The Fenton Process

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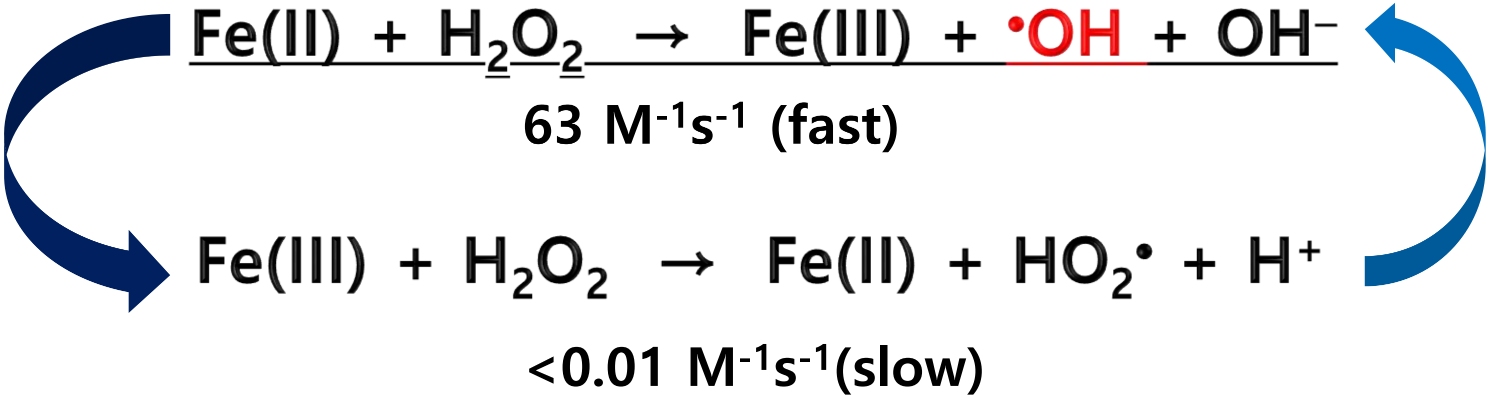
The Fenton Reaction

- **Fenton reaction**

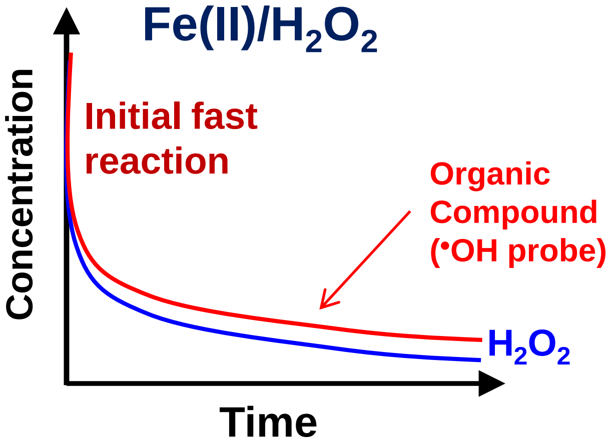


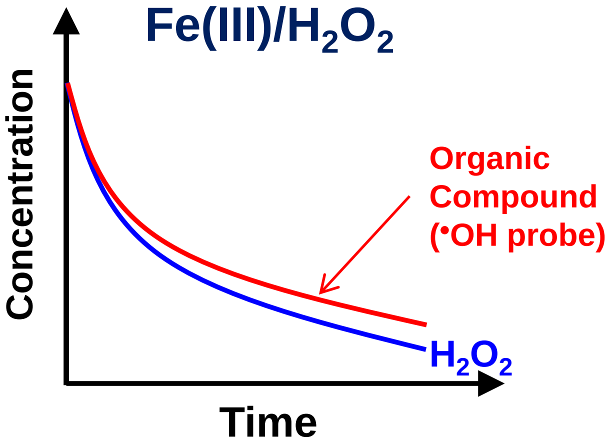
$$Fe(II) + H_2O_2 \rightarrow Fe(III) + {}^{\bullet}OH + OH^-$$

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

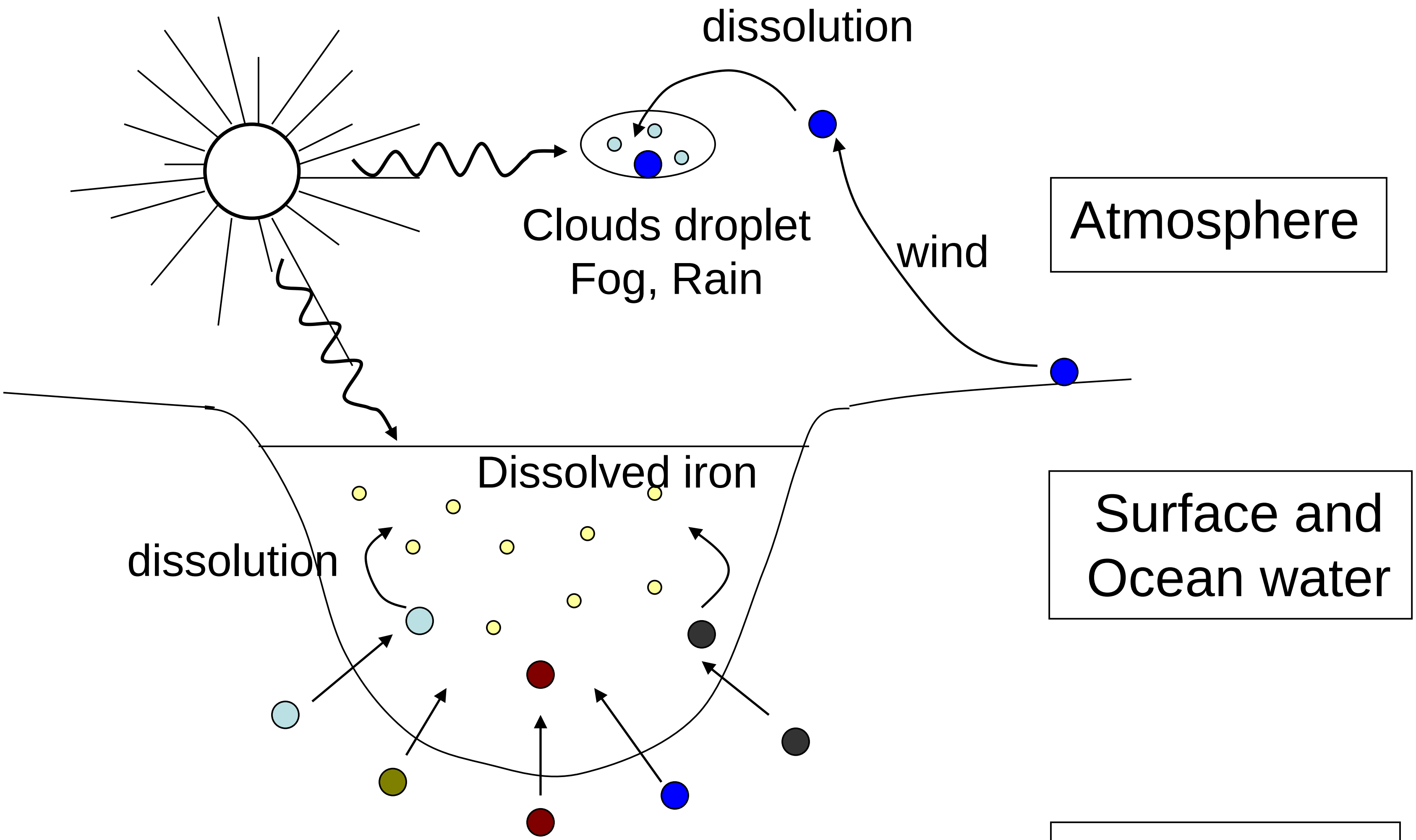
$$Fe(III) + H_2O_2 \rightarrow Fe(II) + HO_2^{\bullet} + H^+$$

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





Iron in the Environment



dissolution

Clouds droplet
Fog, Rain

wind

Atmosphere

Dissolved iron

dissolution

Surface and
Ocean water

Sediments

Various iron oxide

Geothite, hematite, lepidocrocite
Maghemite et.al.

Activity of Other Metal Ions

◆ **Kinetics of metal ion catalyzed oxidative decarboxylation of benzoic acid>**

(Siegel & Lanphear, 1979, *J. Am. Chem. Soc.*)

Metal ion added	$10^3 k_{obsd}$, s^{-1}	Metal ion added	$10^3 k_{obsd}$, s^{-1}	Metal ion added	$10^3 k_{obsd}$, s^{-1}
None	1.6	Co^{2+}	1.4	Cd^{2+}	1.5
Na^{+}	1.5	Ni^{2+}	1.6	In^{3+}	1.8
Mg^{2+}	1.2	Cu^{2+}	4.8	Os^{4+}	1.6
Al^{3+}	1.5	Zn^{2+}	0.9	Ir^{3+}	0.9
V^{3+}	1.5	Mo^{6+}	1.9	Pt^{2+}	1.5
Cr^{3+}	1.5	Ru^{3+}	7.6	Au^{3+}	1.0
Mn^{2+}	1.6	Rh^{3+}	1.6	Hg^{2+}	0.7
Fe^{2+}	28.0	Ag^{+}	0.7	Tl^{1+}	1.3

T = 32℃
pH = 2.0
$[H_2O_2] = 4.8 \times 10^{-4}$ M
EDTA added

$Fe^{2+} = [Ar]3d^6$ $Ru^{2+} = [Kr]4d^6$ $Cu^{2+} = [Ar]3d^9$

Different Fenton Reagents

✓ **Activation of H_2O_2**

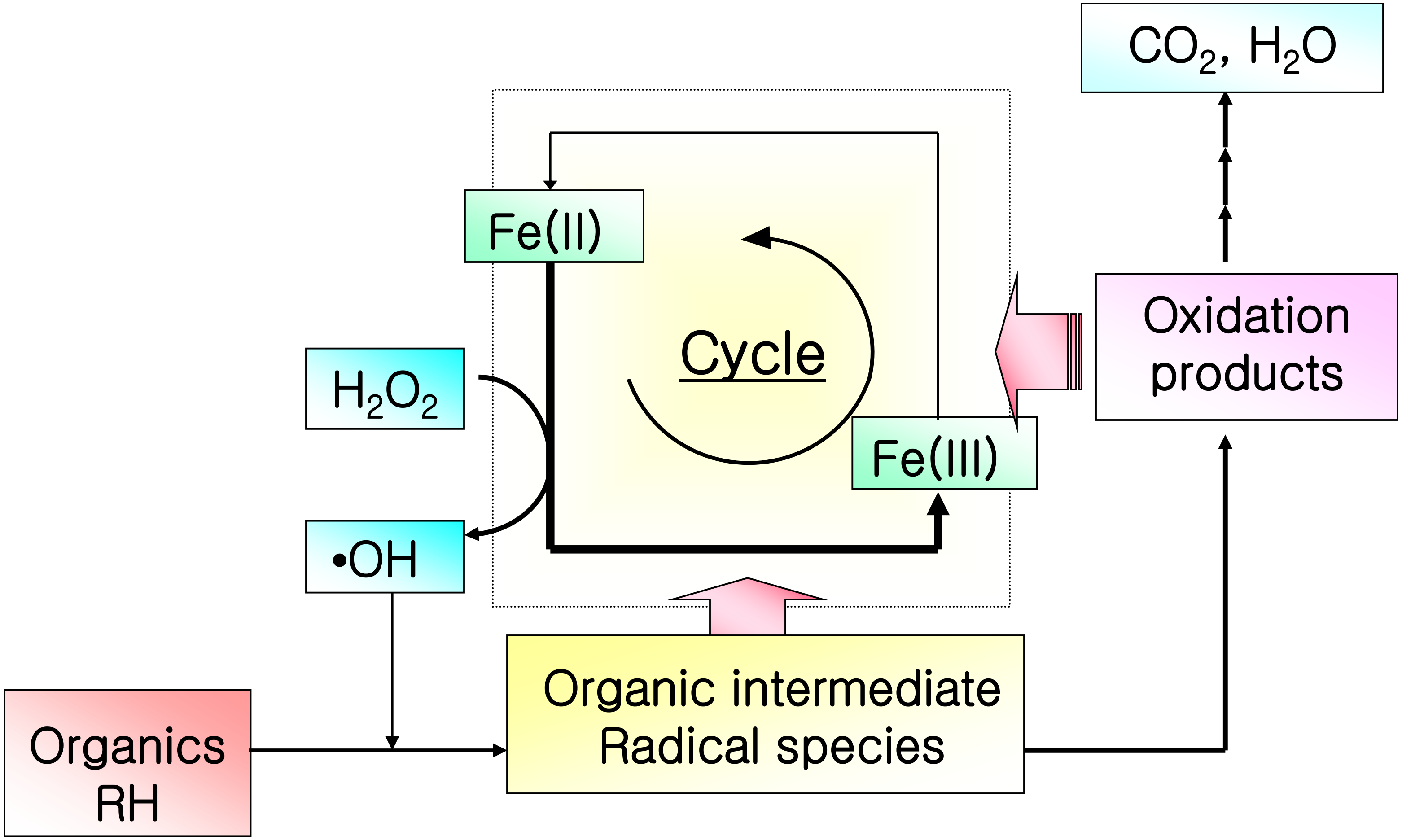
$Fe(II) + H_2O_2$
$Fe(III)$ (+ Reducing agent) $+ H_2O_2$
$Fe^0 + H_2O_2$

✓ **Activation of O_2**

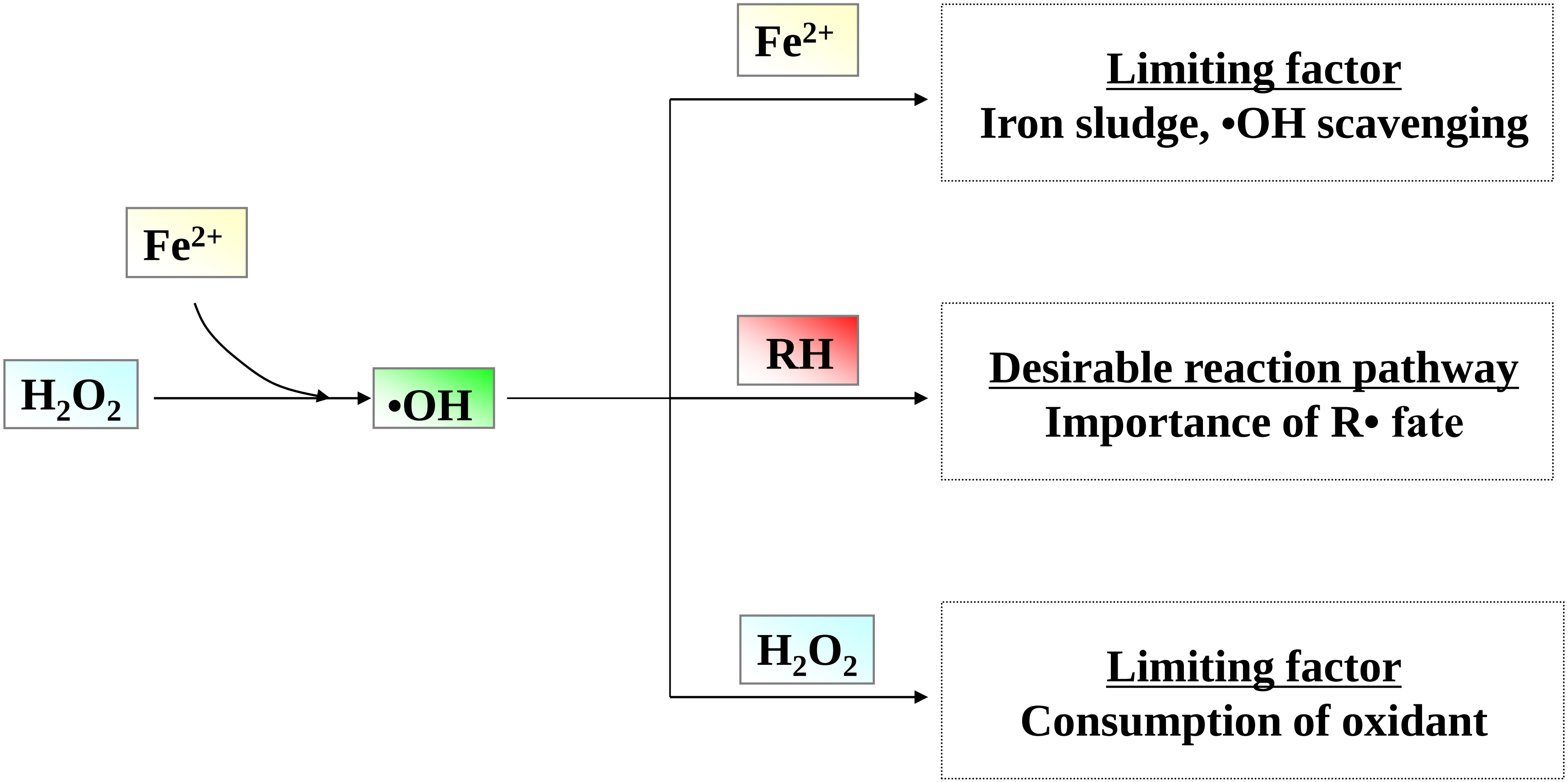
$Fe(II) + O_2$
$Fe(III)$ + Reducing agent $+ O_2$
$Fe^0 + O_2$

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

Oxidation of Organic Compounds by the Fenton System



Fate of •OH in the Fenton System



Fe^{2+}

H_2O_2

•OH

Fe^{2+}

Limiting factor
Iron sludge, •OH scavenging

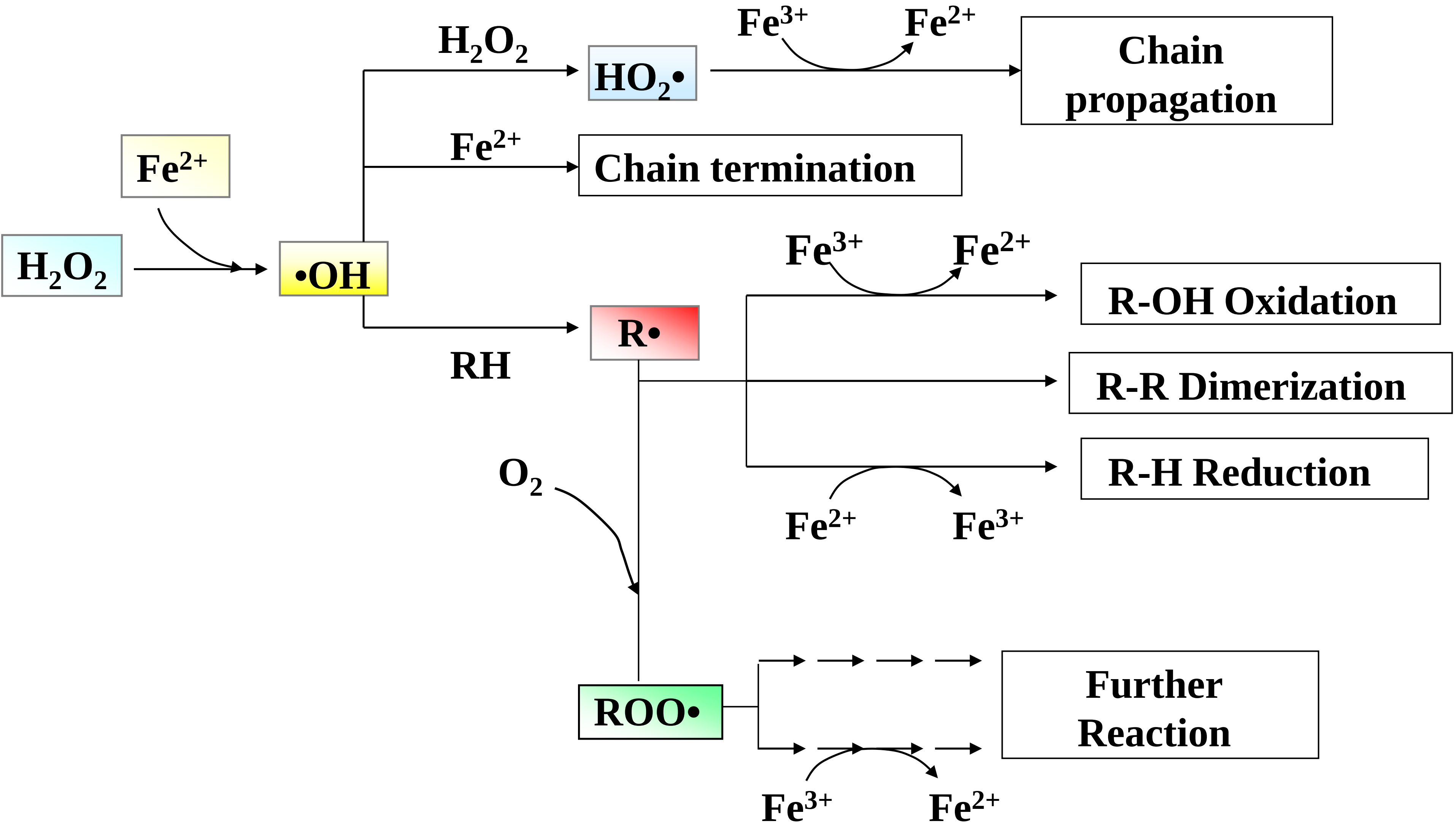
RH

Desirable reaction pathway
Importance of R• fate

H_2O_2

Limiting factor
Consumption of oxidant

Fate of •OH in the Fenton System



Kinetics of the Fe(III)/H_2O_2 System

- **Decomposition of H_2O_2**

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \qquad k_1$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \qquad k_2$$

$$HO_2^{\bullet} + Fe^{3+} \rightarrow Fe^{2+} + O_2 + H^+ \qquad k_3$$

$$HO_2^{\bullet} + Fe^{2+} \rightarrow Fe^{3+} + HO_2^- \ (\leftrightarrow H_2O_2) \qquad k_4$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \qquad k_5$$

The observed decomposition rate of H_2O_2 follows the pseudo-first order kinetics:

$$d[H_2O_2]/dt = -\,k_{H2O2}[H_2O_2]$$

Let’s 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 ($k_1 \sim k_5$).

*Use steady-state approximations for the intermediates

Kinetics of the Fe(III)/H_2O_2 System

$$d[Fe^{2+}]/dt$$
$$= k_1[Fe^{3+}][H_2O_2]-k_2[Fe^{2+}][H_2O_2]+k_3[HO_2\bullet][Fe^{3+}]-k_4[HO_2\bullet][Fe^{2+}]\approx 0$$

$$d[HO_2\bullet]/dt$$
$$= k_1[Fe^{3+}][H_2O_2]-k_3[HO_2\bullet][Fe^{3+}]-k_4[HO_2\bullet][Fe^{2+}]+k_5[\bullet OH][H_2O_2]\approx 0$$

$$d[\bullet OH]/dt$$
$$= k_2[Fe^{2+}][H_2O_2]-k_5[\bullet OH][H_2O_2] \approx 0$$

⇩

$$[\bullet OH]_{ss} = (k_1k_2k_3)^{1/2}[Fe^{3+}]/k_5k_4^{1/2}$$

$$[Fe^{2+}]_{ss} = (k_1k_3)^{1/2}[Fe^{3+}]/(k_2k_4)^{1/2}$$

$$[HO_2\bullet]_{ss} = (k_1k_2)^{1/2}[H_2O_2]/(k_3k_4)^{1/2}$$

Kinetics of the Fe(III)/H_2O_2 System

$d[H_2O_2]/dt$

$= k_4[HO_2\bullet]_{ss}[Fe^{2+}]_{ss} - k_1[Fe^{3+}][H_2O_2] - k_2[Fe^{2+}]_{ss}[H_2O_2] - k_5[\bullet OH]_{ss}[H_2O_2]$

$= -2(k_1k_2k_3)^{1/2}\, k_4^{-1/2}\, [Fe^{3+}][H_2O_2]$

$d[H_2O_2]/dt = -k_{obs}[H_2O_2]$

$$\boldsymbol{k_{obs} = 2(k_1k_2k_3)^{1/2}\, k_4^{-1/2}\, [Fe^{3+}]}$$

Kinetics of the Fe(III)/H_2O_2 System

◆ Oxidation of a organic contaminant (P)

$P + {}^{\bullet}OH \rightarrow \text{Products} \qquad k_6$

d[P]/dt = ?

(1) Low concentration

*The presence of P does not affect the $^{\bullet}$OH concentration in the system.

(2) High concentration

*All $^{\bullet}$OHs produced in the system are scavenged by P.

Factors Affecting the Fenton System

pH

Anions

Ratios (doses) of reagents

Oxygen

Temperature

Light

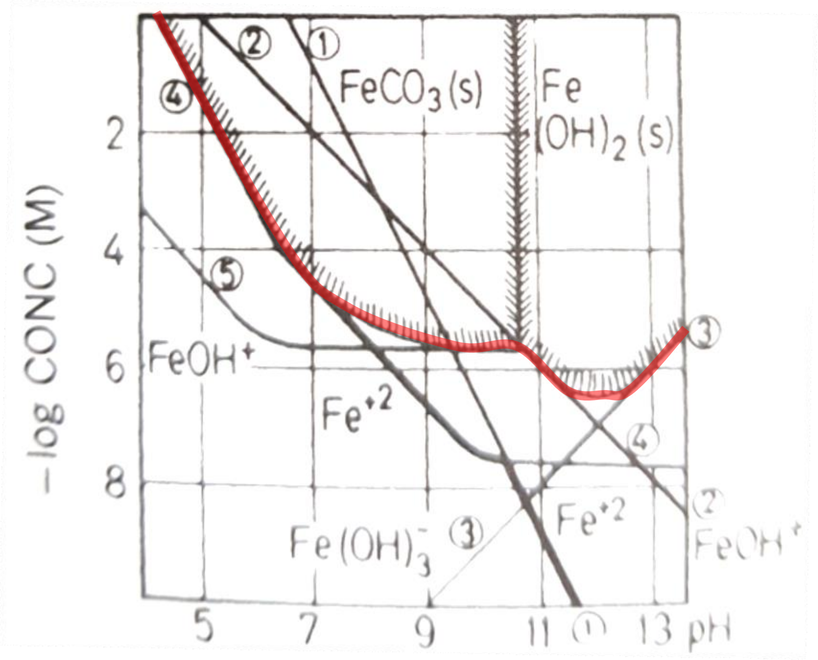
And what else?

Solubility of Iron

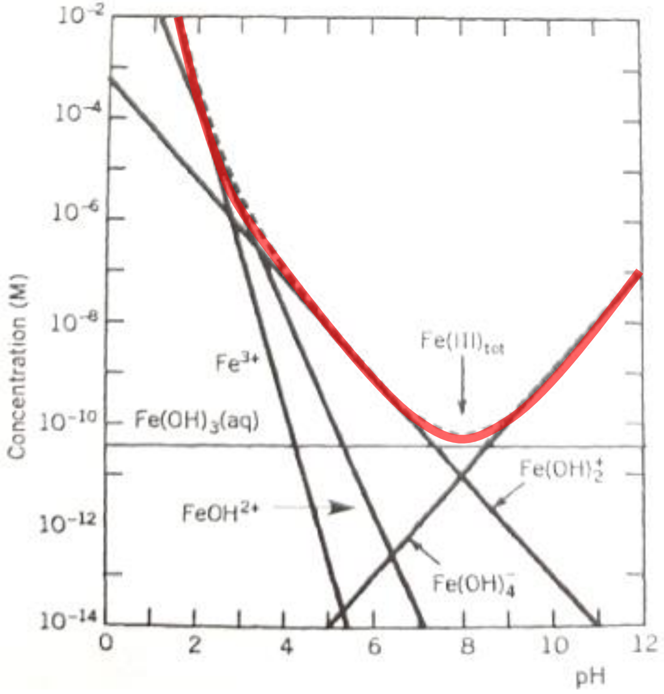
- **pH affects the solubility of iron (both Fe(II) and Fe(III))**

(Stumm & Morgan, 1996, *Aquatic Chemistry*)

Fe(II) (open system)



Fe(III) (closed system)

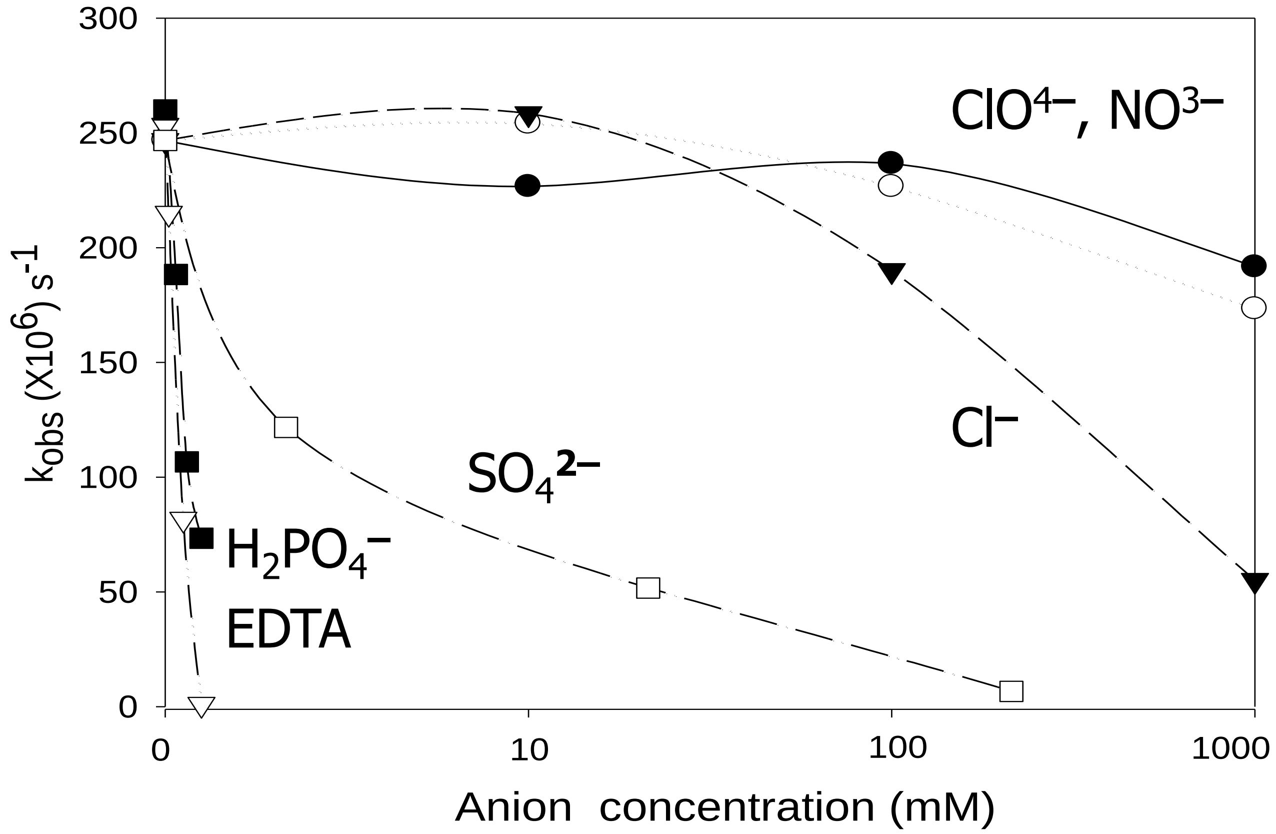


- **pH affects the mechanism of the Fenton reaction**

  (let's talk about it later)

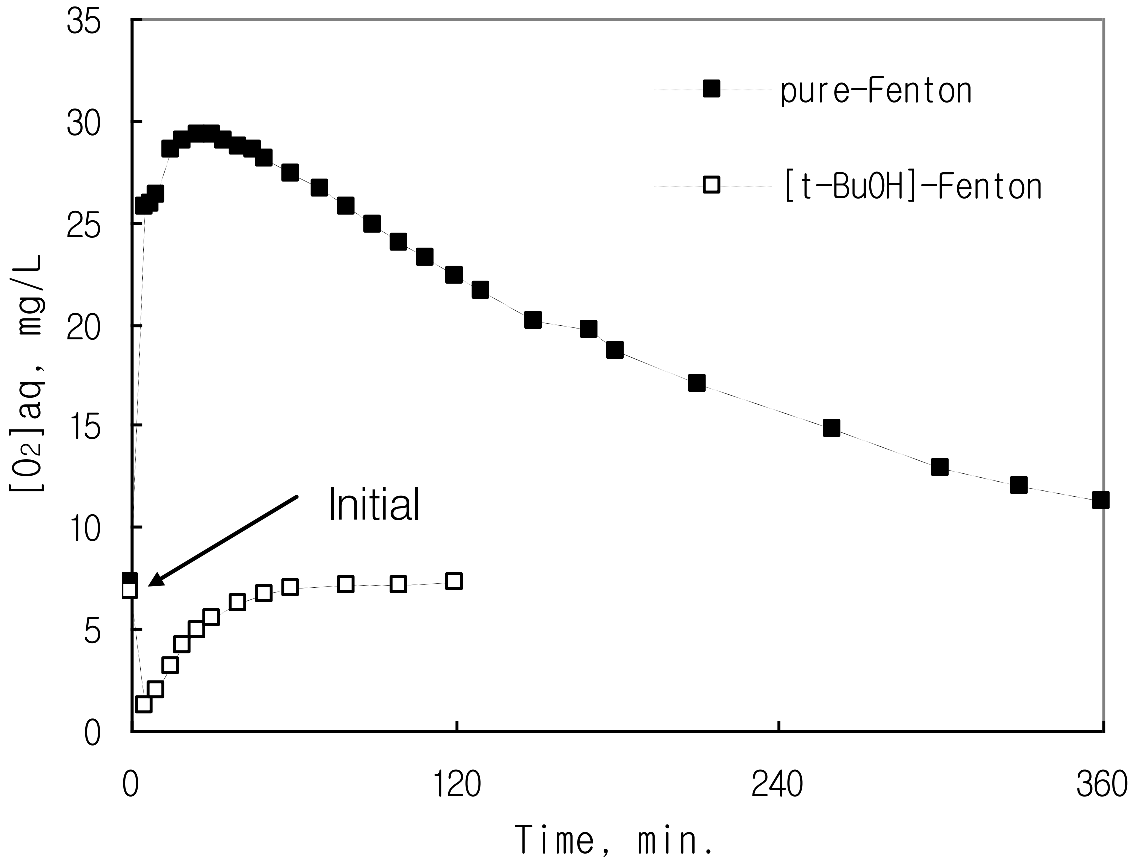
Effects of Anions

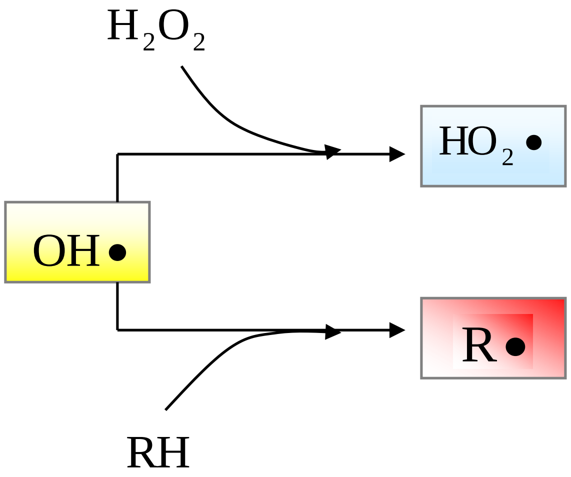
- **Two major roles of anions: iron-complexing agents & •OH scavengers**



$[Fe^{3+}]$ = 1.0 mM , pH_0 = 2.8 , $[H_2O_2]_0$ = 100 mM

Role of Oxygen





H_2O_2

$HO_2\bullet$

$OH\bullet$

$R\bullet$

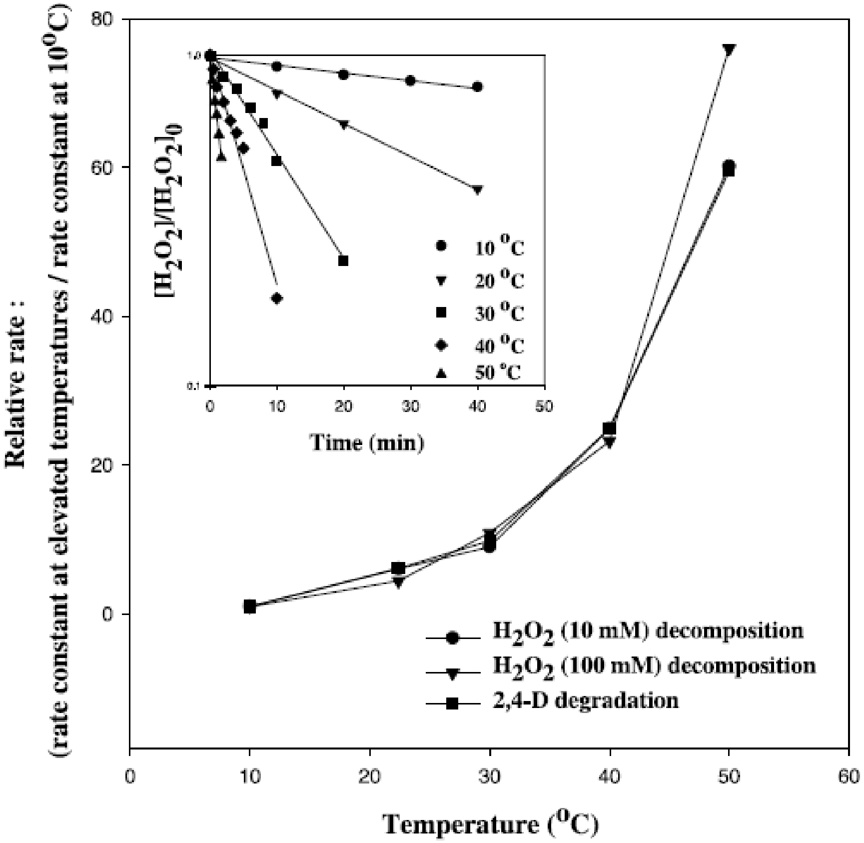
RH

$[Fe^{2+}]_0$ =1 mM(56mg/L) , $[H_2O_2]_0$ = 5 mM(170mg/L) ,

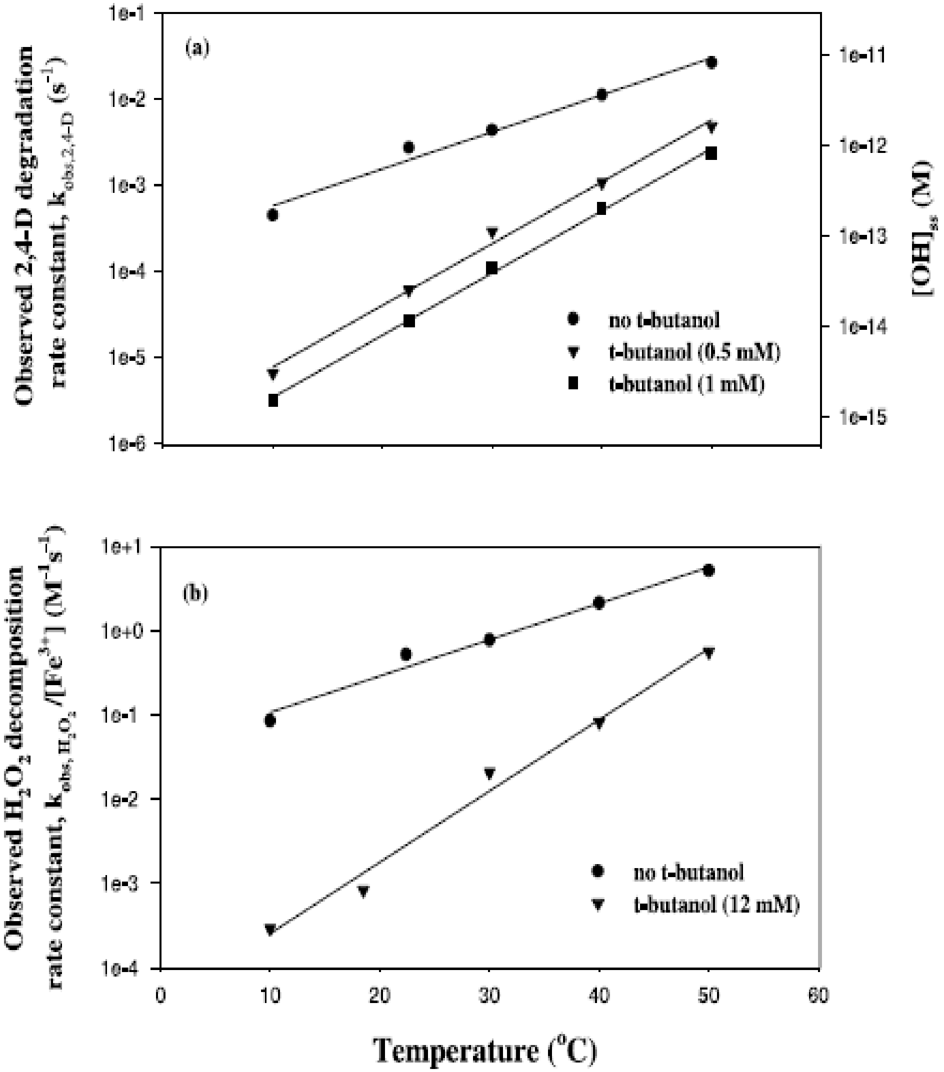
[t-BuOH] = 0 or 30mM

Temperature Effect

- **Temperature-dependent decomposition of H_2O_2 and degradation of 2,4-D**

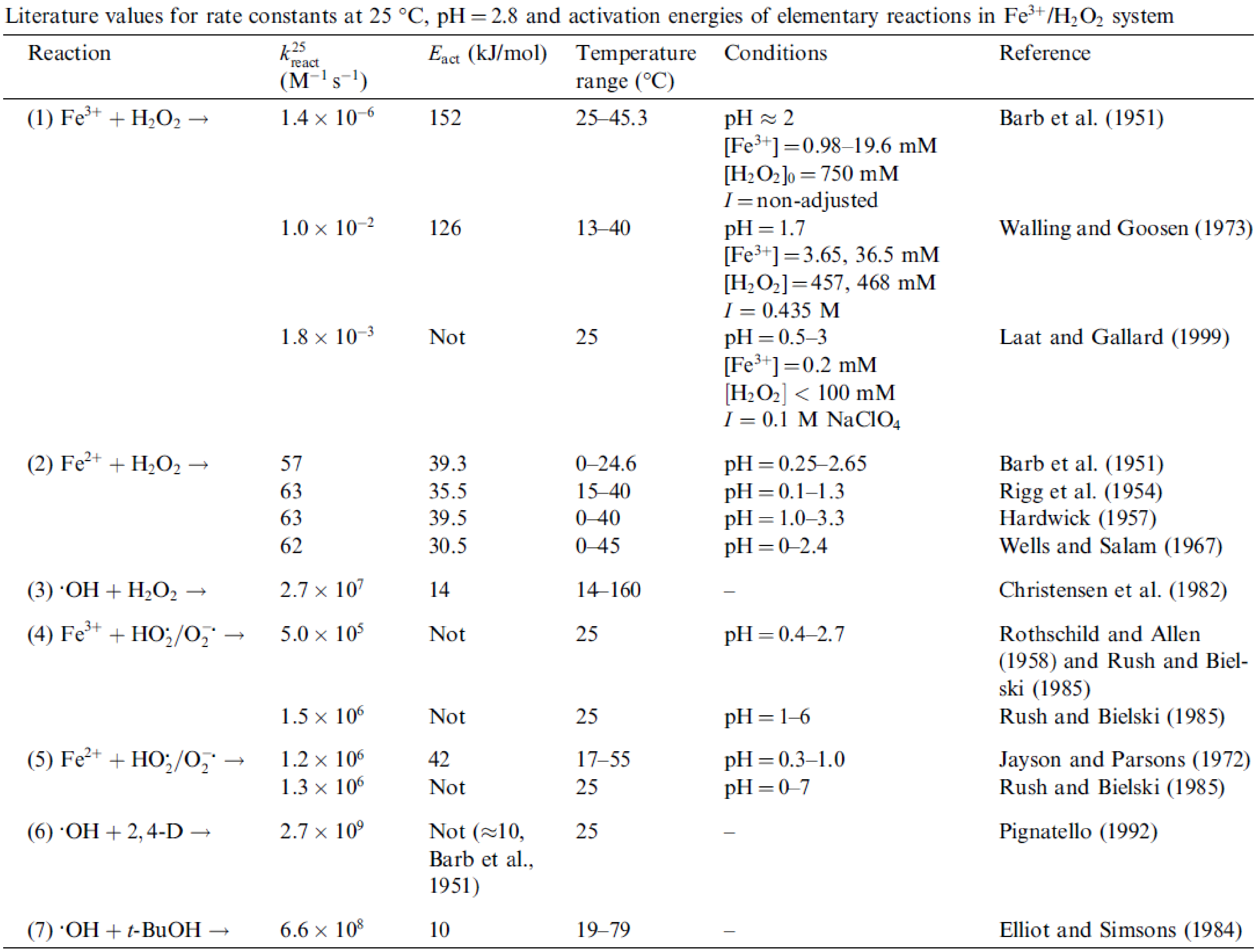


(Lee et al, 2003, *Chemosphere*)



Temperature Effect

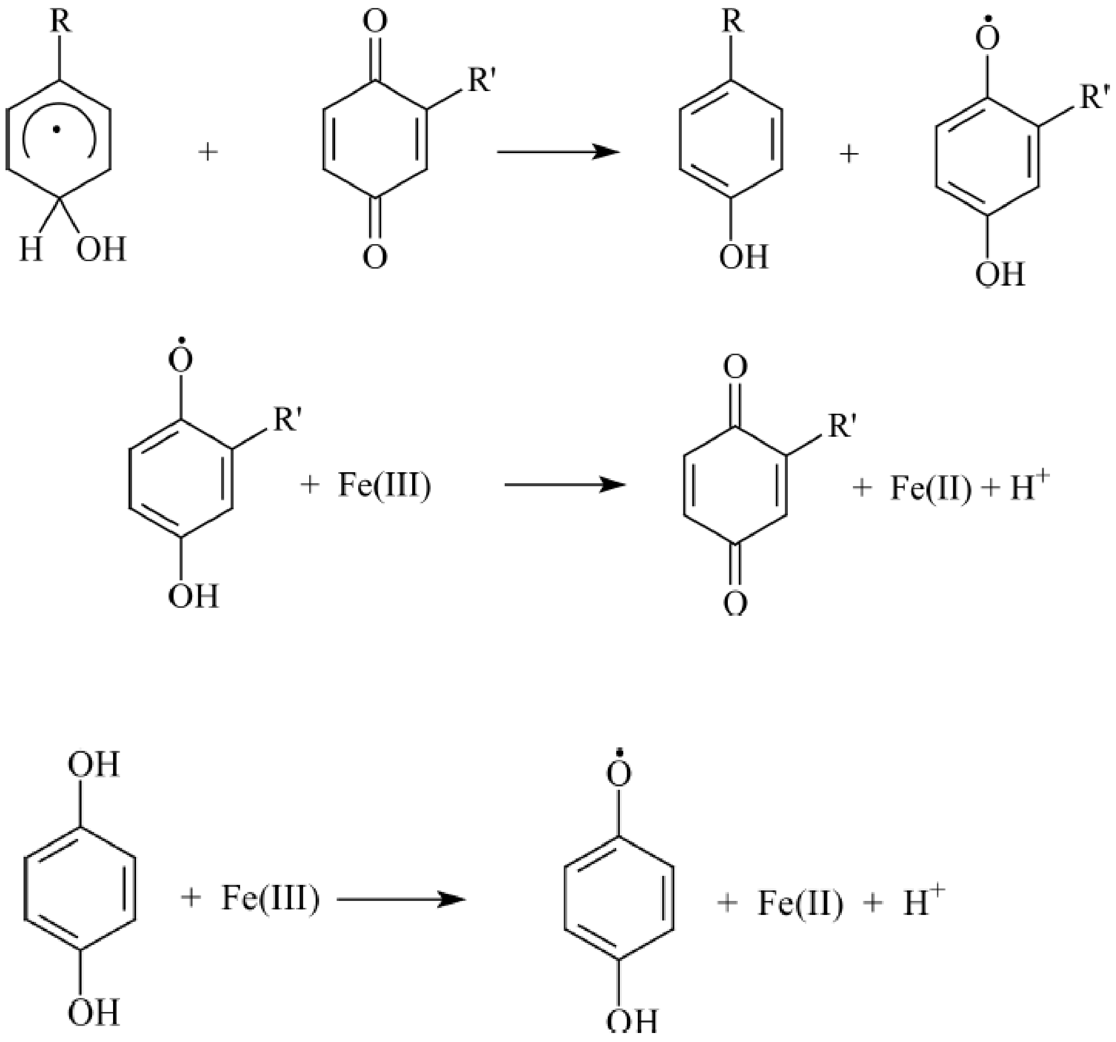
(Lee et al, 2003, *Chemosphere*)



Literature values for rate constants at 25 °C, pH = 2.8 and activation energies of elementary reactions in Fe^{3+}/H_2O_2 system

Reaction	k_{react}^{25} (M^{-1} s^{-1})	E_{act} (kJ/mol)	Temperature range (°C)	Conditions	Reference
(1) $Fe^{3+} + H_2O_2 \rightarrow$	1.4×10^{-6}	152	25–45.3	pH ≈ 2 $[Fe^{3+}] = 0.98$–19.6 mM $[H_2O_2]_0 = 750$ mM I = non-adjusted	Barb et al. (1951)
	1.0×10^{-2}	126	13–40	pH = 1.7 $[Fe^{3+}] = 3.65$, 36.5 mM $[H_2O_2] = 457$, 468 mM $I = 0.435$ M	Walling and Goosen (1973)
	1.8×10^{-3}	Not	25	pH = 0.5–3 $[Fe^{3+}] = 0.2$ mM $[H_2O_2] < 100$ mM $I = 0.1$ M $NaClO_4$	Laat and Gallard (1999)
(2) $Fe^{2+} + H_2O_2 \rightarrow$	57	39.3	0–24.6	pH = 0.25–2.65	Barb et al. (1951)
	63	35.5	15–40	pH = 0.1–1.3	Rigg et al. (1954)
	63	39.5	0–40	pH = 1.0–3.3	Hardwick (1957)
	62	30.5	0–45	pH = 0–2.4	Wells and Salam (1967)
(3) $^{\cdot}OH + H_2O_2 \rightarrow$	2.7×10^{7}	14	14–160	–	Christensen et al. (1982)
(4) $Fe^{3+} + HO_2^{\cdot}/O_2^{-\cdot} \rightarrow$	5.0×10^{5}	Not	25	pH = 0.4–2.7	Rothschild and Allen (1958) and Rush and Bielski (1985)
	1.5×10^{6}	Not	25	pH = 1–6	Rush and Bielski (1985)
(5) $Fe^{2+} + HO_2^{\cdot}/O_2^{-\cdot} \rightarrow$	1.2×10^{6}	42	17–55	pH = 0.3–1.0	Jayson and Parsons (1972)
	1.3×10^{6}	Not	25	pH = 0–7	Rush and Bielski (1985)
(6) $^{\cdot}OH$ + 2,4-D →	2.7×10^{9}	Not (≈10, Barb et al., 1951)	25	–	Pignatello (1992)
(7) $^{\cdot}OH$ + *t*-BuOH →	6.6×10^{8}	10	19–79	–	Elliot and Simsons (1984)

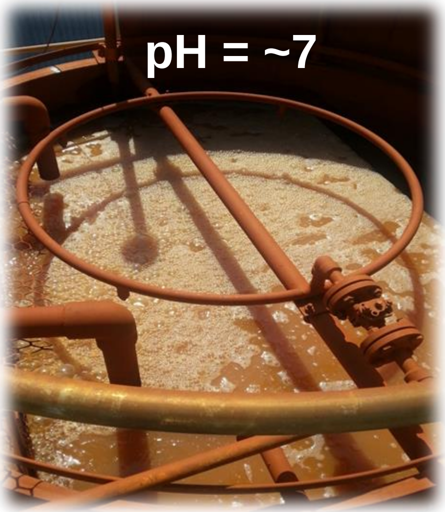
Aromatic Compounds as Promotors

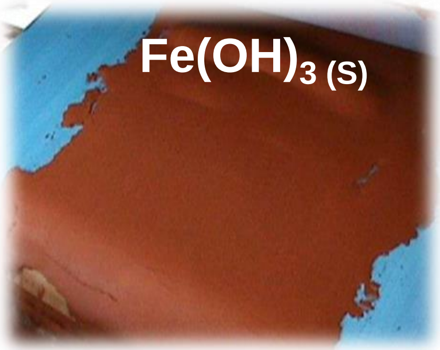


Fenton Processes

✓ Conventional Fenton process

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





Pictures from Prof. Y. H. Huang from NCKU, Taiwan

Fenton Processes

✓ Modified Fenton processes

- Fluidized-bed Fenton process

- Electro-Fenton process
- Photo-Fenton process

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

(fast)

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

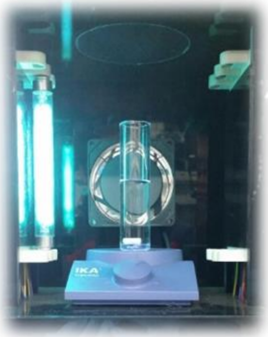
(slow)

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

"Photo-Fenton"

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

"Electro-Fenton"

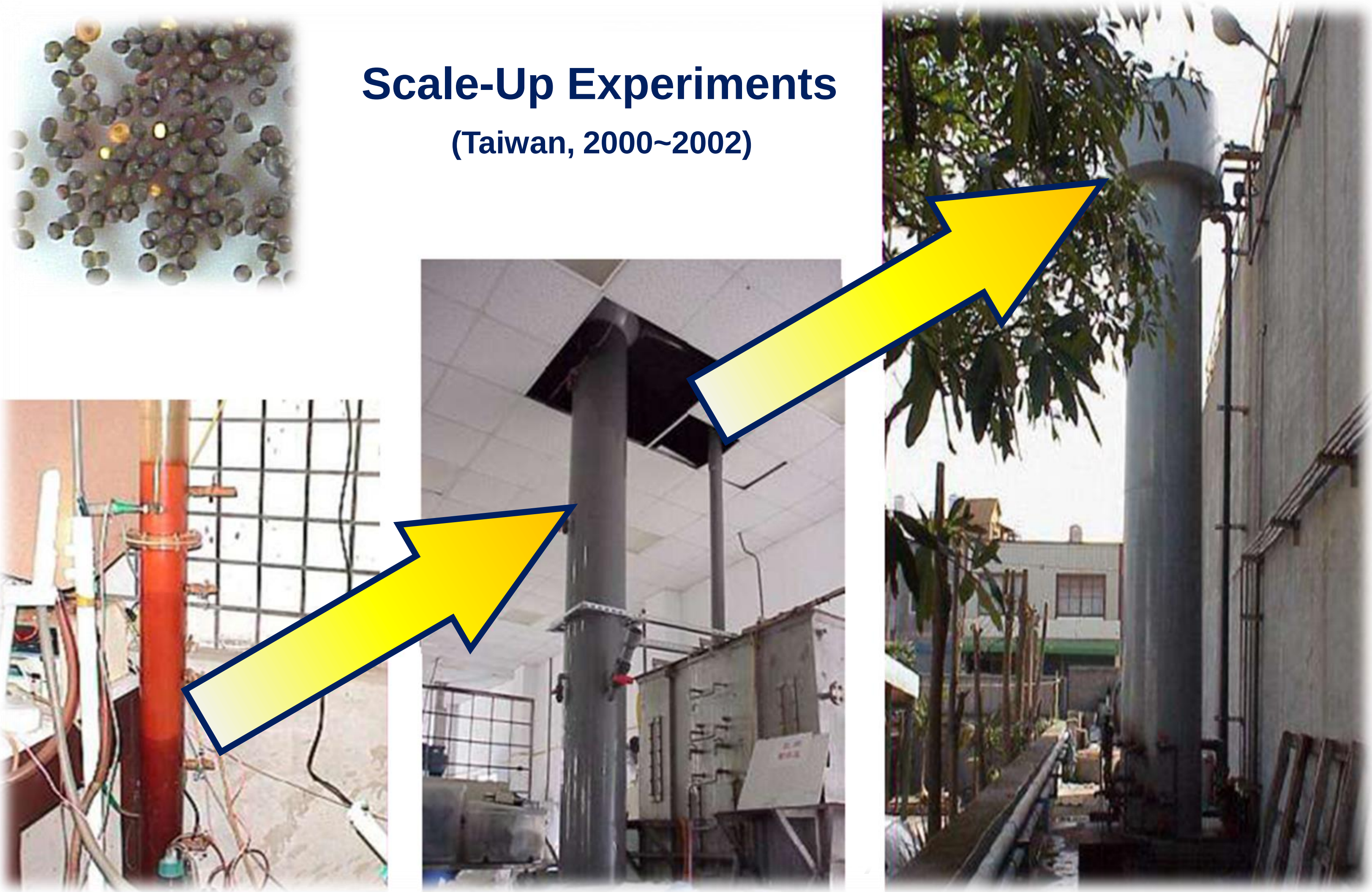


Pictures from MercuryTec, Taiwan & Prof. Y. H. Huang from NCKU, Taiwan

Fluidized Bed Fenton Process

Scale-Up Experiments

(Taiwan, 2000~2002)



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

Fluidized Bed Fenton Process

Built in 2002

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

Fluidized Bed Fenton Process

▲ Capacity: 1,200 CMD
COD: 300 → 100 mg/L

▲ Capacity: 12,500 CMD
COD: 180 → 70 mg/L

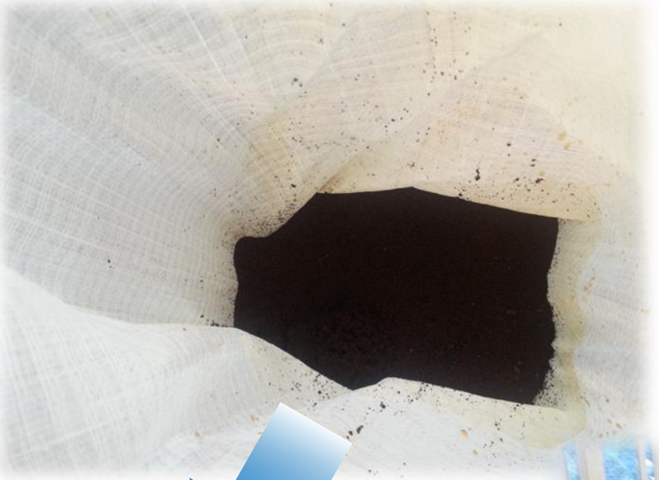
▲ Capacity: 30,000 CMD
COD: 350 → 100 mg/L

▲ Capacity: 4,800 CMD
COD: 250 → 80 mg/L

◄ Capacity: 86,000 CMD
COD: 800 → 100 mg/L

Fluidized Bed Fenton Process (Unseeded)

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



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

A Major Limitation of Fenton Processes

Conventional Fenton process

Fluidized-bed Fenton process

Effective

at acidic pH

Most of others
using different
Fenton reagents

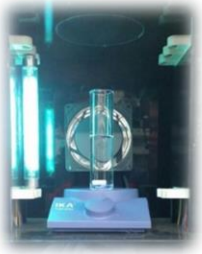


Photo-Fenton
process

Electro-Fenton
process

Pictures from Prof. Y. H. Huang from NCKU, Taiwan

Reactive oxidants produced by the Fenton reaction

✓ **$^{\bullet}$OH vs Fe(IV)**

One-electron transfer

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

Two-electron transfer

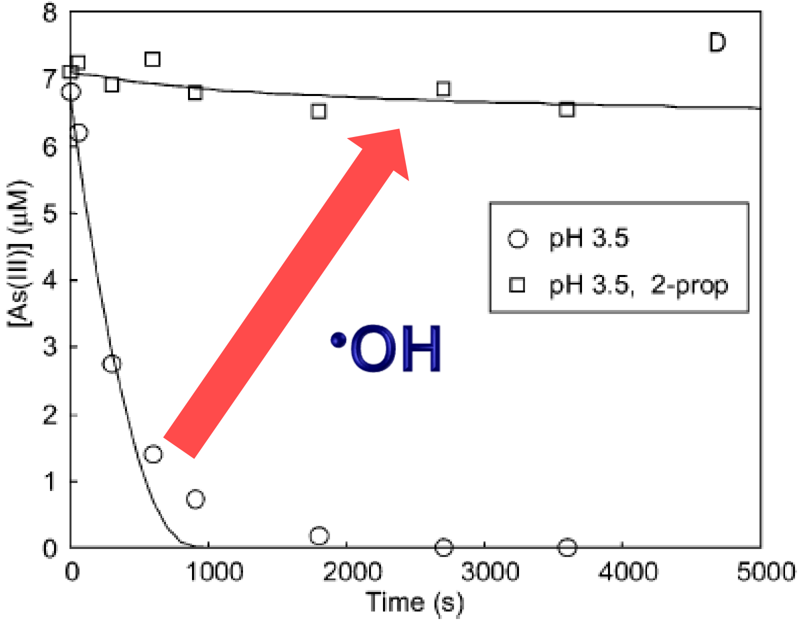
$$\overset{\overset{2e^{-}}{\curvearrowright}}{\mathrm{Fe(II)} + \mathrm{H_2O_2}} \xrightarrow{2\mathrm{H^{+}}} \mathrm{Fe(IV)} + 2\mathrm{H_2O}$$

•OH vs Fe(IV), pH-Dependent?

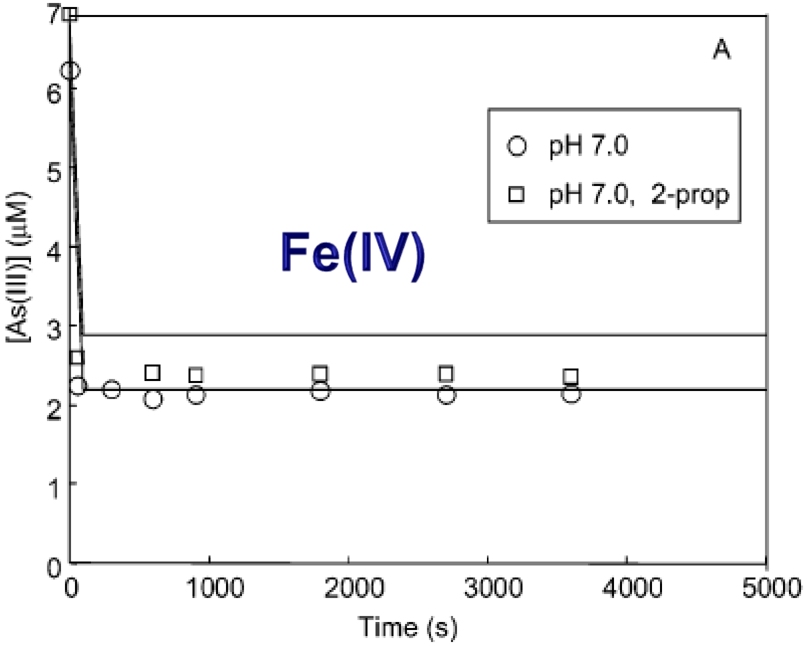
✓ **Effect of a •OH scavenger**

- 2-Propanol inhibits the As(III) oxidation by the Fenton reaction only at acidic pH

Acidic pH



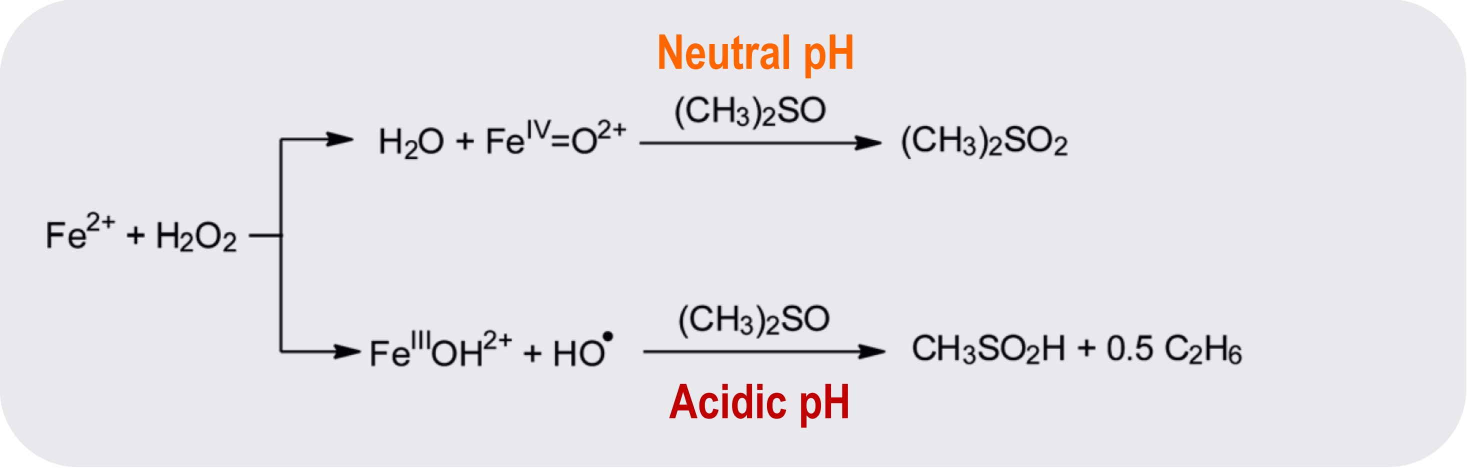
Neutral pH



Hug and Leupin, 2003 (*Environ. Sci. Technol.*)

•OH vs Fe(IV), pH-Dependent?

✓ Oxidation of DMSO by Fe(II)/H_2O_2

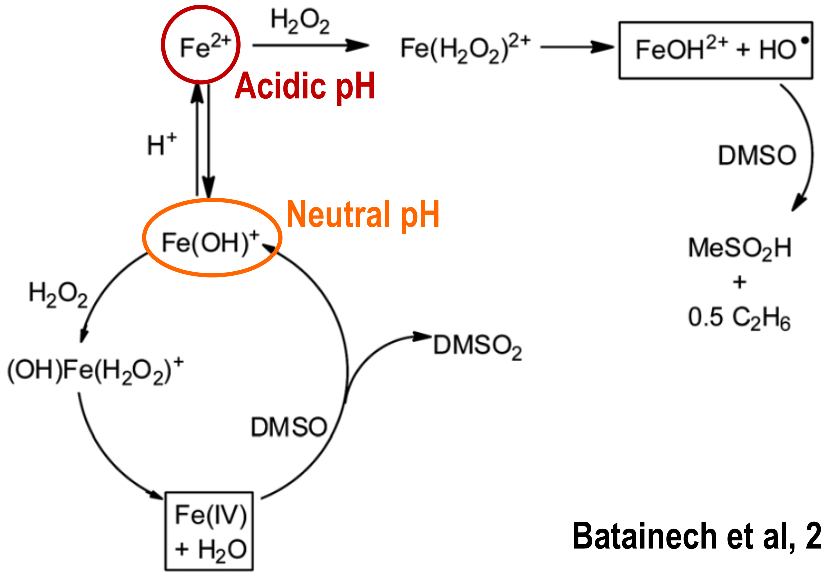


Neutral pH

$$Fe^{2+} + H_2O_2 \rightarrow H_2O + Fe^{IV}{=}O^{2+} \xrightarrow{(CH_3)_2SO} (CH_3)_2SO_2$$

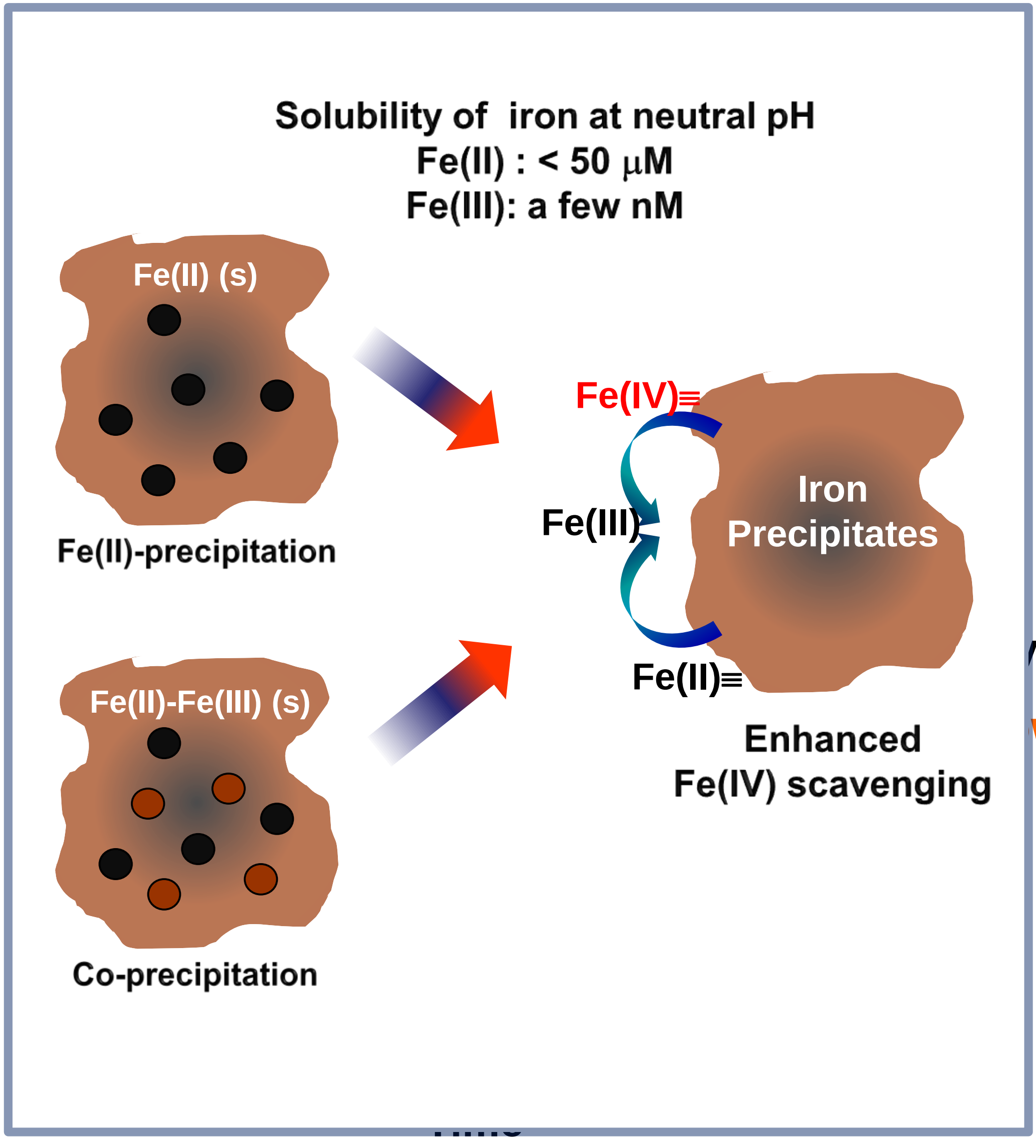
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{III}OH^{2+} + HO^{\bullet} \xrightarrow{(CH_3)_2SO} CH_3SO_2H + 0.5\ C_2H_6$$

Acidic pH



Batainech et al, 2012 (*Chem. Sci.*)

•OH vs Fe(IV), pH-Dependent?



Solubility of iron at neutral pH
Fe(II) : < 50 μM
Fe(III): a few nM

Enhanced Fe(IV) scavenging

Neutral pH

$$Fe(II) + H_2O_2 \rightarrow Fe(IV) + 2H_2O$$

$$Fe(II) + Fe(IV) \rightarrow 2Fe(III)$$

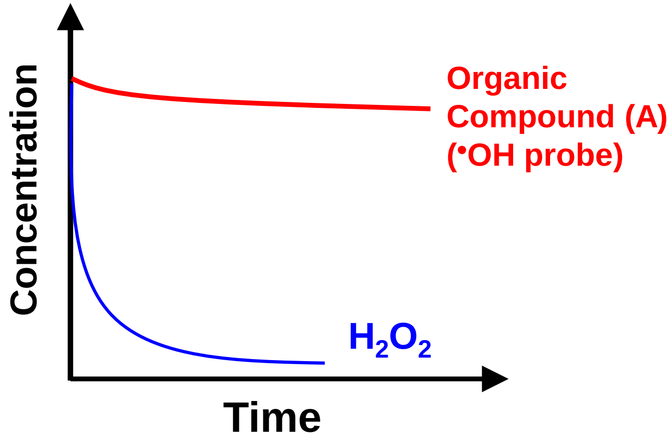
$$H_2O_2 + Fe(IV) \rightarrow Fe(II) + O_2 + 2H^+$$

$$\gg$$

$$A + Fe(IV) \rightarrow Products$$

$(\Delta[A]/\Delta[H_2O_2])$

w

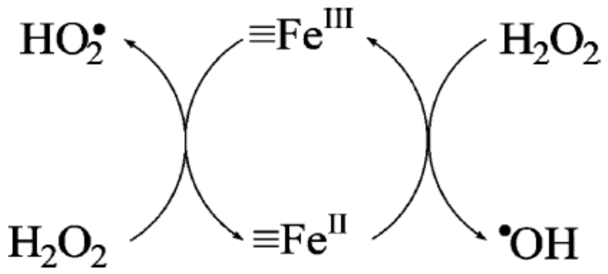


Non-Radical Mechanism Involving Fe(IV) on Heterogeneous Iron Surfaces

Pham et al., 2009 (*Environ. Sci. Technol.*)

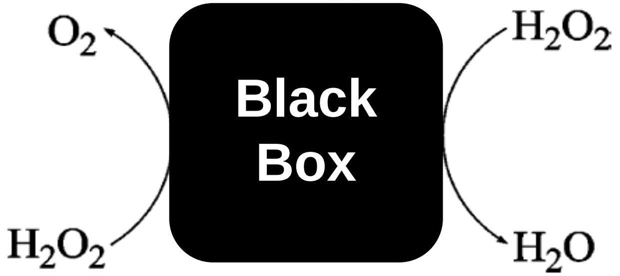
Haber—Weiss Mechanism

Acidic pH



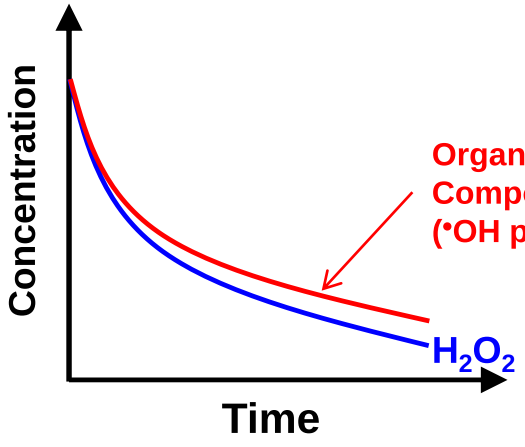
Non-Radical Mechanism

Neutral pH

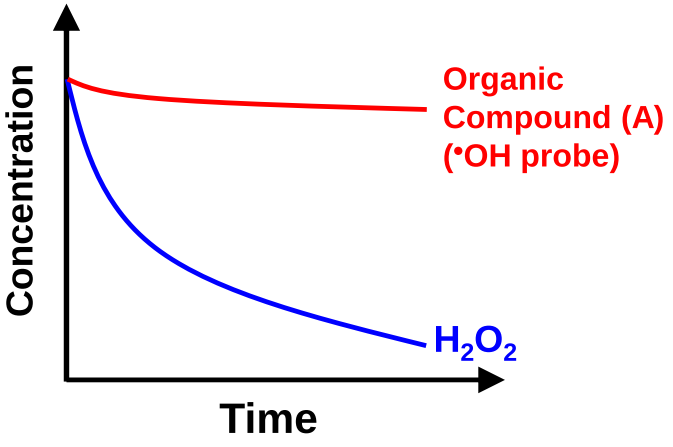


H_2O_2 Utilization Efficiency ($\Delta[A]/\Delta[H_2O_2]$)

High

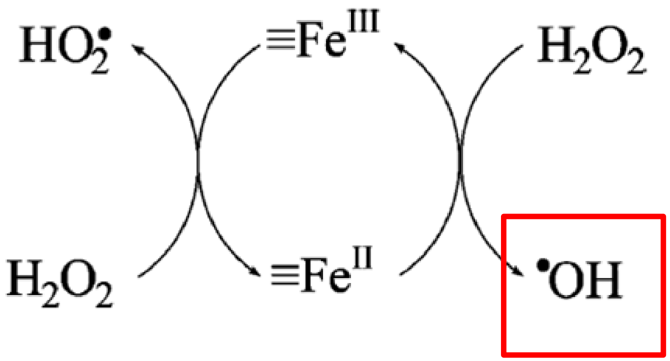


Low



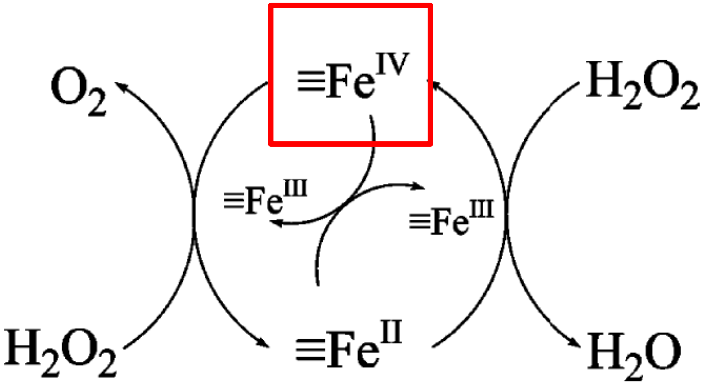
Nonradical Mechanism and Fe(IV)

Haber—Weiss Mechanism



(Acidic pH)

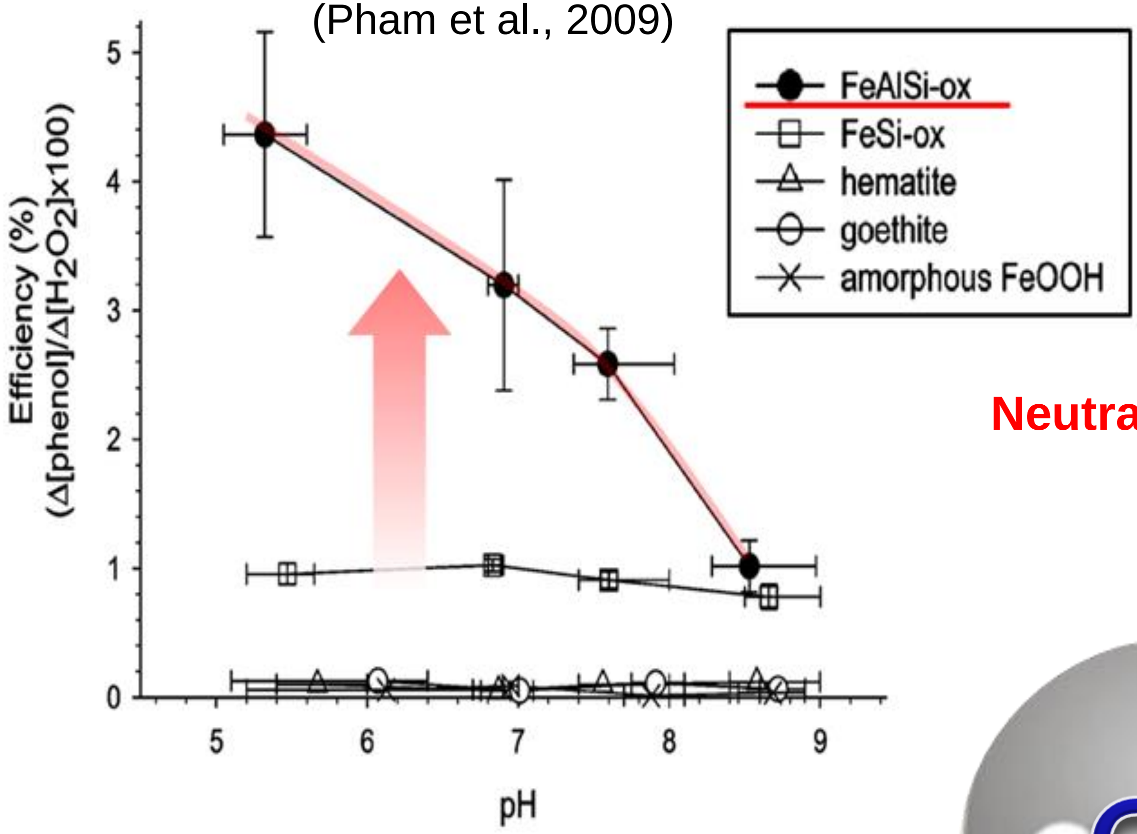
Non-Radical Mechanism



(Neutral pH)

$1e^-$ ⟷ $2e^-$

Neutral-pH Active Fenton Catalysts?


(Pham et al., 2009)

Neutral-pH Active Heterogeneous Fenton Catalyst