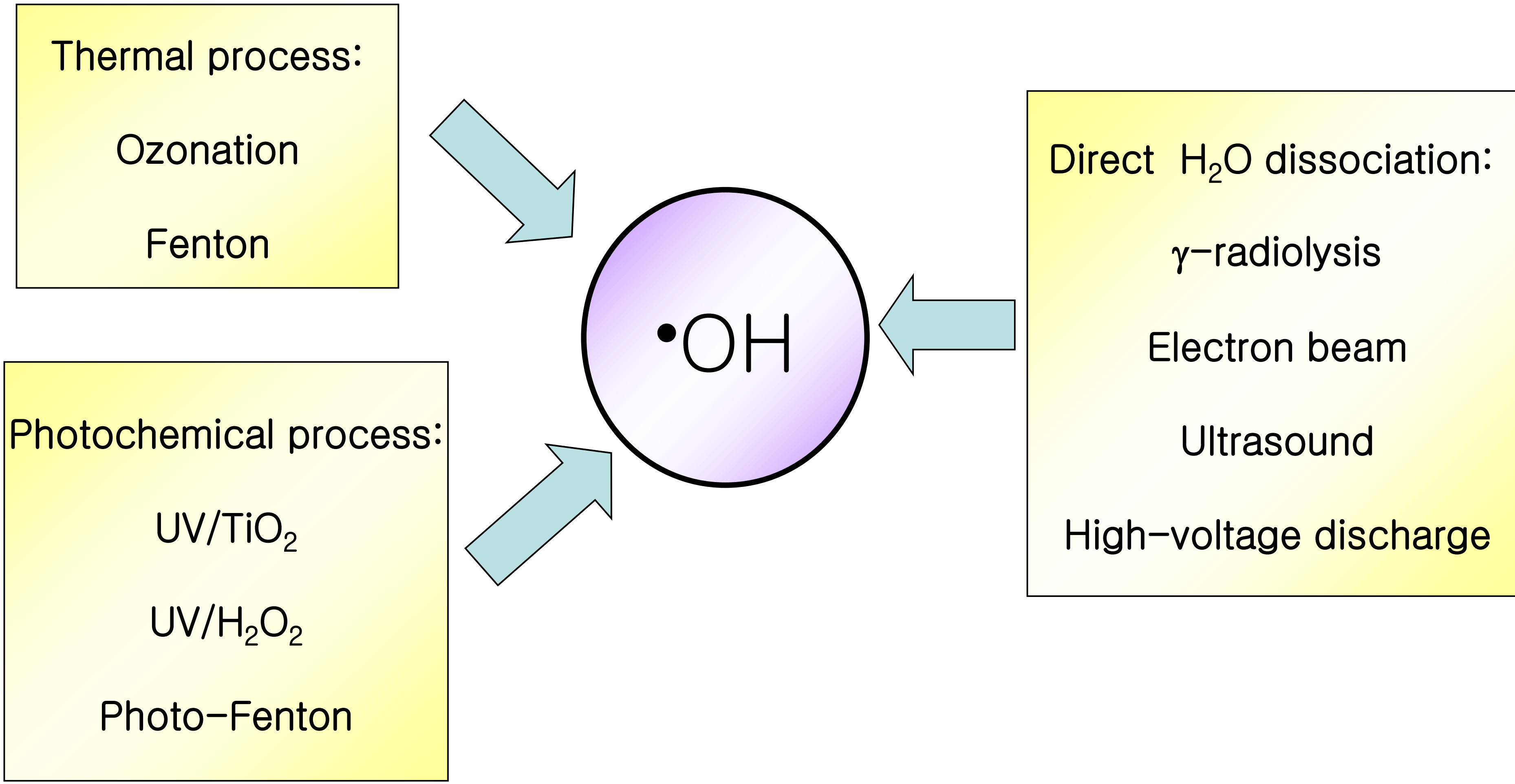
DOM, HCO_3^- , Cl^-
•OH precursors

$-d[T]dt = k_T[T][\bullet OH]_{ss}$

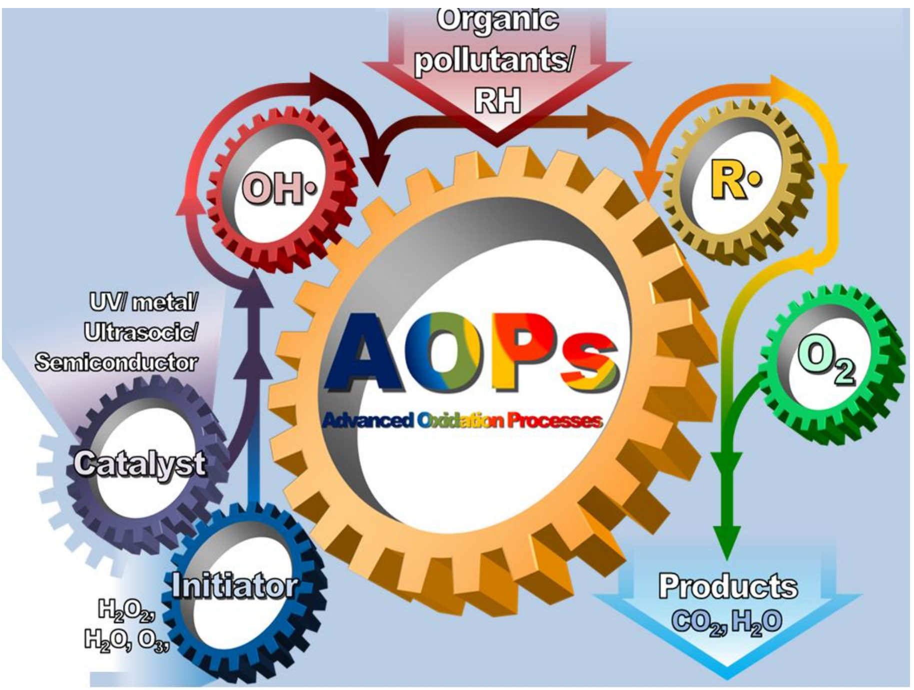
$([\bullet OH]_{ss} = -(d[A]/dt) / (\sum K_{s,i}[S_i])$

$= -k_T \cdot (d[A]/dt)/(\sum K_{s,i}[S_i]) \cdot [T]$

Classification of AOTs



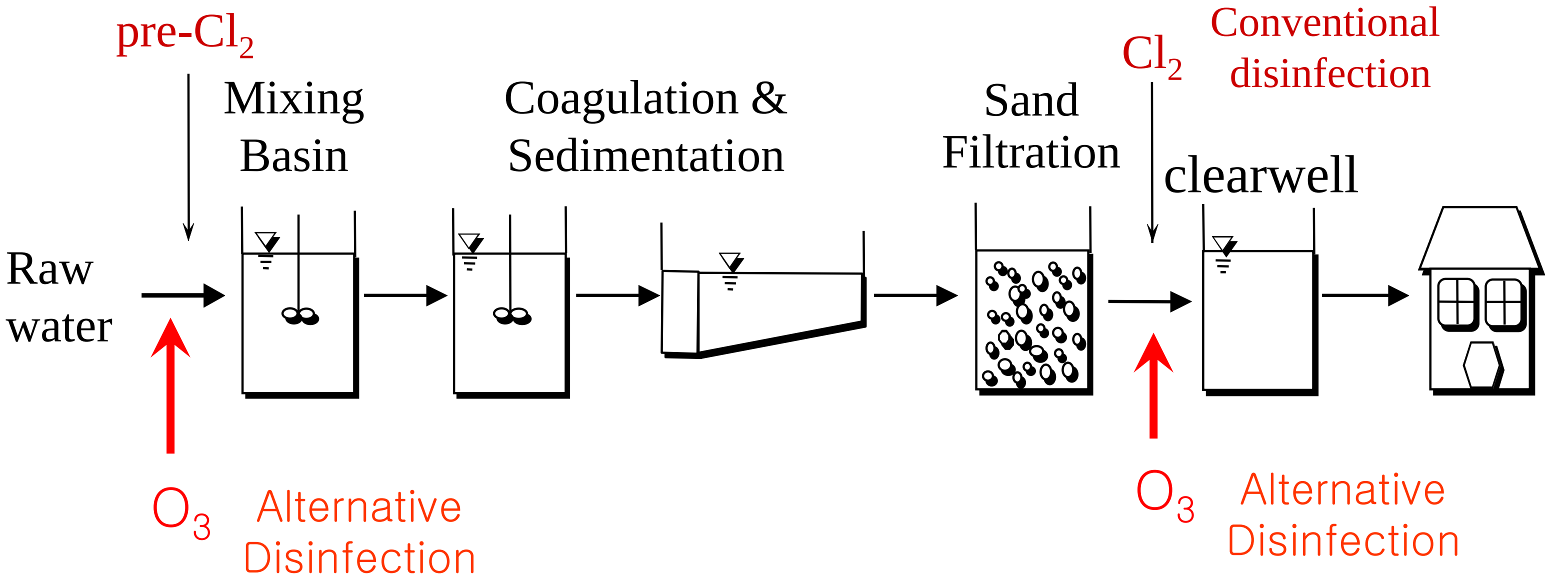
Application of AOTs



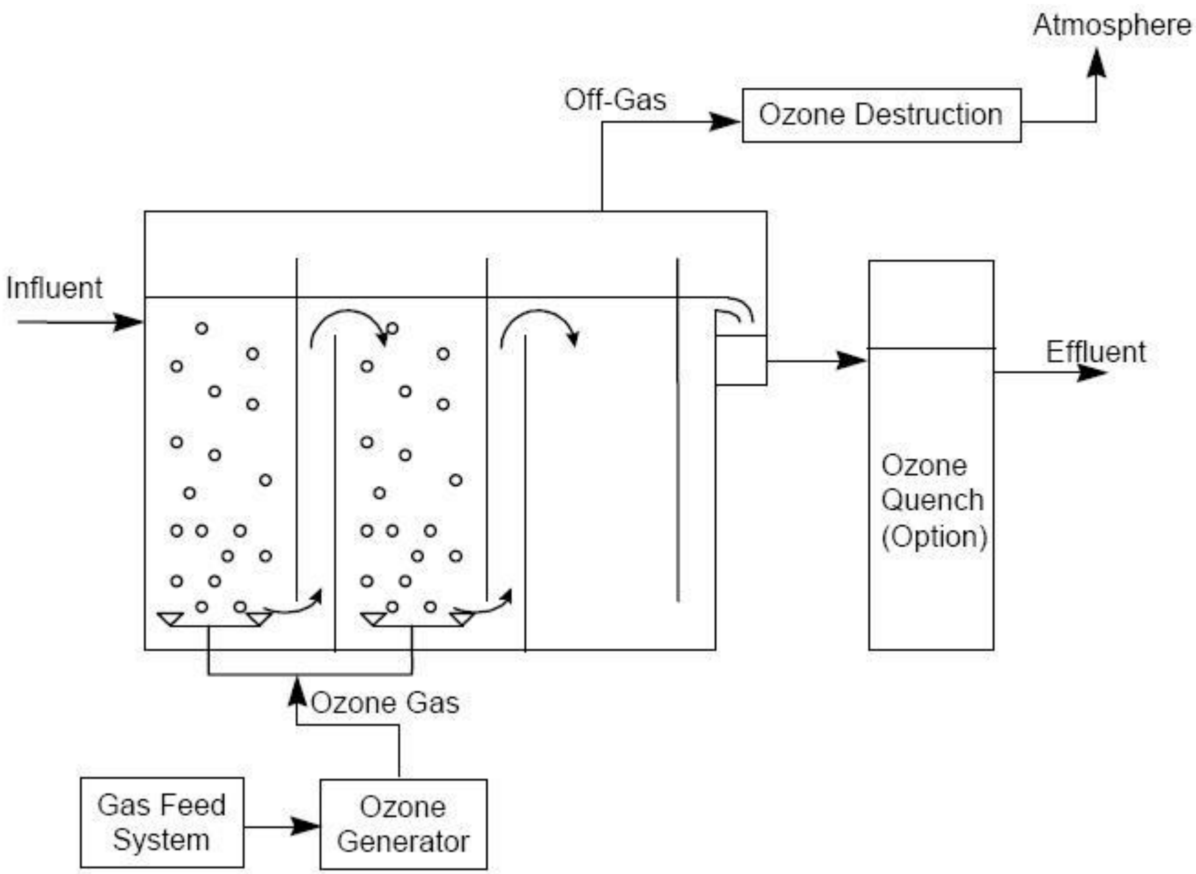
1. Drinking water treatment
   (e.g., ozonation, UV/H_2O_2)
2. Wastewater treatment
   (e.g., Fenton processes, ozonation)
3. Groundwater remediation
   (e.g., Fenton process, ozonation, inorganic oxidants w/ or w/o catalysts)
4. Disinfection and biofilm control
   (e.g., ozonation, photocatalysts)
5. Production of ultrapure water
   (e.g., VUV)
6. Sludge pretreatment

3. Ozonation

Ozonation for drinking water treatment



Ozonation process schematic diagram



Four basic components

Ozone water treatment systems have four basic components;

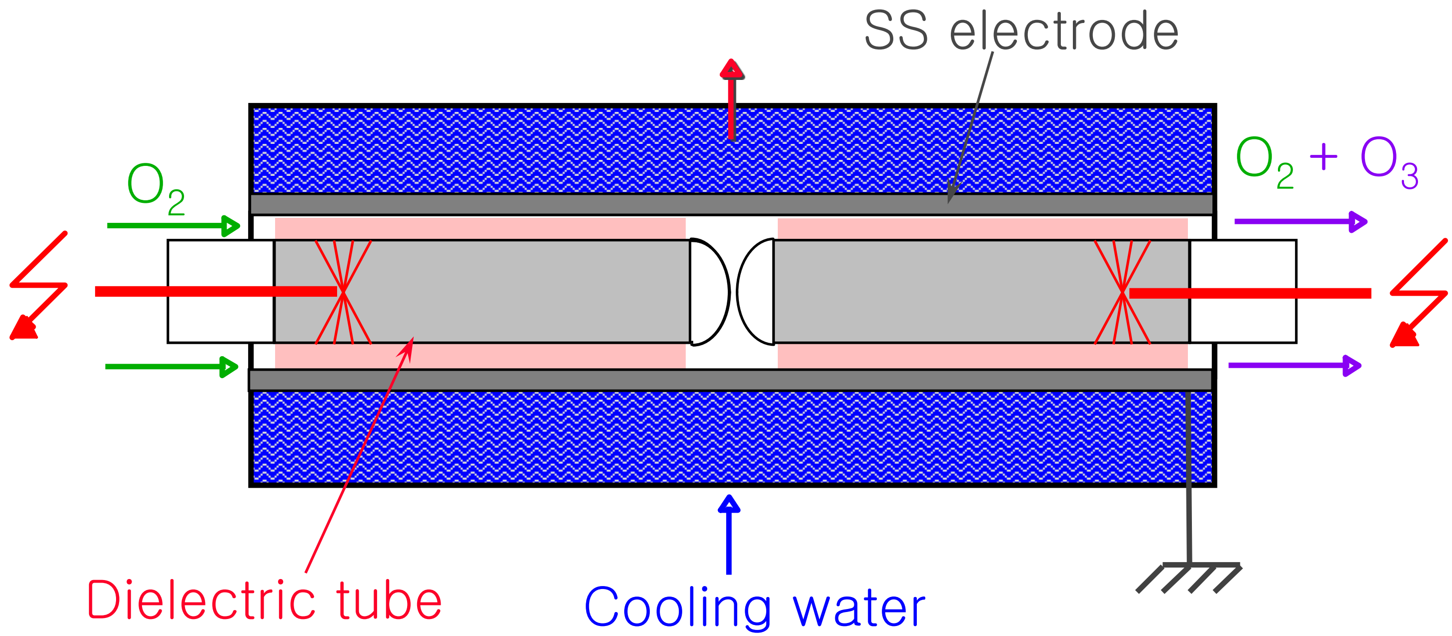
A. Gas feed system

B. Ozone generator

C. Ozone contactor

D. Off-gas destruction system

Ozone generator



Ozone generation

Firstly, ozone was synthetically discovered through the electrolysis of sulfuric acid. Ozone can be produced Several ways, although one method, Corona discharge, predominates in Ozone generation industry

Corona discharge

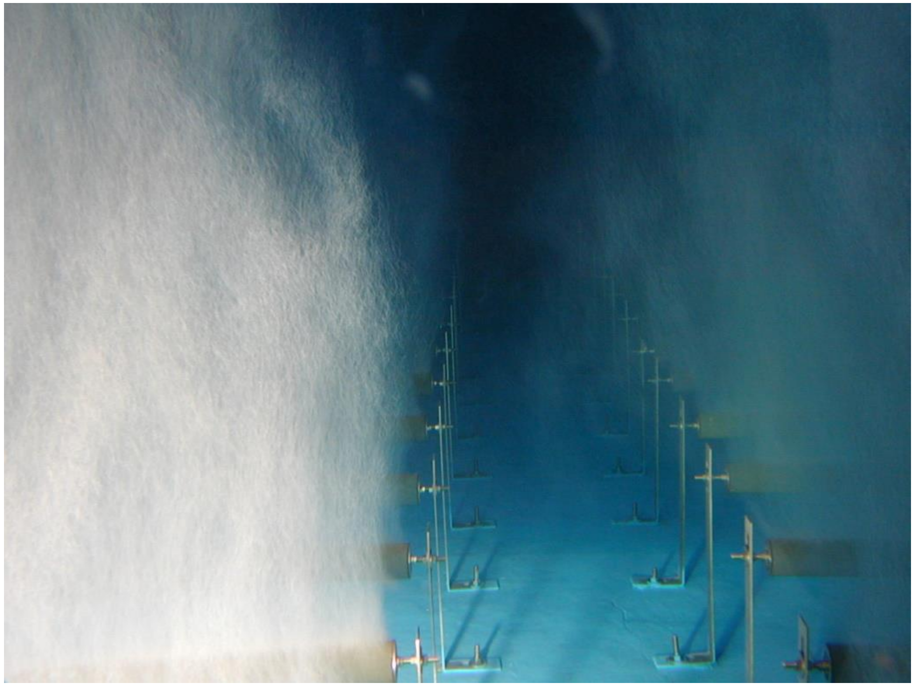
Corona discharge consists of passing an oxygen-containing gas through two electrodes separated by dielectric and a discharge gap. These electrons provide the energy to disassociate the oxygen molecules, leading to the formation of ozone

Ozone generator & ozone contactor

Duksan water treatment plant, Busan, Korea

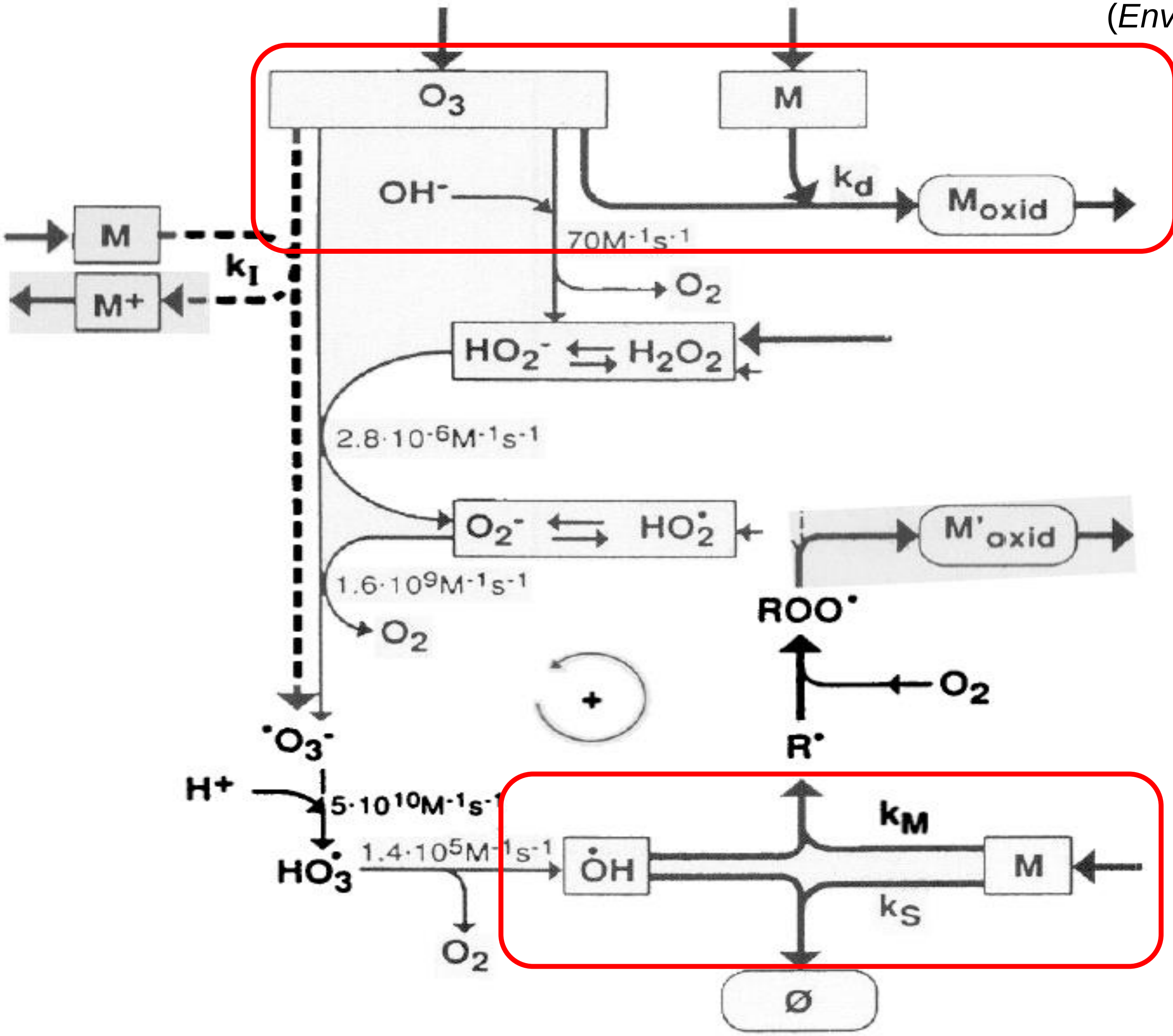
1. Ozone generator

2. Ozone contactor

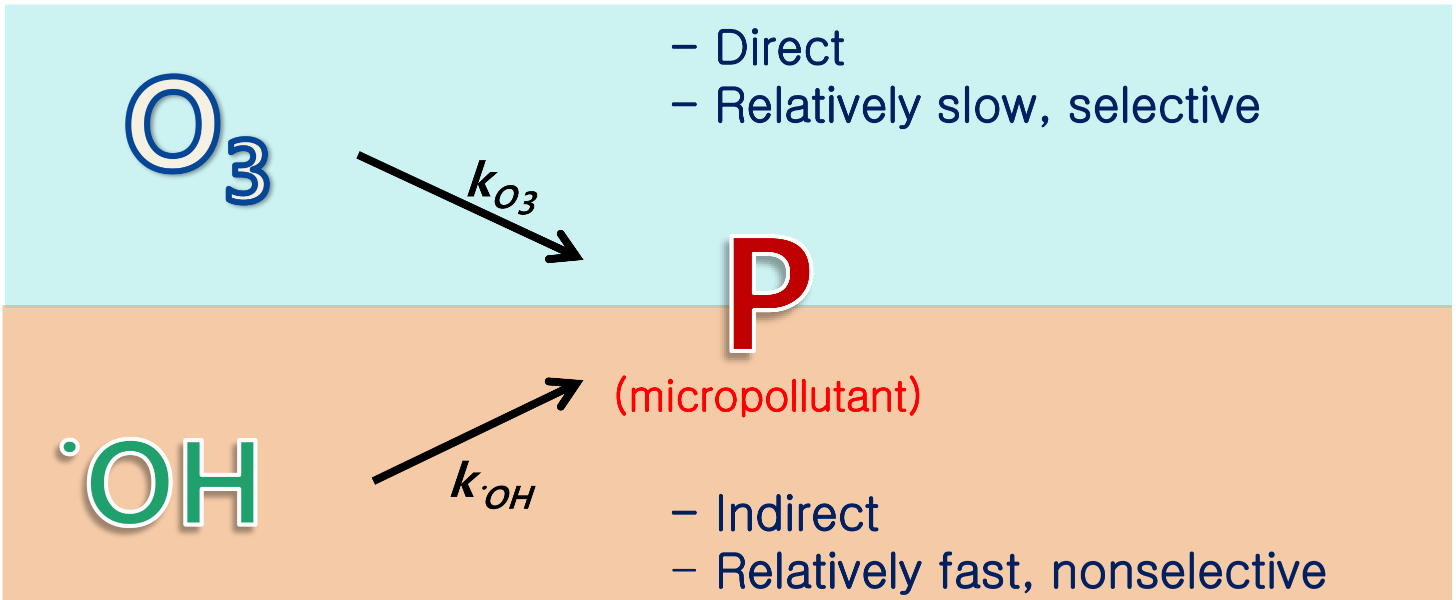


Chemistry of ozonation process

Staehelln and Hoigne, 1985
(*Environ. Sci. Technol.*)



Oxidation of organic pollutants by ozonation



> **Second-Order rate constant for the reaction of ozone and ˙OH**

Compound	k_{O_3} ($M^{-1}s^{-1}$)	$k_{\cdot OH}$ ($M^{-1}s^{-1}$)
Atrazine	6	3×10^{9}
Geosmin	<10	8.2×10^{9}
Carbofuran	620	7×10^{9}
Dinoseb	1.5×10^{5}	4×10^{9}

Modified ozonation processes

O_3/H_2O_2 Process

$$H_2O_2 \Leftrightarrow HO_2^- + H^+ \quad pK_a = 11.8$$

$$O_3 + HO_2^- \rightarrow {}^{\bullet}OH + O_2^{\bullet -} + O_2$$

Source: Applied Process Technology, Inc.

UV/O_3 Process

$$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2$$

$$H_2O_2 \Leftrightarrow HO_2^- + H^+ \quad pK_a = 11.8$$

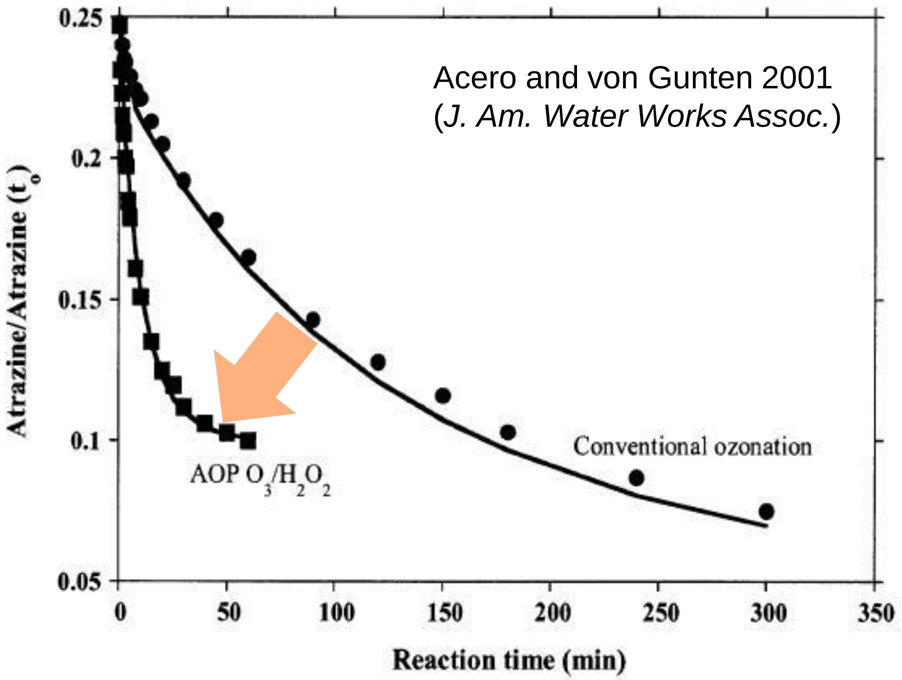
$$O_3 + HO_2^- \rightarrow {}^{\bullet}OH + O_2^{\bullet -} + O_2$$

Source: Spartan Co.

Conventional ozonation vs. O_3/H_2O_2

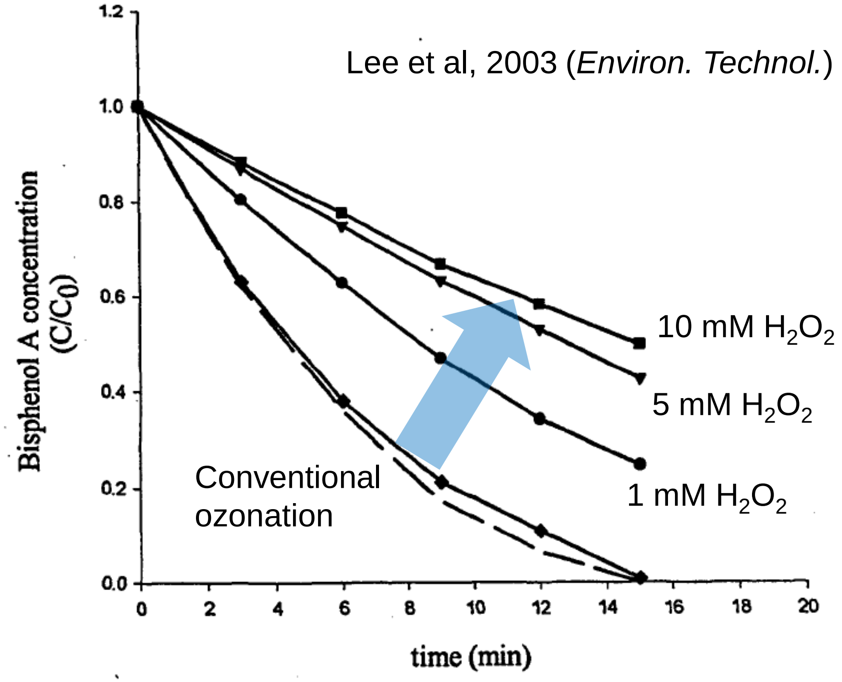
Atrazine

k_{O3} = 6 $M^{-1}s^{-1}$

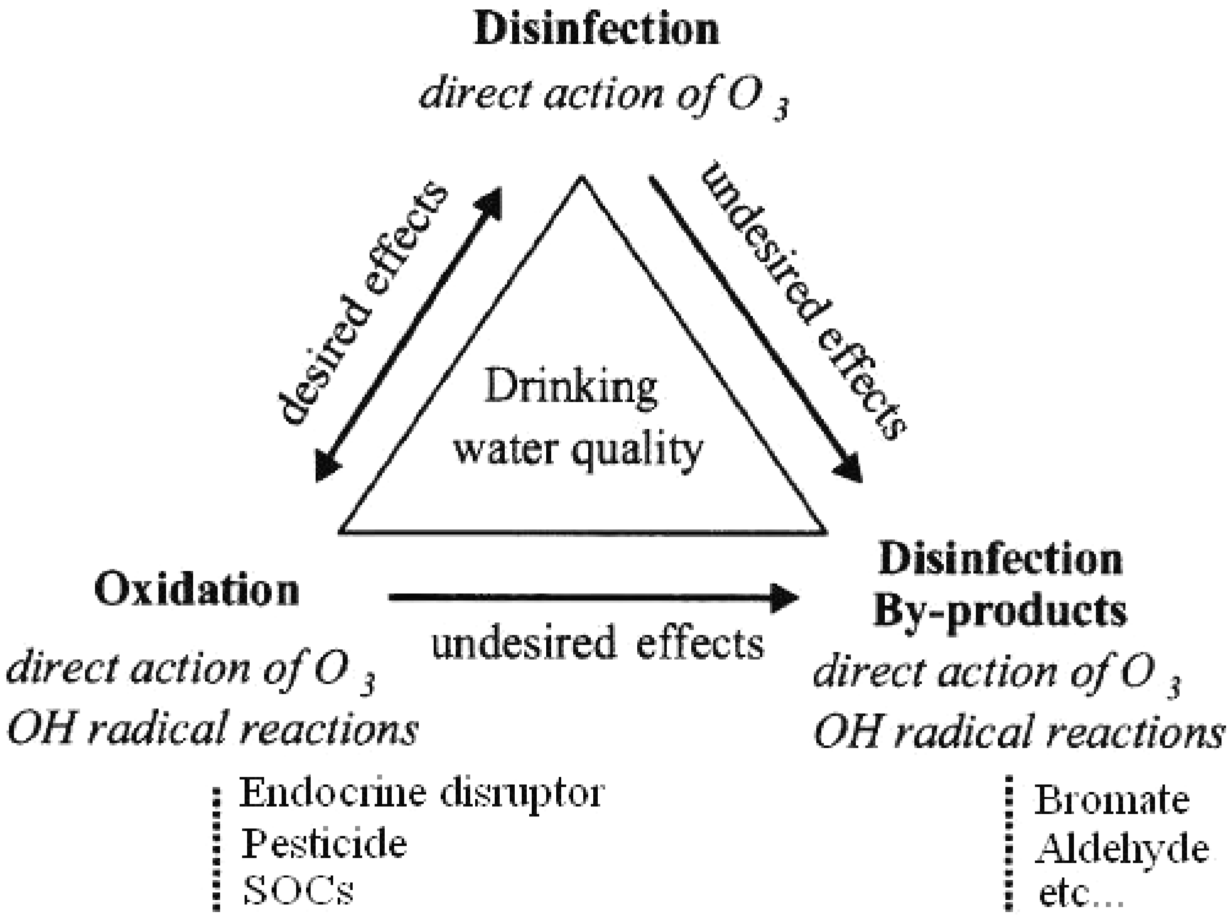


Bisphenol-A

k_{O3} = 2.7 × 10^6 $M^{-1}s^{-1}$ at pH 7



Desired and undesired effects of ozonation



3. Fenton Process

Fenton process

Fenton reaction

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

(fast)

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

(slow)

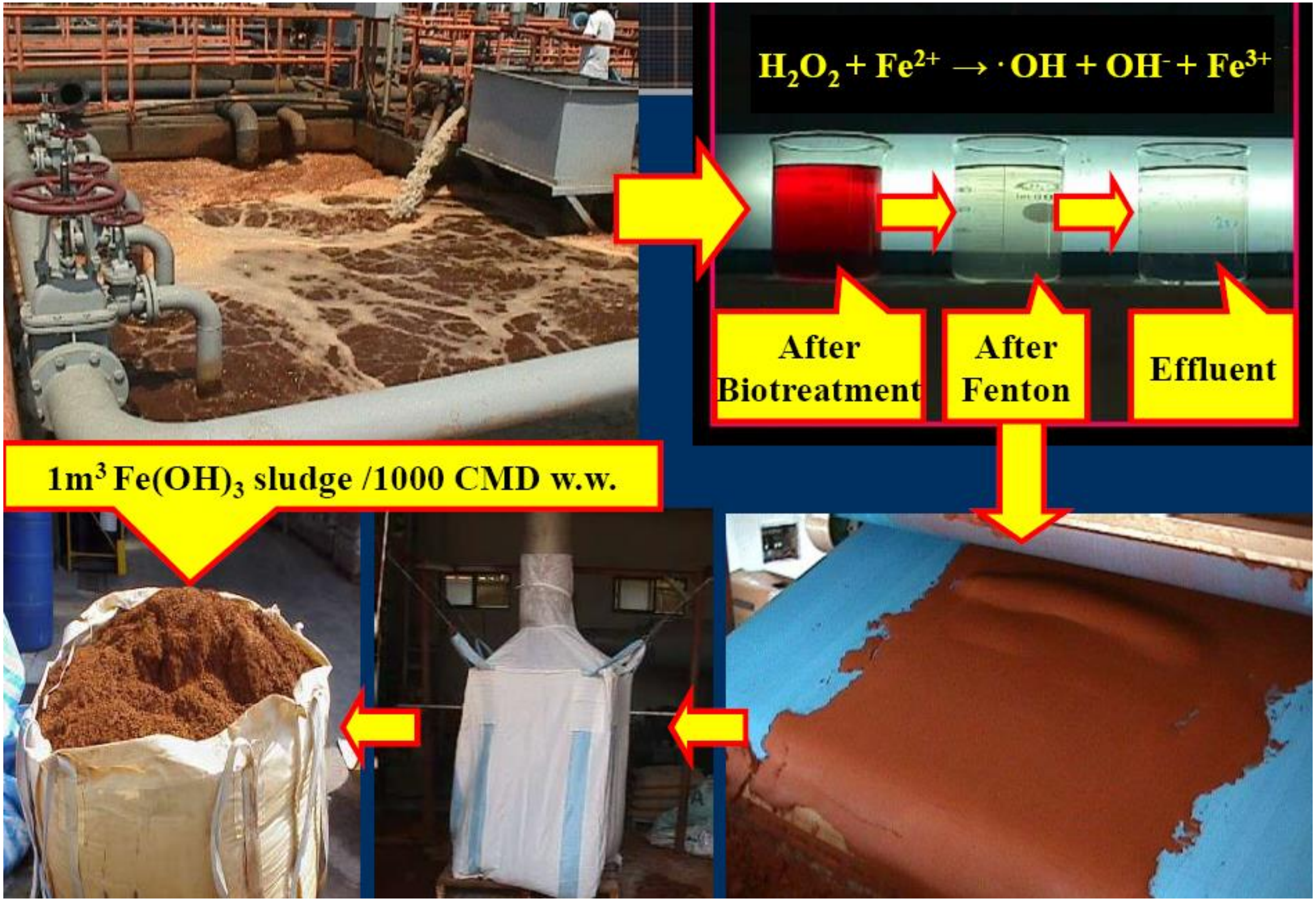
$$Fe(III) + H_2O + h\nu \rightarrow Fe(II) + {}^{\bullet}OH + H^+$$

"Photo–Fenton"

$$Fe(III) + e^- \rightarrow Fe(II)$$

"Electro–Fenton"

Traditional Fenton process



Source: Prof. Y. H. Huang from NCKU, Taiwan

Heterogeneous Fenton process using FBR

Source: Prof. Y. H. Huang from NCKU, Taiwan

Full-scale Fenton process using FBR

Source: Prof. Y. H. Huang from NCKU, Taiwan

Source: Prof. Y. H. Huang from NCKU, Taiwan

處理水量: 50CMD

尺寸: 0.6 m∮ x 5.85mWH x 6mTH

進流水質: phenol:1.5mg/L

放流水質: phenol<0.1mg/L

處理水量: 1200CMD

尺寸: 1.9 m∮ x 9mWH x 9.15mTH

進流水質: COD<300 mg/L

放流水質: COD<100 mg/L

處理水量: 4800CMD

尺寸: 2.8 m∮ x 13mWH x 13.15mTH

進流水質: COD<250 mg/L

放流水質: COD<80 mg/L

處理水量: 12500CMD

尺寸: 3.1 m∮ x 13mWH x 13.15mTH

數量: 2槽

進流水質: COD<180 mg/L

放流水質: COD<70 mg/L

處理水量: 30000CMD

尺寸: 3.35 mφ x 12.5mWH x 12.9mTH

數量: 4座

進流水質: COD<350 mg/L

放流水質: COD<100 mg/L

處理水量: 86000CMD

尺寸: 3.6 m∮ x 12.5mWH x 12.9mTH

數量: 12座

進流水質: COD<800 mg/L

放流水質: COD<100 mg/L

Source: Prof. Y. H. Huang from NCKU, Taiwan

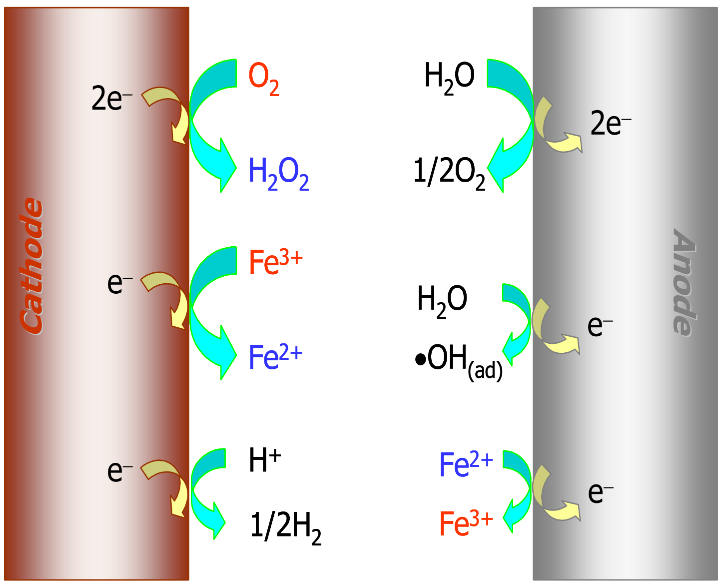
Unseeded FBR Fenton process

▲ **Capacity: 1,000 CMD**
COD: 200 → 80 mg/L

Source: Prof. Y. H. Huang from NCKU, Taiwan

Electro-Fenton process

Schematic diagram for reactions
in the electro-Fenton process



**Source: Prof. Y. H. Huang
from NCKU, Taiwan**

Electro-Fenton Process

Applications of the electro-Fenton process (Taiwan)

Type of wastewater	Influent COD, mg/l	Effluent COD, mg/l	COD removal efficiency (%)
Oil/ink wastewater in a chemical plant	74,600	2,390	97
Hexamine wastewater in a chemical plant	29,600	40	>99
Electroless nickel wastewater in a electro-plating plant	27,900	1,940	93
Black liquor in a pulp/paper plant	30,900	350	99
Acrylonitrile wastewater in a latex plant	5,800	560	90
Resin processing wastewater in a chemical plant	2,500	350	86
Catalyst regenerate wastewater in a manmade fiber plant	24,900	620	97
Waste liquor of laboratory in a college	23,900	4,780	80

Reactive oxidants produced by the Fenton reaction

◆ •OH vs Fe(IV)

One-electron transfer

E^o = 0.771 V $\qquad$ E^o = 2.813 V

$$\text{Fe(II)} + H_2O_2 \rightarrow \text{Fe(III)} + {}^{\bullet}OH + OH^- \qquad H_2O$$

E^o = 0.74 ~ 1.14? V

Two-electron transfer

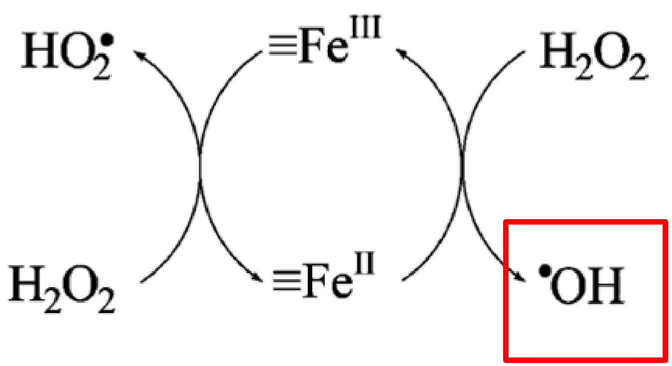
E^o = ~1.3 V $\qquad$ E^o = ~1.8 V

$$\text{Fe(II)} + H_2O_2 \xrightarrow{2H^+} \text{Fe(IV)} + 2H_2O \qquad \text{Fe(III)}$$

E^o = 1.763 V

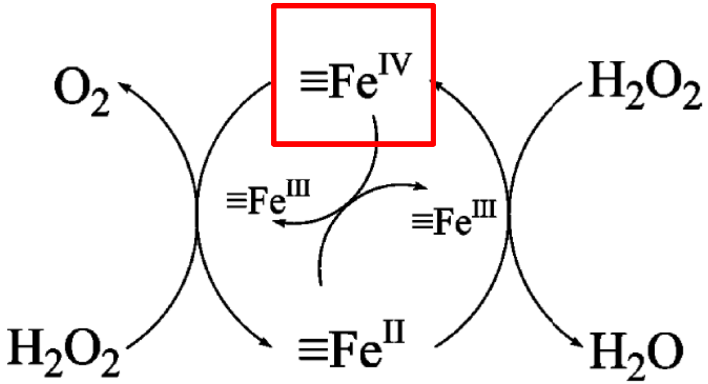
Nonradical mechanism and Fe(IV)

Haber—Weiss Mechanism



(Acidic pH)

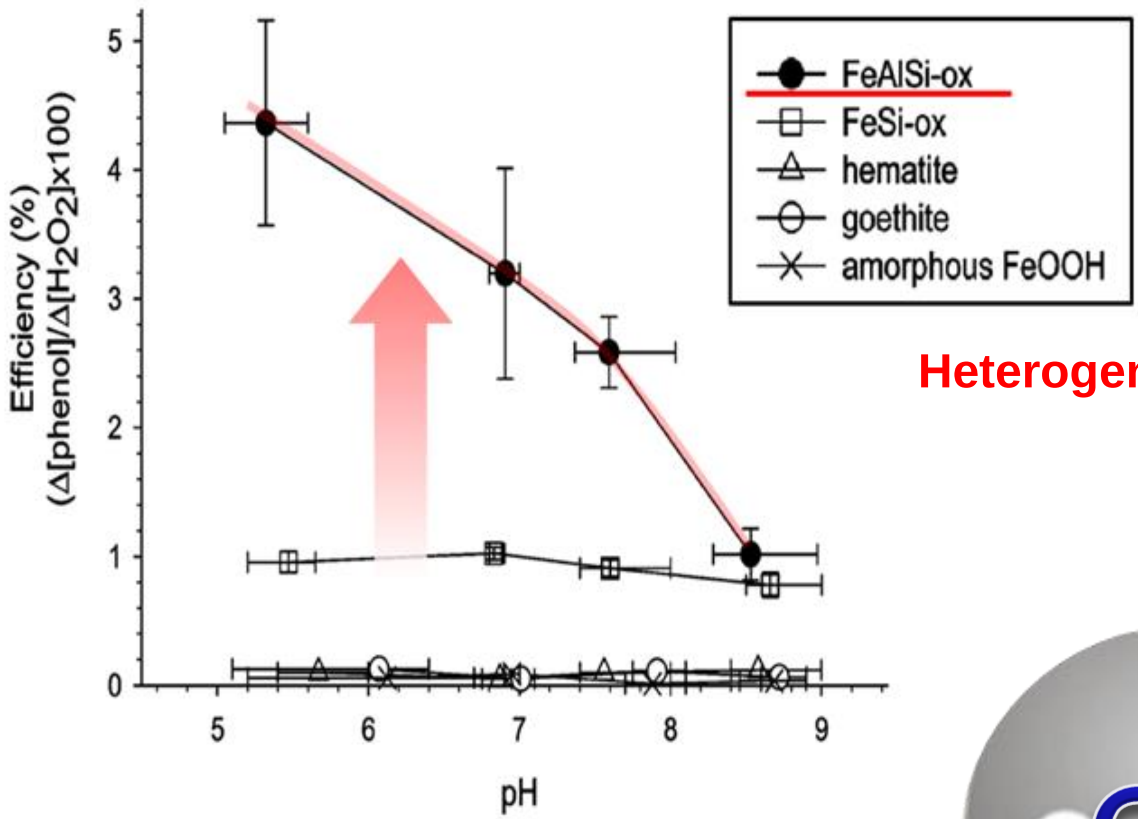
Non-Radical Mechanism



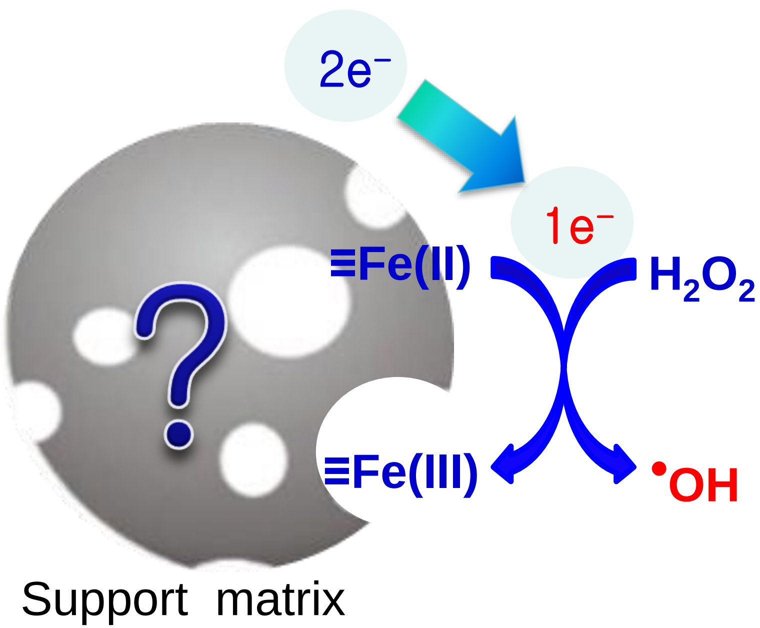
(Neutral pH)

$1e^-$ ⟺ $2e^-$

Neutral-pH active Fenton catalysts



Heterogeneous Fenton Catalyst
(Pham et al., 2009)



Homework

Kinetics of iron-catalyzed decomposition of hydrogen peroxide

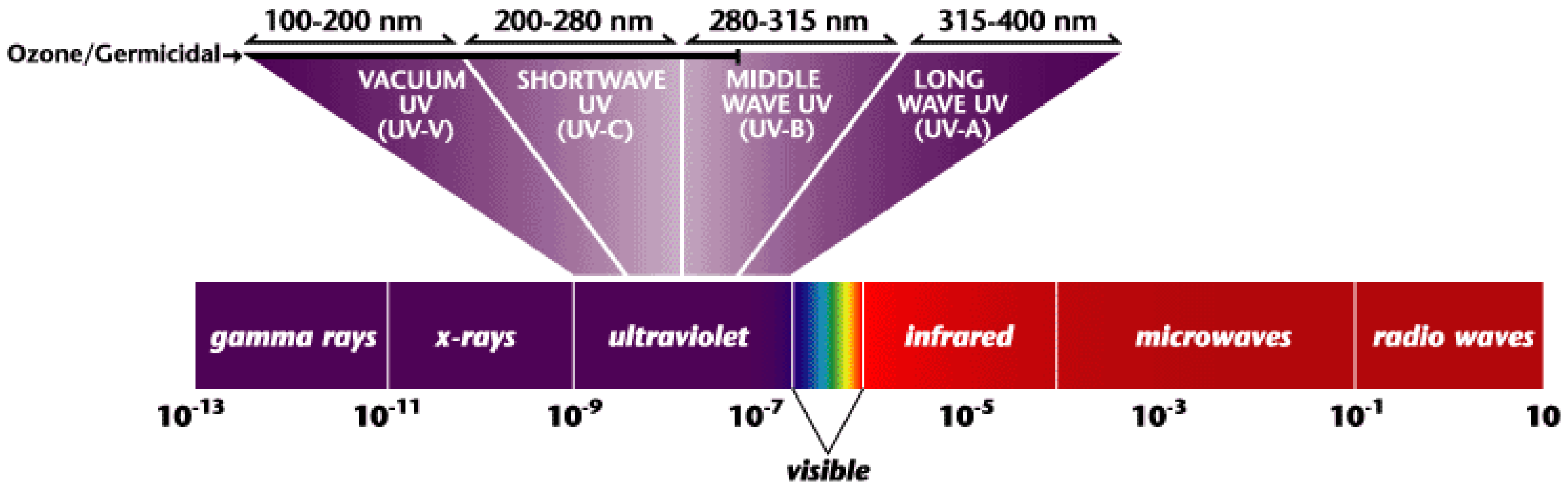
When Fe^{3+} is added into the solution containing H_2O_2, the decomposition of H_2O_2 is accelerated by the catalytic reactions as follows. Also, the decomposition rate of H_2O_2 follows the pseudo-first order kinetics (i.e., $d[H_2O_2]/dt = -k_{H2O2}[H_2O_2]$) .
Derive the pseudo-first order rate constant for the decomposition of H_2O_2 (k_{H2O2}) using the second-order rate constants of the elementary reactions below ($k_1 \sim k_5$) and the concentration of Fe^{3+} ($[Fe^{3+}]$)

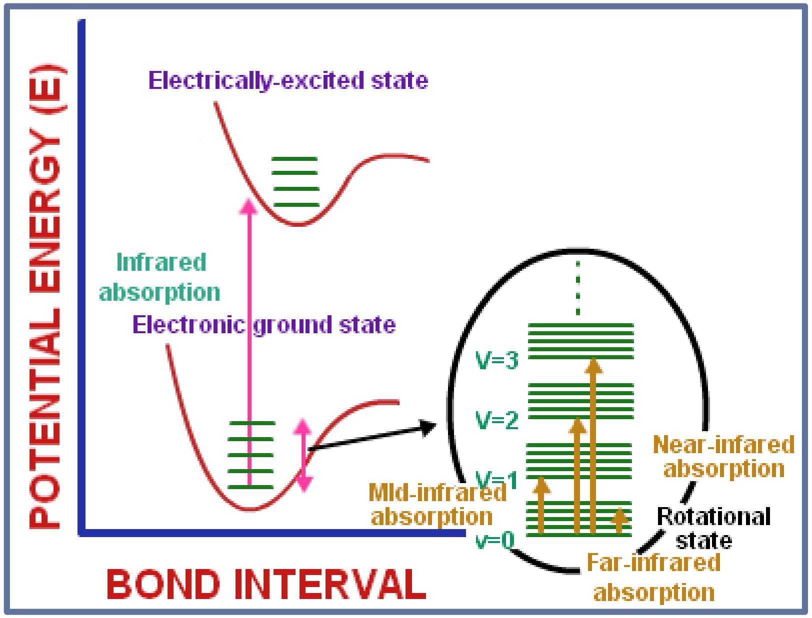
$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \qquad k_1$$
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad k_2$$
$$HO_2^{\bullet} + Fe^{3+} \rightarrow Fe^{2+} + O_2 + H^+ \qquad k_3$$
$$HO_2^{\bullet} + Fe^{2+} \rightarrow Fe^{3+} + HO_2^- \ (\leftrightarrow H_2O_2) \qquad k_4$$
$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \qquad k_5$$

(Tip: Use steady-state approximations for the intermediates)

4. Photochemical Process

Electromagnetic Spectrum





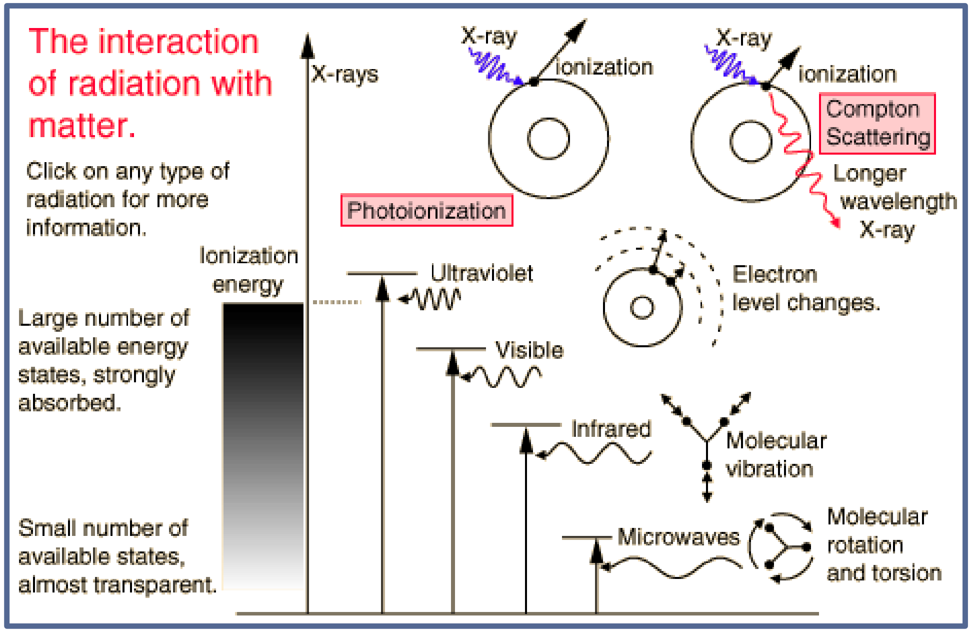


Photo-Excitation and Subsequent Processes

A + *hv* → A*
(photo-excitation)

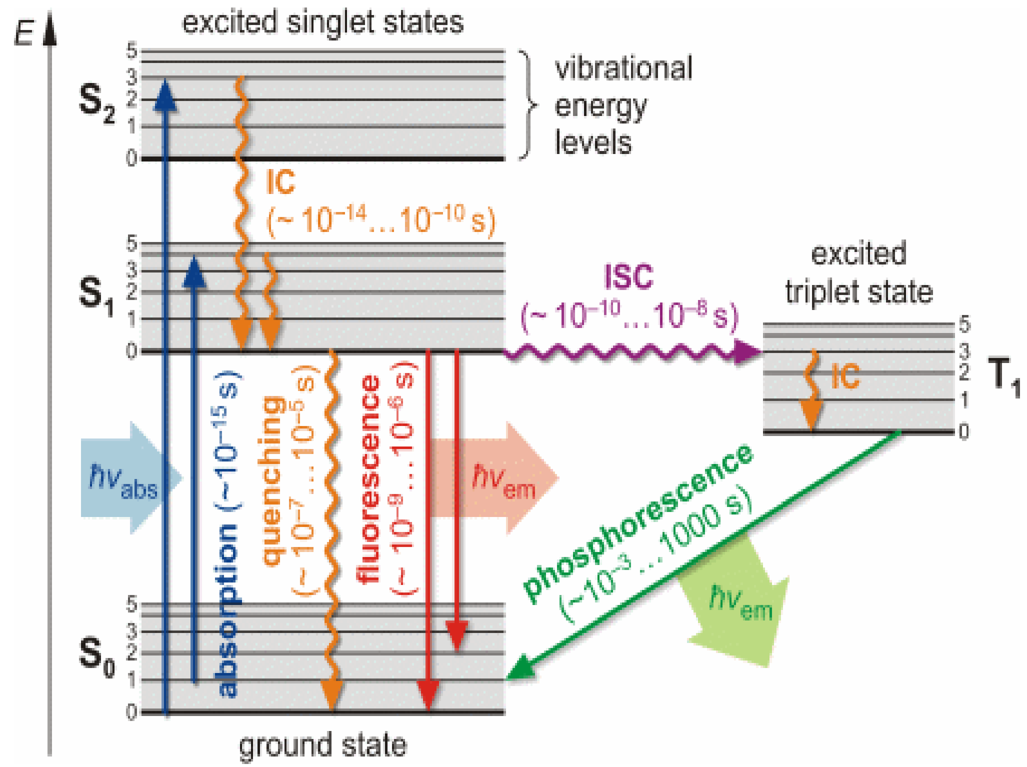
A* → A + heat
(thermal decay)

A* → A + *hv′*
(fluorescence)

A* → A + *hv″*
(phosphorescence)

A* → 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				

오염물질의 광분해(Photolysis)

- 직접 광분해(Direct photolysis)

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

T: Target compound
P: Product

- 간접 광분해(Indirect photolysis)

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

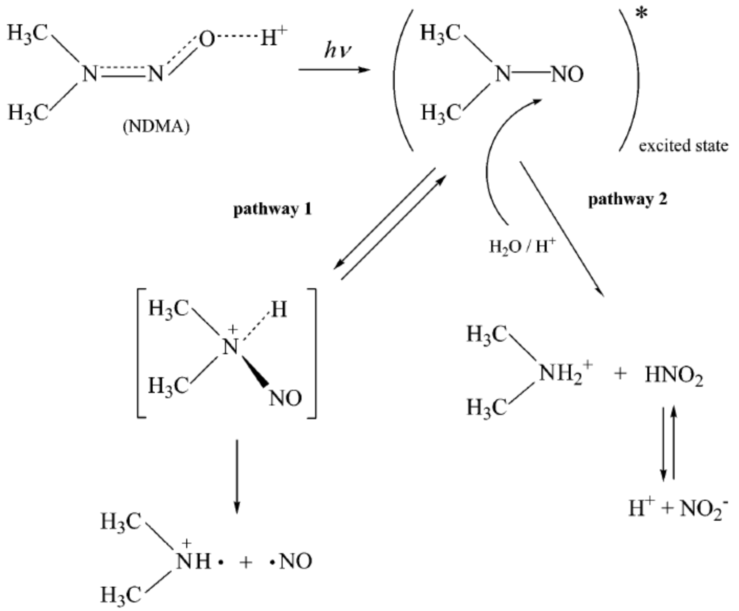
A: Light absorbing compound
R: Reactive compound

- 광촉매(photo-catalytic) 반응

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

C: Photo-catalyst

e.g. NDMA photolysis



e.g. UV/H_2O_2 system

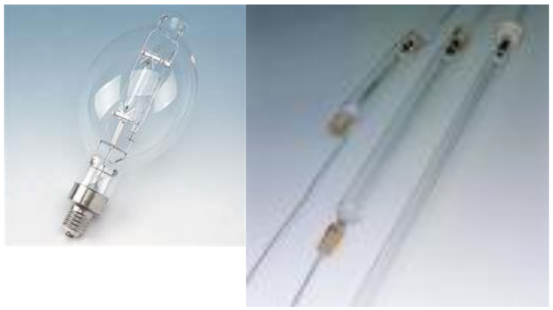
$H_2O_2 + h\nu \rightarrow 2{\bullet}OH$
Compounds + $\bullet OH \rightarrow$ Products

e.g. TiO_2 photo-catalysis

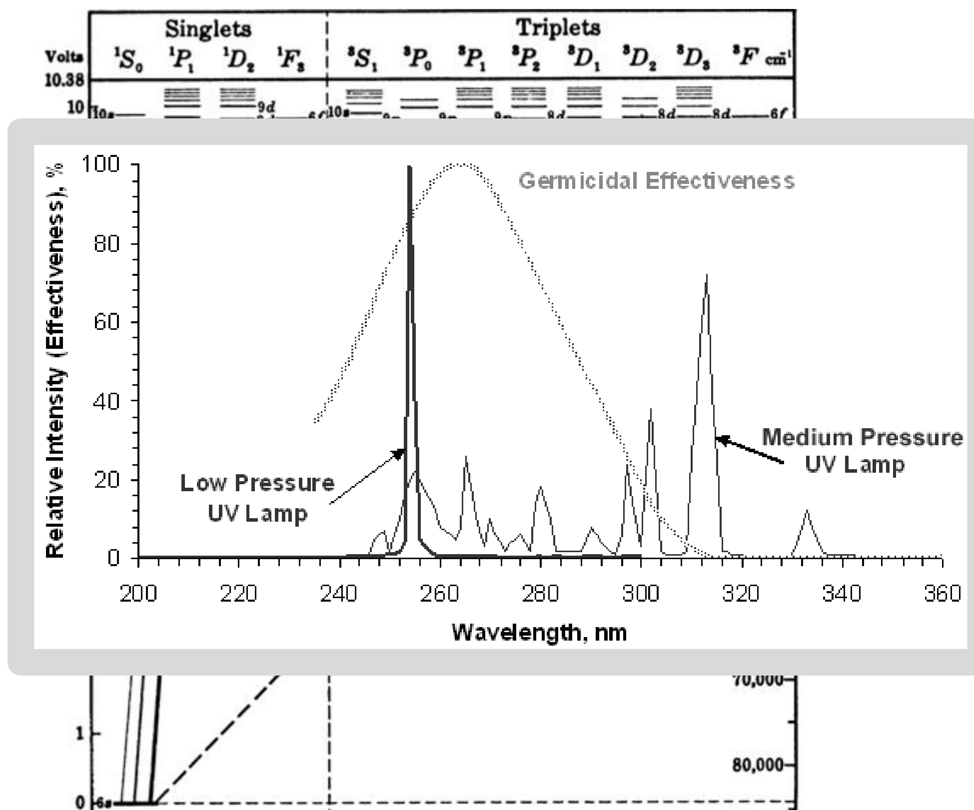
$TiO_2 + h\nu \rightarrow TiO_2(h^+ \,\&\, e^-)$
Compounds + $TiO_2(h^+ \,\&\, e^-) \rightarrow$ Products + TiO_2

UV Lamps

Mercury vapor lamps (수은방전램프)



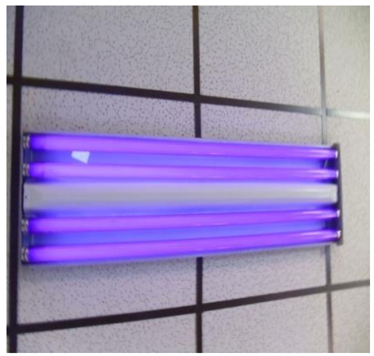
- Low pressure Hg lamps: monochromatic emission at 254 and 185 nm(표준형, 고출력 저압수은 램프)
- Medium and High pressure Hg lamps: polychromatic emission from 200~800 nm(수은 중압, 고압 램프)



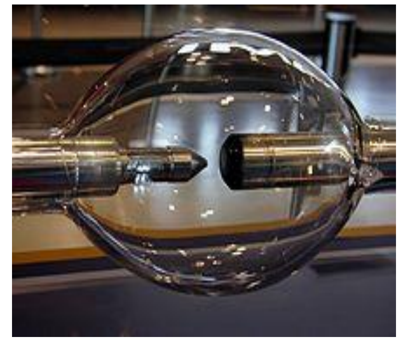
Wavelength (nm)	Color
184.5	VUV
253.7	UVC
365.4	UVA
404.7	Violet
435.8	Blue
546.1	Green
578.2	Yellow-orange

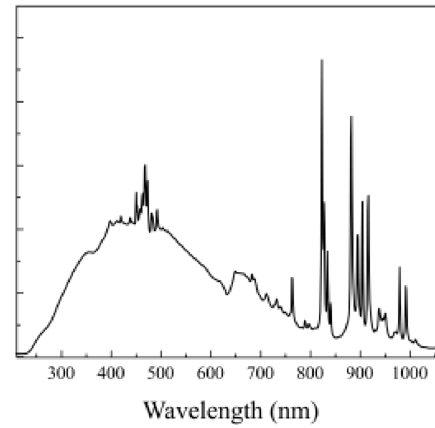
UV Lamps

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

Quantum Yield (ϕ)

$$A + h\nu \rightarrow B$$

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

- Primary quantum yield: quantum yield for the primary photochemical reaction
- overall quantum yield: quantum yield considering the primary photochemical reaction and subsequent thermal reactions

Ex) $A + h\nu \rightarrow B + C$ (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 for 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

$$A + h\nu \rightarrow B$$

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

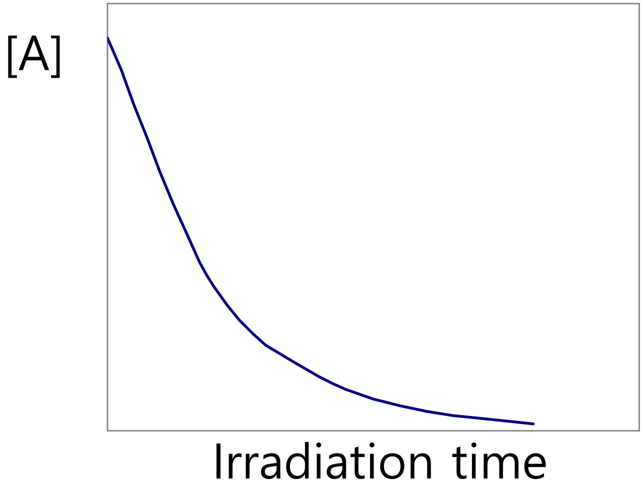
I_0 : incident photon flow (Einstein l^{-1} s^{-1})
ϕ : quantum yield

Kinetics for Photochemical Reactions

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

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

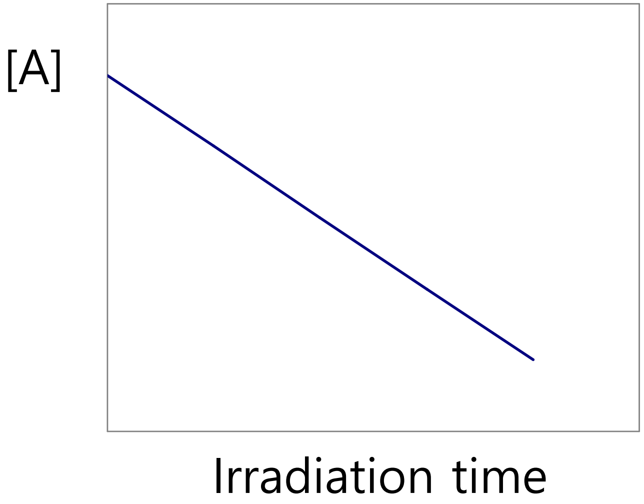
First order kinetics (일차반응)



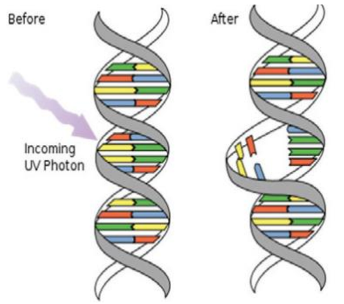
At a high concentration ($\varepsilon bc >> 1$)

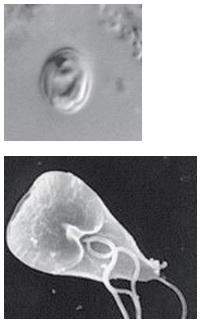
$$d[A]/dt = -I_0(1-10^{-\varepsilon b[A]}) \times \phi \approx -I_0 \phi$$

Zero order kinetics (영차반응)



Photochemical Water Treatment



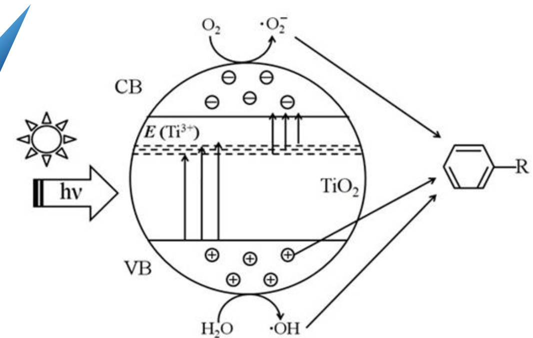


UV Disinfection

Ultrapure Water
Production
(VUV)

Photochemical Reactions

Drinking Water Treatment
(UV/H_2O_2 system)



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

UV/H_2O_2 System

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

(<300 nm)

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

Solvent cage

Primary quantum yield: 0.5

Overall quantum yield for •OH: 0.5 x 2 = 1

Subsequent reactions

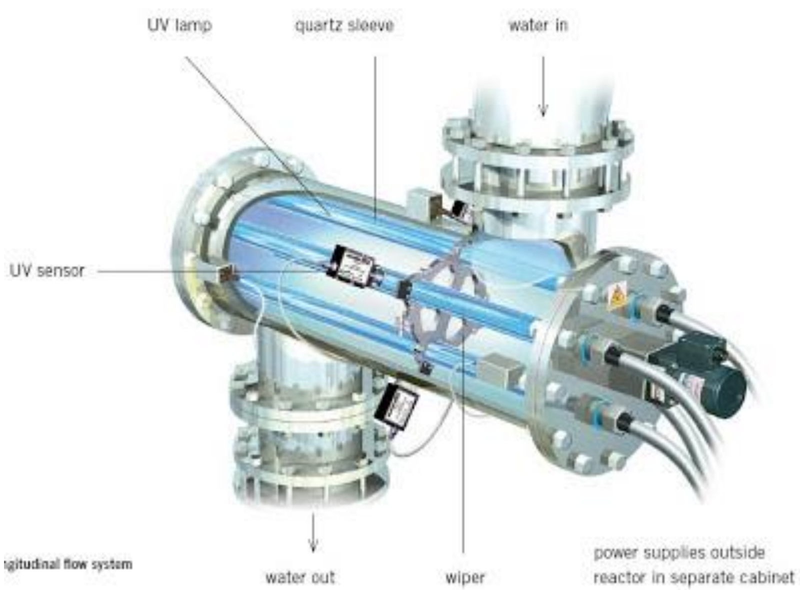
$${}^{\bullet}OH + H_2O_2 \rightarrow HO_2{\bullet} + H_2O$$

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

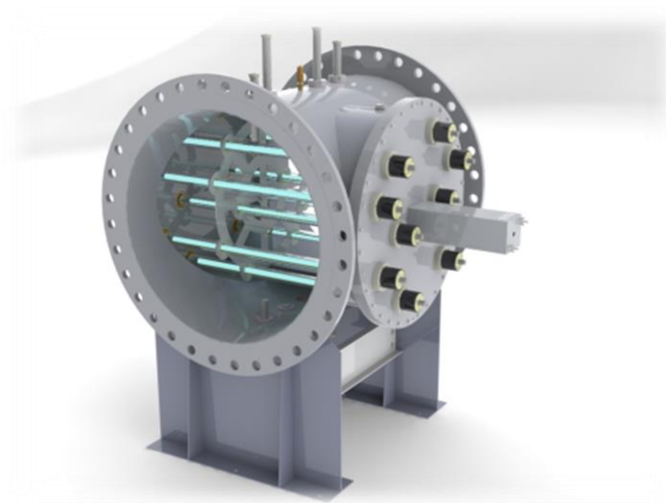
$$2{\bullet}OH \rightarrow H_2O_2$$

UV/H_2O_2 Reactor

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



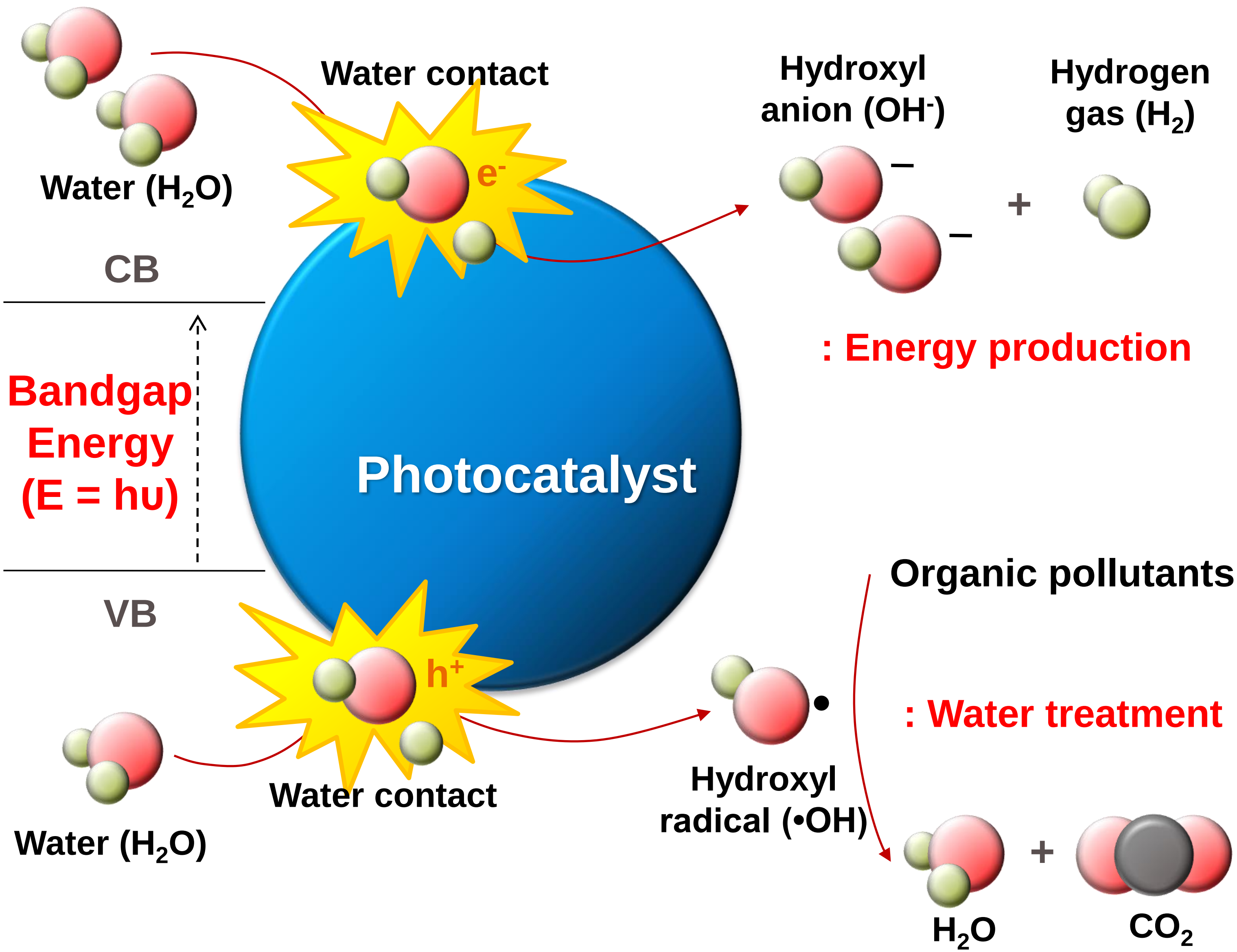
▲ Longitudinal flow system



Source: Ozonia Co. (Aquaray® H_2O)

▲ Cross flow system

Principles of semiconductor photocatalysis



Modification of photocatalytic process