# Use of Iron In Advanced Oxidation Processes.

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# 연 구 배 경

- **Application of Fenton process ( 국내 )**
  - 염색 폐수 처리 **(** 반월**,** 시화 **)**
  - 매립지 침출수 처리 **(** 수도권**,** 김해 **)**

- 수도권 매립지 침출수 처리**(1997**년 기준**)**
  - **4000 ~ 6000 m$^3$/day**
  - **High operation cost due to large $H_2O_2$ use ( 1500 ~ 3000 mg/L )**

- 대부분 경험에 의존한 운전 인자 결정

→ **Fenton** 반응 메커니즘 이해를 통한 공정 효율성 증가**.**

# 연 구 배 경

Fenton 반응 메커니즘 연구 → 실제 처리 공정에서의 의미 파악

- 펜톤 반응의 폐수 처리 적용에 있어서 핵심 인자.

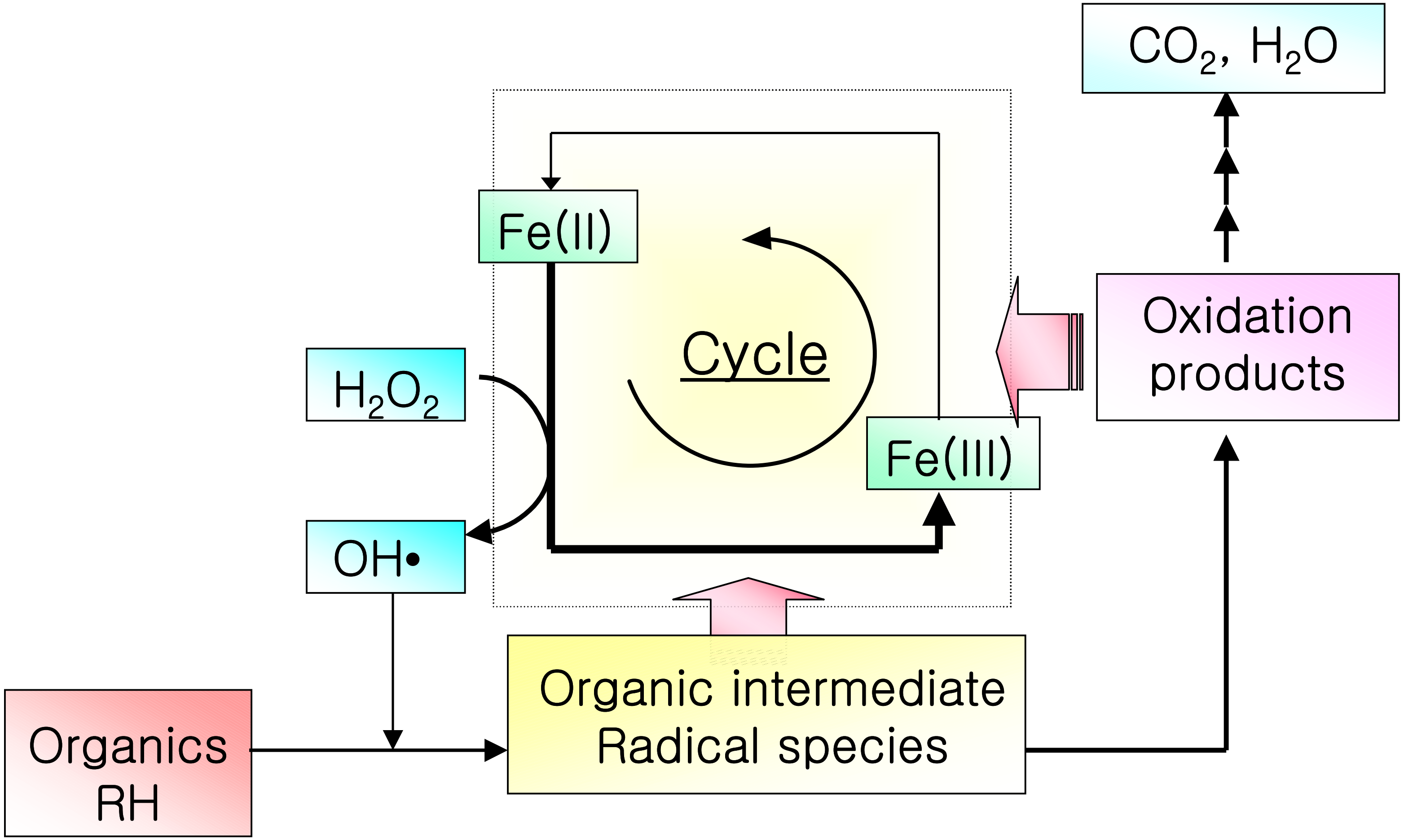
**1. Reagents condition**

**( ex. [$Fe^{2+}$], [$Fe^{3+}$] and [$H_2O_2$] )**

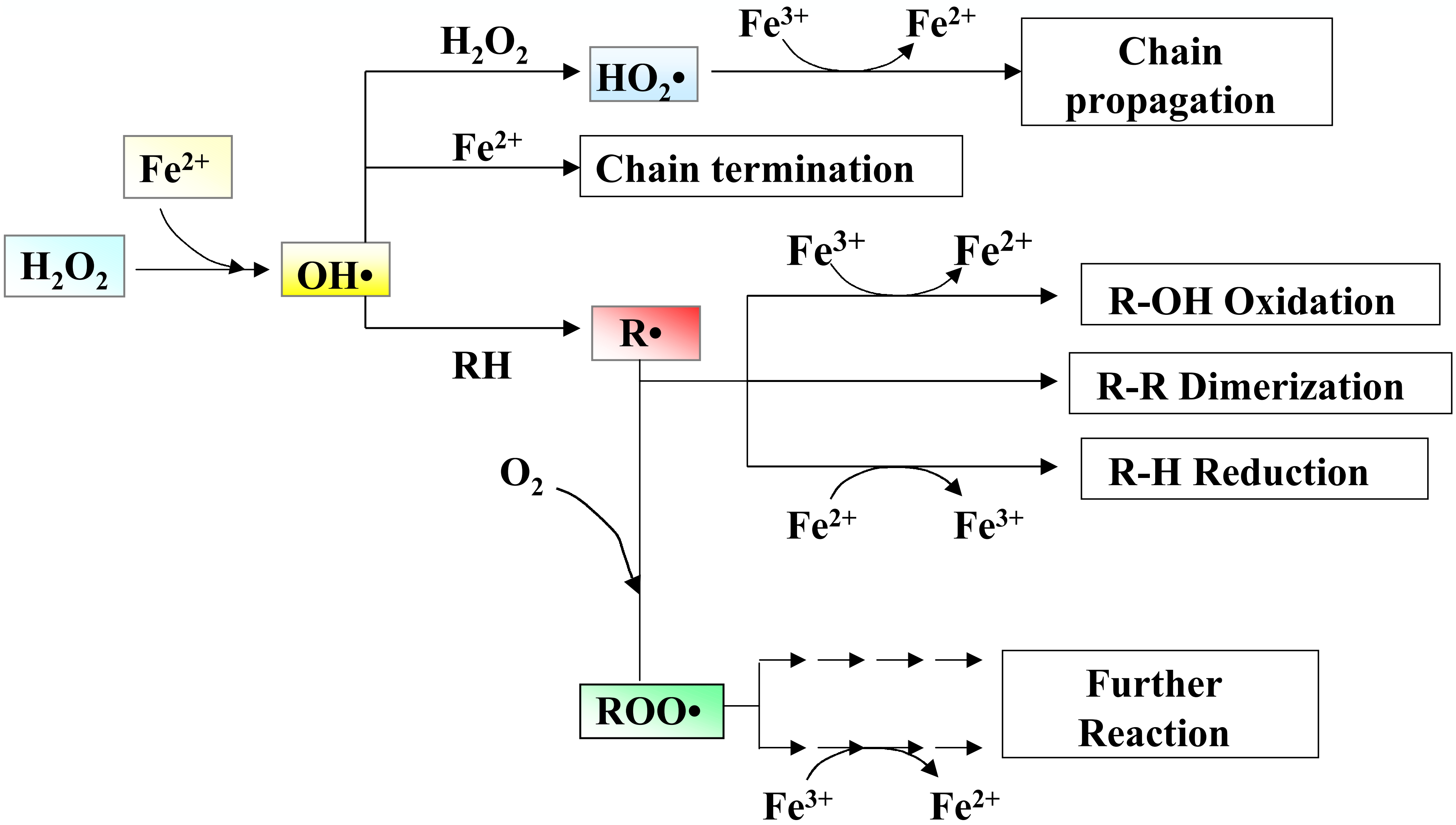
**2. Characteristics of wastewater**

**( type and quantity of organic or inorganic constituents, pH, and temperature of solution)**

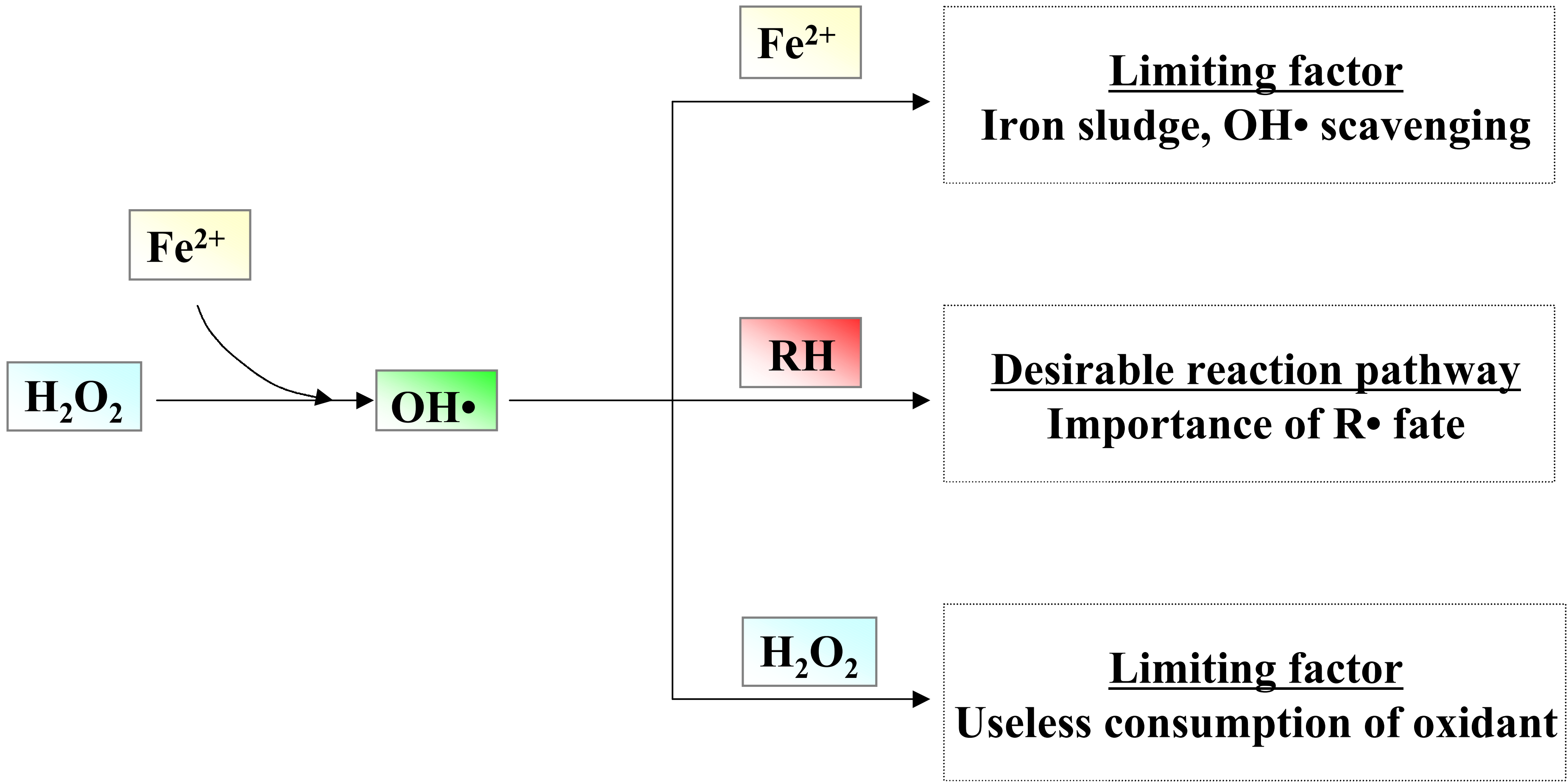
# Fenton oxidation mechanism



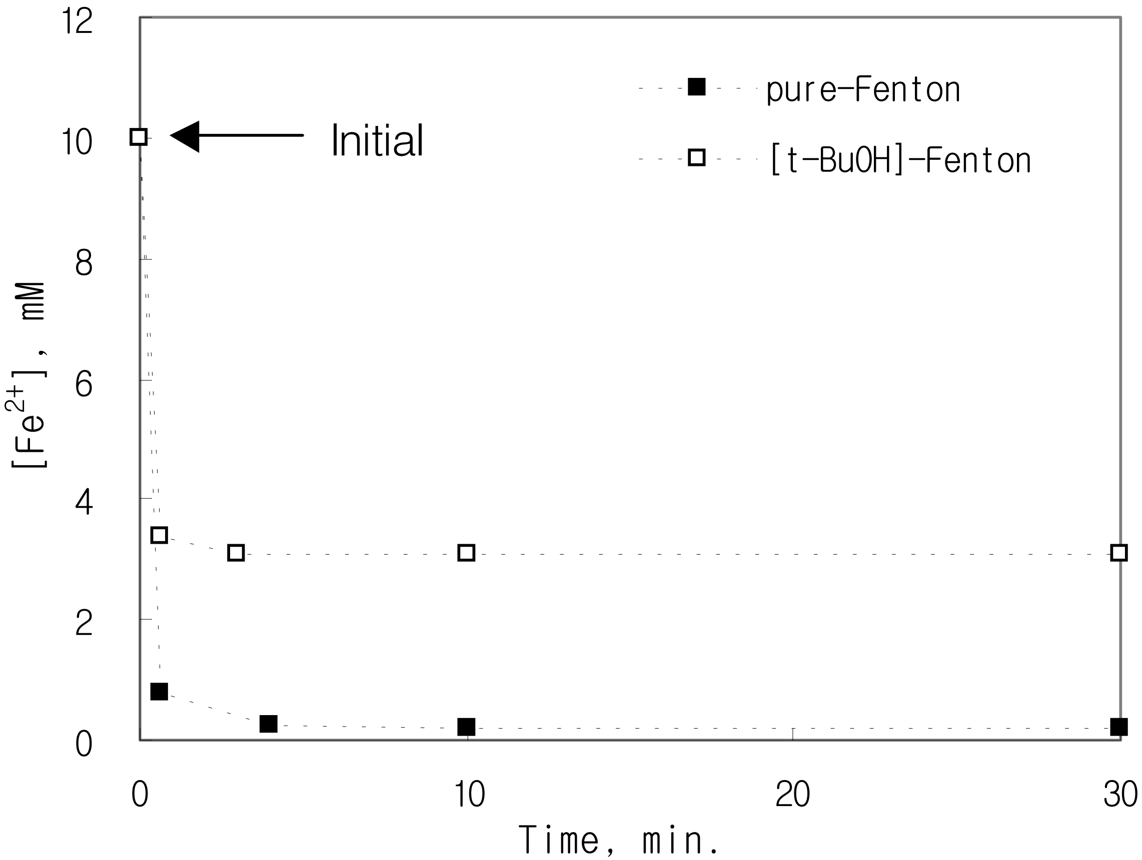
# Fenton oxidation mechanism



# 1. Reagnet 조건($[Fe^{2+}]_0/[H_2O_2]_0$ )에 따른 반응 특성 고찰



# High ratio of $[Fe^{2+}]_0/[H_2O_2]_0$( ≥ 2 )




- **Pure Fenton : [t-BuOH] = 0 mM**
- **[t-BuOH] Fenton : [t-BuOH] = 30 mM**

**$[Fe^{2+}]_0$ =10 mM( 560mg/L) , $[H_2O_2]_0$ = 5 mM( 170mg/L) , $[t\text{-}BuOH]_0$ = 0 or 30mM**

# Competitive reactions for OH•

**High ratio of $[Fe^{2+}]_0/[H_2O_2]_0$ ( ≥ 2 )**

- **[t-BuOH] = 0 mM**

$$OH\bullet + Fe^{2+} \rightarrow Fe^{3+} + OH^- \qquad k_1 = 3.2\times10^8\ M^{-1}s^{-1}$$

$$OH\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O \qquad k_2 = 3.3\times10^7\ M^{-1}s^{-1}$$

**This makes the consumption ratio to <u>2</u> ($\triangle[Fe^{2+}]/\triangle[H_2O_2] = 2$ )**

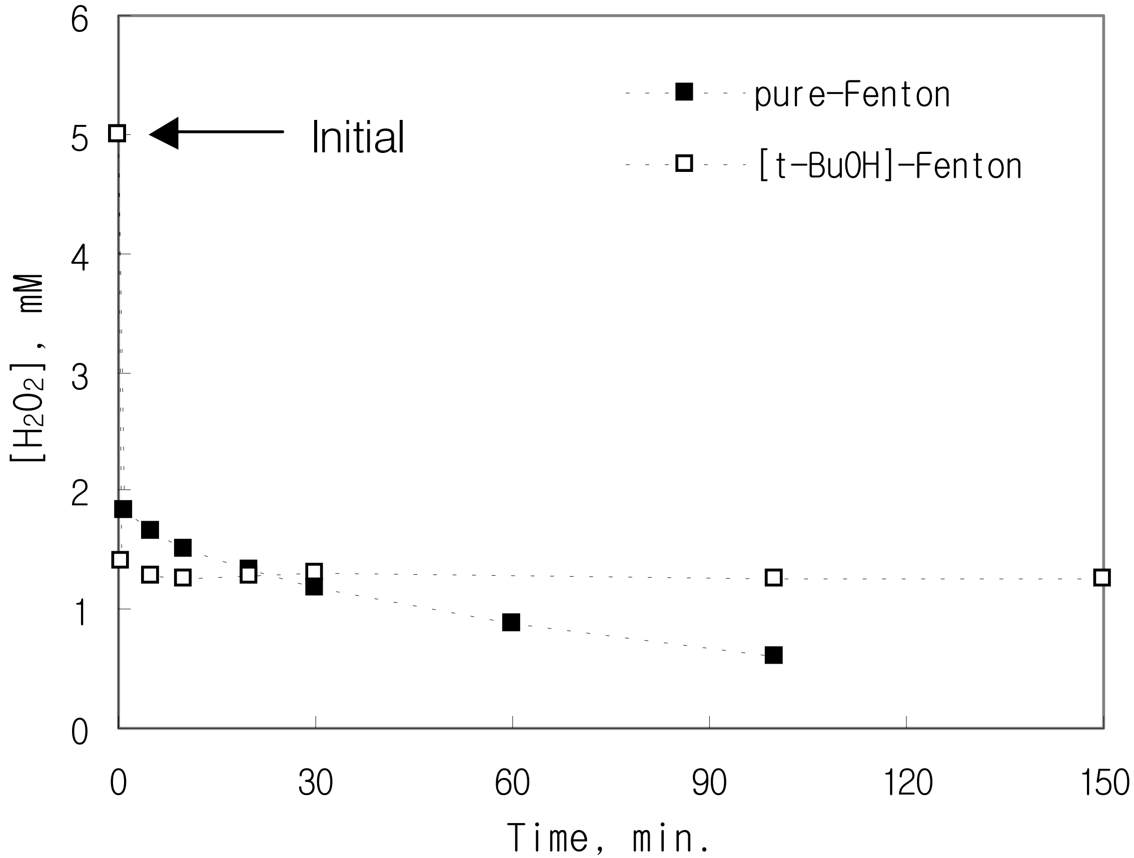
- **[t-BuOH] = 30 mM**

$$OH\bullet + t\text{-}BuOH \rightarrow R_{tB}\bullet + H_2O \qquad k_6 = 5.9\times10^8\ M^{-1}s^{-1}$$

**This makes the consumption ratio less than <u>2</u> ($[Fe^{2+}]/\triangle[H_2O_2] < 2$)**

- **In this condition, $H_2O_2$ was not detected in a few seconds after the beginning of reaction**

## Medium ratio of $[Fe^{2+}]_0/[H_2O_2]_0$( = 1 )




**$[Fe^{2+}]_0$ =5 mM( 280mg/L) , $[H_2O_2]_0$ = 5 mM( 170mg/L) ,**

**[t-BuOH] = 0 or 30mM**

# Two initiation reactions in Fenton reaction

## Medium ratio of $[Fe^{2+}]_0/[H_2O_2]_0$ ( = 2 )

- **Ferrous system**

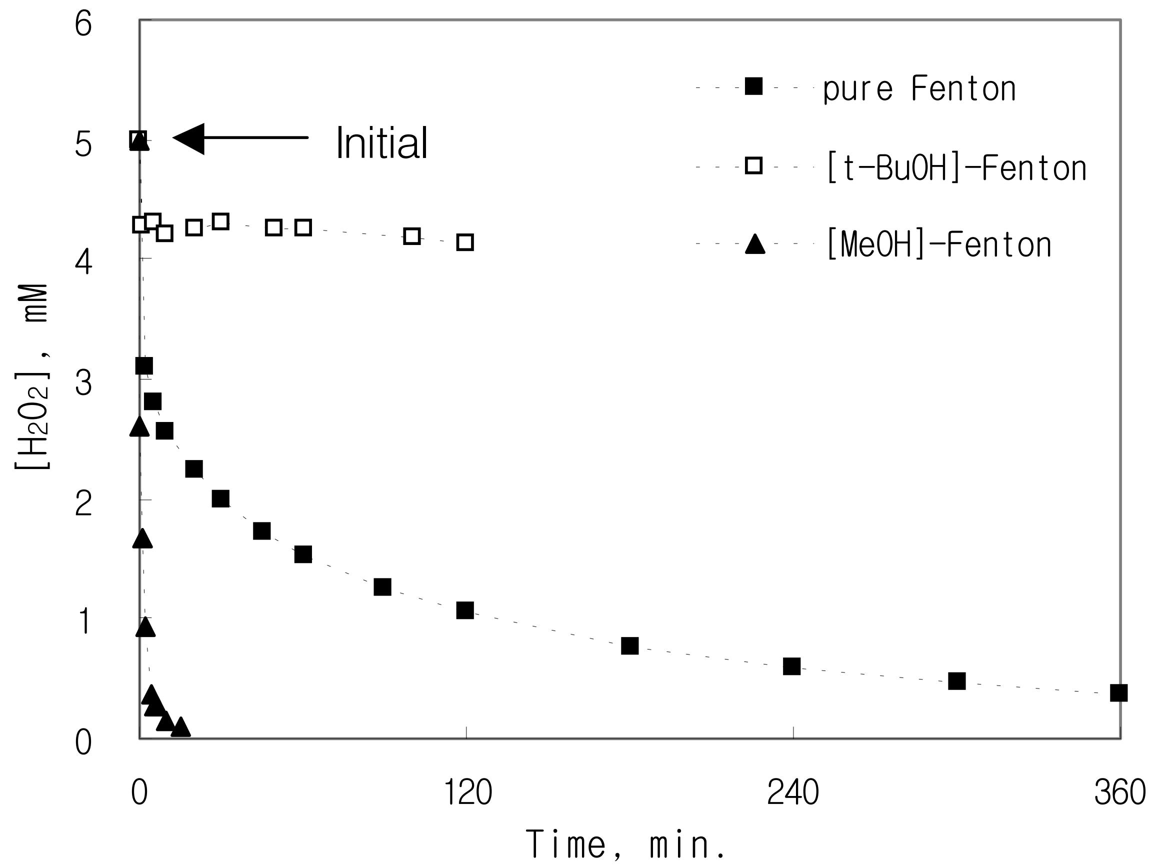
  : $Fe(II) + H_2O_2 \rightarrow Fe(III) + OH\bullet + OH^-$ $k_A \approx 70\ M^{-1}s^{-1}$

- **Ferric system**

  : $Fe(III) + H_2O_2 \rightarrow Fe(II) + HO_2\bullet$ $k_{app} \approx 0.01\ M^{-1}s^{-1}$

- **In case of $[Fe^{2+}]_0/[H_2O_2]_0 < 1$, $[Fe^{2+}]_0$ can't decompose all $[H_2O_2]_0$ in the early stage of Fenton reaction.**
- **Therefore, residual $[H_2O_2]$ decomposes slowly through Ferric system in the absence of [t-BuOH].**
- **However, in the presence of [t-BuOH], the decomposition of residual $[H_2O_2]$ stops completely.**

# Low ratio of $[Fe^{2+}]_0/[H_2O_2]_0$( << 1 )

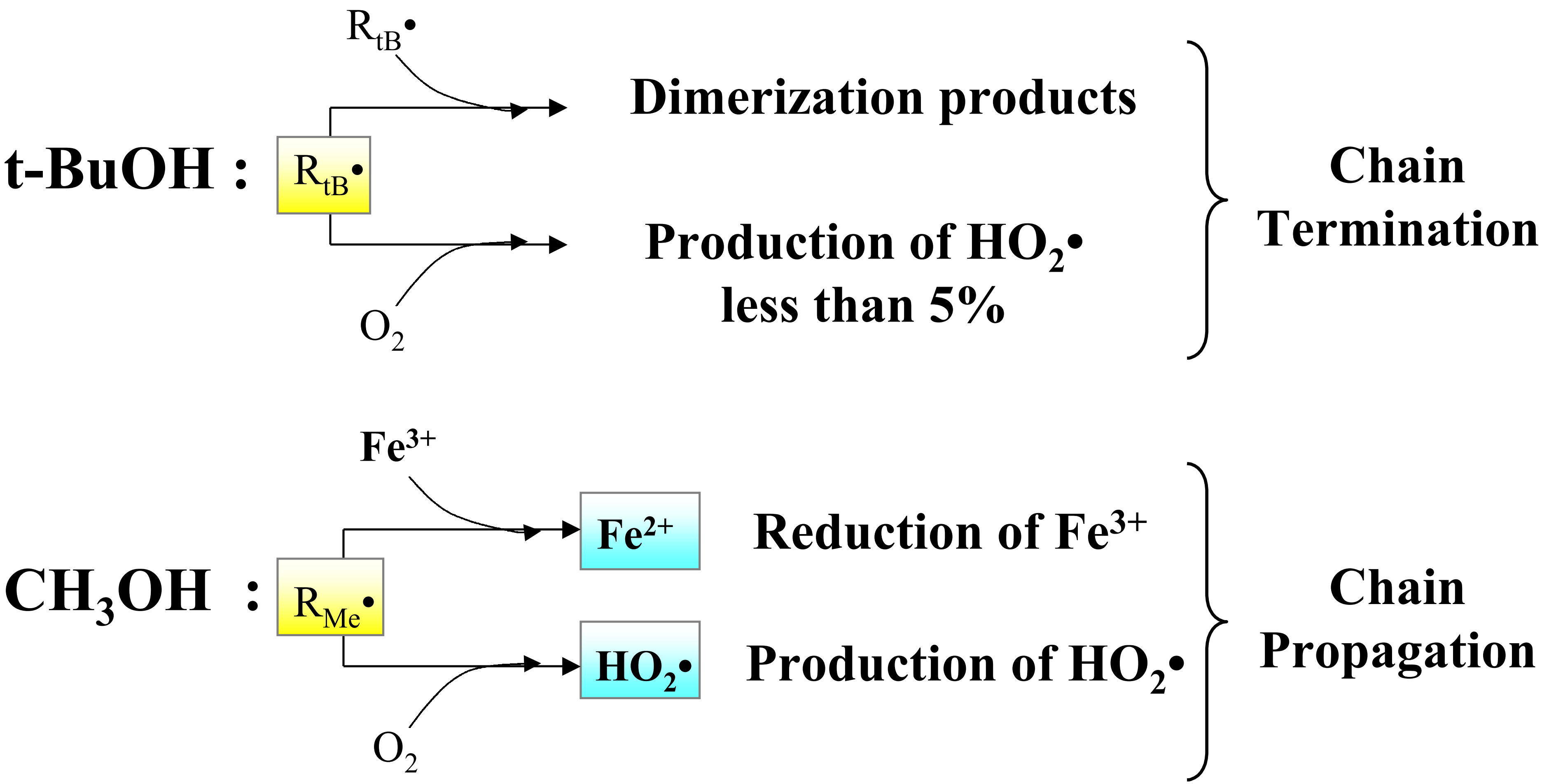



**$[Fe^{2+}]_0$ =1 mM( 56mg/L) , $[H_2O_2]_0$ = 5 mM( 170mg/L) ,**

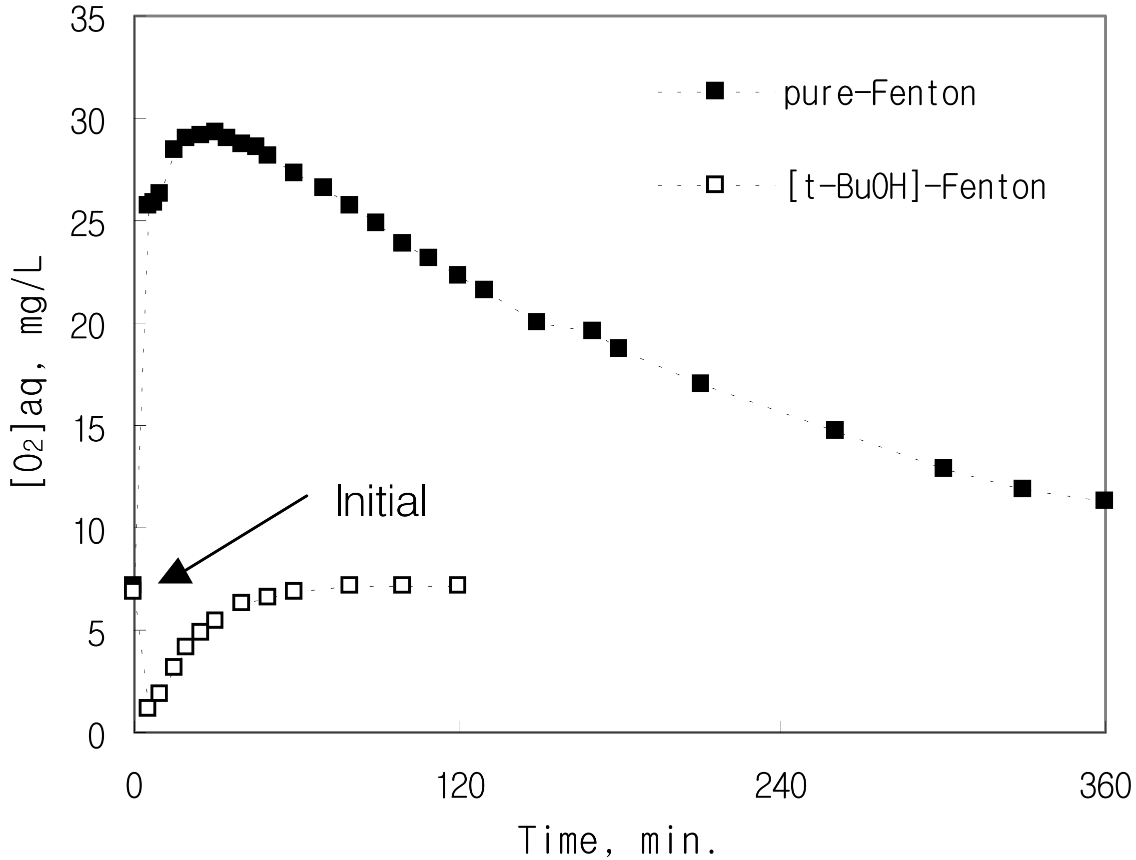
**$[t\text{-}BuOH]_0$ = 0 or 30mM, $[MeOH]_0$ = 0 or 30 mM**

# Two different roles of organics

**Low ratio of $[Fe^{2+}]_0/[H_2O_2]_0$ ( = 2 )**



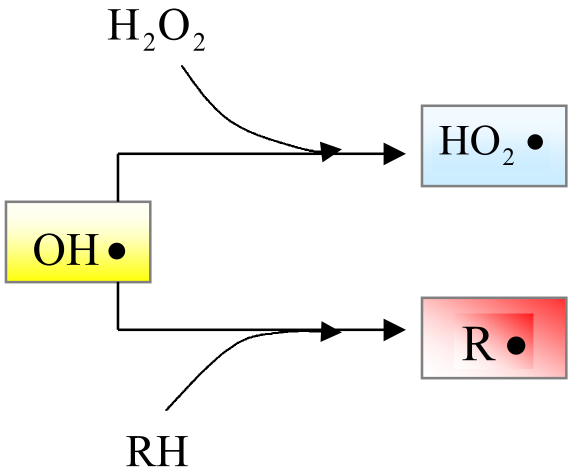
# Role of oxygen in Fenton system




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

**[t-BuOH] = 0 or 30mM**

# Production and consumption of dissolved oxygen




☞ $HO_2\bullet + Fe(III) \rightarrow Fe(II) + O_2 + H^+$

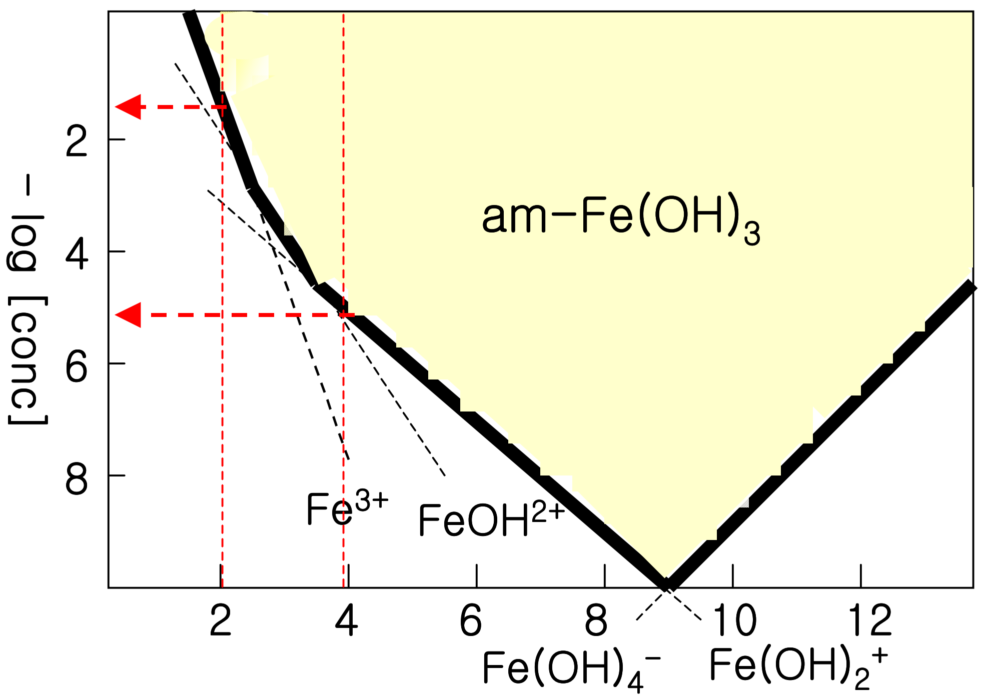
**Oxygen evolution in the absence of organics**

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

**Oxygen depletion in the presence of organics**

- **Instantaneous depletion of dissolved oxygen occurs in the condition of high reagents and organics**
- **It can has a great impact on oxidation products in Fenton system**

# Precipitation of ferric ion




< Solubility equilibria of amorphous $Fe(OH)_3$ (s) >

- **In using high conc. of iron ( > 10mM), the precipitation of ferric ion can occur even at acidic pH ( 2 ~ 4 )**
- **Losing ability to decompose $H_2O_2$**
- **Coagulation effects for organic removal**

# Conclusion

- In high $[Fe^{2+}]_0$ ( $\geq$ 1mM )
  - Scavenging effect by $Fe^{2+}$ for OH•
  - Instantaneous depletion of oxygen
  - Precipitation of ferric ion (iron sludge)

- In low(catalytic) $[Fe^{2+}]_0$ or $[Fe^{3+}]_0$ ( < 1mM)
  - Importance of R•'s reaction pathway (relatively slow reaction)

# 2. 폐수 성상(용존 유기물의 양과 특성)에 따른 반응 특성 고찰 ( low iron concentration, < 1mM )

- **Decomposition of $H_2O_2$ by ferric ion (Walling's kinetic scheme, 1973)**

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

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

$OH\bullet + H_2O_2 \rightarrow HO_2\bullet + H_2O$

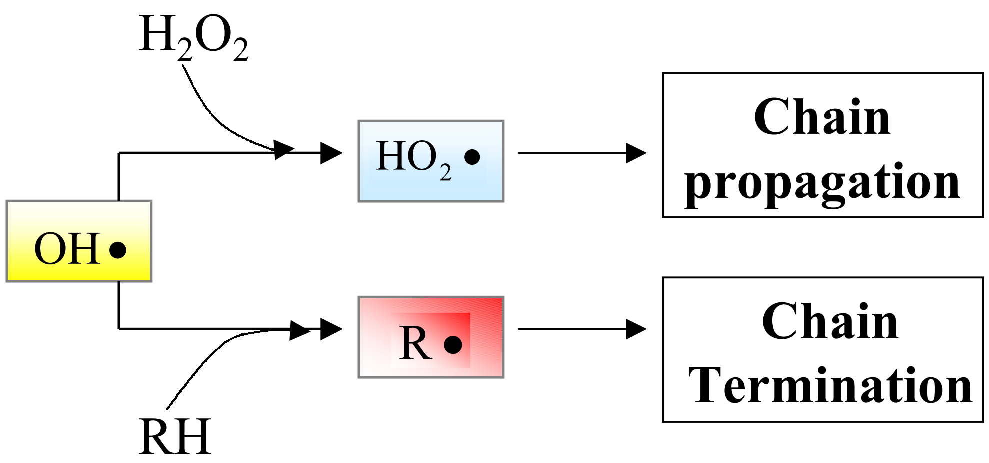
$HO_2\bullet + Fe^{3+} \rightarrow O_2 + Fe^{2+} + H^+$

$HO_2\bullet + Fe^{2+} \rightarrow HO_2^- + Fe^{3+}$

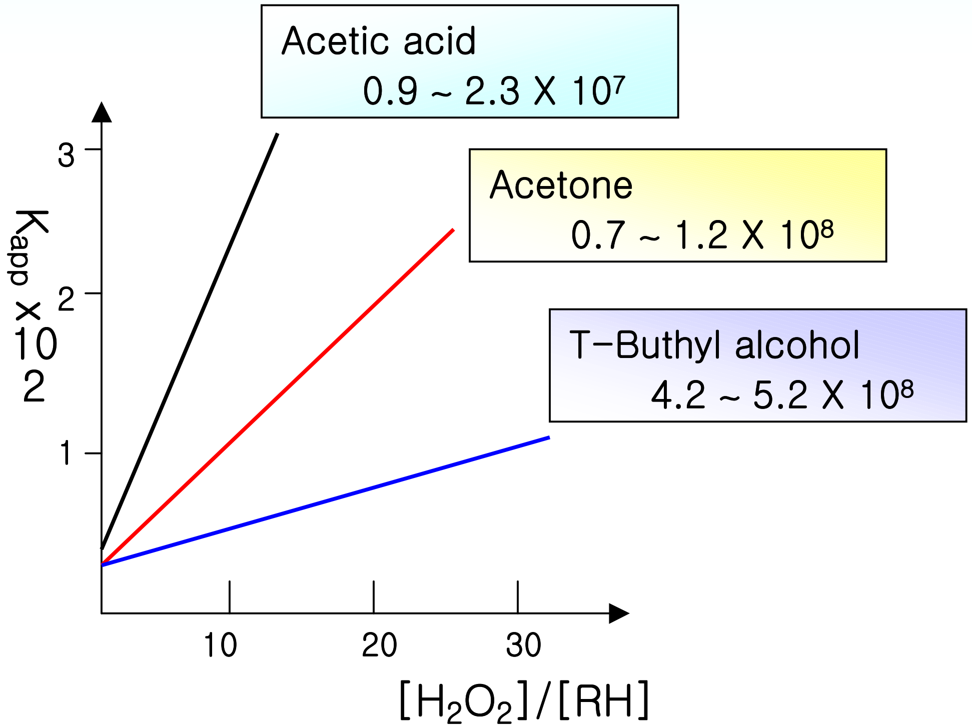
$OH\bullet + RH \rightarrow H_2O + R\bullet$

$R\bullet + O_2 \rightarrow RO_2\bullet$

$RO_2\bullet + Fe^{2+} \rightarrow RO_2^- + Fe^{3+}$



# Walling's kinetic scheme




- 보충되어야 할 점
  - 유기물 라디칼의 reducing effect
  - 유기물과 철 이온의 착물 형성
  - Aromatic 화합물의 영향

$$\frac{-dLn[H_2O_2]}{dt} = 2k_1[Fe^{3+}]\times(1+\frac{k_3}{k_6}\frac{[H_2O_2]}{[RH]})$$

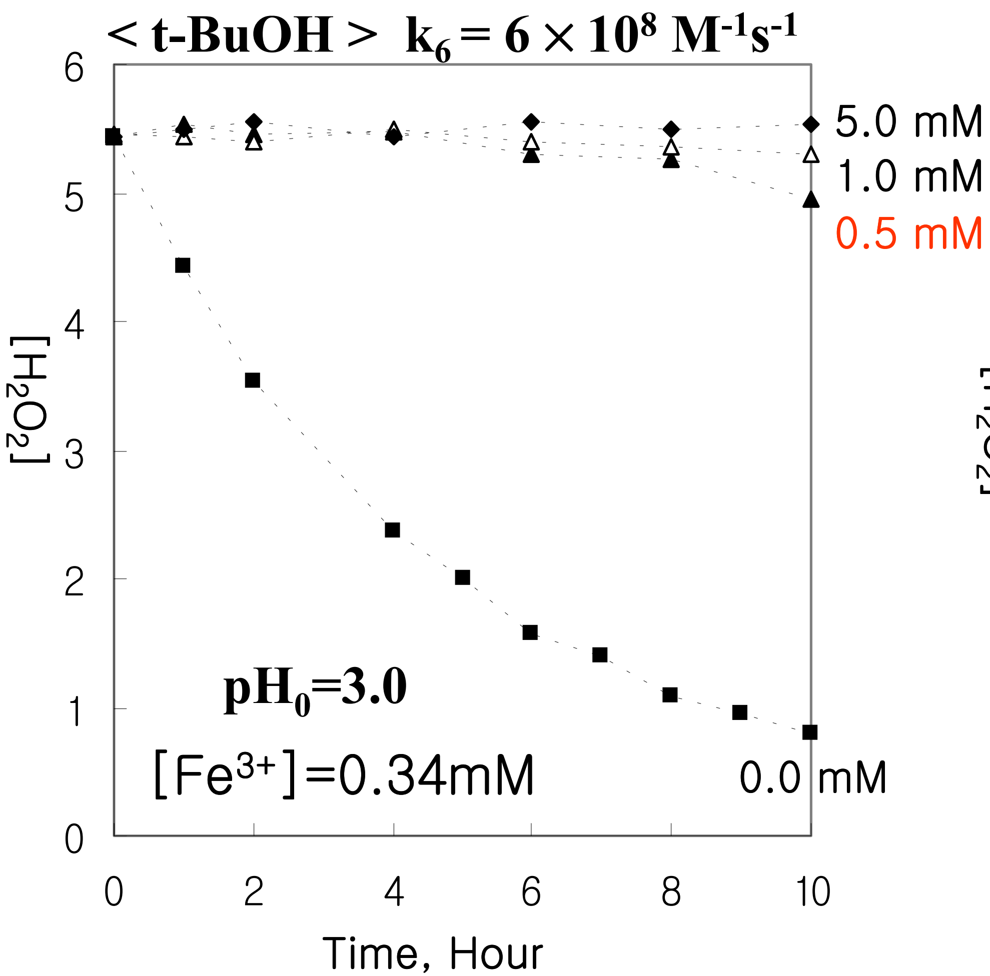
$$\frac{k_{app}}{[Fe^{3+}]} = 2k_1\,(1+\frac{k_3[H_2O_2]}{k_6[RH]})$$

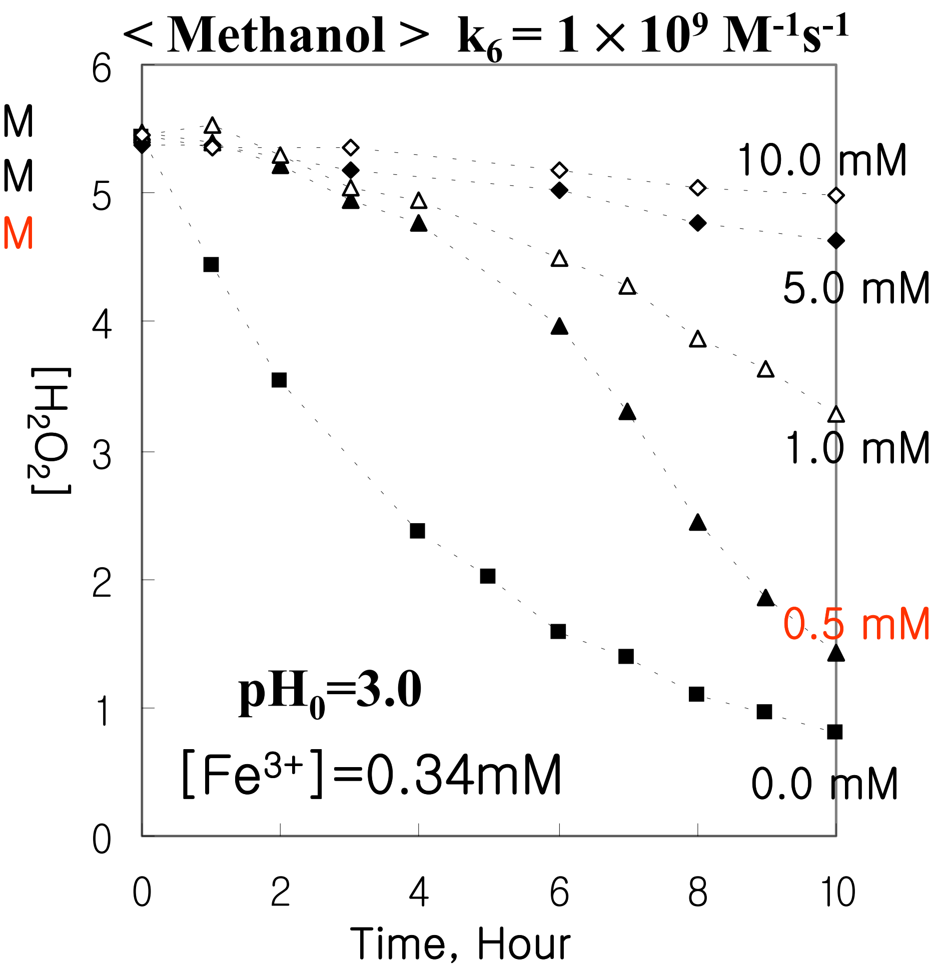
$k_1$ = $Fe^{3+}$ + $H_2O_2$

$k_3$ = $H_2O_2$ + OH• , 3 ×$10^7$

$k_6$ = RH + OH•

- **Simple aliphatic alcohol ( tert-buthyl alcohol and methanol )**



## Simple aliphatic alcohol ( tert-buthyl alcohol VS methanol )

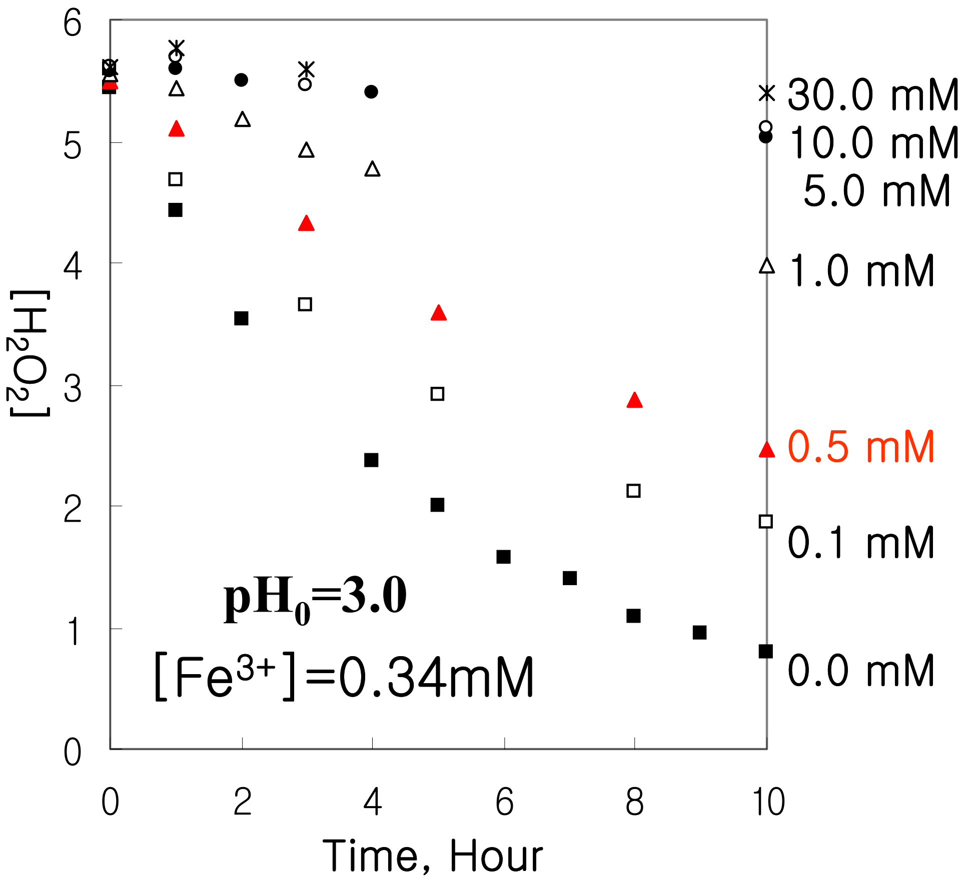
- t-BuOH
  - complete OH• scavenger :β-hydroxy alcohol (inert)

- Methanol
  - partial OH• scavenger :α-hydroxy alcohol

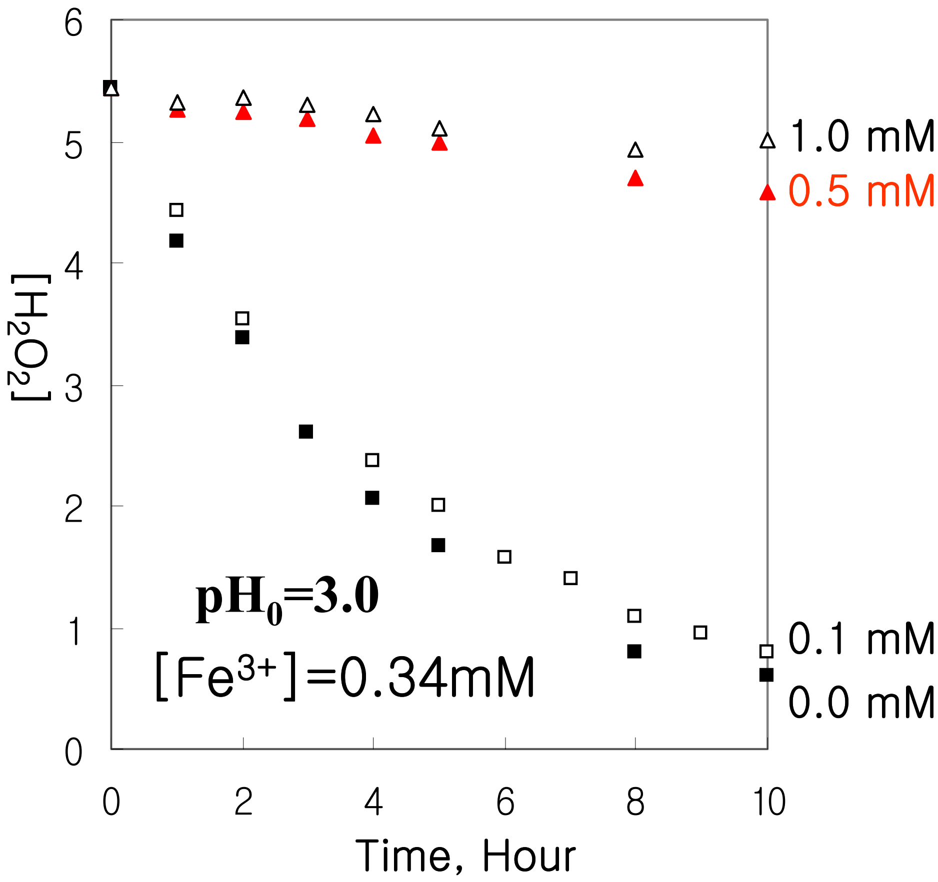
| | |
|---|---|
| $\bullet CH_2OH + Fe^{3+} \rightarrow CH_2O + Fe^{2+}$<br>$\bullet O_2CH_2OH \rightarrow HO_2\bullet + CH_2O$ | **Radical chain propagation** |
| $\bullet O_2CH_2OH + Fe^{2+} \rightarrow HOOCH_2OH + Fe^{3+}$ | **Radical chain termination** |

## Simple aliphatic acids ( Acetic acid and Oxalic acid )

< Acetic acid > $k_6 = 2 \times 10^7$ $M^{-1}s^{-1}$




< (H)oxalate ion > $k_6 = 4 \times 10^7$ $M^{-1}s^{-1}$



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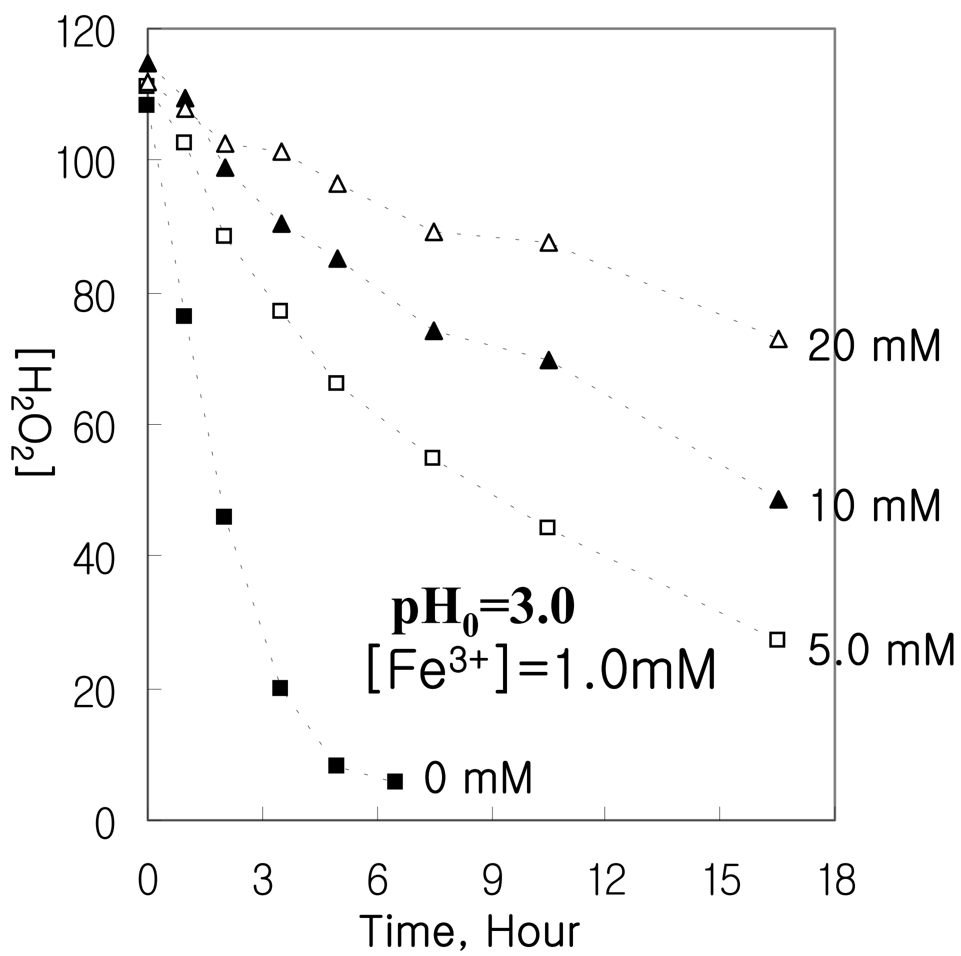


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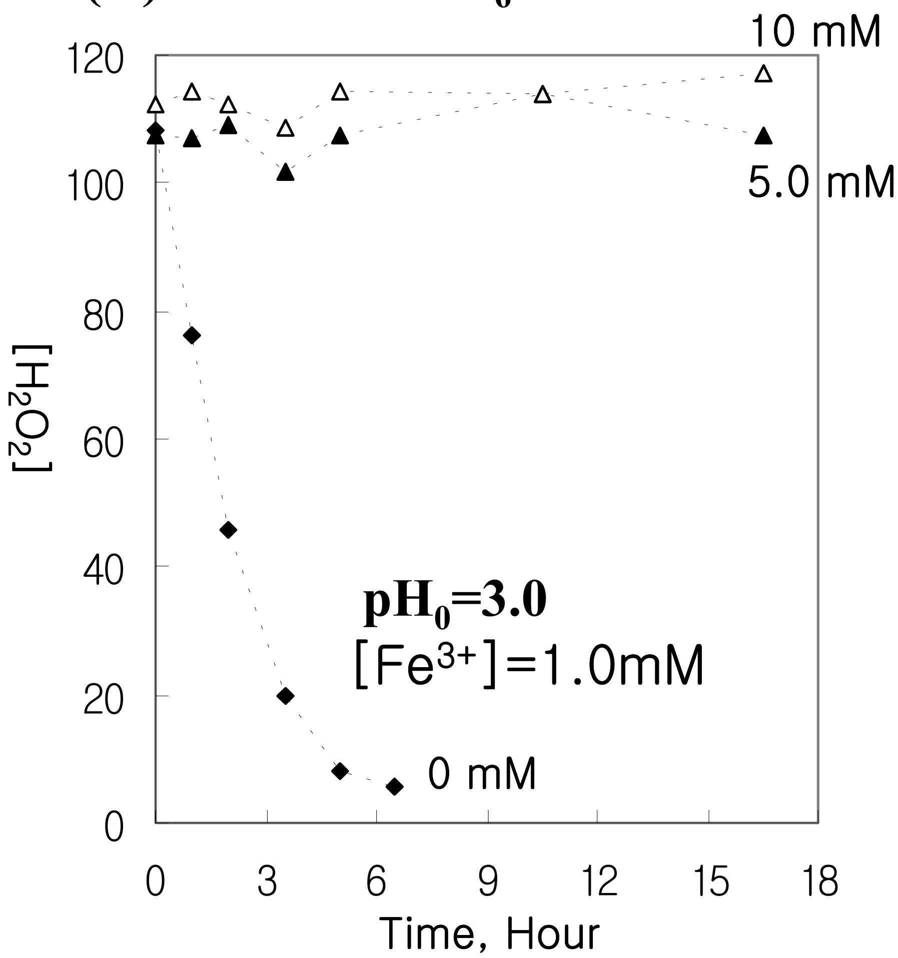
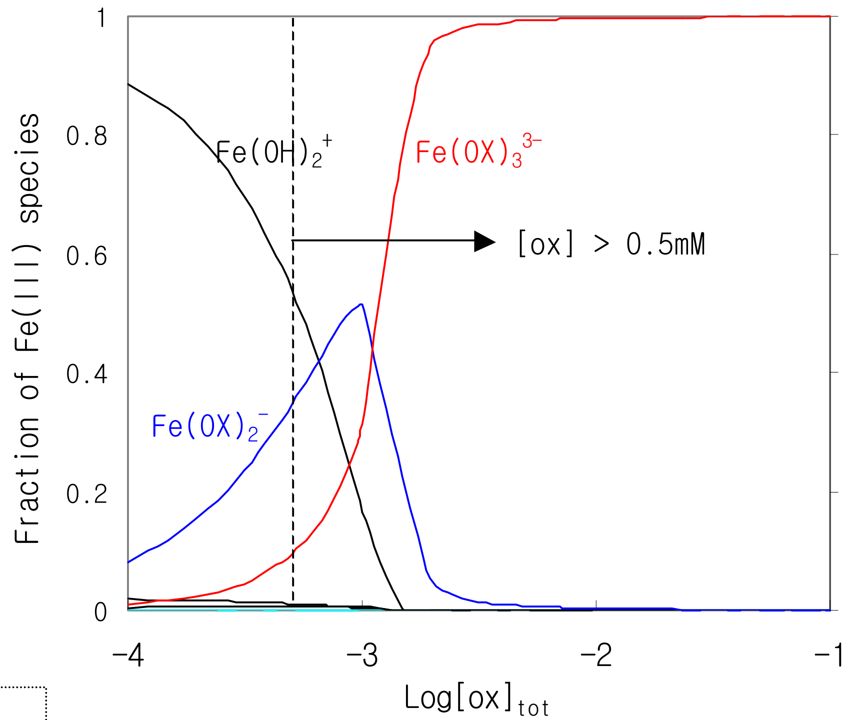


# Simple aliphatic acids ( Acetic acid VS Oxalic acid )

- **Acetic acid**
  - **complete OH• scavenger**
    **: reducible radical**

- **Oxalic acid (hydrogen oxalate ion)**
  - **complete OH• scavenger**
  - **formation of strong ferric-oxalato complex**

| | |
|---|---|
| $Fe^{3+} + C_2O_4^{2-} \rightarrow Fe(C_2O_4)^+$ | K1 |
| $Fe(C_2O_4)^+ + C_2O_4^{2-} \rightarrow Fe(C_2O_4)_2^-$ | K2 |
| $Fe(C_2O_4)_2^- + C_2O_4^{2-} \rightarrow Fe(C_2O_4)_3^{3-}$ | K3 |

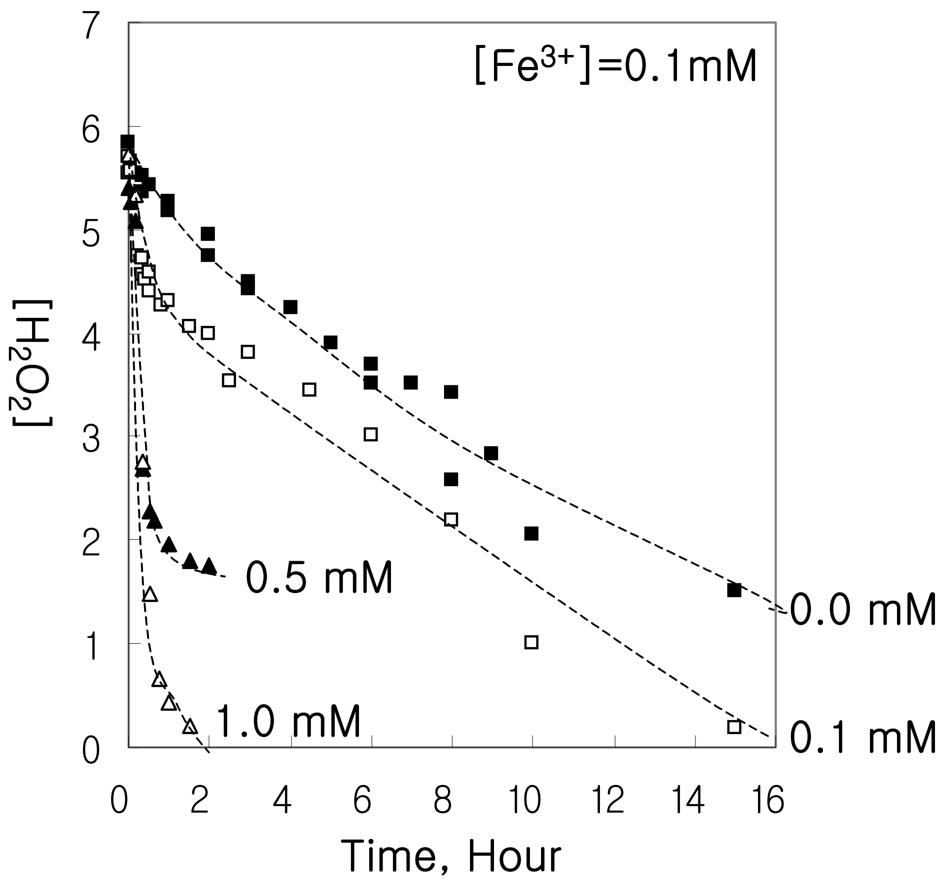


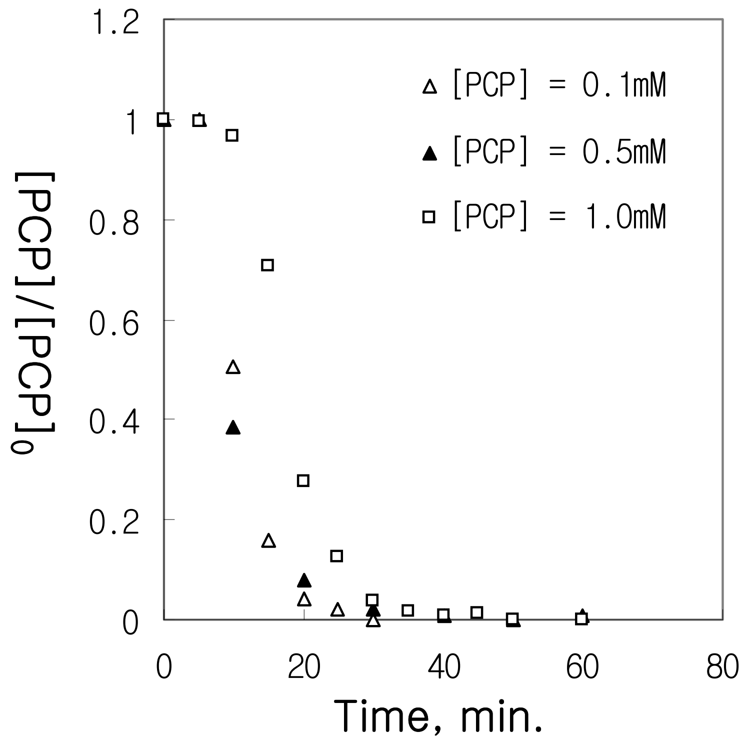

< Mole-fraction distribution of the iron(III)-oxalate complexes.>

298K, pH 3, [Fe(III)] = 0.5mM
OX = oxalate

- **Phenolic compounds (para-chlrorphenol (PCP))**

**< P-CP > $k_6 = 6.0 \times 10^9\ M^{-1}s^{-1}$**



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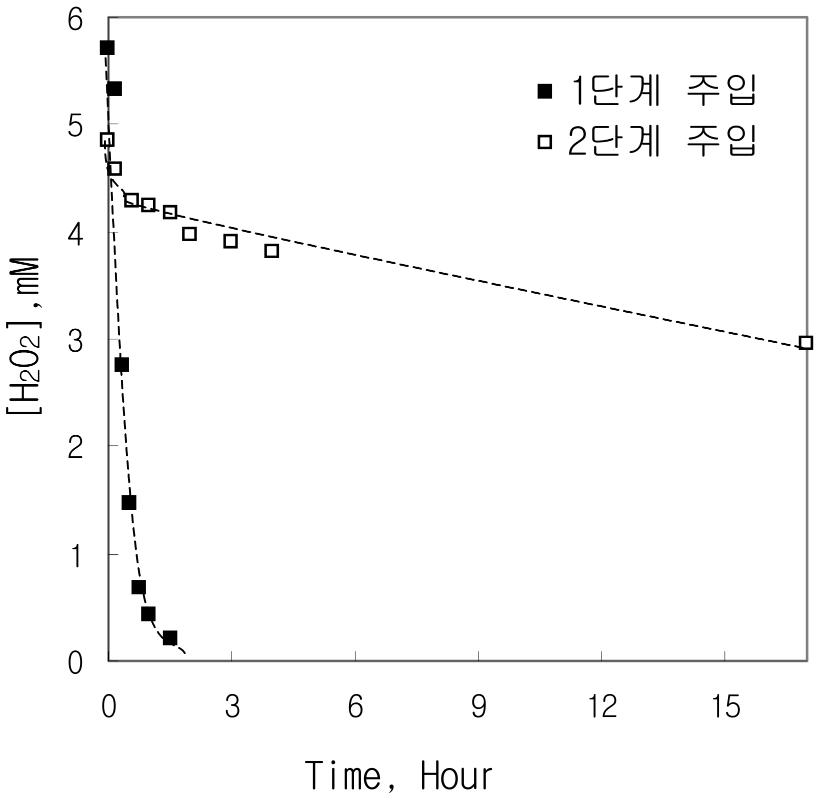
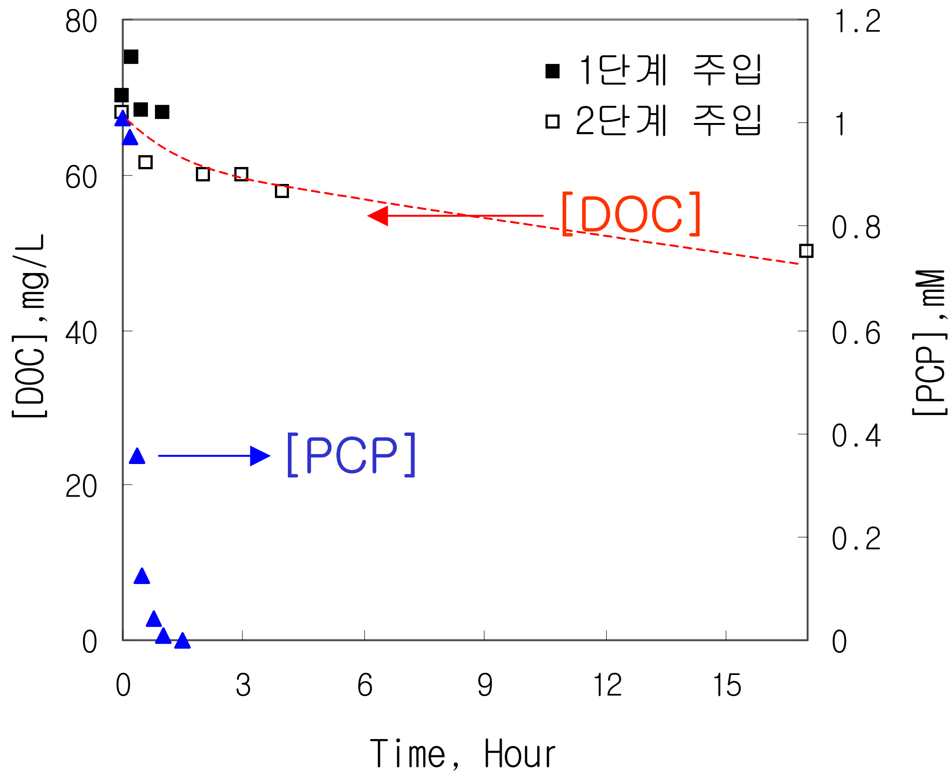
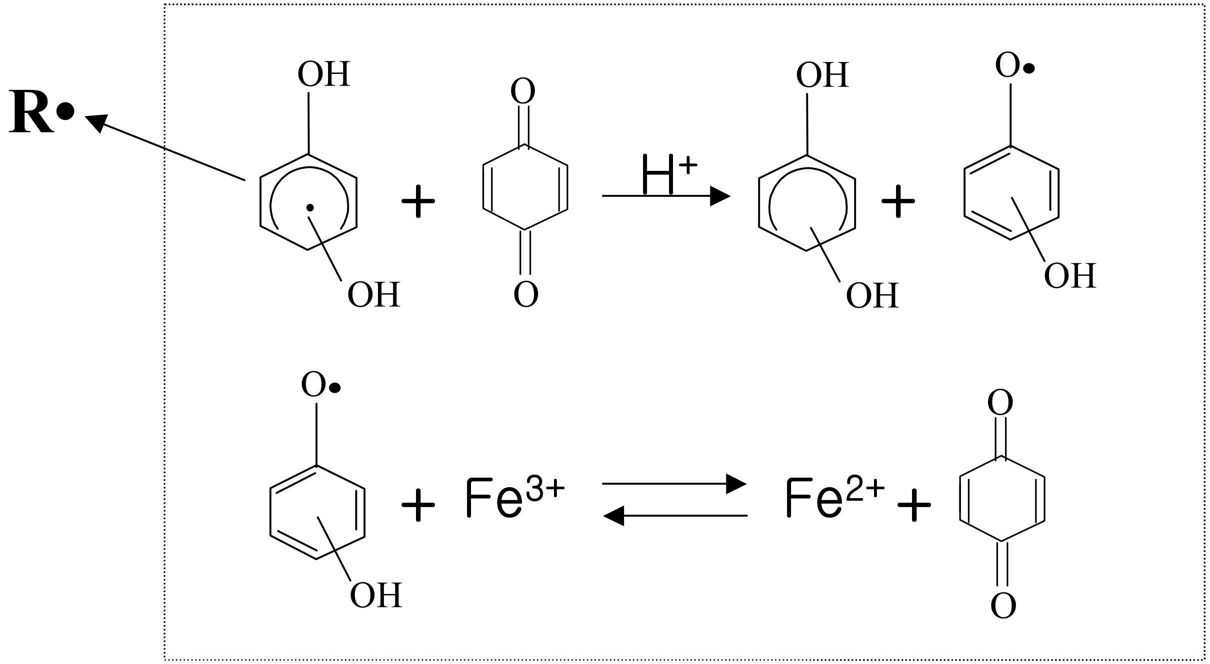



$[Fe^{3+}]_0$=0.1mM , $[PCP]_0$ = 1.0 mM,

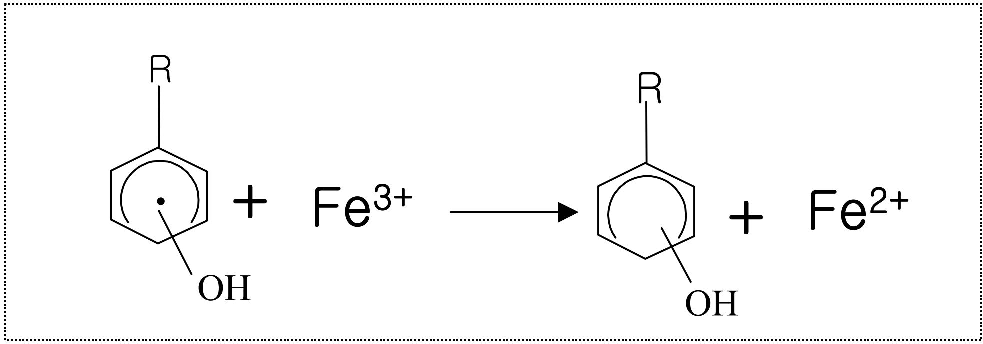
- **Phenolic compounds (para-chlrorphenol (PCP))**
  - **Promotion of iron-redox cycles ( Fe(III) ⇒ Fe(II) )**

**1. Role of quinone-intermediates (Pignatello J.J., 1997)**



- **Phenolic compounds (para-chlrorphenol (PCP))**
  - **Promotion of iron-redox cycles ( Fe(III) ⇒ Fe(II) )**

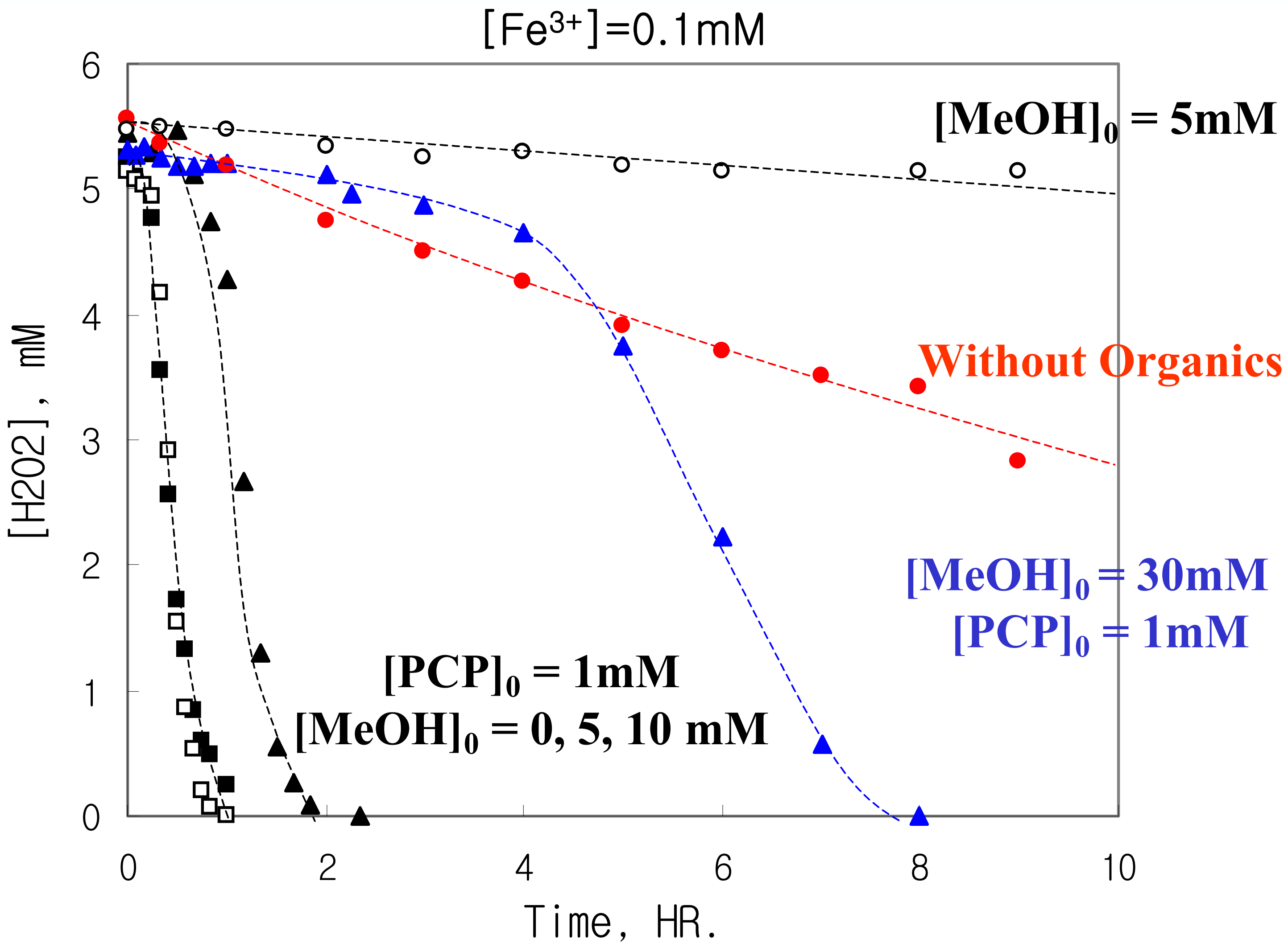
**2. Role of cyclohexadienyl radical**



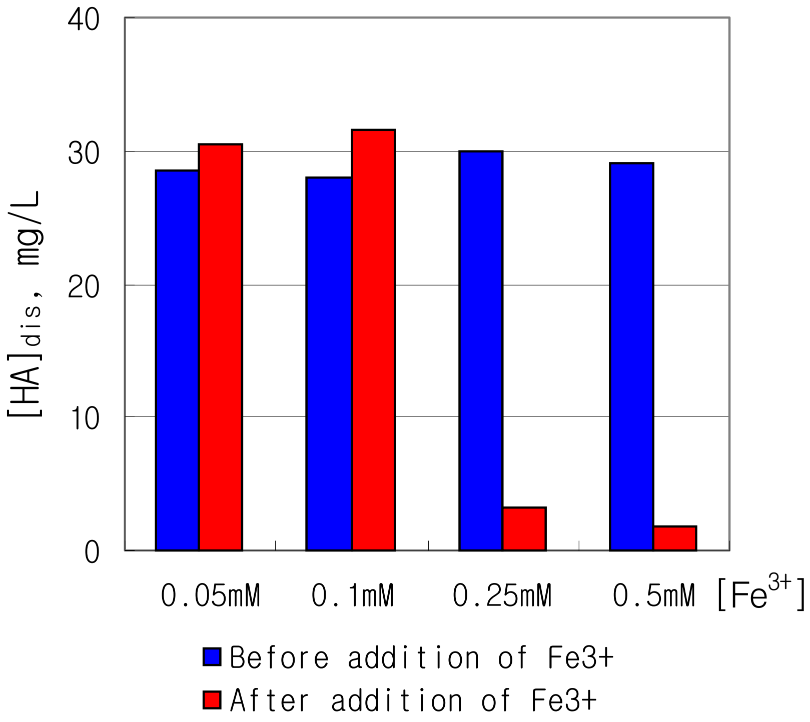

- Phenolic compounds → Ring-opened Products

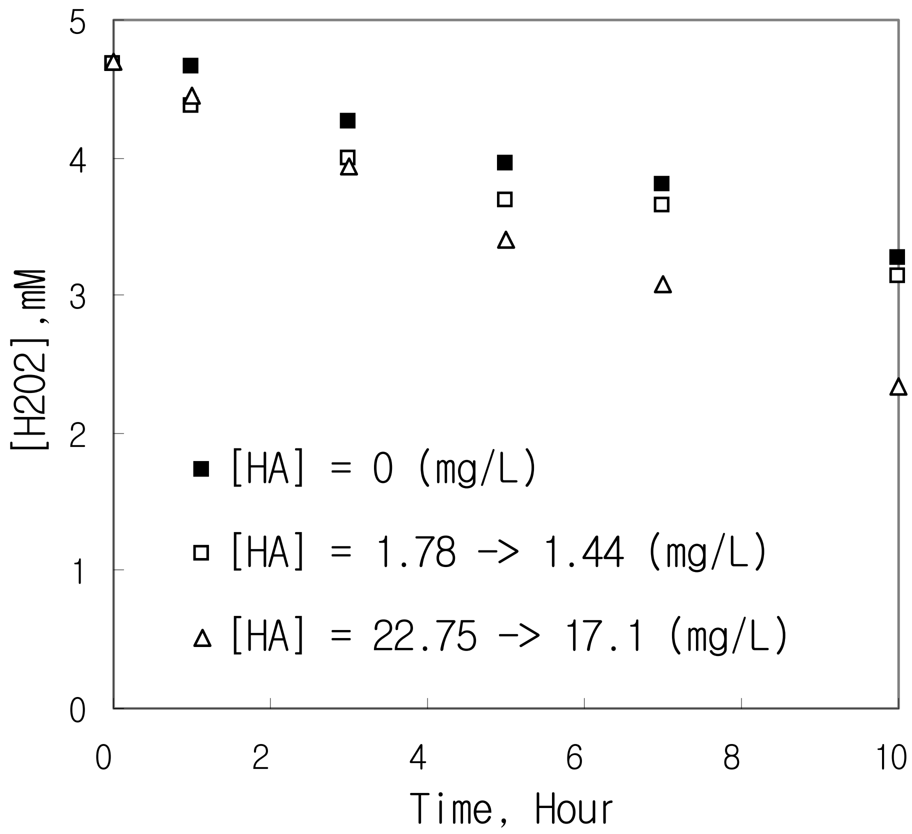
  Promotor → Scavenger

- **Phenolic(PCP) + Alcohol(Methanol) compounds**



# Humic acid (Commercial (Fluka))




pH = 3.0 ± 0.1

$[Fe^{3+}]$ = 0.1mM

- **Humic acid (Commercial (Fluka))**

- **Precipitation of humic acid at high [Fe(III)] ( > 0.25mM, pH=3.0)**
  - **Removal of metal ion makes humic acid soluble even at pH = 1.0 ( Jansen S. et al., 1996)**
  - **Cations associates with anionic groups on the humic acid, drawing the humic acid molecule together and enhances the formation of hydrophobic pseudo-micelles ( pH = 6.9 ~ 7.2, Engebretson., 1998 )**

- **Humic acid as <u>promoter</u> or <u>scavenger!</u>**
  - **Various functional groups**
    **phenol, quinone : promotor , carboxylic, carbonyl : scavenger**
  - **Humic acdis are typically insoluble to any measurable degree at pH < 4**

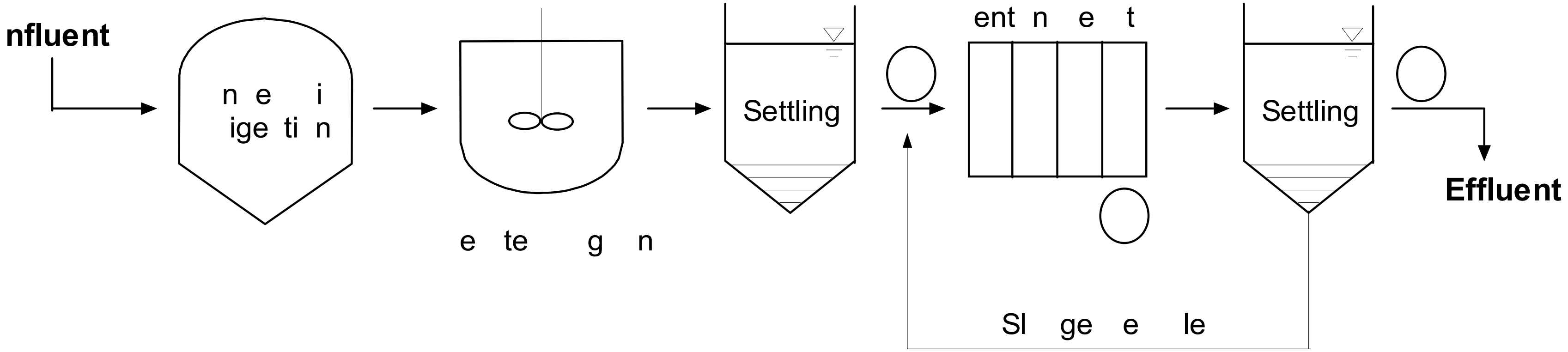
# Conclusion

- **Aliphatic alcohol and Acids**
  - **Retardation the decomposition rate of $H_2O_2$**
  - **t-BuOH, Acetic acid : Complete OH• scavneger**
  - **Methanol : Partially OH• scavenger**
  - **Oxalic acid : inert ferric-oxalic complex**

- **(chloro)Phenol**
  - **Promotion the decomposition rate of $H_2O_2$**
  - **Oxidative intermediates (ring-opened products) retard again the decomposition rate of $H_2O_2$**

- **Humic acid**
  - **Precipitation of humic acid at high [Fe(III)] ( $\geq$ 0.25mM, pH = 3 )**
  - **Small effect for the decomposition rate of $H_2O_2$ (in our experimental condition)**

# 3. Roles of oxidation and coagulation in Fenton process for the removal of organics in landfill leachate




< Schematic of the leachate treatment process (A,B,C : sampling point>

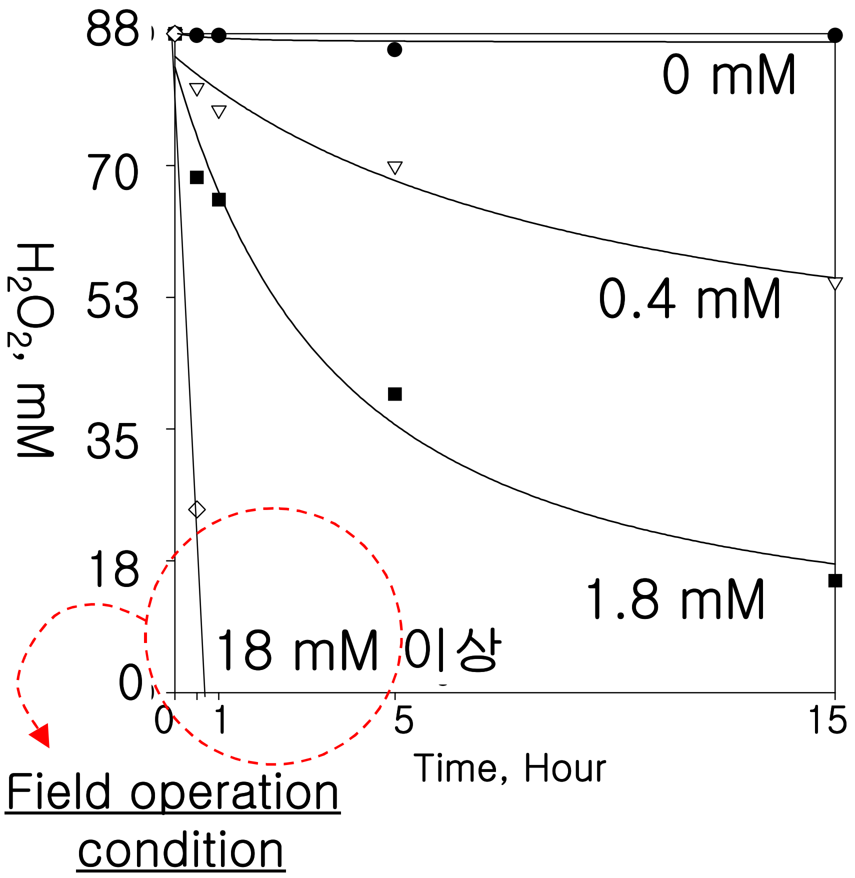
- Operation in six years (97년 기준)
- Fresh leachate, TOC :1000 ~ 1500 mg/L
  BOD : 1500 ~ 3000 mg/L
  COD : 4000 ~ 7200 mg/L
- Influent of the Fenton process, TOC : 229 ~ 494 mg/L

# Characteristics of landfill leachate

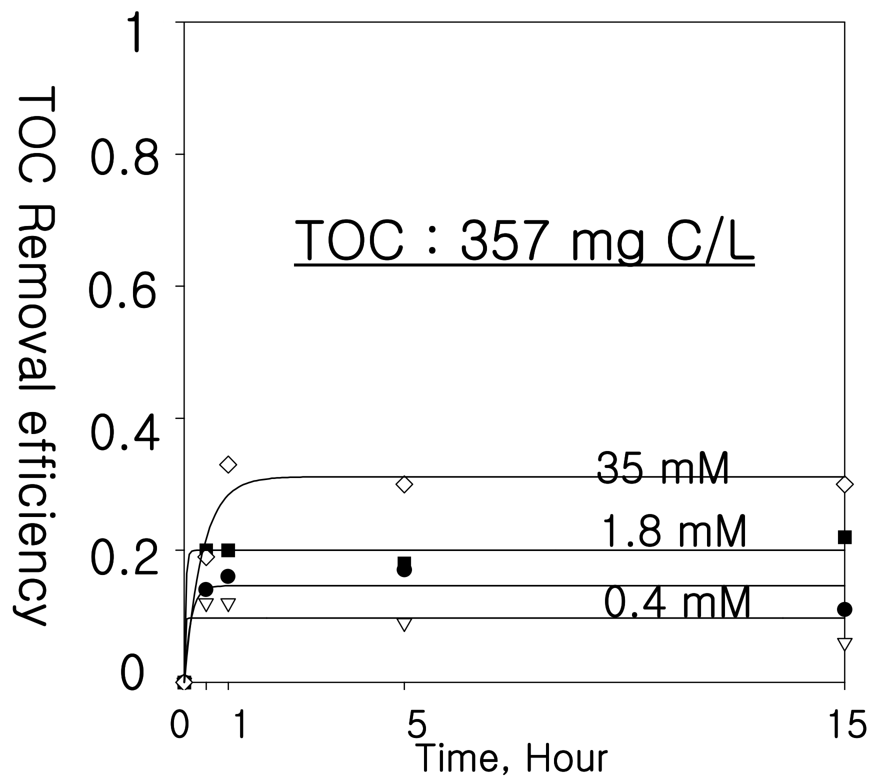
| Sample ID | Sampling point | Organics Characteristics | |
|---|---|---|---|
| | | TOC(mg C/L) | $COD_{cr}$(mg $O_2$/L) |
| F1 | A | 335 | 1020 |
| F2 | A | 341 | - |
| F3 | A | - | 1120 |
| F4 | A | 229 | 800 |
| | B | 277 | 840 |
| | C | 158 | 480 |
| F5 | A | 357 | 1040 |
| | B | 331 | 920 |
| | C | 89 | 368 |
| F6 | A | 320 | 920 |
| | B | 415 | 860 |
| | C | 100 | 372 |

| Other characteristics | |
|---|---|
| Parameter | Range |
| pH | 8.4~8.8 |
| BOD (mg/L) | 43 ~ 372 |
| T-N (mg N/L) | 949 ~ 1730 |
| Alkalinity (mg/L) | 7305 ~ 8673 |

# The decay of $H_2O_2$ (Fenton Oxidation)




Change of $H_2O_2$
as a function of $Fe^{2+}$



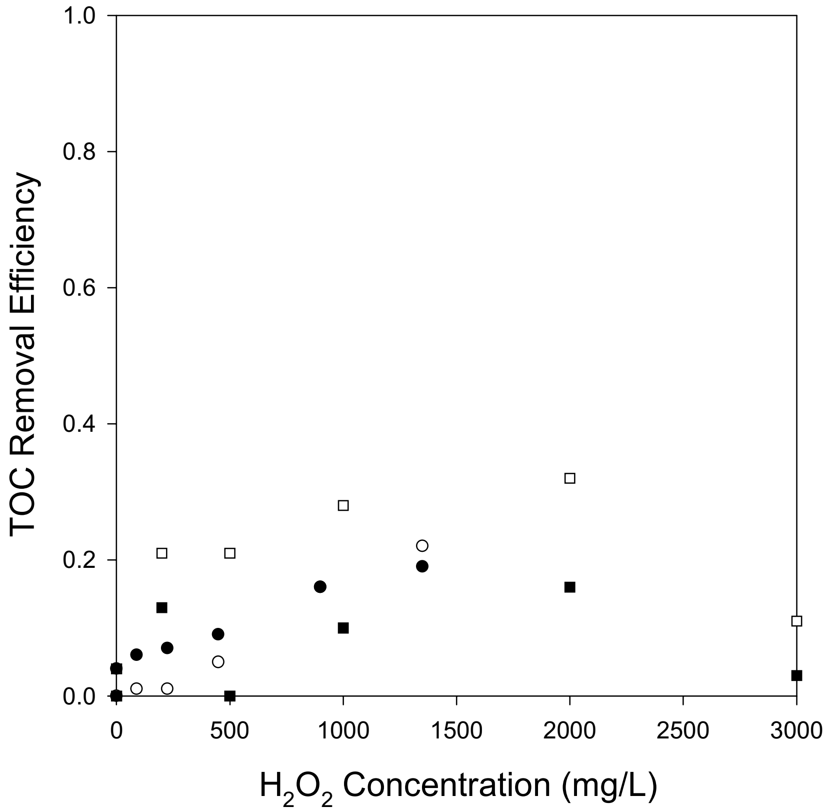

Change of TOC
as a function of $Fe^{2+}$

# Pathway of OH• in field operating condition

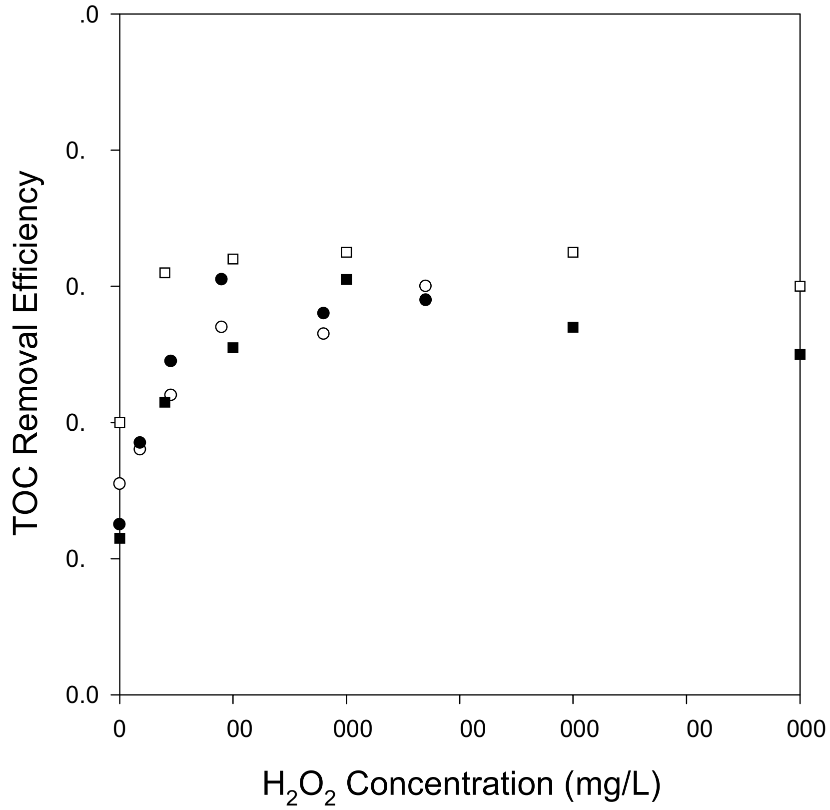
| OH• → | Initial conc. (mM) | Rate const. ($M^{-1}s^{-1}$) | Approximate |
|---|---|---|---|
| $Fe^{2+}$ | 18 | 3.2 X $10^8$ | |
| RH | 1 ~ 10 | 1.0 X $10^9$ | Below 50 % |
| | 30 ~ 300 g C/Mol<br>TOC = 300 mg/L | | |
| $H_2O_2$ | 88 | 3.2 X $10^7$ | |
| | Other unknown reaction<br>e.g. $Cl^-$ | | |

- $Fe^{2+}$ 와 $H_2O_2$ 는 소모되지만, 유기물은 제거되지 않는다.
- 유기물에 대한 정보 부족. (OH• 과의 반응 속도 상수)

# Effects of $H_2O_2$ conc. on TOC removal
# Oxidation VS Coagulation




< Oxidation >




< Coagulation >

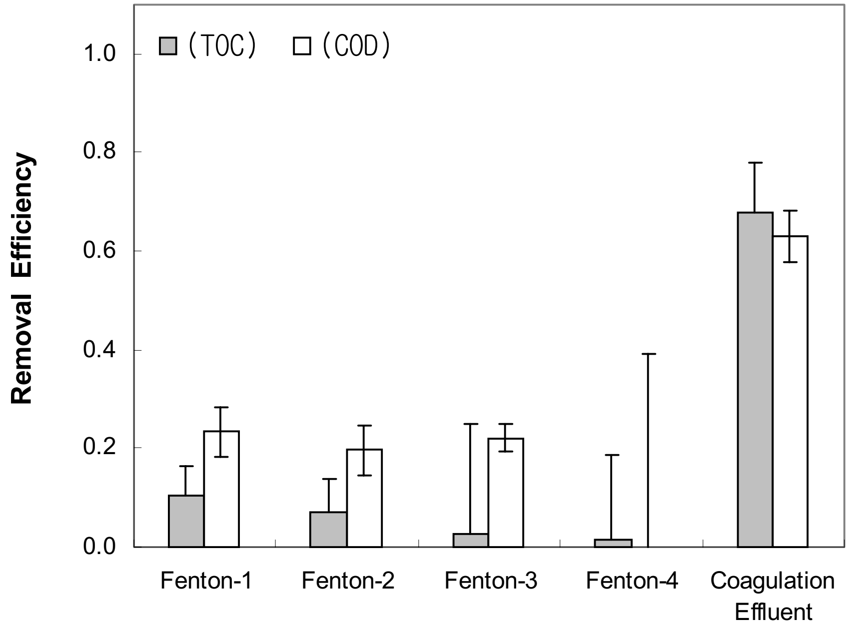
○ $[Fe^{2+}]$ = 22 mM[F1] □ $[Fe^{2+}]$ = 22 mM[F4-A]
● $[Fe^{2+}]$ = 44 mM[F1] ■ $[Fe^{2+}]$ = 44 mM[F4-A]

# Oxidation VS Coagulation

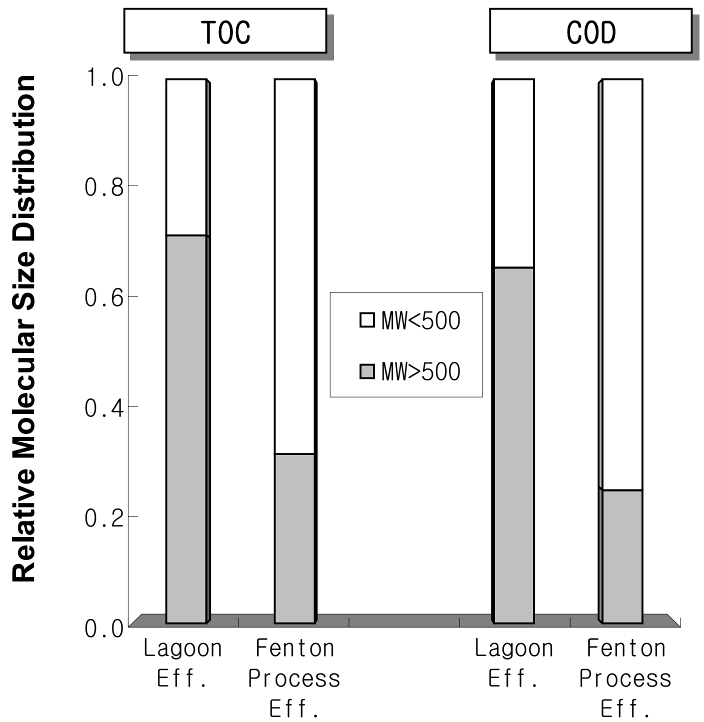
- Oxidation
  - Oxidation reaction is over within 60 min
  - Possibility of ferric precipitation or organic precipitation
  - Partial oxidation of large organic molecules
    ( low TOC removal efficiency : 10 ~ 30% )

- Coagulation
  - Most of the organics removed by the coagulation step
    not by oxidation step, 53 ~ 65%
  - Enhanced coagulation by $H_2O_2$,

# Investigation of Field Fenton process



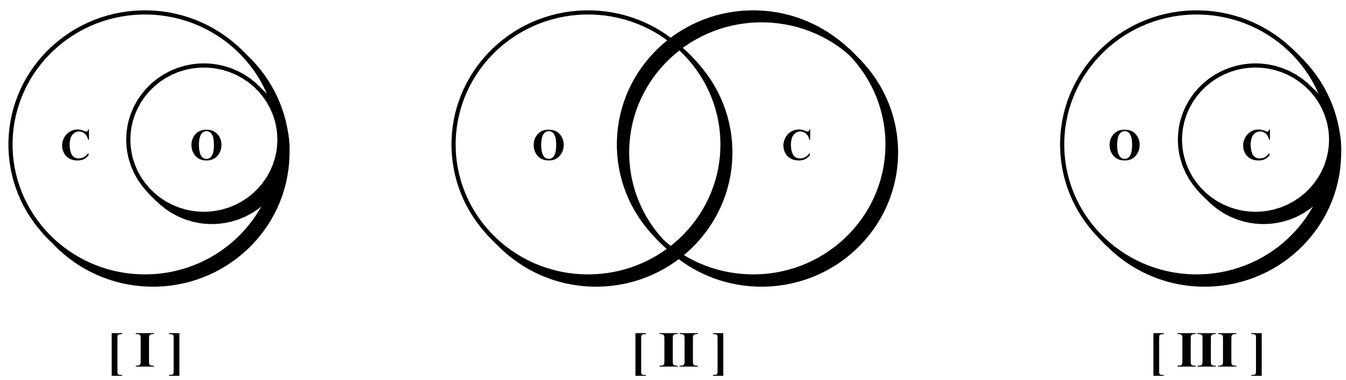

On-site organic removal by the Fenton Process as estimated with TOC and COD in samples F4 through F6




On-site change in Molecular size Distribution of organics as estimated with TOC and COD

# Conclusion

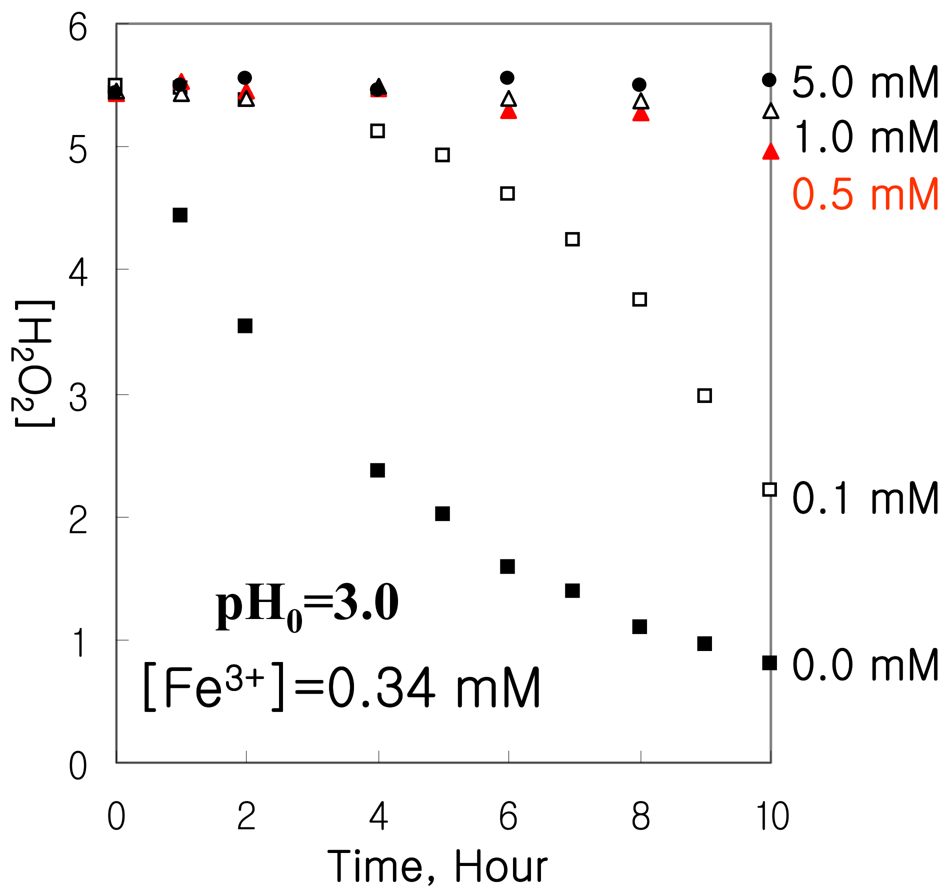
- Coagulation may serve a more significant organic removal process
- Fenton oxidation process (dark) is not appropriate for TOC removal in this $H_2O_2$ dose ( TOC : 300 mg/L , $H_2O_2$ : 88 mM )
- Condition of Landfill leachates treatment are typical of Type I




O : Oxidation in Fenton Process    C : Coagulation in Fenton Process

## Simple aliphatic alcohol ( tert-buthyl alcohol and methanol )

**< t-BuOH > $k_6 = 6 \times 10^8\ M^{-1}s^{-1}$**




**< Methanol > $k_6 = 1 \times 10^9\ M^{-1}s^{-1}$**