AOP

Using Photochemical Reactions

Characteristics of light

Planck Law of Radiation

$$\mathbf{u = hv = hc/\lambda = h\,c\;\bar{v}}$$

$$\mathbf{U = N_A hv = h\,c\,N_A/\lambda = hcN_A\;\bar{v}}$$

Where u = energy (J) of one photon

v = frequency (s^{-1})

λ = wavelength (m)

$\bar{v}$ = wave number (m^{-1})

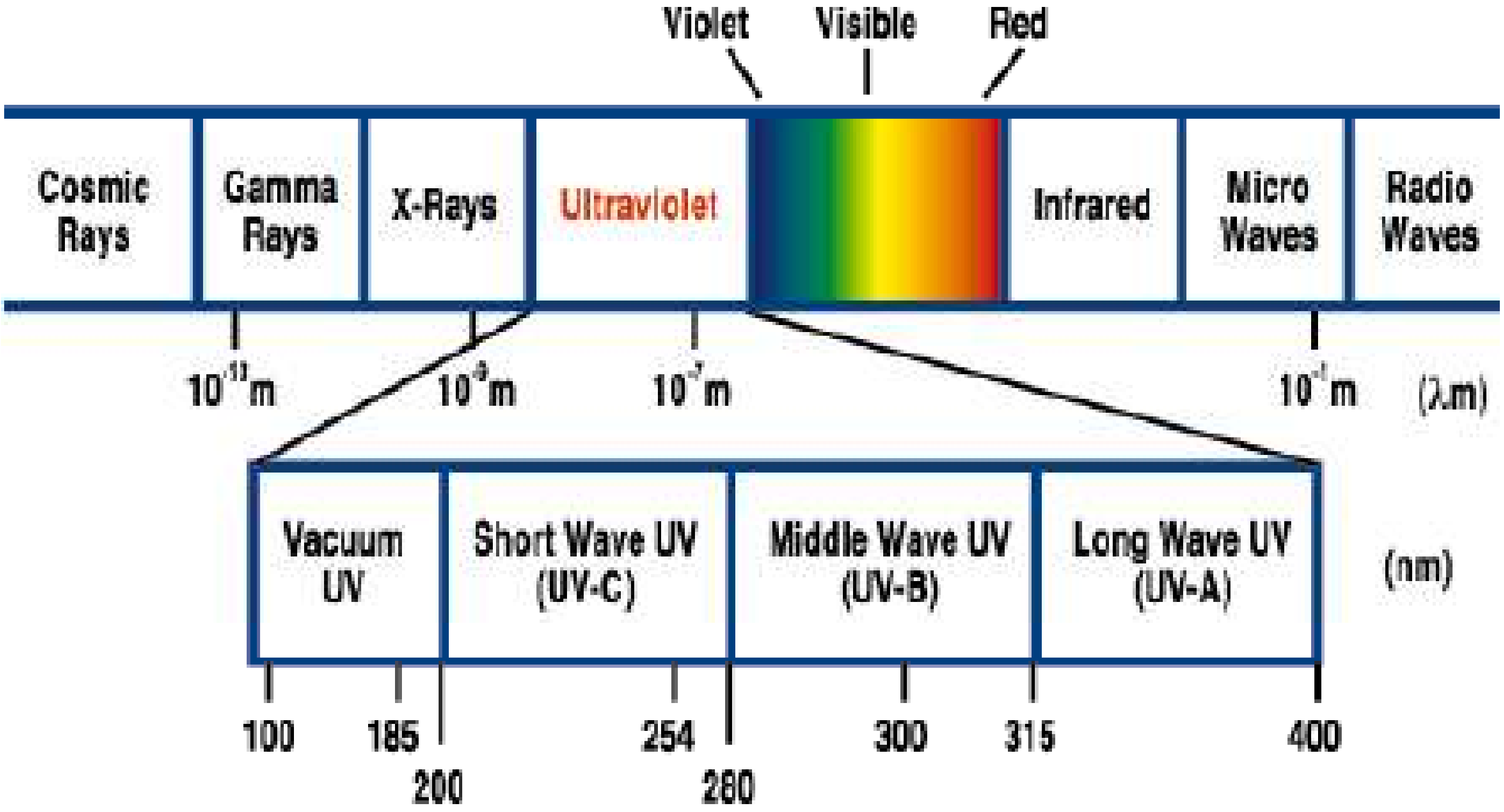
c = speed of light (2.9979×10^{8} m s^{-1})

h = Planck constant (6.6261×10^{-34} J s)

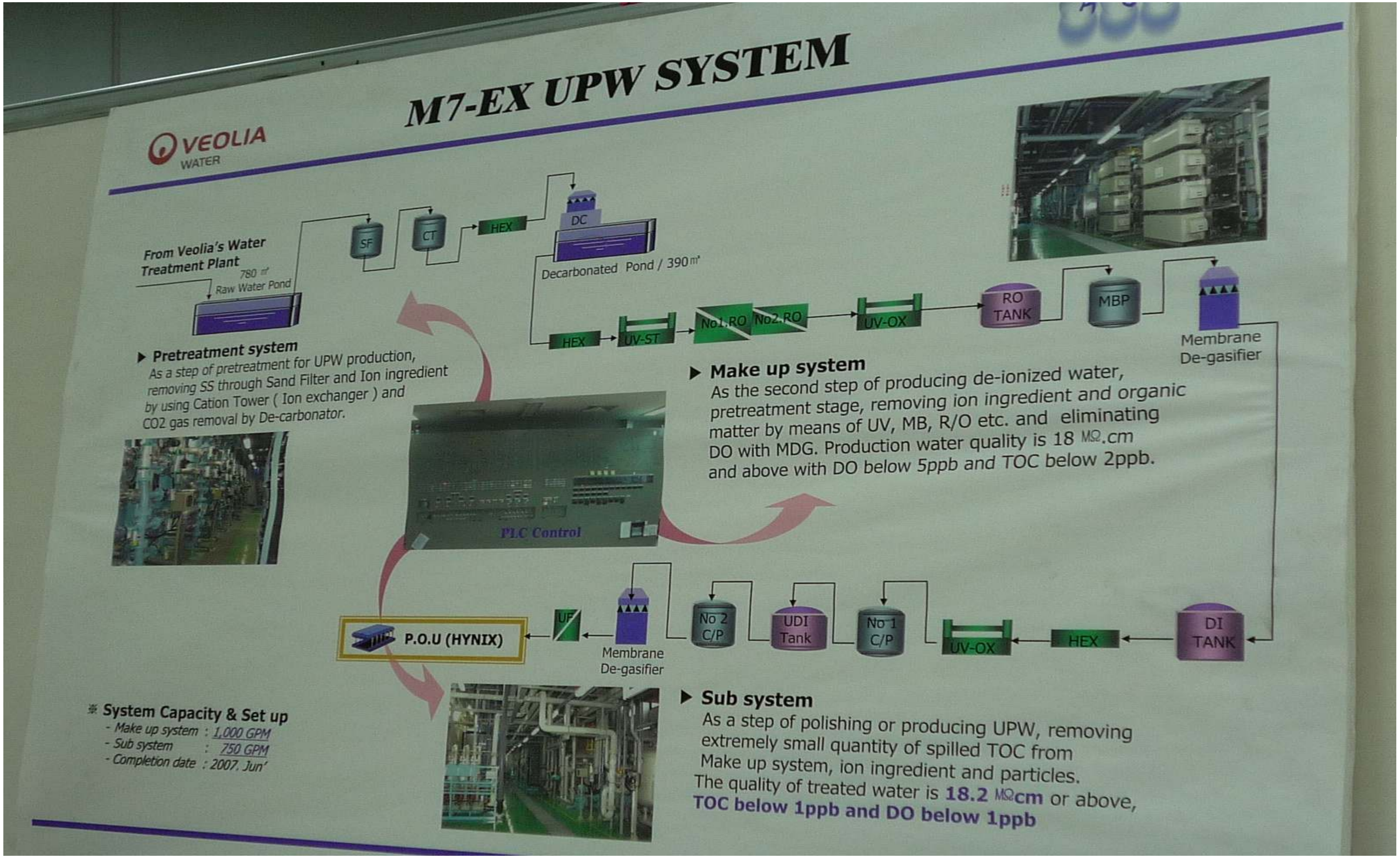
N_A = Avogadro number (6.02214×10^{23} mol^{-1})

U = energy per einstein

- Electromagnetic Spectrum



Hynix ultrawater supply system



M7-EX UPW SYSTEM

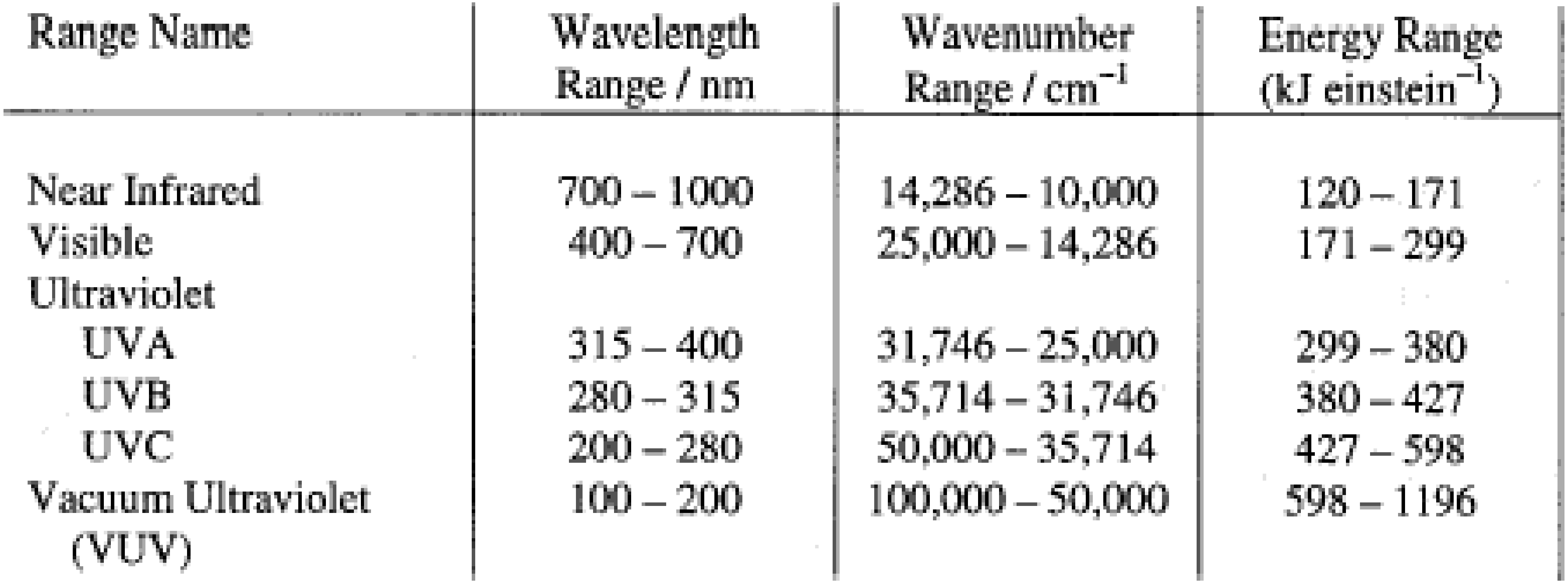
▶ **Pretreatment system**
As a step of pretreatment for UPW production, removing SS through Sand Filter and Ion ingredient by using Cation Tower (Ion exchanger) and CO2 gas removal by De-carbonator.

▶ **Make up system**
As the second step of producing de-ionized water, pretreatment stage, removing ion ingredient and organic matter by means of UV, MB, R/O etc. and eliminating DO with MDG. Production water quality is 18 ㏁.cm and above with DO below 5ppb and TOC below 2ppb.

▶ **Sub system**
As a step of polishing or producing UPW, removing extremely small quantity of spilled TOC from Make up system, ion ingredient and particles.
The quality of treated water is **18.2 ㏁cm** or above,
TOC below 1ppb and DO below 1ppb

※ **System Capacity & Set up**
- *Make up system : 1,000 GPM*
- *Sub system : 750 GPM*
- *Completion date : 2007. Jun'*

Spectral ranges of interest in Photochemistry



Range Name	Wavelength Range / nm	Wavenumber Range / cm^{-1}	Energy Range (kJ $einstein^{-1}$)
Near Infrared	700 – 1000	14,286 – 10,000	120 – 171
Visible	400 – 700	25,000 – 14,286	171 – 299
Ultraviolet			
UVA	315 – 400	31,746 – 25,000	299 – 380
UVB	280 – 315	35,714 – 31,746	380 – 427
UVC	200 – 280	50,000 – 35,714	427 – 598
Vacuum Ultraviolet (VUV)	100 – 200	100,000 – 50,000	598 – 1196

Photons with wavelength > 1000 nm photon energy too small

< 100 nm photon energy so much

파장 종류별 특성

UVA	파장의 범위는 315-400 nm 이고 피부에 흡수되면 “sun tanning” 을 일으킨다.
UVB	파장의 범위는 280-315 nm 이고 피부에 흡수되면 “sun burning” 을 일으킨다.
UVC	파장의 범위는 200-280 nm 이고 피부 조직의 DNA에 의해 흡수되어 피부암을 일으키는 원인이 된다. 또한 미생물의 DNA 혹은 RNA에 흡수되어 복제를 억제시켜 미생물을 불활성화 시킨다.
Vacuum UV	파장의 범위는 100-200 nm 이고 공기 중의 물과 산소에 의해 흡수된다.

The laws of photochemical reaction

- Beer-Lambert absorption law

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

$$I_a = I_o - I$$

T: transmittance
I : irradiance (Einstein l^{-1} s^{-1})
ε: molar aborption coefficient (M^{-1} cm^{-1})
b: optical pathlength (cm)
C: molar concentration of photon absorber (M)

- Kinetic raw of photochemical reaction

$$A + hv \rightarrow B$$

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

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

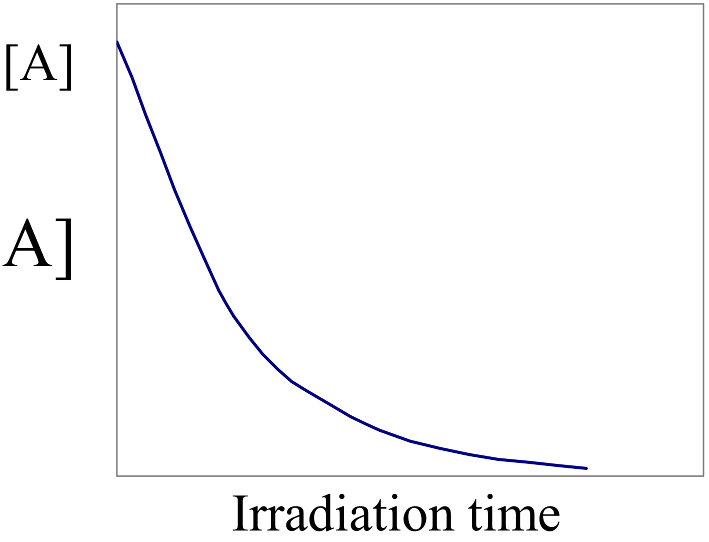
Controlling factors : I_0 , ε, ϕ

The laws of photochemical reaction

At a low concentration ($\varepsilon b[A] << 0.1$)

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

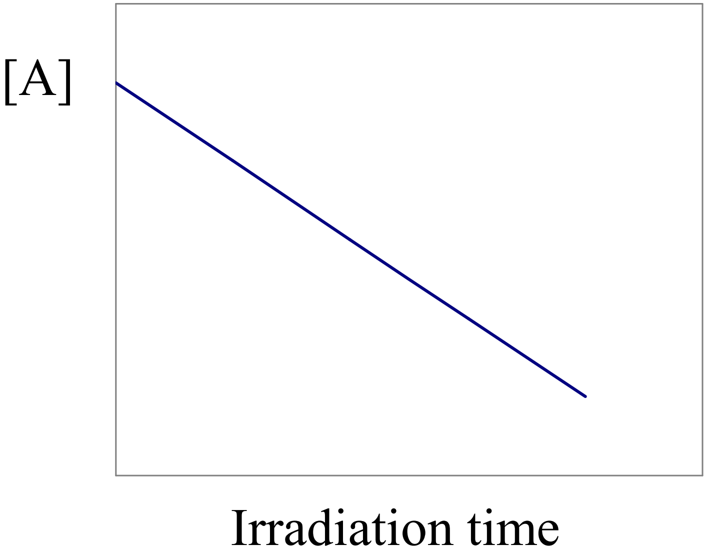
First order kinetics



At a high concentration ($\varepsilon b[A] >> 1$)

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

Zero order kinetics



Quantum yield (양자수득률: 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 photo-process
- Overall quantum yield: quantum yield considering the primary photochemical reaction and the further 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

$$Fe(C_2O_4)_3^{3-} + h\nu \rightarrow Fe^{2+} + 2C_2O_4^{2-} + C_2O_4^{-}\bullet \qquad (1)$$

$$C_2O_4^{-}\bullet \rightarrow CO_2^{-\bullet} + CO_2 \qquad (2)$$

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

Example : Calculate Quantum yield (ϕ)

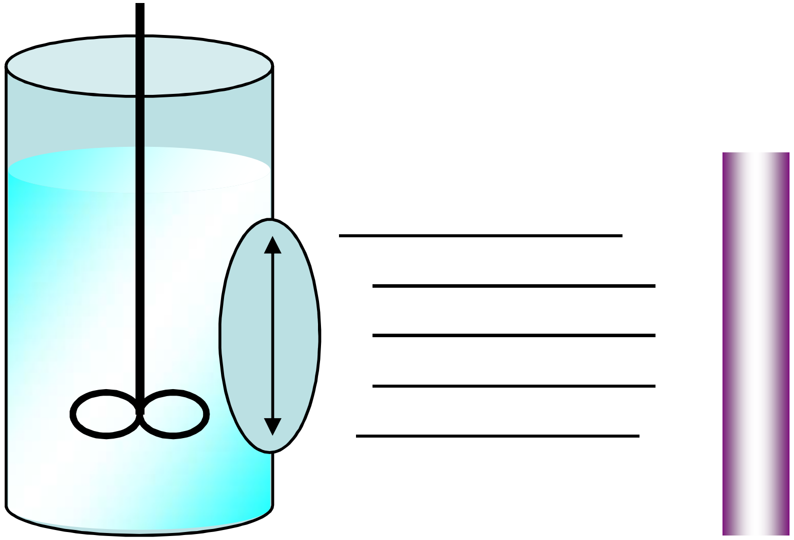
Ferrioxalate ($Fe(C_2O_4)_3^{3-}$) 는 아래와 같은 광화학반응들 (1) ~ (3)을 거쳐서 2가철 (Fe^{2+})로 환원된다. 그림 1과 같은 반응기를 이용하여 10 mM ferrioxalate 용액 100 ml에 low pressure Hg lamp (99% 254 nm emission)로 빛을 조사하며 시간에 따른 2가철 농도를 측정하여 표 1과 같은 실험결과를 얻었다.실험결과를 이용하여 아래 광화학 반응의primary quantum yield와 2가철 생성의 overall quantum yield를 구하여라.

(단, 입사면은 원형으로 지름 10cm이, 입사면에서 빛세기는 11.5 mW/cm² 이다. Ferrioxalate의 몰흡광계수는 254 nm에서 약 8000 M^{-1} cm^{-1}이며 optical pathlength는10 cm로 가정)

$$\mathbf{Fe(C_2O_4)_3^{3-} + h\nu \rightarrow Fe^{2+} + 2C_2O_4^{2-} + C_2O_4^{-}\bullet} \qquad \mathbf{(1)}$$

$$\mathbf{C_2O_4^{-}\bullet \rightarrow CO_2^{-\bullet} + CO_2} \qquad \mathbf{(2)}$$

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



<표 1> 시간에 따른 2가철 농도

Time (s)	$[Fe^{2+}]$ (μM)
0	0
60	0.056
240	0.10
480	0.17
720	0.22
960	0.28

Quantum yield (양자수득률: ϕ) 계산 예제

풀이:

우선, Ferrioxalate에 의해서 흡수되는 빛의 양(I_a)을 정확히 계산하자.

$$I_a = I_0(1-10^{-\varepsilon b[A]})$$

문제에서, $\varepsilon = 8000\ M^{-1}\ cm^{-1}$, $b = 10\ cm$, $[A] = 10\ mM = 10^{-2}\ M$
$\varepsilon b[A] = 8000 \times 10 \times 10^{-2} = 800 >> 1$ 이므로,

$$I_a \approx I_0 \quad \text{(조사되는 빛이 모두 흡수되는 조건)}$$

이제, 문제에서 $I_0 = 11.5\ mW/cm^2 = 1.15\times10^{-2}\ J/s.cm^2$ 로 주어진 값을 이용하여

양자수득률 계산을 위해 단위 부피당 빛의 양(Einstein/L.s)으로 환산해야 한다

254 nm에서 광자 1 mole 이 가지는 에너지는
$(hc/\lambda)\ N_A = (6.6\times10^{-34})\times(3\times10^{8})/(254\times10^{-9})\times(6.02\times10^{23}) = 4.69\times10^{5}\ J$

따라서, $1.15\times10^{-2}\ J/s.cm^2 = (1.15\times10^{-2})/(4.69\times10^{5}) = 2.45\times10^{-8}\ Einstein/s.cm^2$

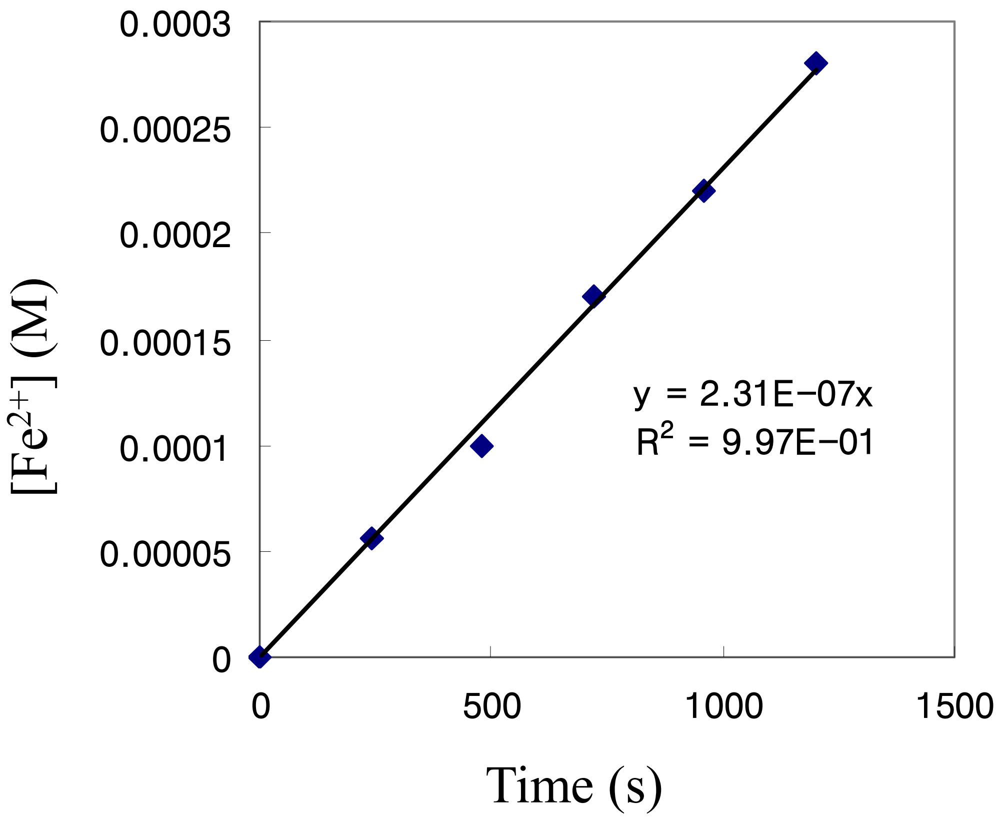
Quantum yield (양자수득률: ϕ) 계산 예제

한편, 빛의 입사면적은 $\pi \times 5^2 = 78.5\ cm^2$ 이고, 반응용액의 부피는 100 ml = 0.1 L 이므로,

2.45×10^{-8} Einstein/s.cm^2 $\times$ 78.5 cm^2 / 0.1 L = 1.92×10^{-7} Einstein/L.s

결국, **I_a = 1.92×10^{-7} Einstein/L.s**

이제, <표 1>의 결과로 부터 2가철의 생성 속도를 구하자.
결과를 도시하면 오른쪽그림과 같다.



기울기로부터

2가철 생성속도 = 2.31×10^{-7} M/s

Quantum yield (양자수득률: ϕ) 계산 예제

결국 양자수득률 = 광화학반응 진행 속도 / 흡수되는 광자 속도

$$= \mathbf{(2.31\times10^{-7}\ M/s) / (1.92 \times 10^{-7}\ Einstein/L.s)}$$

= 1.20   (2가철 생성의 Overall quantum yield)

한편, 반응식 (1) ~ (3)에서 보는 바와 같이, Ferrioxalate의 광화학반응의 경우 $CO_2^{-}\bullet$ 에 의한 2차적인 2가철의 생성이 포함되어 있으므로

Primary quantum yield = **1.20 / 2 = 0.6** 이 된다.

UV/H_2O_2 process

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

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

Solvent cage

Subsequent reactions

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

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

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

Photochemical reactions of ferric complexes

- Ferric-hydroxo complexes

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

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

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

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

- Other ferric complexes

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

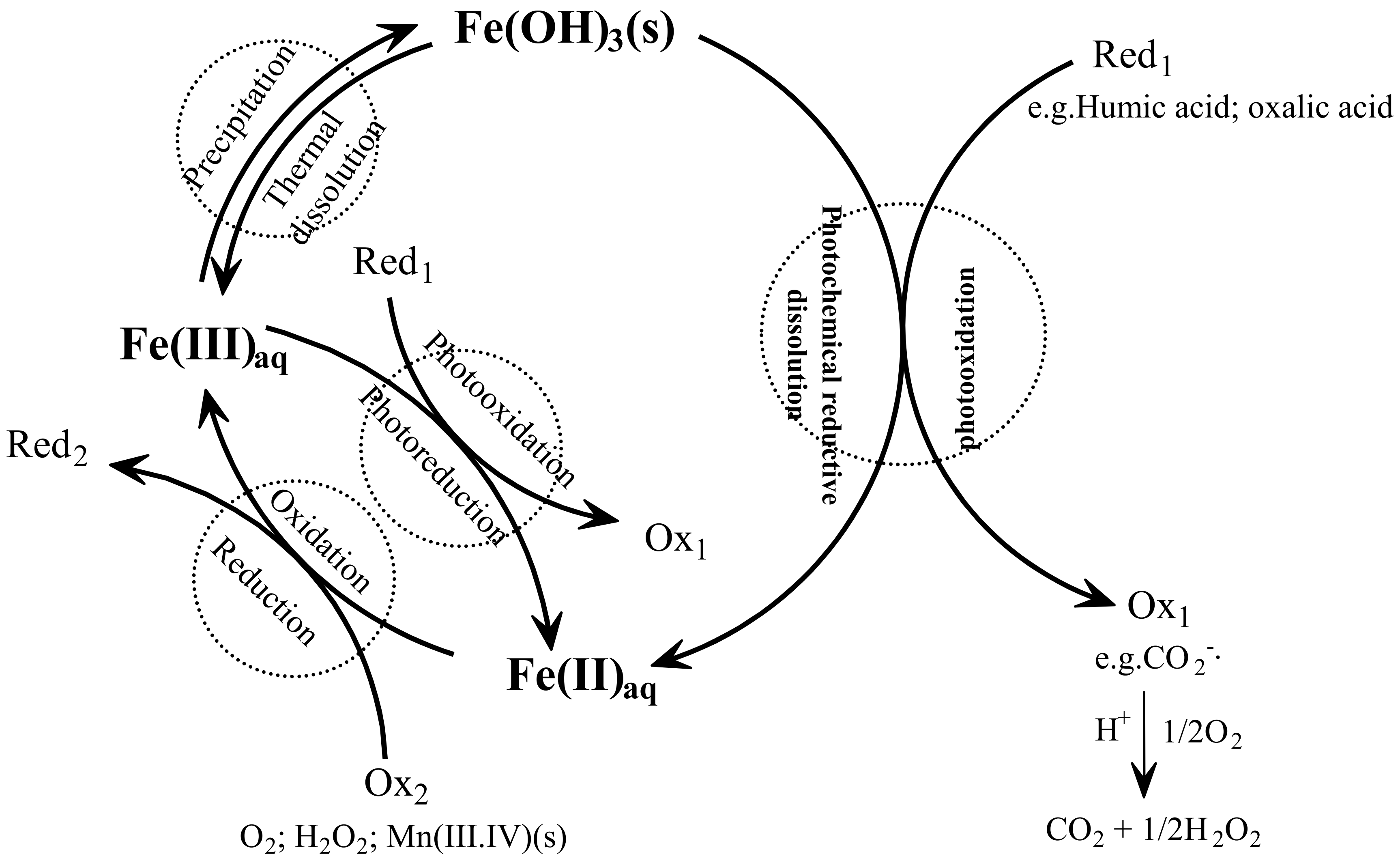
Ex) $Fe(SO_4)^+ + h\nu \rightarrow Fe^{2+} + SO_4^{-}\bullet$

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

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

Photoredox cycles of iron species in environment

(Sulzberger et.al.)



$Fe(OH)_3(s)$

Precipitation

Thermal dissolution

Photochemical reductive dissolution

photooxidation

Red_1

e.g.Humic acid; oxalic acid

$Fe(III)_{aq}$

Red_1

Photooxidation

Photoreduction

Ox_1

Red_2

Oxidation

Reduction

$Fe(II)_{aq}$

Ox_2

O_2; H_2O_2; Mn(III.IV)(s)

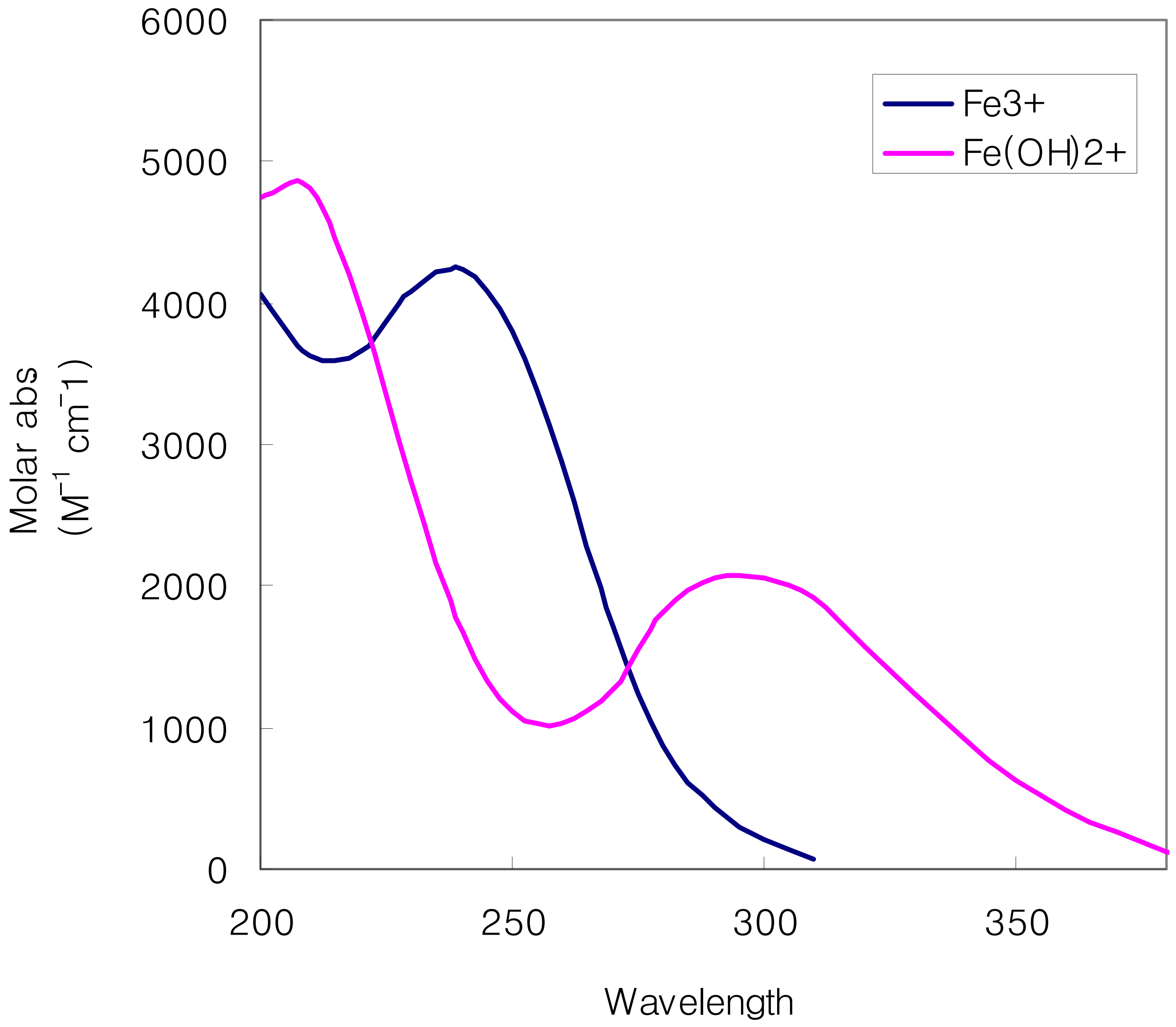
Ox_1

e.g.$CO_2^{-\cdot}$

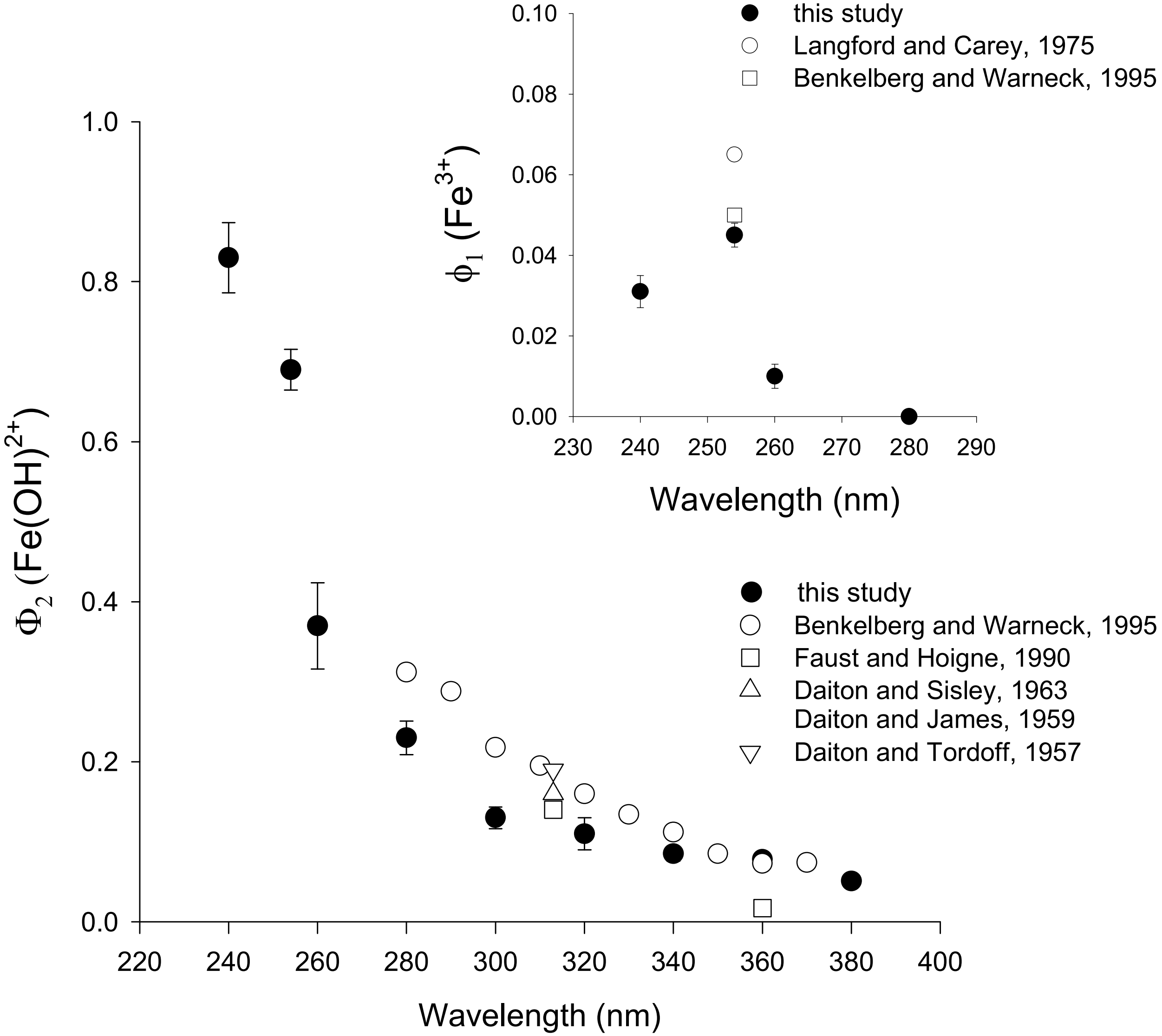
H^+ $1/2O_2$

$CO_2 + 1/2H_2O_2$

Molar absorption coefficients of ferric–hydroxo complexes



Individual quantum yields for the photolysis of Fe(III)–hydroxo complexes as a function of wavelength



Quantum yields for photolysis of several ferric complexes

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

Fe(III) species	wave length	Quantum yield (Fe(II))
Fe^{3+}	254	0.05
$Fe(OH)^{2+}$	313	0.14
$Fe_2(OH)_2^{4+}$	350	0.007
$Fe(SO_4)^+$	280 ~ 350	$(1.51 \sim 7.28) \times 10^{-3}$
$Fe(Cl)^{2+}$	347	0.5
$Fe(C_2O_4)_3^{3-}$	250 ~ 480	1.0 ~ 1.2
α-FeOOH(geothite)	300 ~ 400	$(0.19 \sim 2.9) \times 10^{-4}$

Photo/ferrioxalate system

- Classical Fenton and photofenton system

Classical Fenton

- $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^{-}$
- Available only in acidic medium
- Producing a lot of iron sludge

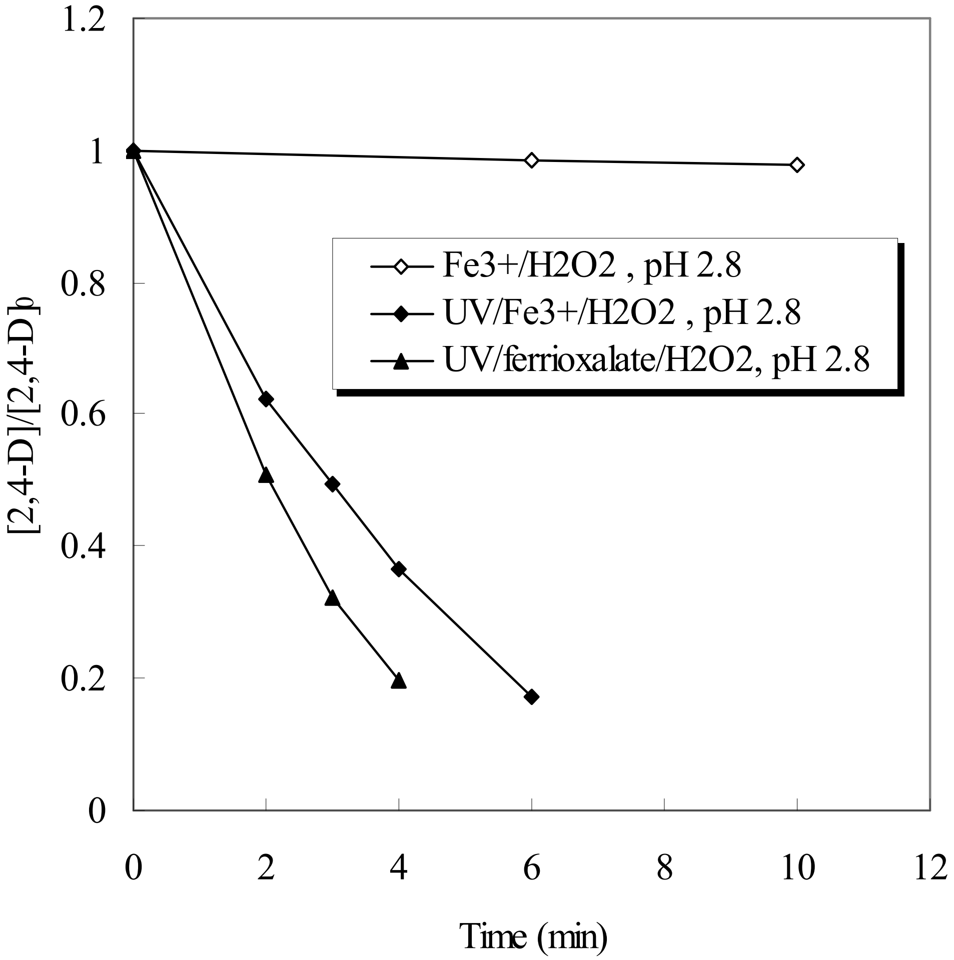
Photofenton

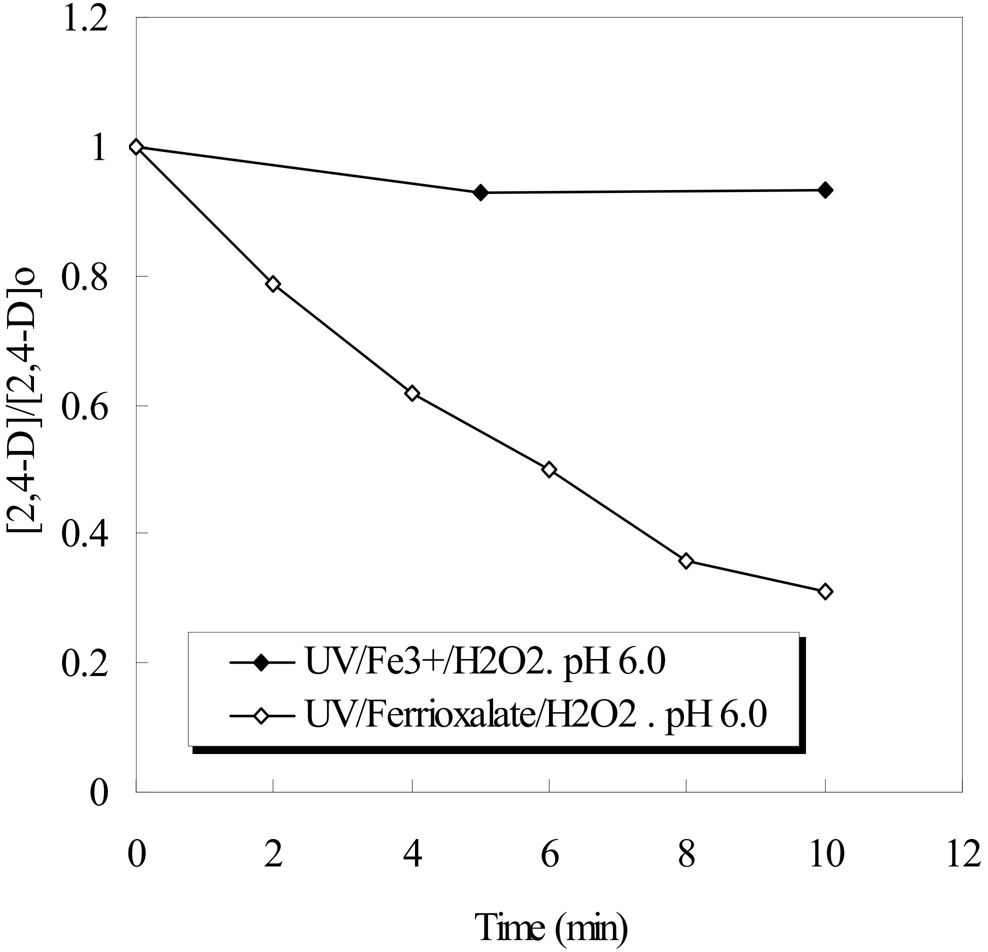
- $Fe^{III}(OH)^{2+} + h\nu \rightarrow Fe^{2+} + \bullet OH$
- Low quantum yield for Fe(II) generation
- Available only under UV light irradiation

- What is the photo/ferrioxalate system?

; New type of photofenton system using ferric oxalate complex, which makes it possible to utilize a **visible light (sunlight)** as irradiation source.

Comparison of 2,4-D removal by dark, photo-Fenton, photo-ferrioxalate system





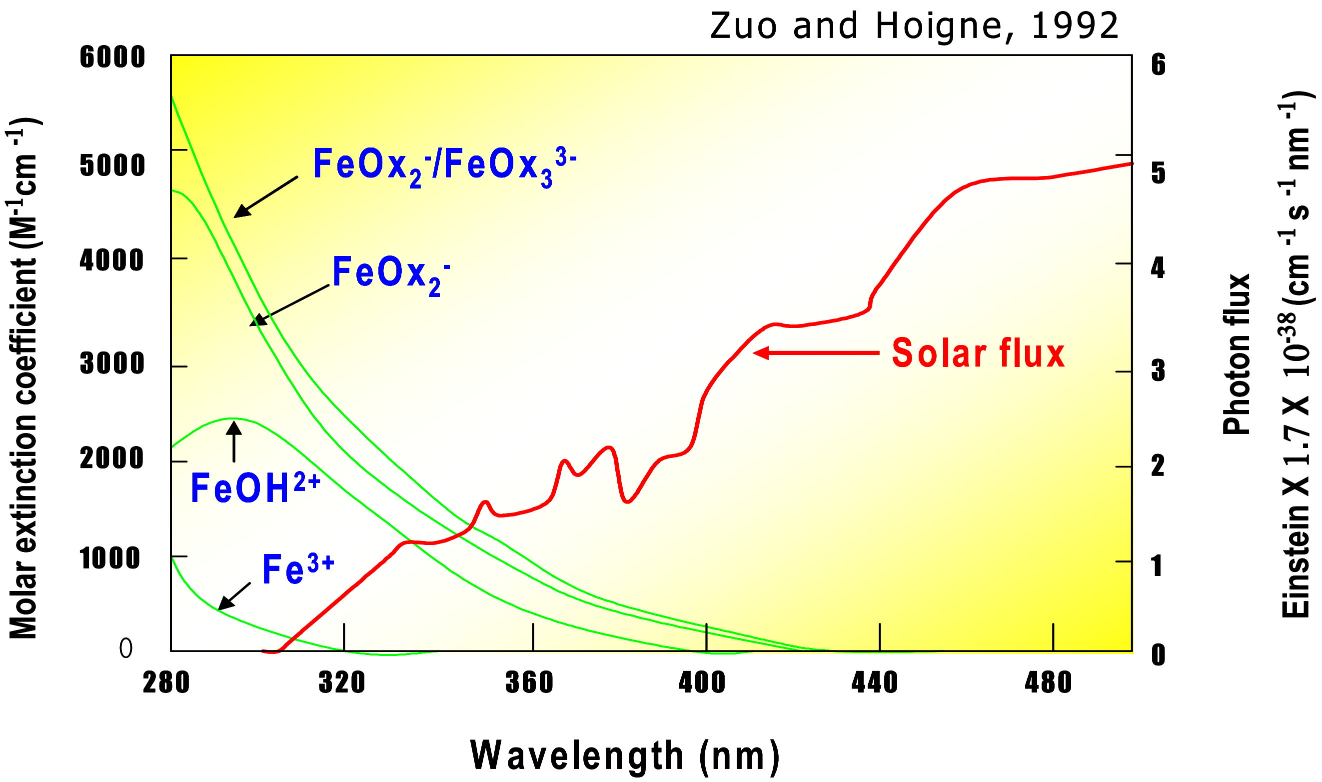
$[Fe(III)]_0 = 0.1$ mM, $[H_2O_2]_0 = 10$ mM, $[2,4\text{-}D]_0 = 0.1$ mM

Characteristics of photo/ferrioxalate system

- High molar absorptivity
- High quantum yields for Fe(II) generation
- Production of highly reductive radical intermediate ($CO_2^{-\bullet}$)
- Available in neutral pH

High molar absorptivity

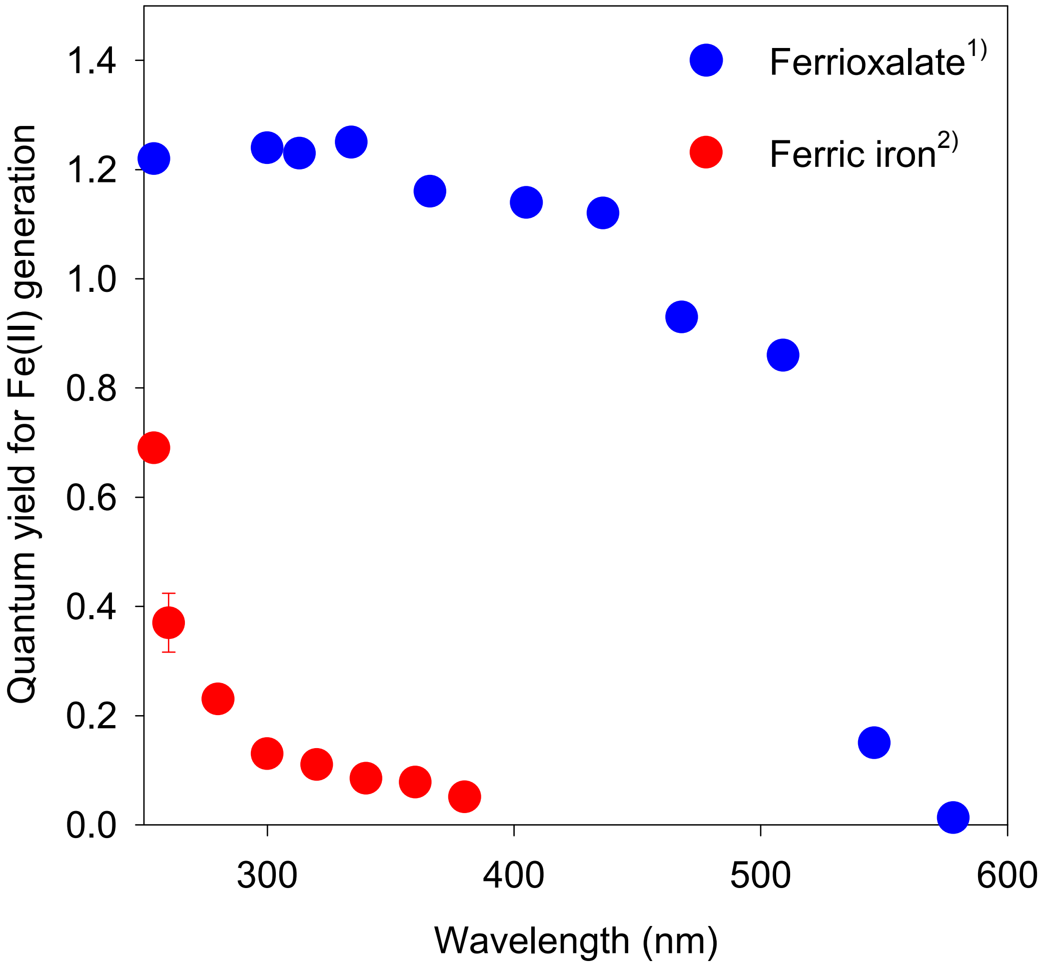
- Light absorption spectrum of ferrioxalate



- 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) C. Lee *et al.*, submitted

Ferric iron

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

Ferrioxalate

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

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

- High quantum yield for Fe(II) generation

Highly reductive radical intermediate

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

Photolysis of ferrioxalate

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

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

Fe(II) generation

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

H_2O_2 generation

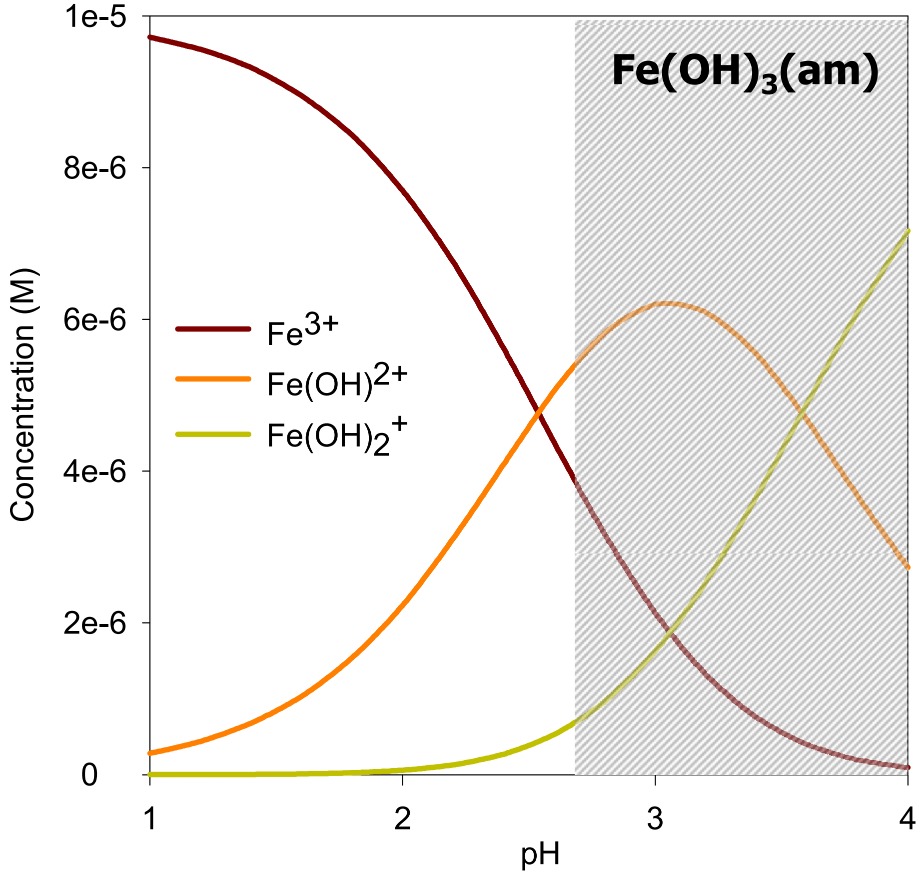
$\mathbf{CO_2^{-}\bullet} + O_2\ (+ H^+) \rightarrow O_2^{-}\bullet(HO_2\bullet) + CO_2 \rightarrow\rightarrow H_2O_2$

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	- 0.3

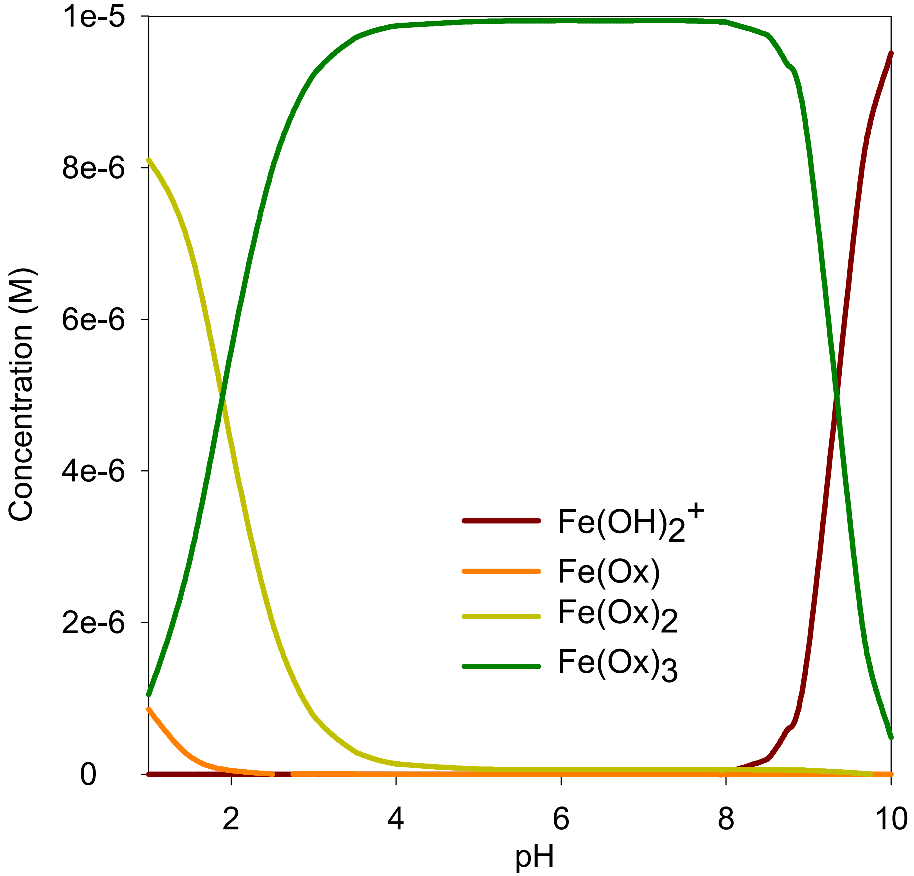
Available in neutral pH

- Iron species distribution ($[Fe^{3+}]_0 = 10\ \mu M$)

Without oxalate

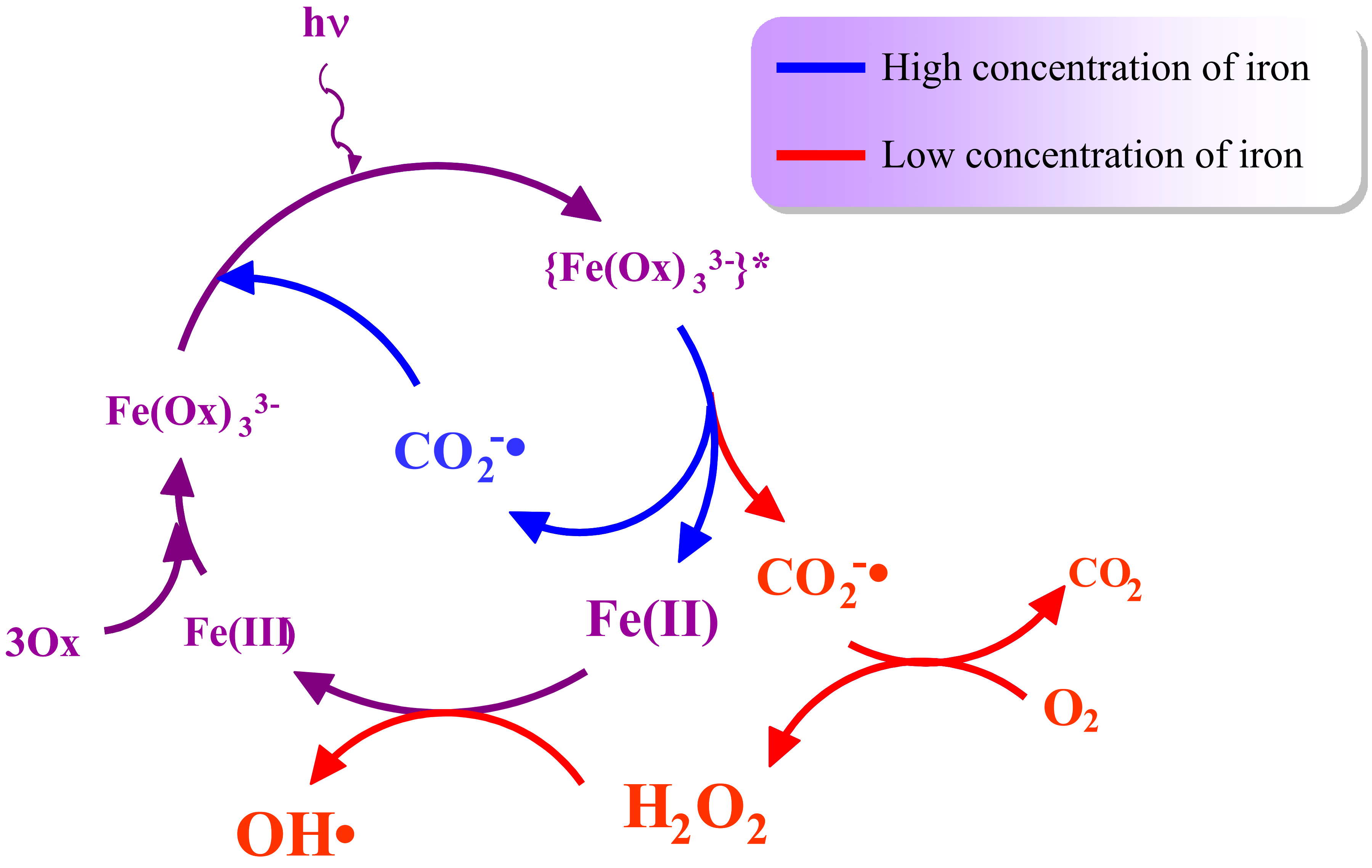


With oxalate

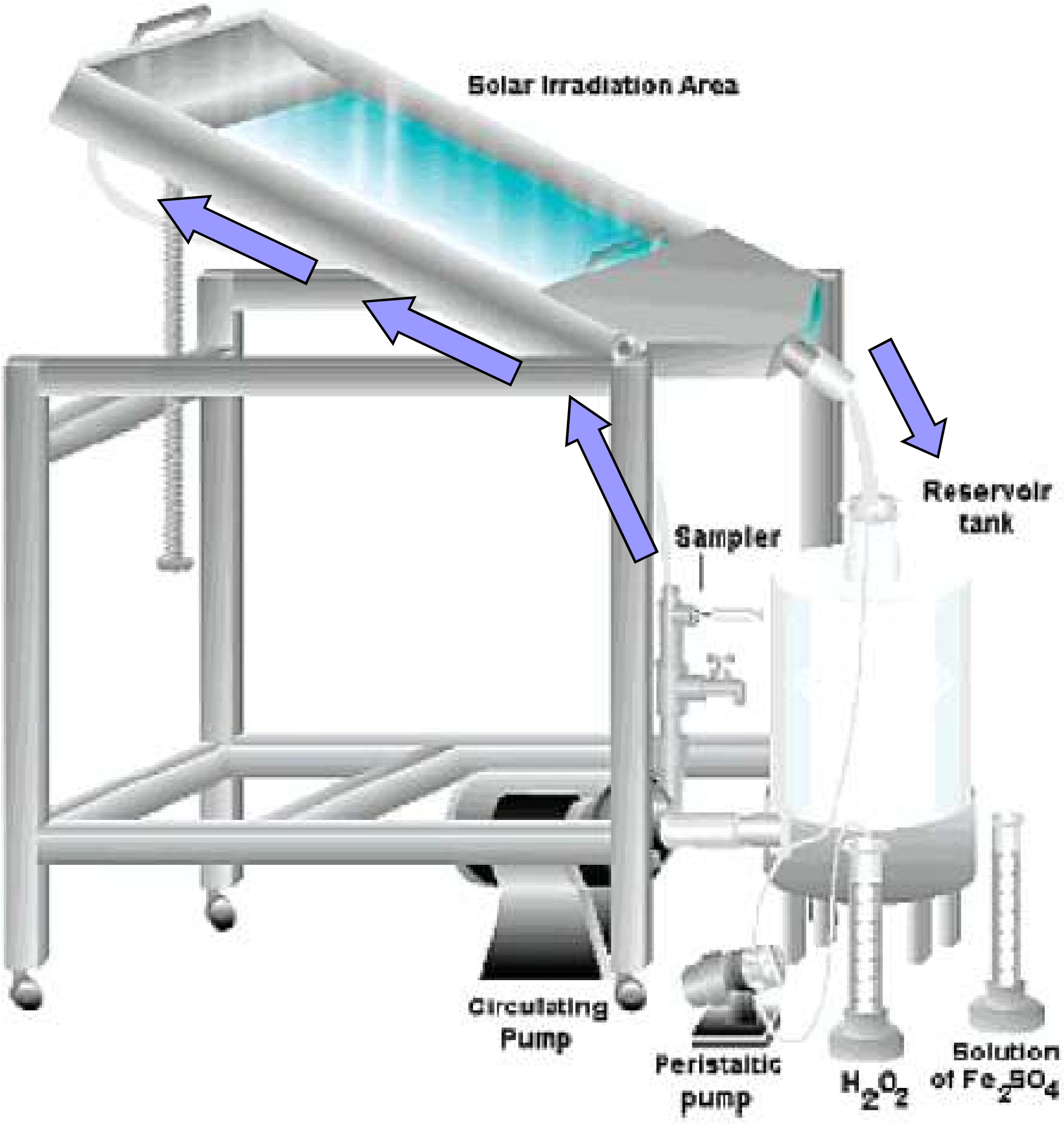


- Available in a wide range of pH

Reaction Scheme of $CO_2^{-}\bullet$

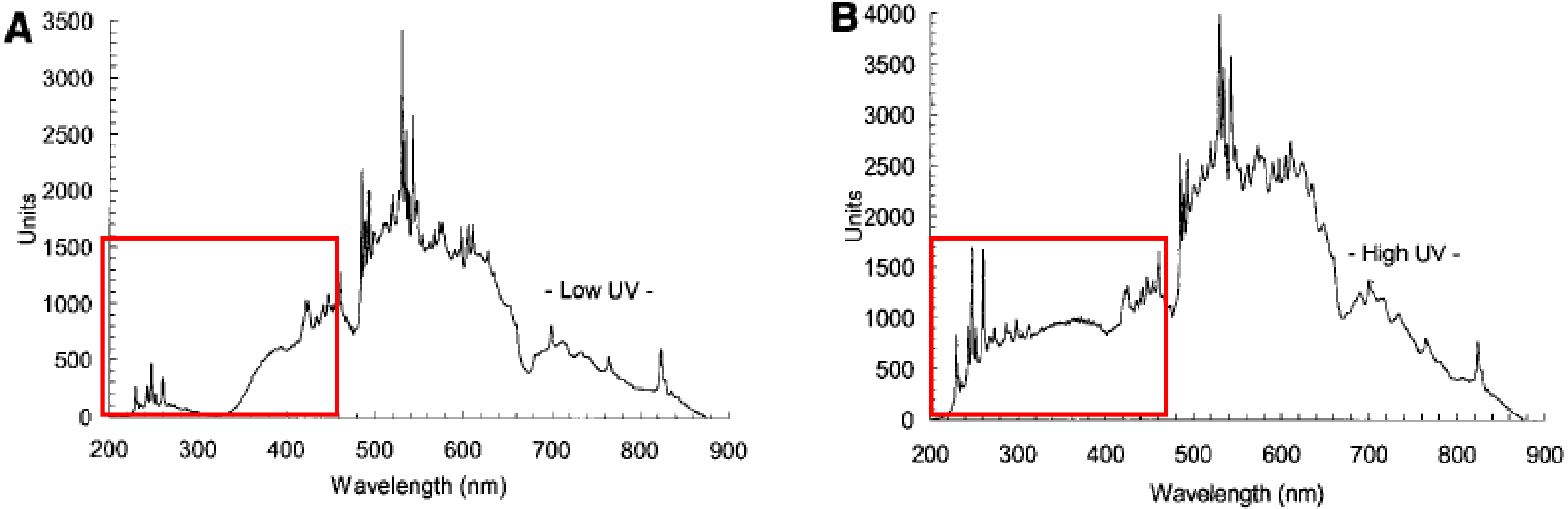


Solar/Fenton process


Solar Irradiation Area
Reservoir tank
Sampler
Circulating Pump
Peristaltic pump
H_2O_2
Solution of Fe_2SO_4

Pulsed UV technique

Pulsed and continuous UV light sources



A: Continuous lamp

B: Pulsed lamp

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

Photochemical Degradation Processes

Outline

- Introduction and Basic Concepts
- Advanced Oxidation Technologies(AOTs)
- Figures-of Merit for AOTs – the EE/O and the EE/M
- UV/H_2O_2 Treatment (Rayox^R)

Photochemical Processes

- Consider only homogeneous processes.
- Treatment driven by the absorption of photons

$$E = \frac{hc}{\lambda}$$

where h is Planck's constant, c is the speed of light and λ is the wavelength of the light.

- Smaller λ means higher energy photons, so photolysis usually requires ultraviolet light

Advanced Oxidation Technologies

- Advanced Oxidation Technologies (AOTs) usually involve the generation of hydroxyl radicals(·OH).

- Called "Advanced" because the reactions are just highly accelerated oxidation reactions that occur when pollutants enter the environment.

- The ·OH radicals react with organic pollutants to initiate a series of oxidative degradation reactions.

- The overall process often leads to mineralization (i.e., conversion to CO_2, H_2O and mineral acids) of the pollutants.

AOT Mechanism

- ·OH radicals react with organic compounds by:
  - ☐ Hydrogen abstraction from aliphatic componds

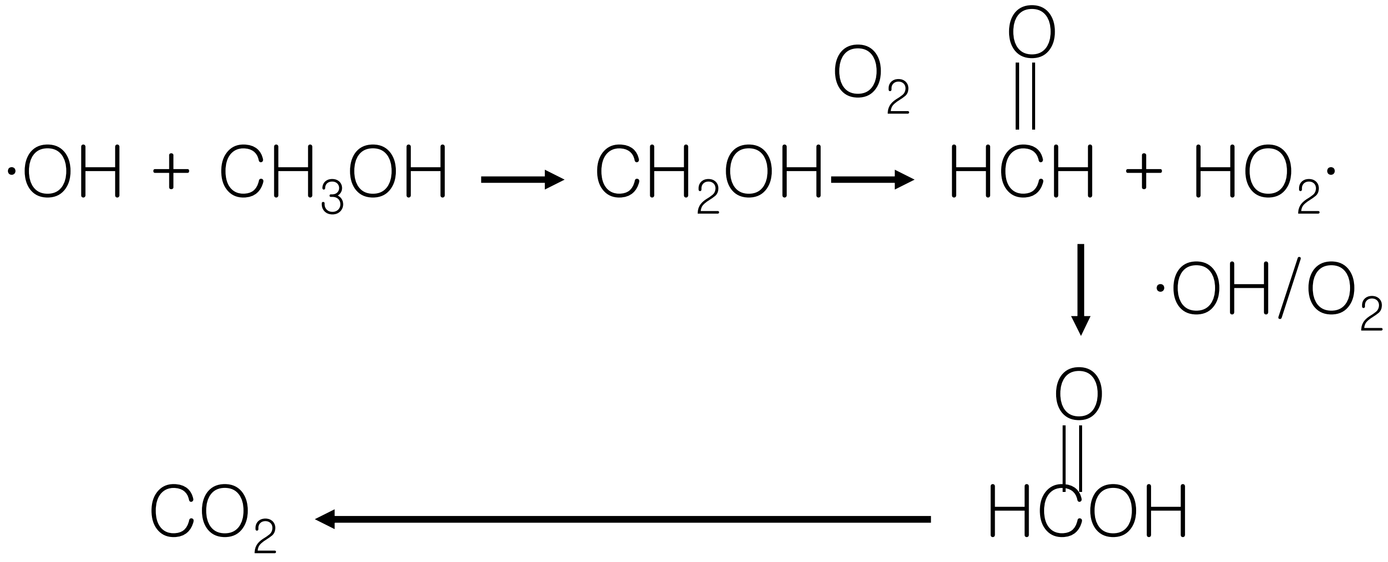
$$\cdot OH + CH_3OH \rightarrow \cdot CH_2OH + H_2O$$

  - ☐ Addtion to unsaturated compounds

$$\cdot OH + CH_2 = CH_2 \rightarrow \cdot CH_2CH_2OH$$

- This is followed by reaction with oxygen initiating a series of degradative oxidation reactions

Mechanism of Methanol Degradation



$$\cdot\mathrm{OH} + \mathrm{CH_3OH} \longrightarrow \mathrm{CH_2OH} \xrightarrow{\mathrm{O_2}} \mathrm{H}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{H} + \mathrm{HO_2}\cdot$$

$$\mathrm{H}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{H} \xrightarrow{\cdot\mathrm{OH/O_2}} \mathrm{H}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OH} \longrightarrow \mathrm{CO_2}$$

- Other organic are more complex, but generally:

  Pollutant ⟶ aldehydes ⟶ carboxylic acids ⟶ bicarbonate

Kinetic Scheme

$$H_2O_2 \xrightarrow{h\nu} 2\cdot OH \qquad R_{OH} = G\chi\phi_{OH}/V$$

$$\cdot OH + P \xrightarrow{k_p} \text{Products} \qquad k_p[\cdot OH][P]$$

$$\cdot OH + S \xrightarrow{k_s} \text{Products} \qquad k_S[\cdot OH][S]$$

$$\frac{d[P]}{dt} = k_P[\cdot OH]_{ss}[P] = \frac{G\chi\phi_{OH}/V}{k_p[P]+k_s[S]} k_P[P]$$

- G(Einstein/s) is the total emitted light flux from the lamp.
- χ is the fraction of the emitted light flux absorbed in the water.
- Φ_{OH} is the quantum yield for generation of ·OH radicals.
- P=pollutant; S=scavenger

$$\frac{d[P]}{dt} = k_P[\cdot OH][P]$$

$$\frac{d[S]}{dt} = k_S[\cdot OH][S]$$

$$\frac{d[P]}{dt} = -k_P[\cdot OH][P]$$

$$\frac{d[\cdot OH]}{dt} = Gx\varphi_{OH}/V - [\cdot OH]\left\{k_P[P] + k_S[S]\right\}$$

$$\mathrm{A} \longrightarrow \mathrm{Z}\cdot \qquad \mathrm{Rate}_1 = \mathrm{CP/V}$$

$$\mathrm{Z}\cdot + \mathrm{C} \longrightarrow \mathrm{Products} \qquad \mathrm{Rate}_2 = \mathrm{k}_\mathrm{C}[\mathrm{Z}\cdot][\mathrm{C}]$$

$$\mathrm{Z}\cdot + S_1 \longrightarrow \mathrm{Products} \qquad \mathrm{Rate}_{3a} = \mathrm{k}_{\mathrm{S}_1}[\mathrm{Z}\cdot][\mathrm{S}_1]$$

$$\mathrm{Z}\cdot + \mathrm{S}_\mathrm{i} \longrightarrow \mathrm{Products} \qquad \mathrm{Rate}_{3\mathrm{i}} = \mathrm{k}_{\mathrm{S}_\mathrm{i}}[\mathrm{Z}\cdot][\mathrm{S}_\mathrm{i}]$$

$$\mathrm{C} = \mathrm{Gx}\varphi_\mathrm{z}/\mathrm{P}$$

$$rate = \frac{CPk_c[V]/V}{k_c[C] + \sum_i K_{S_i}[S_i]}$$

$$\mathrm{k_c[C]} >> \sum_{\mathrm{i}} \mathrm{k_{S_i}[S_i]}$$

$$rate = CP/V$$

$$\mathrm{k_c[C]} << \sum_{\mathrm{i}} \mathrm{k_{S_i}[S_i]}$$

$$rate = \frac{CPk_c[C]/V}{\sum_i K_{S_i}[S_i]}$$

$$\frac{dC}{C} = \frac{CPk_c/V}{\sum K_{S_i}[S_i]} dt$$

~ **100 mg/L 기준**

~ **<u>the dosage requirement with zero order regime</u>**

⇨ **with mass**

~ **<u>the dosage requirement with 1st order regime</u>**

⇨ **orders of magnitude of reduction per unit volume**

Figures−of−Merit for AOTs

- Electrical energy is usually the principal factor in the operating cost of AOT systems.

- For low concentrations, define 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 concentrations, define Electrical Energy per Mass (EE/M) as the electrical energy (kWh) necessary to remove 1kg of pollutant. EE/M can also be based on TOC (1kg of C).

Electrical Energy per Mass (EE/M)

- Batch Operation

$$\mathrm{EE/M} = \frac{\mathrm{P} \times \mathrm{t} \times 10^6}{\mathrm{V} \times 60 \times (\mathrm{C_i} - \mathrm{C_f})}$$

- Flow-through Operation

$$\mathrm{EE/M} = \frac{\mathrm{P} \times 10^6}{\mathrm{R} \times 60 \times (\mathrm{C_i} - \mathrm{C_f})}$$

P is the lamp power (kW), t(min) is the time of irradiation, V is the total system volume(L), R is the flow rate (gpm), C_i, C_f are the initial and final pollutant concentrations (mg/L).

Relation of EE/O to Fundamental Parameters

$$\mathrm{EE/O} = \frac{2.422\ \mathrm{P}\sum_{\mathrm{i}} \mathrm{k}_{\mathrm{s_i}}[\mathrm{S_i}]}{\mathrm{G}\chi\phi_{\mathrm{OH}}\mathrm{k_P}}$$

P is the lamp power (kW)

K_{S_i} are rate constants ($M^{-1}\ S^{-1}$) for the reaction of ·OH with scavengers S_i. K_P is the corresponding rate constant for the pollutant P.

G (Einsteins/s) is the total emitted light flux from the lamp.

χ is the fraction of the emitted light flux absorbed in the water

Φ_{OH} is the quantum yield for generation of ·OH radicals.

<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 !

<Solution 1>

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

$E = Nh\nu = Nhc/\lambda = (6.02\times10^{23})\times(6.6\times10^{-34})\times(3\times10^{8})/(254\times10^{-9})$
$= 469\ \mathrm{kJ} = 0.13\ \mathrm{kWh}$

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

<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 !

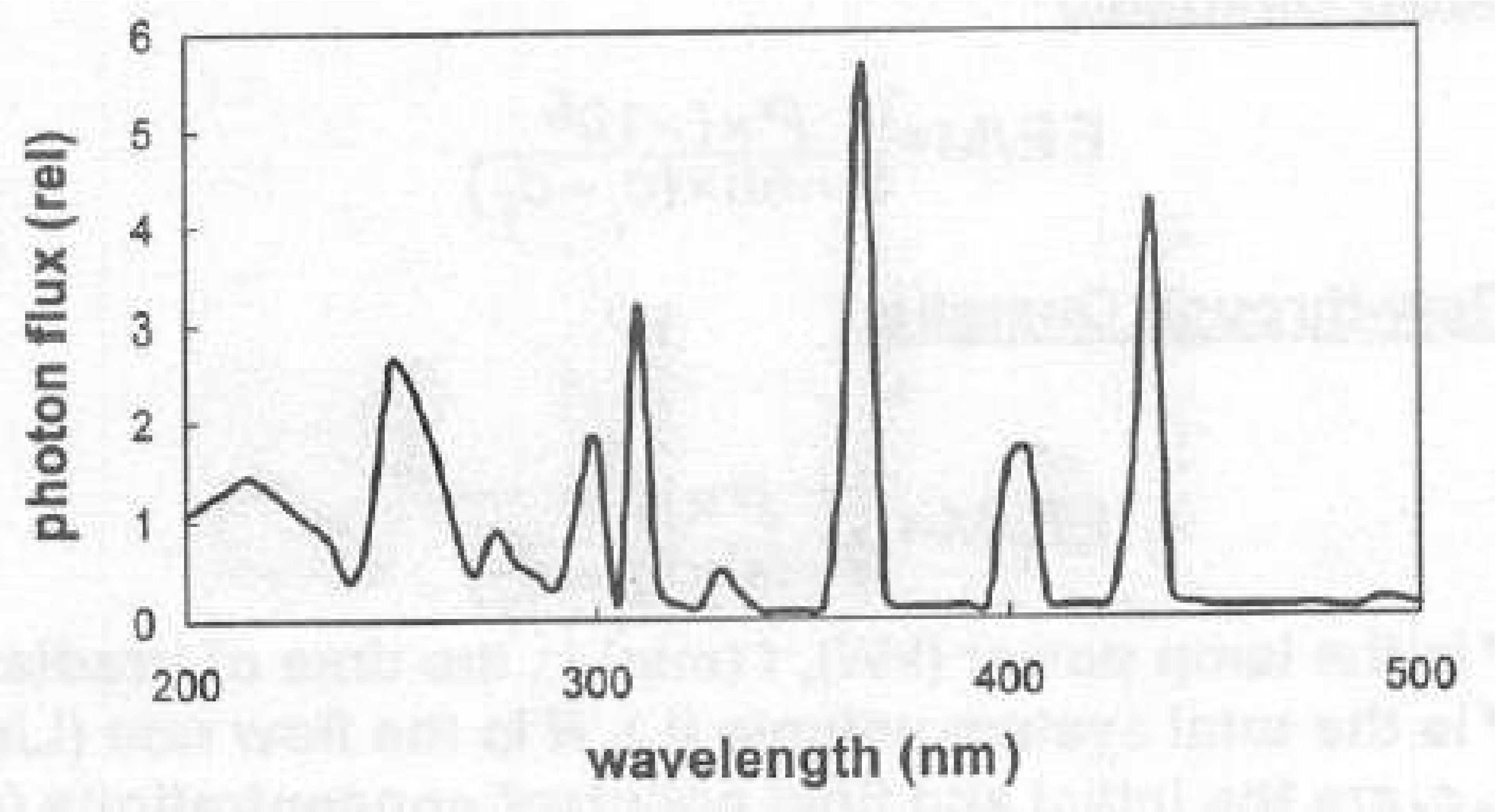
<Solution 2>
The mass of TOC removed is 2000 (L) x 0.00040 (kg/L) = 0.8 kg TOC
Thus the EE/M value is (30 x 10)/0.8 = 375 kWh/kg

<Example 3>

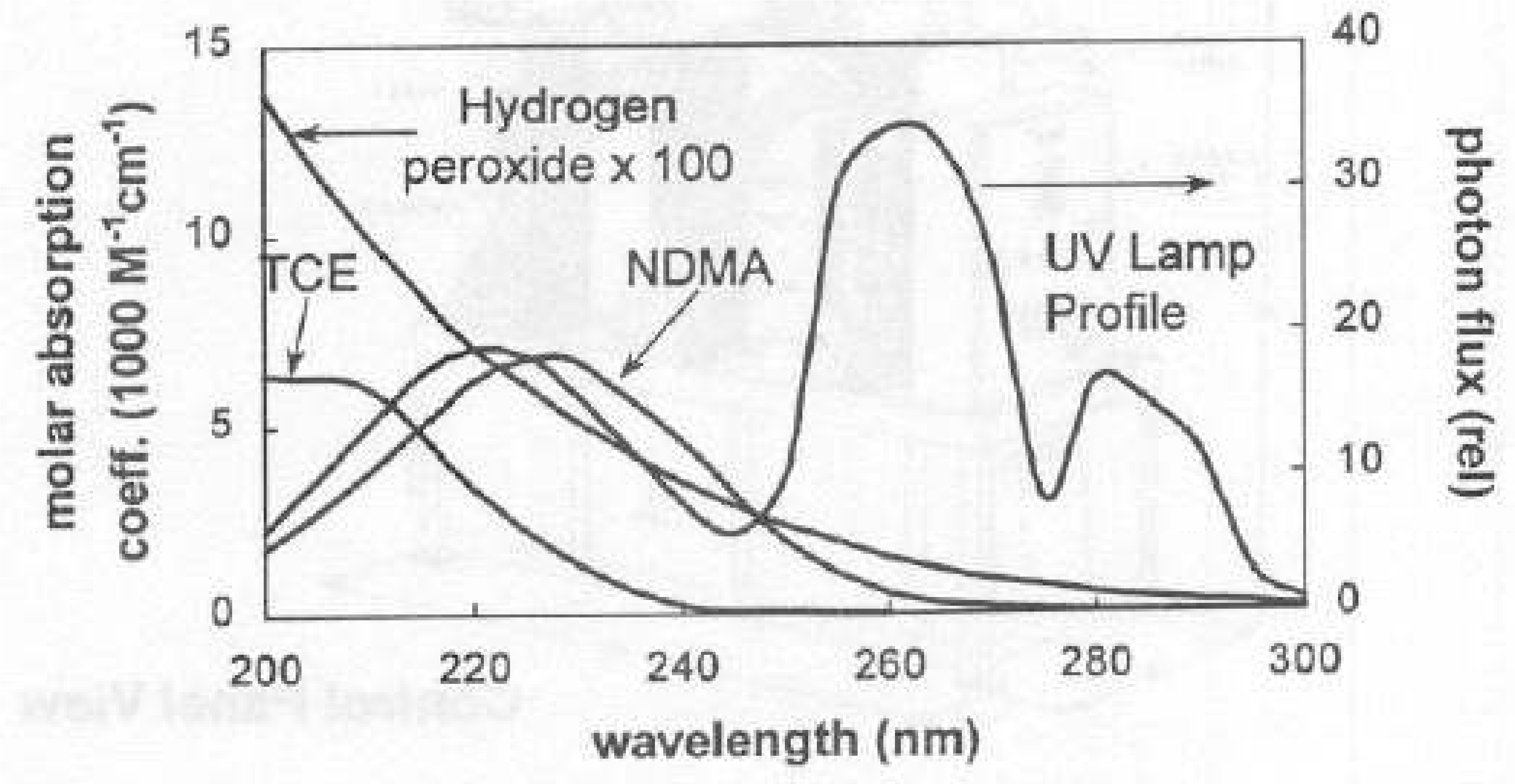
A groundwater containing 20 mg/L of trichloroethylene (TCE) flowing at 8.5 m^3/h is treated with an AOP rated at 25 kW. It was found that the effluent concentration of TCE had dropped to 5 ug/L.
Calculate the EE/O value !

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

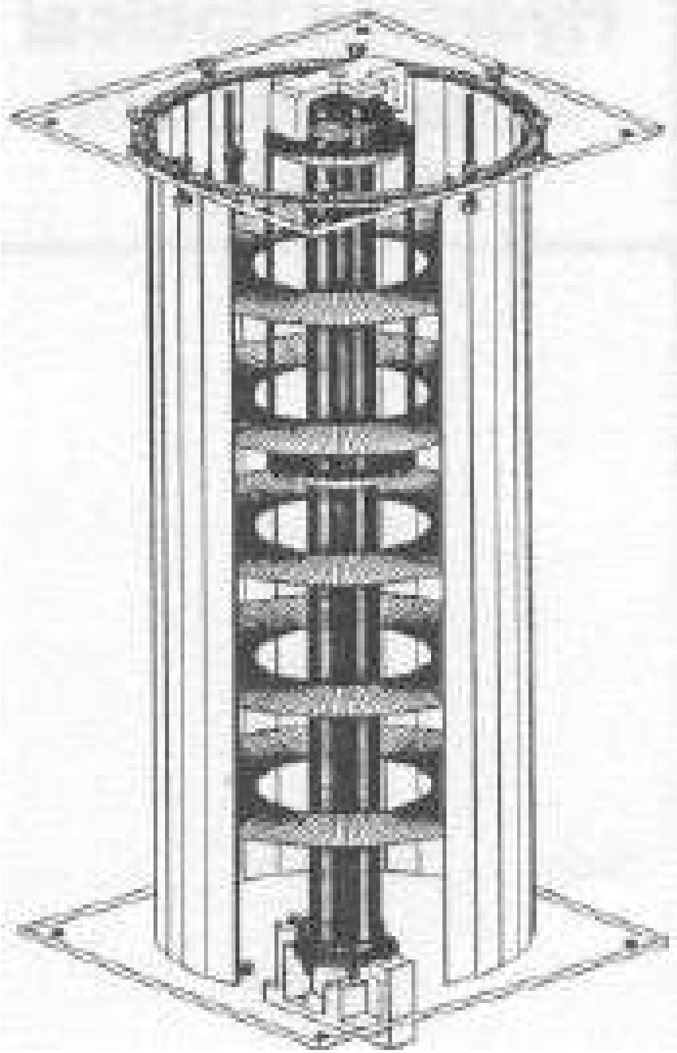
UV Lamp Emission Spectrum



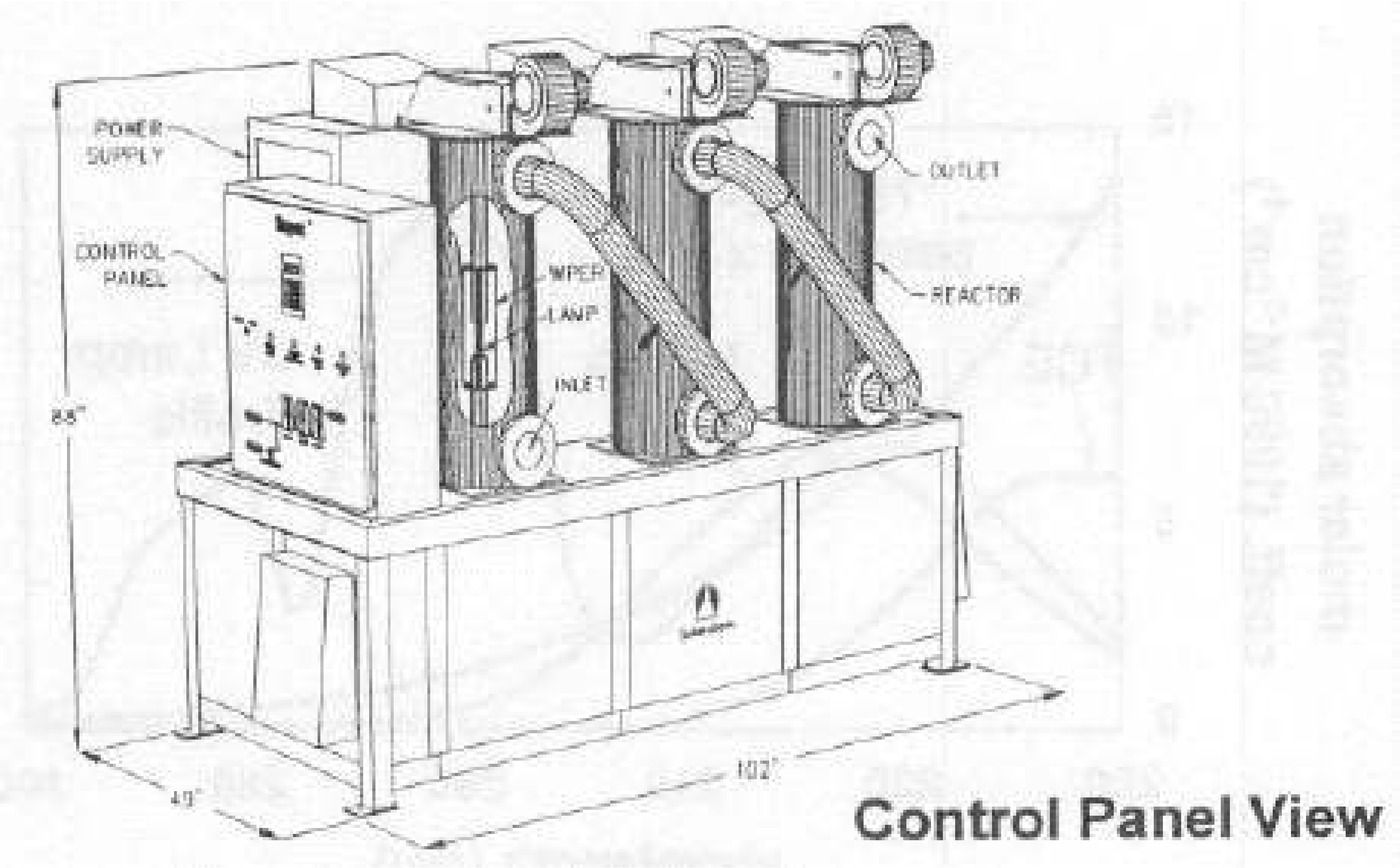
Pollutant Absorption Spectra



Rayox UV Reactor



Model 30-3 (90kW System)



Control Panel View

Pollutant Removal Rates

Pollutant	OH Radical Rate Constant /10^9 M-1 s-1	EE/O kWh per 1000 gal per order
Benzene & derivatives	4-7	2-10
Chlorinated alkenes	4-7	4-20
CH_2Cl_2	0.058	20-100
$CHCl_3$	0.005	40-250
CCl_4	0.001	>250

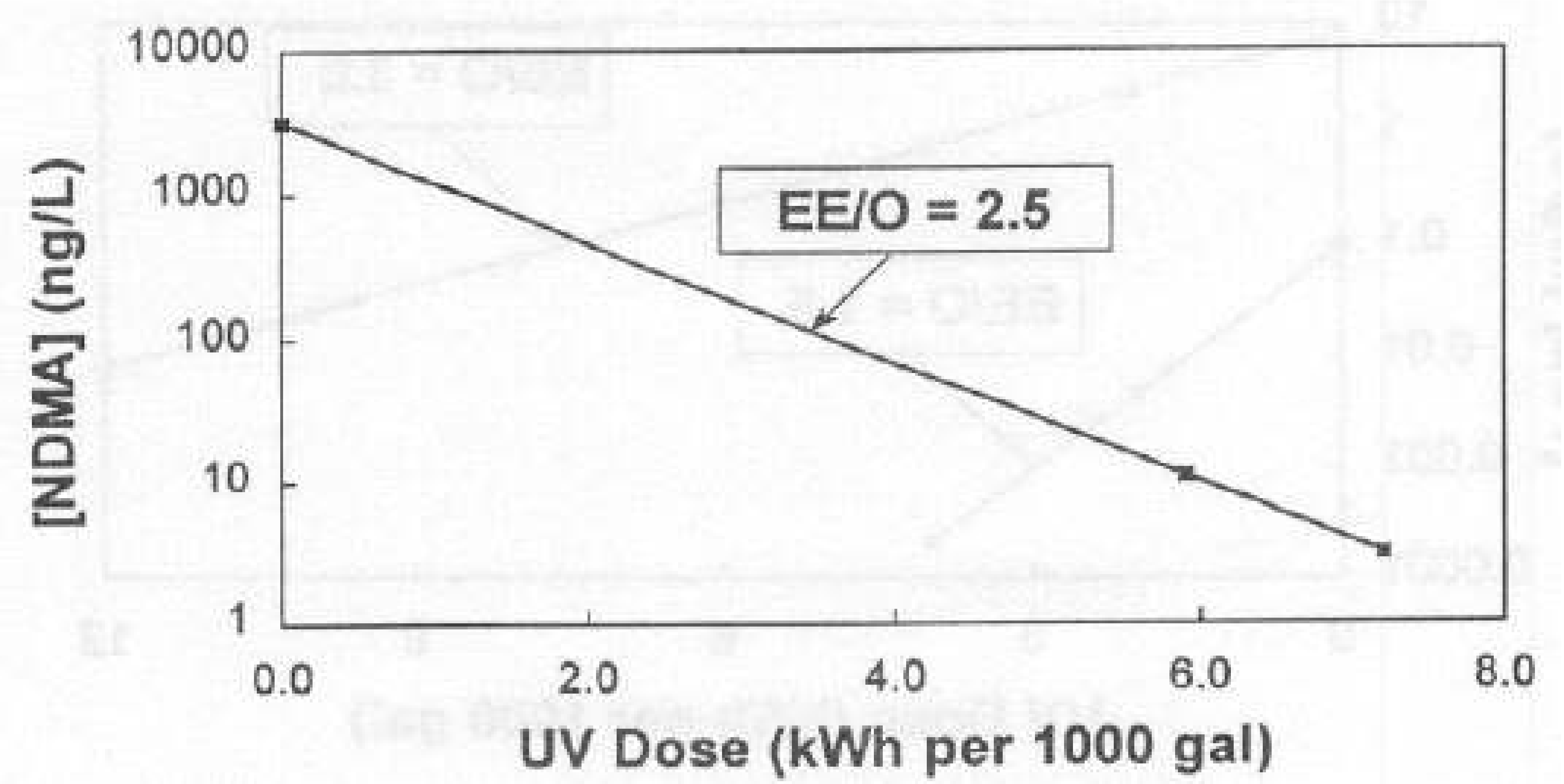
Treatment of NDMA

NDMA (nitrosodimethylamine) is a carcinogen that is often found in industrial effluennts. It does not biodegrade nor does it absorb well to activated carbon. However, it does photolyze very efficiently.

$$(CH_3)_2NNO \xrightarrow{h\nu} (CH_3)_2N\cdot + NO$$

NDMA absorbs only in the range 200-240nm; thus, a UV lamp with strong output in this region is essential for effective treatment.

Direct Photolysis Rayox^R Treatment of NDMA in Groundwater



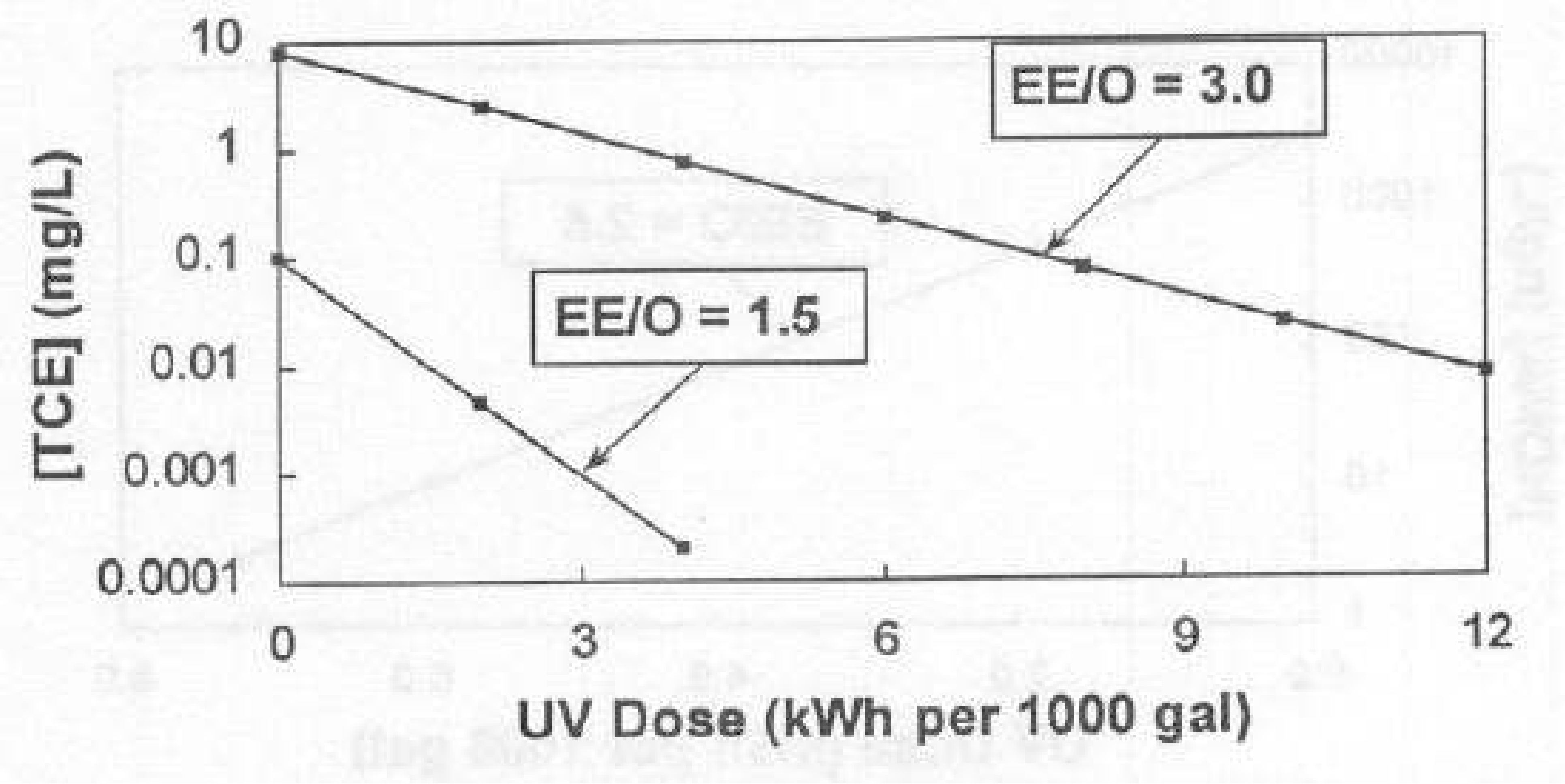
Rayox^R UV/H2O2 Process

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

$$H_2O_2 + h\nu \longrightarrow 2 \cdot OH \qquad \varphi = 1.0$$

- Molar absorption coefficients are small, so significant levels(>100 ppm) of H2)2 are required to absorb most of the emitted UV.
- Important to have a UV lamp with strong output is the 200-300 nm region.

RayoxR Treatment of TCE in Groundwater



Practical Applications

- There are now nearly 300 commercial UV/oxidation systems installed worldwide treating waste waters at up to 1000 gpm.
- Catalyzed processes and technology hybrids have dramatically increased the range of application for UV/oxidation.
- This presentation presents six unique applications as examples.

Conclusions

- Fundamentals of AOTs reviewed
- UV/H_2O_2 (RayoxR) is very effective in mineralizing pollutants
- UV/Fe/H_2O_2 (RayoxR-F) and UV/ferrioxalate/H_2O_2 (RayoxR-A) are alternate processes for the generation of hydroxyl radicals.
- Combining treatment technologies often results in lower overall costs.