


Application of alkaline-activated persulfate to remediate organic contaminants in groundwater

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July 23, 2014

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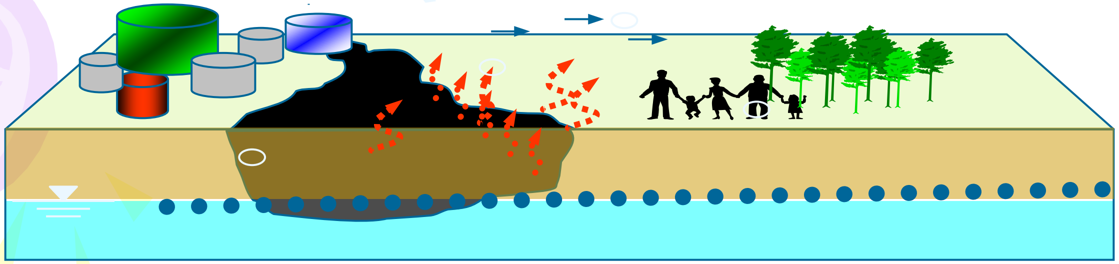


Introduction (1/5)

- Contamination of soil and groundwater by petroleum and chlorinated hydrocarbons (HC) has become a serious issue worldwide due to the large amount of use.
- Sources of petroleum HC contamination
  - Leakage of USTs and pipelines
  - Accidental spills
- Sources of chlorinated HC contamination
  - Discharge of wastewater
  - Inappropriate storage and disposal

Introduction (3/5)

- Groundwater remediation technologies
  - Chemical oxidation
  - Bioremediation
  - Pump and treat
  - Air sparging
  - Adsorption

- Chemical oxidation is a powerful remediation technology that is capable of destroying an extensive range of contaminants effectively.

Introduction (4/5)

Oxidants

- Hydrogen peroxide (Fenton's reagent, Fenton-like reaction)
- Ozone
- Permanganate
- Persulfate

Persulfate

- Chlorinated ethylenes
- Chlorinated ethanes
- Chlorophenols
- Bisphenol A
- PAHs
- Gasoline components
- Gasoline additives
- Various volatile organic compounds

Persulfate activation

- Persulfate can be thermally or chemically activated by initiators such as heat or transition metals (e.g., Fe^{2+}) to produce more powerful sulfate free radicals ($SO_4^{-}\cdot$).

Thermal activation

$$S_2O_8^{2-} + \text{heat} \rightarrow 2SO_4^{-}\cdot$$

$$SO_4^{-}\cdot + e^- \rightarrow SO_4^{2-} \quad E^0 = 2.6\ V$$

Chemical activation

$$Fe^{2+} + S_2O_8^{2-} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{-}\cdot$$

$$SO_4^{-}\cdot + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-}$$

$$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2\ SO_4^{2-}$$

Persulfate activation

- Heat
- Transition metals (Fe^{2+}, Ag^{+}, Cu^{2+}, Mn^{2+})
- Strong base (pH > 10)
- Fe-chelating agents (oxalic, citric, EDTA, NTA…)
- (n)ZVI
- UV
- Activated carbon (AC surface-OOH, AC surface-OH)

Introduction (6/6)

- Methyl tert-butyl ether (MTBE) and 1,2-dichloroethane (1,2-DCA) are commonly found groundwater pollutants.

- MTBE is widely used as a gasoline additive.

- 1,2-DCA is used for the production of vinyl chloride (VC).

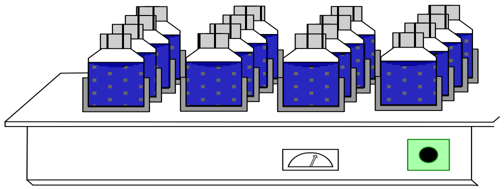
Objectives

- Determine the required pH for alkaline-activated persulfate.
- Evaluate the degradation efficiency of 1,2-DCA and MTBE by alkaline-activated persulfate.
- Evaluate the potential of industrial waste to drive alkaline-activated persulfate process.

Materials and Methods (1/4)

Batch Experiments

- Batch experiments were conducted to evaluate MTBE and 1,2-DCA removal by persulfate under different alkaline conditions (pH 10-13, 25 ^{o}C, 150 rpm).
- 50 mL serum bottles were used as reactors.
- Each bottle was filled with a mixed solution of the contaminant and persulfate.
- pH of the mixed solution was adjusted by NaOH.
- Basic oxygen furnace (BOF) slag was also used to evaluate its feasibility to increase pH.



Materials and Methods (2/4)

Table1. 1,2-DCA and MTBE degradation by PS under different pH

pH	Persulfate (%)	1,2-DCA or MTBE (mg/L)	NaOH/Persulfate (mole ratio)
3 (unactivated)	1	50	0：1
10			0.03：1
11			0.12：1
12			1.2：1
13			6：1

Materials and Methods (3/4)

Table 2. 1,2-DCA and MTBE degradation by PS with different dosages of BOF slag

Slag (g/L)	PS (%)	1,2-DCA or MTBE (mg/L)	Slag/Persulfate (Weight ratio)
0 (unactivated)	1	50	0：1
20			2：1
40			4：1
60			6：1
80			8：1
100			10：1

Materials and Methods (4/4)

Analysis

- 1,2-DCA, MTBE, and their degradation byproducts (vinyl chloride (VC), tributyl formate (TBF), tributyl alcohol (TBA)) were analyzed by GC-FID.
- VC was reconfirmed by GC-MS.
- Heavy metals (Cr, Cd, Zn, Ni, Pb, Cu) were analyzed by ICP-AES.

Results and Discussion (1/11)

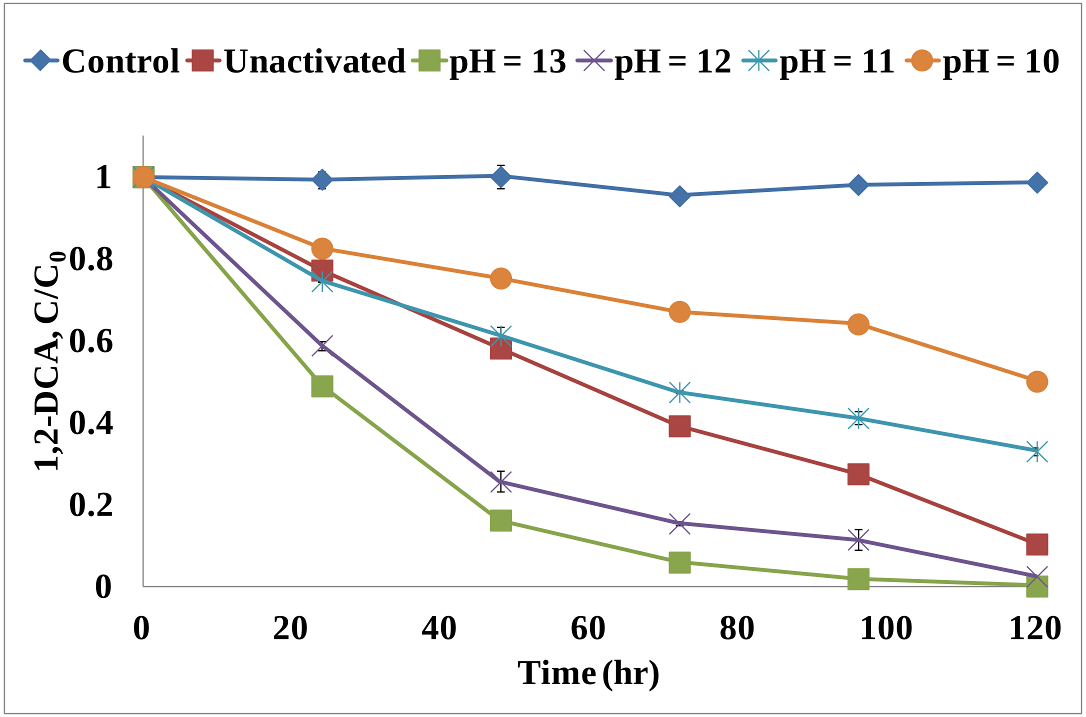


Fig. 1. 1,2-DCA removal by persulfate under different alkaline conditions

- 1,2-DCA degradation was increased with increasing pH under alkaline conditions.
- 1,2-DCA removal was stalled at pH 10 and 11.
- 1,2-DCA degradation was enhanced with pH higher than 12.

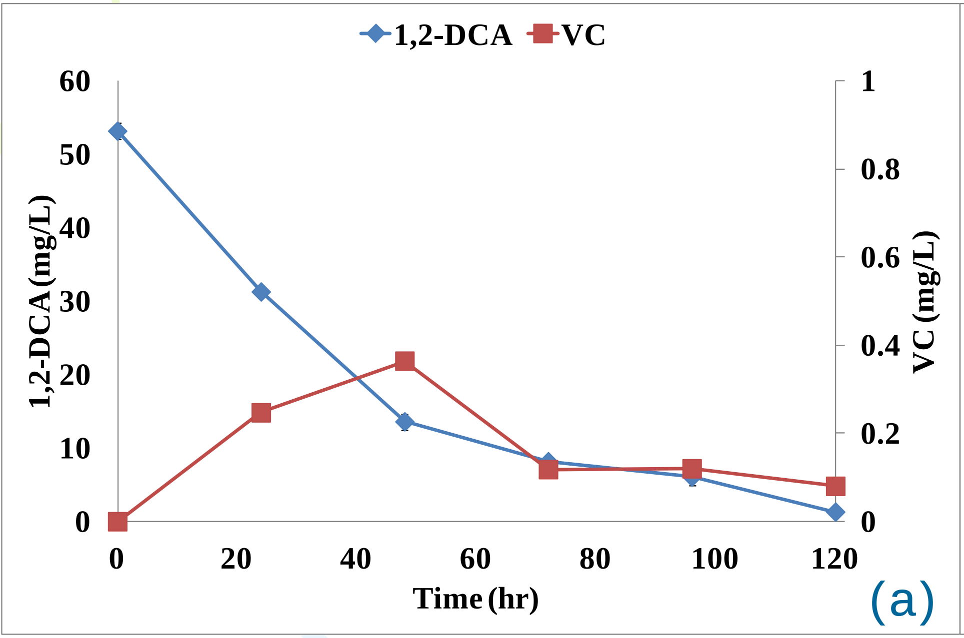
Results and Discussion (2/11)

Table 3. Rate constants of 1,2-DCA degradation by PS under different alkaline conditions

1,2-DCA (mg/L)	PS (%)	pH	k (1/s)	R^2
50	1	3 (unactivated)	3.77×10^{-6}	0.993
		10	1.43×10^{-6}	0.962
		11	2.51×10^{-6}	0.992
		12	6.57×10^{-6}	0.976
		13	11.7×10^{-6}	0.994

Results and Discussion (3/11)

pH 12 | pH 13



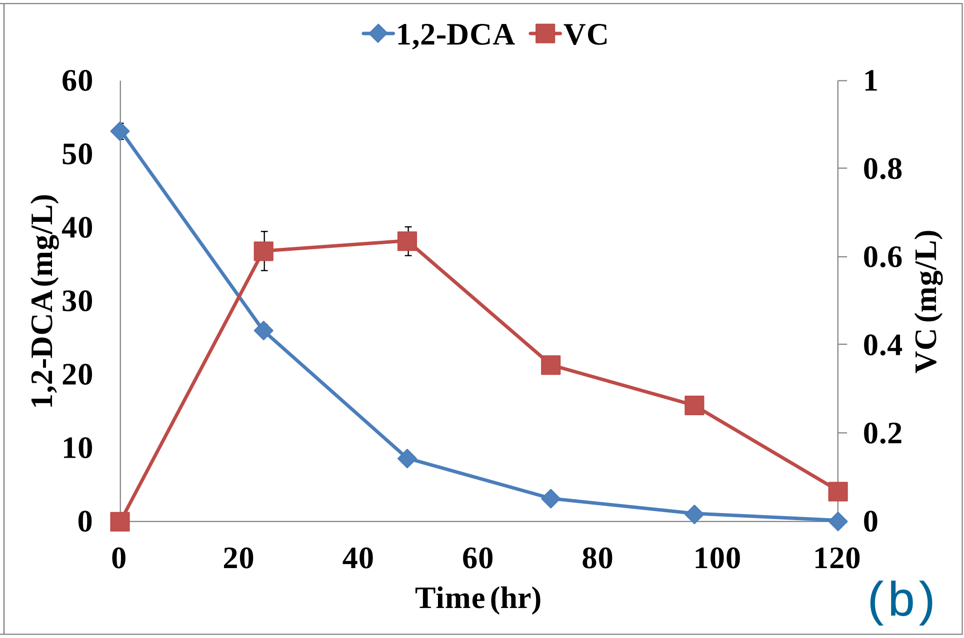


Fig. 2. Degradation of 1,2-DCA and production of VC during alkaline-activated PS oxidation (a) pH 12, (b) pH 13.

- VC is a byproduct of the reductive dechlorination of 1,2-DCA

Results and Discussion (4/11)

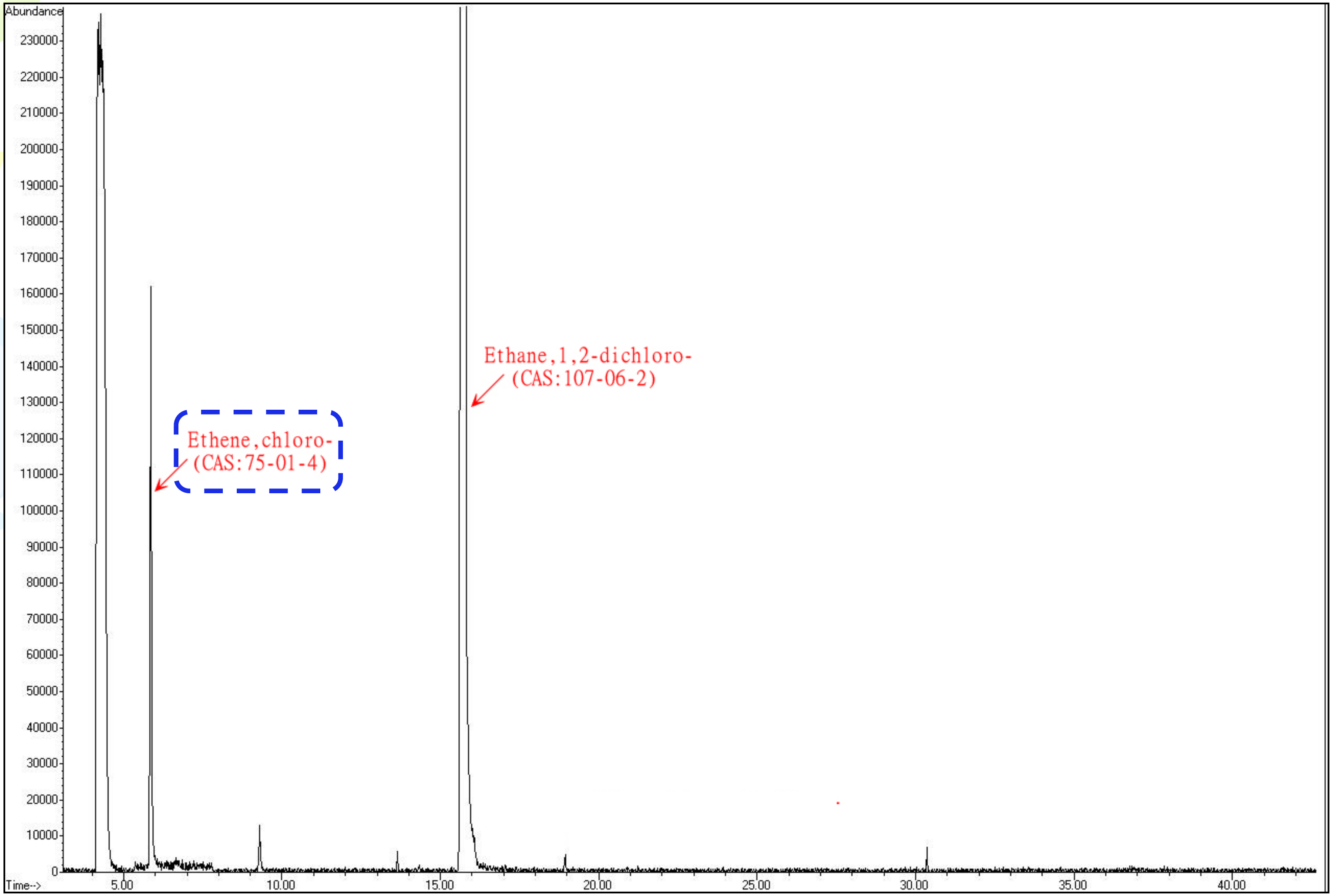


Fig. 3. Identification of VC production by GC-MS

Results and Discussion (5/11)

I

$$S_2O_8^{2-} + H_2O \xrightarrow{OH^-} SO_5^{2-} + SO_4^{2-} + 2H^+$$

$$SO_5^{2-} + H_2O \xrightarrow{OH^-} HO_2^- + SO_4^{2-} + H^+$$

$$HO_2^- + S_2O_8^{2-} \rightarrow SO_4^{\cdot -} + SO_4^{2-} + H^+ + O_2^{\cdot -}$$

$$2S_2O_8^{2-} + 2H_2O \rightarrow 3SO_3^{2-} + SO_4^{\cdot -} + O_2^{\cdot -} + 4H^+$$

$$SO_4^{\cdot -} + OH^- \rightarrow SO_4^{2-} + OH^{\cdot}$$

II

$$S_2O_8^{2-} \rightarrow 2SO_4^{\cdot -}$$

$$SO_4^{\cdot -} + OH^- \rightarrow OH^{\cdot} + SO_4^{2-}$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2$$

$$S_2O_8^{2-} + 2H_2O \rightarrow 2HSO_4^- + H_2O_2$$

$$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$$

$$H_2O_2 + HO_2^- \rightarrow O_2^{\cdot -} + OH^{\cdot} + H_2O$$

$O_2^{\cdot -}$ may contribute the production of VC via the reductive dechlorination of 1,2-DCA

Results and Discussion (6/11)

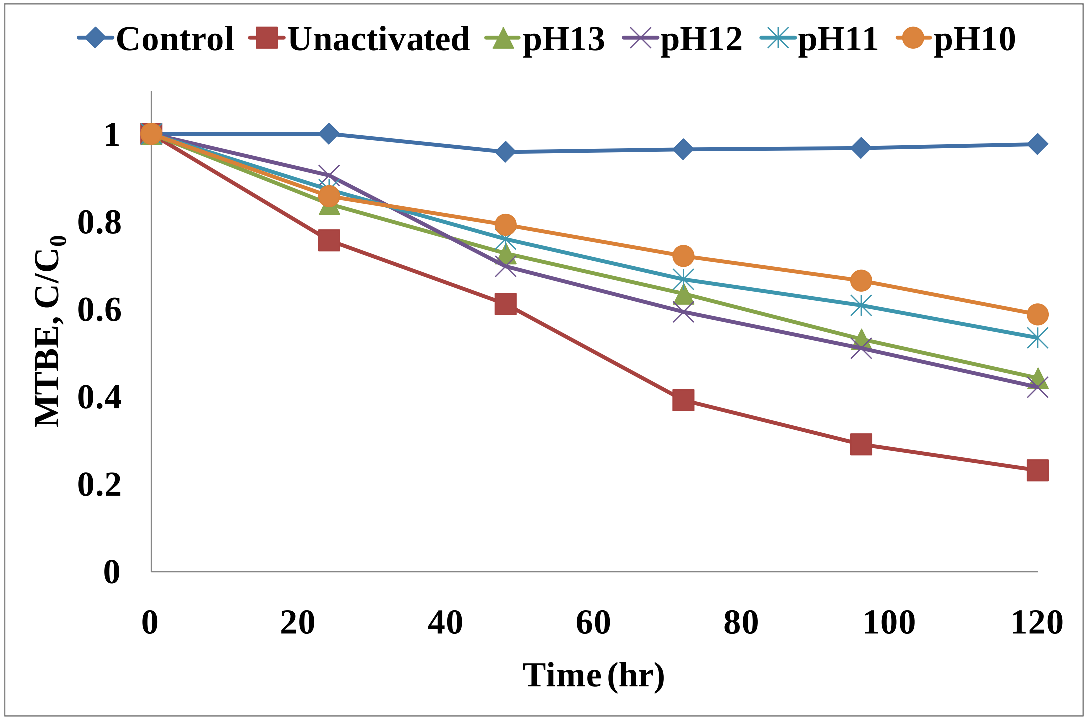


Fig. 4. MTBE removal by persulfate under different alkaline conditions

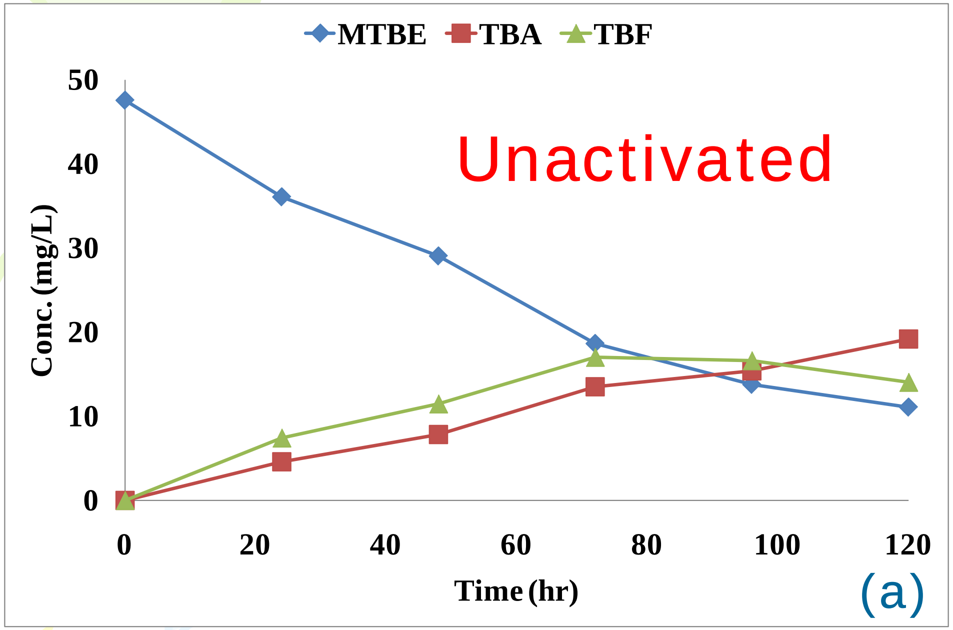
- MTBE degradation was stalled under alkaline conditions.
- Superoxide radicals are ineffective on the degradation of MTBE.
- Only sulfate and hydroxyl radicals contributed the removal of MTBE.

Results and Discussion (7/11)

Table 4. Rate constants of MTBE degradation by PS under different alkaline conditions

MTBE (mg/L)	PS (%)	pH	k (1/s)	R^2
50	1	3 (unactivated)	3.51×10^{-6}	0.991
		10	1.16×10^{-6}	0.990
		11	1.44×10^{-6}	0.997
		12	2.05×10^{-6}	0.992
		13	1.84×10^{-6}	0.997

Results and Discussion (8/11)



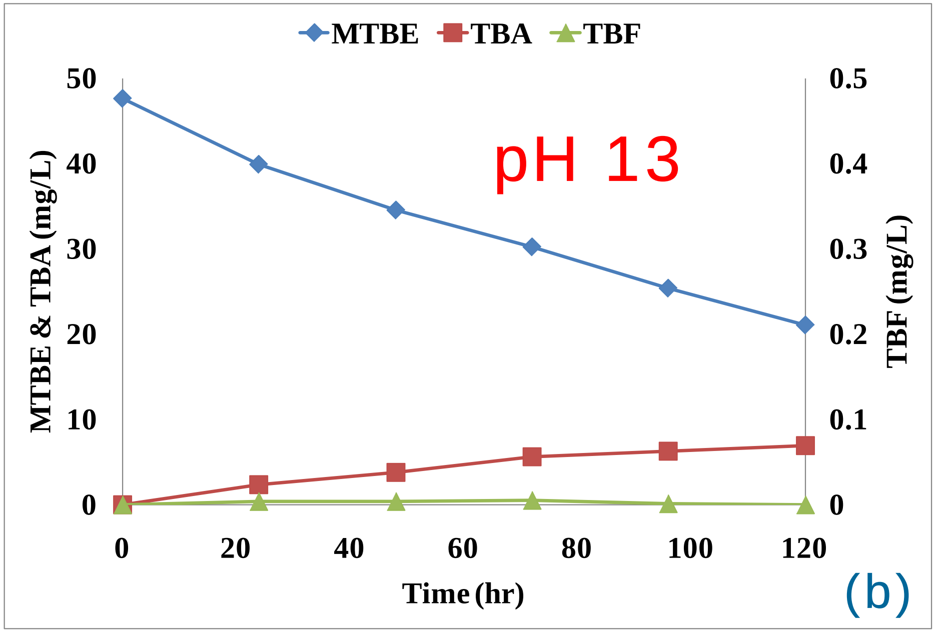


Fig. 5. Degradation of 1,2-DCA and production of TBF and TBA during (a) unactivated and (b) alkaline-activated PS oxidation.

- TBF and TBA were produced during MTBE oxidation.
- Production of TBF and TBA was inhibited under all alkaline conditions.

Results and Discussion (9/11)

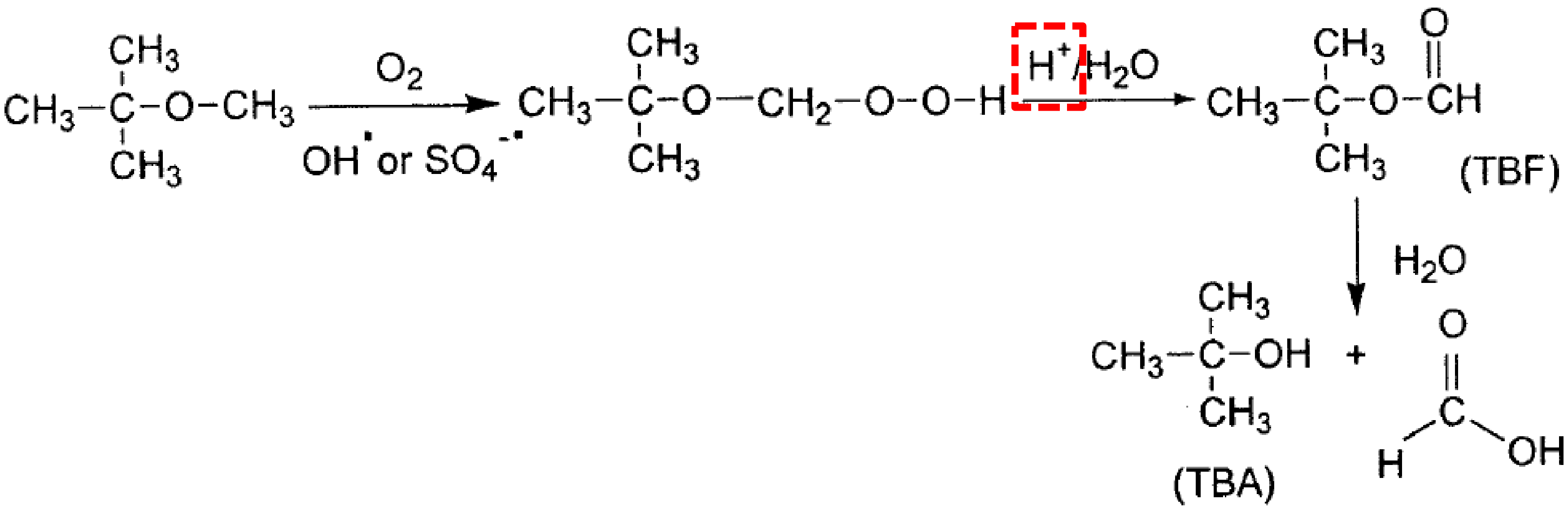
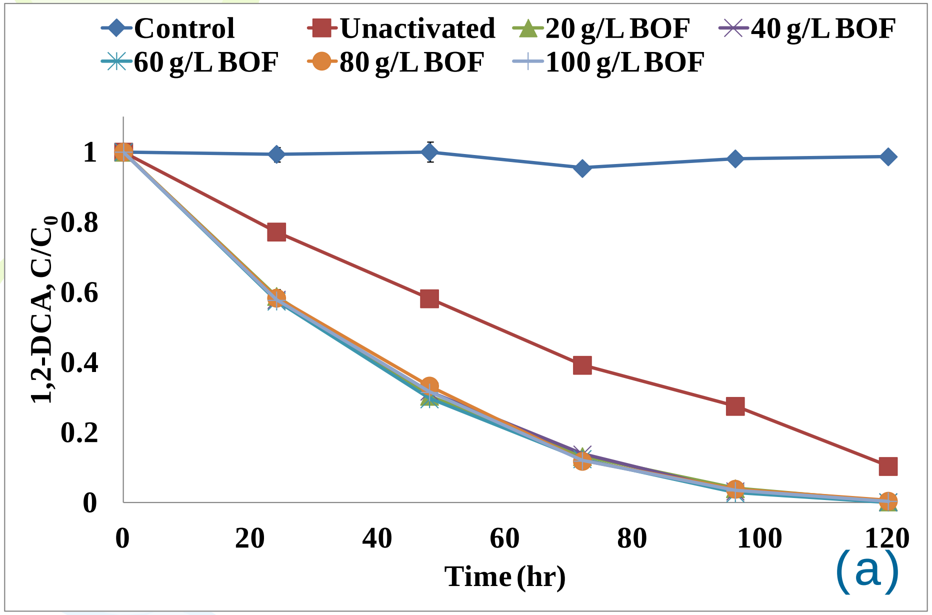


Fig. 6. Scheme of MTBE degradation with advanced oxidation processes
Source: K.C. Huang et al., Chemosphere, 49,413-420, 2002

- Acid-catalyzed hydrolysis was limited under alkaline conditions.
- Production of TBF was limited.
- TBA formation was also inhibited since TBA is produced from the hydrolysis of TBF.

Results and Discussion (10/11)



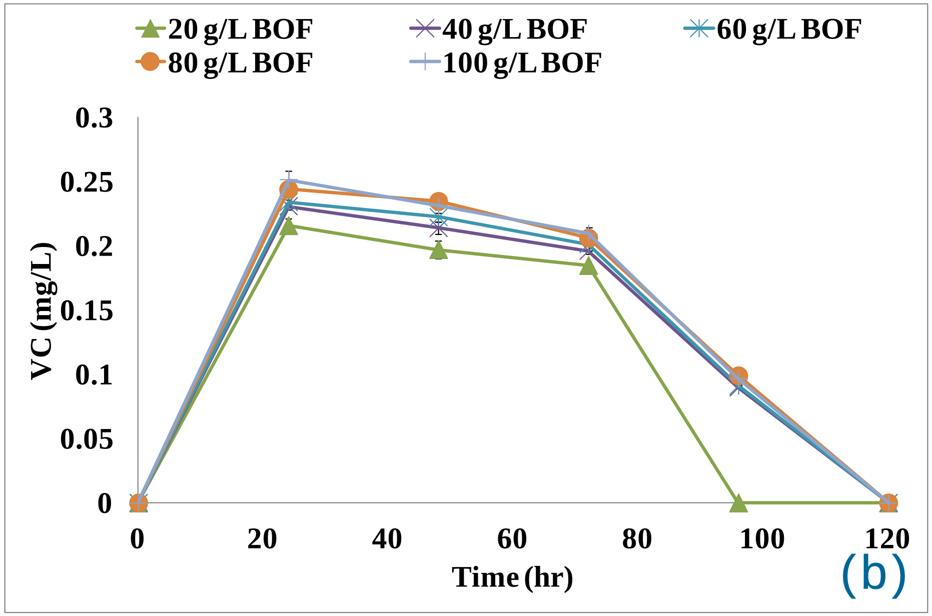
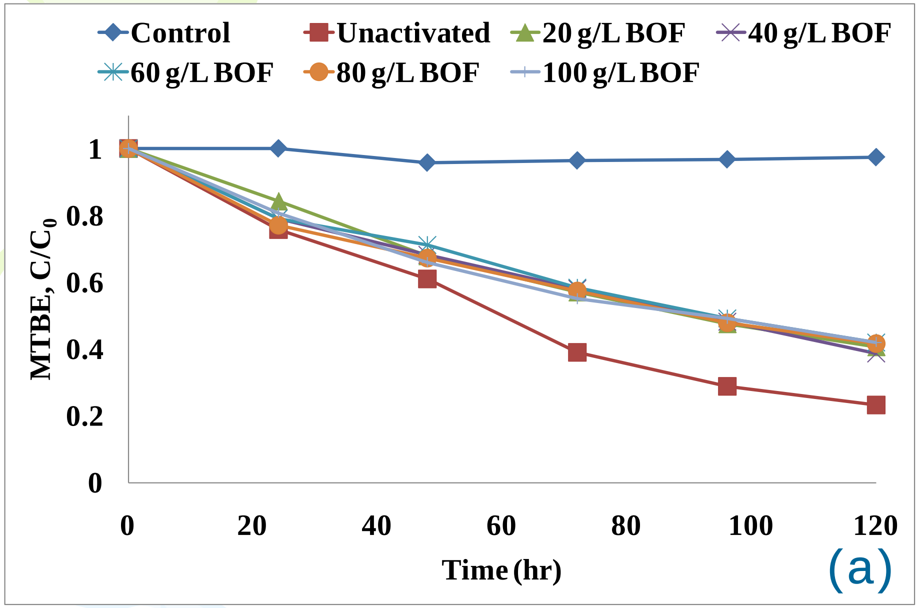
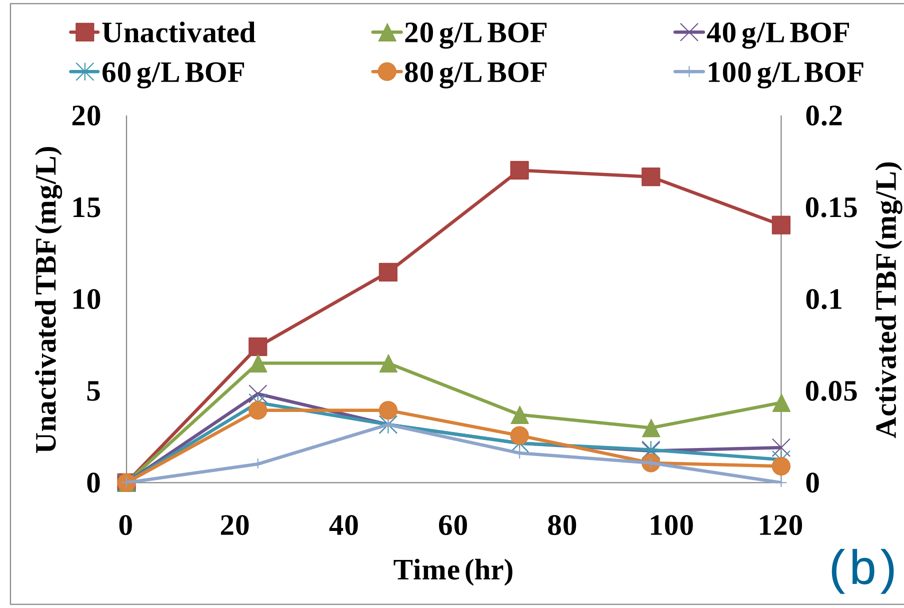


Fig. 7. Degradation of 1,2-DCA (a) and the production of VC (b) during PS oxidation with the addition of different dosages of BOF slag.

- pH reached 12 immediately in all runs after BOF slag was added.
- Removal of 1,2-DCA was enhanced with the addition of BOF slag.
- Production of VC was also observed.
- The addition of 20 g/L of BOF slag could effectively activate persulfate to enhance 1,2-DCA degradation.
- Heavy metals were not released during the treatment.

Results and Discussion (11/11)





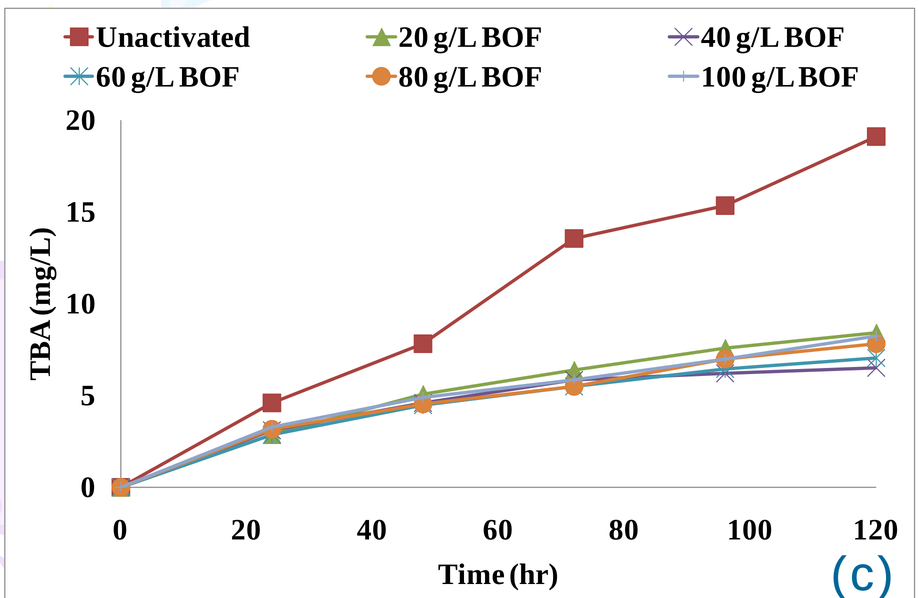


Fig. 8. Degradation of MTBE (a) and production of TBF(b) and TBA (c) during PS oxidation with the addition of different dosages of BOF slag.

- MTBE degradation was stalled with BOF slag addition.
- Production of TBF and TBA was limited in all runs.

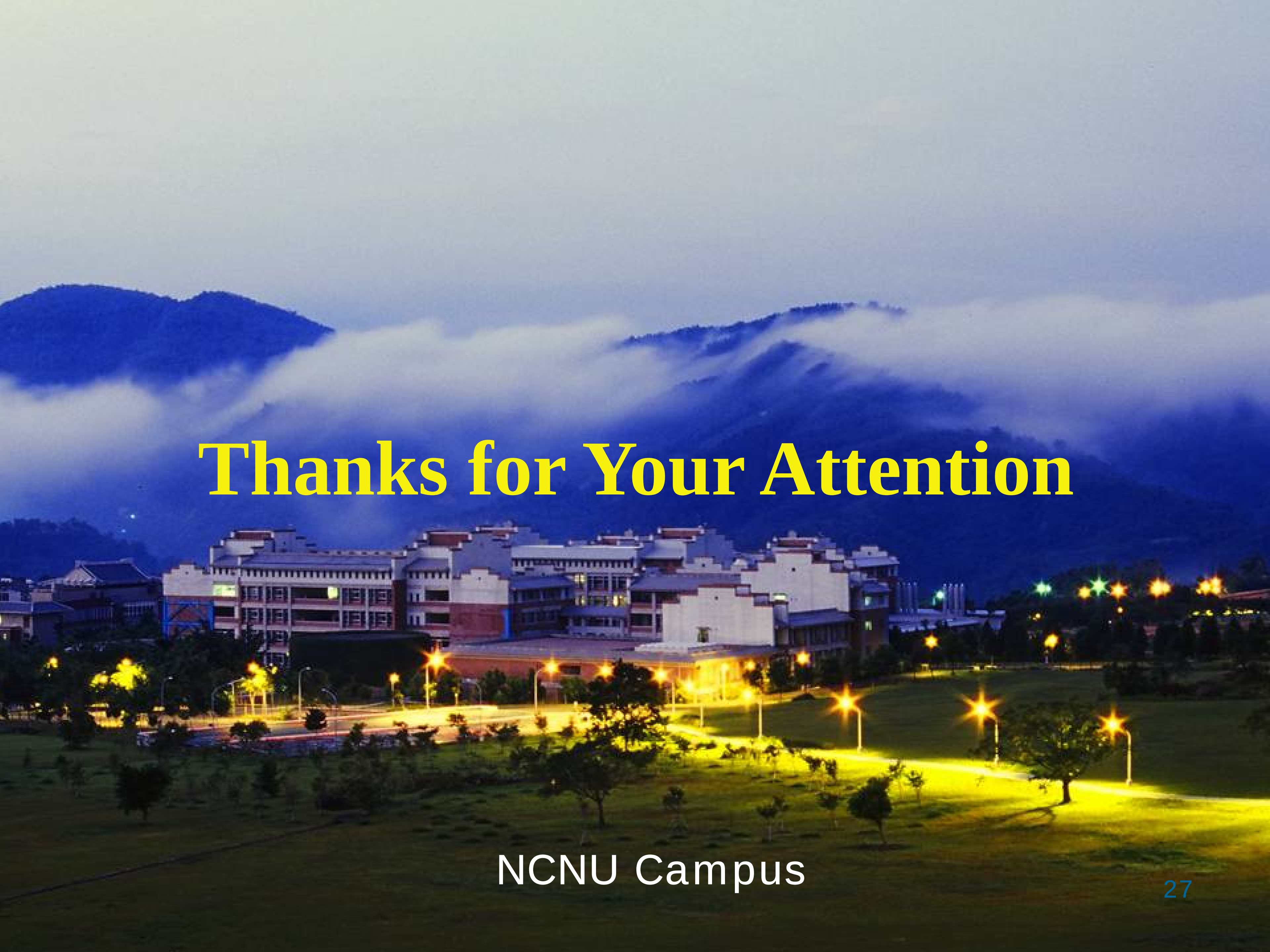
Conclusions (1/2)

- Superoxide radicals, hydroxyl radicals, and sulfate radicals may all exist in alkaline-activated PS.
- Removal of 1,2-DCA could be enhanced by alkaline-activated PS with pH above 12.
- 1,2-DCA might be dechlorinated by superoxide radicals to produce VC during alkaline-activated PS oxidation.
- MTBE degradation was stalled under alkaline conditions, possibly due to the presence of superoxide radicals.
- BOF slag could effectively increase the solution pH to derive alkaline-activated PS reaction.

Conclusions (2/2)

- EPR (electron paramagnetic resonance) analysis needs to be conducted to confirm the role of the reduced superoxide radicals in contaminant removal.
- Since the mechanisms of contaminant removal by alkaline-activated PS are complicated, a feasibility study is necessary before alkaline-activated persulfate is applied to other target compounds to avoid the retardation of contaminant degradation.

Thanks for Your Attention



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