出國報告（出國類別：會議）

參加「亞洲土木、材料及環境科學研討會」

服務機關：國立暨南國際大學
姓名職稱：陳谷汎　副教授
派赴國家：日本
出國期間：**2014** 年 **7** 月 **22** 日 **7** 至 **26** 日
報告日期：**2014** 年 **7** 月 **23** 日

摘要

申請人參與 2014 亞洲土木、材料及環境科學研討會議的目的如下：(1)針對申請人研究成果 Application of alkaline-activated persulfate to remediate organic contaminants in groundwater (以鹼活化過硫酸鹽氧化法處理地下水中有機污染物之研究)進行口頭報告發表；(2)與與會專家學者交流討論研究心得與經驗；及(3)未來研究方向之學習思考。口頭發表後，承蒙與會學者提供未來研究相當寶貴之建議。各相關發表場次之參與學習，亦提供申請人未來研究延伸之方向。綜觀此次會議參與之成果，申請人未來研究可加強及借鏡之處包含：

一、鹼活化過硫酸鹽氧化法現地應用對微生物及重金屬溶出之影響；

二、鹼活化過硫酸鹽氧化法對不同污染物移除機制之探討；

三、鹼活化過硫酸鹽氧化本土整治技術適用參數之建立；及

四、TiO_2光催化技術於地下水污染整治之應用可行性研究。

壹、目的

亞洲土木、材料及環境科學研討會議涵蓋土木、材料及環境科學，為一跨領域之國際會議，旨在提供學者、科學家、工程師及學生一發表其研究成果之國際交流平台，並促進學術界及工業界之交流，達成產學合作之目的。本次會議為第三屆舉辦，共有世界各國超過 300 篇論文在此研討會發表，為亞太地區重要學術交流平台之一。申請人參與此會議的目的如下：

一、針對申請人研究成果 Application of alkaline-activated persulfate to remediate organic contaminants in groundwater (以鹼活化過硫酸鹽氧化法處理地下水中有機污染物之研究)進行口頭報告發表。

二、與與會專家學者交流討論研究心得與經驗；

三、學習國際研究新知；及

四、未來研究方向之學習思考。

貳、出國行程及議程

一、7 月 22 日

研討會報到日，並著手準備次日口頭報告及議程主持相關工作。

二、7 月 23 日

8:00 於會場報到後，隨即至 Environmental Sciences II 場次進行發表，該場次時段為 8:30-10:00，共有 5 位學者進行口頭發表。申請人為第一位發表者，且亦擔任該場次之主持人，於該時段進行 15 分鐘報告，發表題目為 Application of alkaline-activated persulfate to remediate organic contaminants in groundwater，並與在場專家學者進行 3 分鐘之問題討論。口頭發表完畢後，亦至其他場次聆聽環境科學及工程如水資源管理及污染物處理相關之論文及海報發表，並與各國專家學者交流討論，吸取新知。

三、7 月 24 日

本日有申請人指導之博士生進行口頭發表，發表題目為Treatment of methyl tert-butyl ether (MTBE)- and benzene-contaminated groundwater using bamboo charcoal coupled with persulfate oxidation。博士生發表結束後，申請人亦至會場聆聽環境科學及工程如水資源管理及污染物處理相關之論文及海報發表，並與各國專家學者交流討論，吸取新知。

四、7 月 25 日

進行環境保護技術交流，瞭解當地河川水質保護及生態保育之相關工作。

五、7 月 26 日

結束研討會行程。

參、心得與建議

口頭發表後，承蒙與會學者提供相當寶貴之建議，加強本論文內容之完整性，並提供未來研究延伸之方向。申請人發表題目為 Application of alkaline-activated persulfate to remediate organic contaminants in groundwater，主要利用高 pH 條件活化過硫酸鹽，加強其對污染物之氧化移除。交流討論過程中，與會學者特別提及過硫酸應用後對現地微生物之影響及可能造成之重金屬溶出是否有因應對策。此外，鹼活化過硫酸鹽法對不同污染物降解效率之差異，或與自由基生成物種有關，此部分機制仍待更進一步之釐清。上述建議皆為過硫酸鹽氧化法研究及應用待解決之問題，申請人已將會場學者之建議納入未來研究工作之重點，期能使申請人在鹼活化過硫酸鹽氧化法之相關研究更為深入。此外，目前鹼活化過硫酸鹽氧化法於國外已有不少的現地應用成果，惟國內相關現地應用仍較為缺乏，建議未來國內應著手進行現地試驗/整治，以建立本土整治技術適用之相關參數，提供未來整治應用之參考。

本次研討會主題相當廣泛，因時間有限，申請人僅參加與自身有關之環境科學與工程領域相關發表之討論，從中學習其他研究團隊相關的研究成果及技術。近年來，水資源匱乏已成為全球關注之議題，又因地表及地下水體水質受到污染，影響水資源之可利用性。因此，發展經濟有效的污染技術，解決水污染問題已成為各國專家學者研究發展之重點方向。除此之外，進行妥善之水資源及流域管理，方為有效解決水資源使用及污染之方法。

本次會議中，各項有關水資源議題之發表，包含奈米處理技術、化學氧化技術、環境法醫技術、環境微生物技術及水資源與流域管理等，內容相當豐富，使申請人對水資源議題方面之研究進展，有更為深入之瞭解及認識。與申請人研究具有關聯性之議題部分，如奈米級TiO_2經改質後對水中污染物之移除具有相當良好之效果，惟由於需光源進行催化，應用於地下水整治上較為缺乏。然而，目前地下水中有許多難分解之有機污染物，如農藥及申請人持續進行研究之污染物甲基第三丁基醚，目前雖有相關整治方法，惟仍待更多整治技術之嘗試，以提供更彈性之整治方案。未來研究上

或可利用抽取處理法配合TiO_2氧化於現場進行處理，或利用整治牆之方式於地表下裝設光源進行現地處理，以增進難分解有機物之整治效率。

環保技術交流部分，可以發現日本縱使在大都市當中，河川水質都相當良好，且水中生態亦相當豐富。顯見下水道系統及污水處理廠之建置，仍是有效解決河川污染之方法。目前許多縣市皆將河川水質整治工作列為施政重點，惟台灣下水道普及率仍有待加強，進入河川之污水若未能妥善處理，河川整治將事倍功半。因此河川整治工作，仍應從基本的下水道建設著手，列為重點加速進行，以使台灣受污染河川能有真正乾淨的一天。

藉由此次國際研討會之參與，確實有效增廣自身研究相關之見聞，並從中學習其他團隊之研究成果。綜觀此次會議參與之成果，申請人未來研究可加強及借鏡之處包含：

一、鹼活化過硫酸鹽氧化法現地應用對微生物及重金屬溶出之影響；

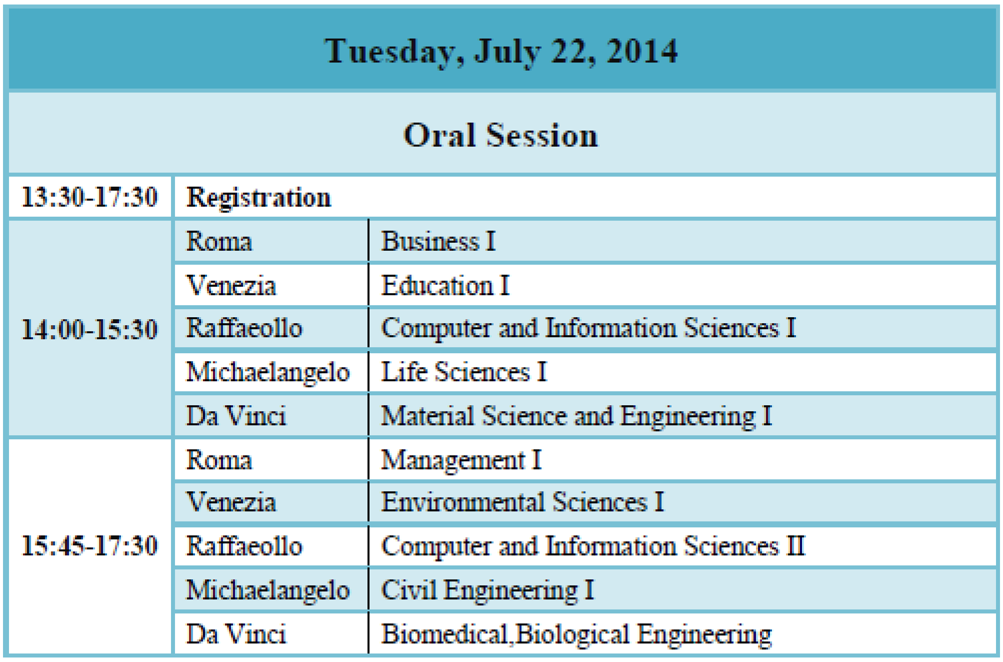
二、鹼活化過硫酸鹽氧化法對不同污染物移除機制之探討；

三、鹼活化過硫酸鹽氧化本土整治技術適用參數之建立；及

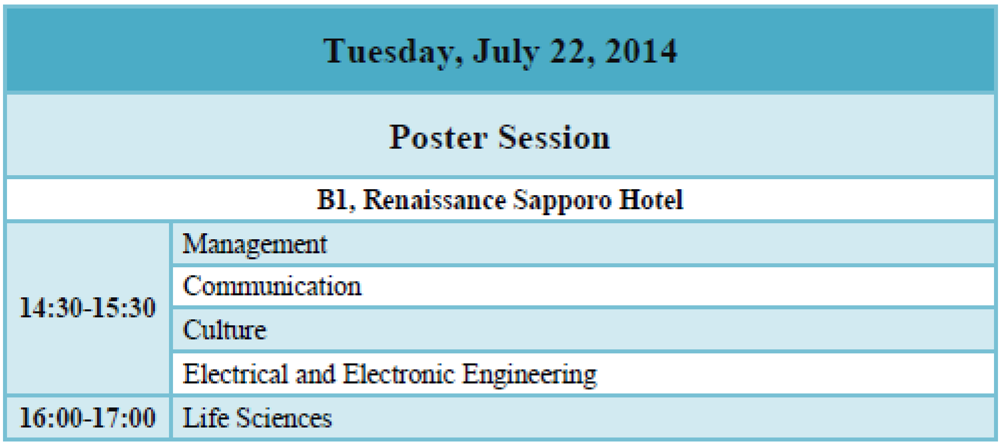
四、TiO_2光催化技術於地下水污染整治之應用可行性研究。

肆、附錄

一、研討會議程



Tuesday, July 22, 2014		
Oral Session		
13:30-17:30	Registration	
14:00-15:30	Roma	Business I
	Venezia	Education I
	Raffaeollo	Computer and Information Sciences I
	Michaelangelo	Life Sciences I
	Da Vinci	Material Science and Engineering I
15:45-17:30	Roma	Management I
	Venezia	Environmental Sciences I
	Raffaeollo	Computer and Information Sciences II
	Michaelangelo	Civil Engineering I
	Da Vinci	Biomedical,Biological Engineering



Tuesday, July 22, 2014	
Poster Session	
B1, Renaissance Sapporo Hotel	
14:30-15:30	Management
	Communication
	Culture
	Electrical and Electronic Engineering
16:00-17:00	Life Sciences

Wednesday, July 23, 2014

Oral Session

Time	Information	
08:15-17:30	**Registration**	
08:30-10:00	Roma	Language & Literature I
	Venezia	Education III
	Raffaeollo	Finance I
	Michaelangelo	Environmental Sciences II
	Da Vinci	Chemical Engineering I
10:00-10:15	**Tea Break**	
10:15-12:00	Venezia	Management II
	Michaelangelo	Material Science and Engineering II
	Da Vinci	Computer and Information Sciences III
10:30-11:45	Roma	Keynote Speech Keynote Speaker: Dr.Jun Mizuno
	Raffaeollo	Keynote Speech Keynote Speaker: Jonathan Damiani
12:00-13:00	**Lunch Time**	
13:00-14:30	Roma	Business II
	Venezia	Education II , Psychology
	Raffaeollo	Linguistics I
	Michaelangelo	Life Sciences II
	Da Vinci	Fundamental and Applied Sciences
14:30-14:45	**Tea Break**	
14:45-16:15	Roma	Management III
	Venezia	Economics I
	Raffaeollo	Biological Engineering II
	Michaelangelo	Electrical and Electronic Engineering I
	Da Vinci	Mechanical Engineering I
16:15-16:45	**Tea Break**	
16:30-18:00	Roma	Culture
	Venezia	Communication I
	Raffaeollo	Politics & Sociology
	Michaelangelo	Civil Engineering II
	Da Vinci	Computer and Information Sciences IV

Wednesday, July 23, 2014	
Poster Session	
09:30-10:30	Education
	Psychology
	Computer and Information Sciences
	Electrical and Electronic Engineering
11:00-12:00	Life Sciences
	Fundamental and Applied Sciences
12:00-13:00	**Lunch Time**
14:00-15:00	Environmental Sciences
	Chemical Engineering
	Material Science and Engineering
16:00-17:00	Biological Engineering
	Life Sciences
	Biomedical Engineering

Thursday, July 24, 2014	
Poster Session	
09:00-10:00	Business
	Education
	Finance
	Mechanical Engineering
11:00-12:00	Life Sciences
14:00-15:00	Civil Engineering
	Material Engineering
	Biomedical Engineering
16:00-17:00	Material Science and Engineering
	Mechanical Engineering

Thursday, July 24, 2014		
Oral Session		
08:15-16:30	**Registration**	
08:30-10:00	Roma	Management IV
	Venezia	Communication II
	Raffaeollo	Linguistics II
	Michaelangelo	Chemical Engineering II
	Da Vinci	Life Sciences III
10:00-10:15	**Tea Break**	
10:15-12:00	Roma	Economics II
	Venezia	Finance II
	Raffaeollo	Business III
	Michaelangelo	Computer and Information Sciences V
	Da Vinci	Material Engineering I
12:00-13:00	**Lunch Time**	
13:00-14:45	Roma	Management V
	Venezia	Business IV
	Raffaeollo	Civil Engineering III
	Michaelangelo	Computer and Information Sciences VI
	Da Vinci	Electrical and Electronic Engineering II
14:45-15:00	**Tea Break**	
15:00-16:45	Roma	Language & Literature II
	Venezia	Education IV
	Raffaeollo	Environmental Sciences III
	Michaelangelo	Electrical and Electronic Engineering III
	Da Vinci	Mechanical Engineering II

Environmental Sciences II

Michaelangelo

2014/07/23 Wednesday 8:30-10:00

Session Chair: ***Prof.Kuan-Yu Liu***

ACCMES-1482

Application of Alkaline-Activated Persulfate to Remediate Organic Contaminants in Groundwater

Kuan-Yu Liu | *National Chi Nan University*
Yu-Chen Chang | *National Chi Nan University*
Ku-Fan Chen | *National Chi Nan University*

ACCMES-1403

The Floor Area Ratio Transfer for Carbon Emissions Feedback Inhibition of Taichung New Civic Center Area

Kuo-Wei Hsu | *Chaoyang University of Technology*
Peng-shiang Wang | *Chaoyang University of Technology*

ACCMES-1406

The Study in Ecological Restoration Indicators of Industrial Ruins

Min-chih Yang | *Chaoyang University of Technology*
Yu-Ju Chen | *Chaoyang University of Technology*

ACCMES-1415

Exploring the Impact of Cultural Performance Facilities on Urban Development from an Economic Value Added Perspective – Using Taichung City as an Example

Chao Jen Chih | *Chaoyang University of Technology*
Hsu Kuo-Wei | *Chaoyang University of Technology*

ACCMES-1478

A Study on the Promotion of the Cultual Creative Industry in Central Taiwan

Jen Shih Feng | *Chaoyang University of Technology*
Hua Yi Chiang | *Chaoyang University of Technology*
Chih Min Yang | *Chaoyang University of Technology*

二、發表論文全文

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

Kuan-Yu Liu
Department of Civil Engineering, National Chi Nan University, 1 University Rd., Puli,
Nantou 54561, Taiwan
happywolf2100@gmail.com

Yu-Chen Chang
Department of Civil Engineering, National Chi Nan University, 1 University Rd., Puli,
Nantou 54561, Taiwan
yu.chen73108@gmail.com

Ku-Fan Chen
Department of Civil Engineering, National Chi Nan University, 1 University Rd., Puli,
Nantou 54561, Taiwan
kfchen@ncnu.edu.tw

The corresponding author: Ku-Fan Chen

Abstract

Methyl tert-butyl ether (MTBE) and 1,2-dichloroethane (1,2-DCA) are common groundwater pollutants. MTBE is widely used as a gasoline additive while 1,2-DCA is used for the production of vinyl chloride (VC). Both pollutants are difficult to be remediated and may cause cancer. In this study, alkaline-activated persulfate was used to treat MTBE- and 1,2-DCA-contaminated groundwater. Batch experiments were conducted under different pH to determine the required pH for alkaline-activated persulfate reaction. Furthermore, the potential of alkaline-activated persulfate by industrial waste was also evaluated. The main objectives were to: (1) investigate the required pH for alkaline-activated persulfate; (2) evaluate the degradation efficiency of MTBE and 1,2-DCA by alkaline-activated persulfate; and (3) evaluate the potential of industrial waste to drive alkaline-activated persulfate process.

Results show that alkaline-activated persulfate can effectively accelerate the degradation of 1,2-DCA. Alkaline-activated persulfate reduced the degradation rate of MTBE and inhibited the production of MTBE-degrading byproducts, tert-butyl alcohol (TBA) and tert-butyl formate (TBF). Persulfate activated by industrial waste basic oxygen furnace slag (BOF Slag) enhanced the degradation of 1,2-DCA. No heavy metals were released from BOF slag during the experiments. Results of this study would be helpful to design a practical system for the treatment of contaminated sites. Since the mechanisms of contaminant removal by alkaline-activated persulfate are complicated, feasibility study is necessary before alkaline-activated persulfate is applied to other target compounds to avoid the retardation of contaminant degradation.

Keywords: MTBE, 1,2-DCA, persulfate, alkaline activation, industrial waste, basic oxygen furnace (BOF) slag

1. Introduction

Contamination of soil and groundwater by petroleum and chlorinated hydrocarbons has become a serious issue worldwide due to the large amount of use. Generally, petroleum and chlorinated hydrocarbons are most commonly detected pollutants in groundwater. These pollutants may be released to the environment due to the leakage of underground storage tanks (USTs) and pipelines, accidental spills, discharge of wastewater, and inappropriate discharge and disposal.

Many technologies such as chemical oxidation, bioremediation, and air sparging have been used to remediate contaminated. Among these technologies, chemical oxidation is a very powerful technology that can destroy many contaminants effectively (ITRC, 2005). Hydrogen peroxide, ozone, and permanganate are common oxidants used for the remediation of organic pollutants. Recently, persulfate oxidation has been applied to in situ chemical oxidation. Persulfate is a strong oxidant, which can be thermally (Johhnson et al., 2008; Costanza et al., 2010) or chemically (Anipsitakis and Dionysiou, 2004; Liang et al., 2004a) activated to produce more powerful sulfate free radicals to degrade organic pollutants .

Thermal activation

$S_2O_8^{2-} + \text{heat} \rightarrow 2SO_4^{-}\cdot \qquad (1)$

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

Chemical activation

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

$SO_4^{-}\cdot + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} \qquad (4)$

$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2\ SO_4^{2-} \qquad (5)$

In addition to heat and transition metals, many other activation technologies such as chelated Fe(II) (Liang et al., 2004b; Liang et al., 2008), zero valent iron (ZVI) (Oh et al., 2009; Hussain et al., 2012), nanoscale ZVI (Yan et al., 2011), ultraviolet light (Lin et al., 2011; Gao et al., 2012), and activated carbon (Yang et al., 2011) have also been developed to activate persulfate. Recently, alkaline-activated persulfate has been used to treat some groundwater pollutants (Block et al., 2004; Liang et al., 2013). However, no comparison study has been conducted to evaluate the difference of removal efficiency between chlorinated and petroleum hydrocarbons. Since methyl tert-butyl ether (MTBE) and 1,2-dichloroethane (1,2-DCA) are typical petroleum hydrocarbon and chlorinated hydrocarbon found in groundwater, respectively, the two compounds were selected as the target compounds for this study. The main objectives of this study were to:

(1) determine the required pH for alkaline-activated persulfate;

(2) evaluate the degradation efficiency of 1,2-DCA and MTBE by alkaline-activated persulfate; and

(3) evaluate the potential of industrial waste to drive alkaline-activated persulfate process.

2. Materials and Methods

In this study, batch experiments were conducted using 50 mL serum bottles to evaluate MTBE and 1,2-DCA removal by persulfate under different alkaline conditions (pH 10-13, 25 ^{o}C, 150 rpm). Each bottle was filled with a mixed solution of the contaminant and persulfate. pH of the batch experiments was adjusted by NaOH. Table1 shows the component of 1,2-DCA and MTBE degradation by PS under different pH. In addition to NaOH, basic oxygen furnace (BOF) slag was also used to evaluate its feasibility to increase pH. The components of 1,2-DCA and MTBE degradation by PS with different dosages of BOF slag were shown in Table 2.

GC-FID was mainly used for the analysis of 1,2-DCA, MTBE, and their degradation byproducts including vinyl chloride (VC), tert-butyl formate (TBF), and tert-butyl alcohol (TBA). The production of VC was reconfirmed by GC-MS. In addition, heavy metals in the experiments with slag addition were analyzed using ICP-AES to evaluate the potential of heavy metal release from slag.

Table1. Component of 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

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

Slag (g/L)	Persulfate (%)	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

3. Results and Discussion

Figure 1 shows the results of 1,2-DCA removal by different alkaline conditions. Although 1,2-DCA degradation was increased with increasing pH under alkaline condition, its removal was stalled at pH 10 and 11 compared to that of unactivated PS. The results show that 1,2-DCA degradation was enhanced with pH higher than 12. Results also show that the degradation of 1,2-DCA by PS followed the pseudo-first-order reaction. The rate constants of 1,2-DCA removal at pH 12 and 13 were significant higher than that of unactivated PS, respectively (Table 3).

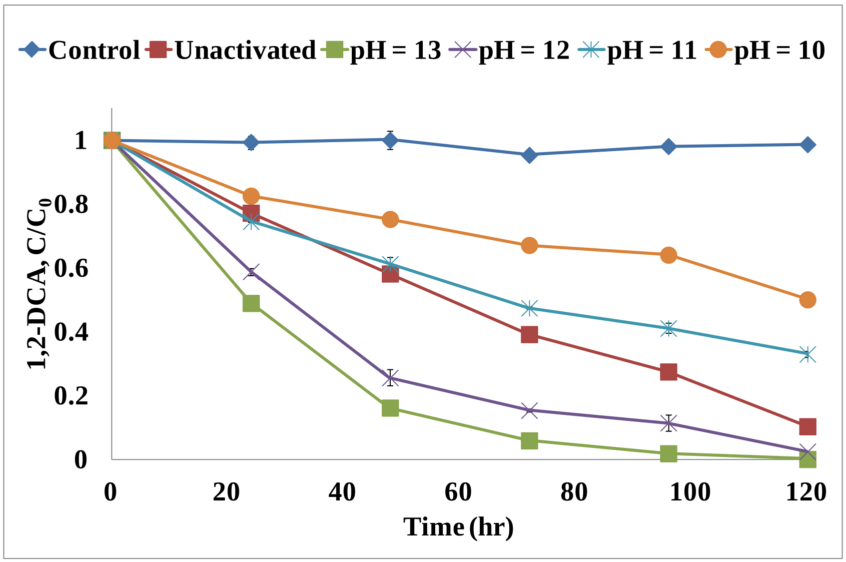
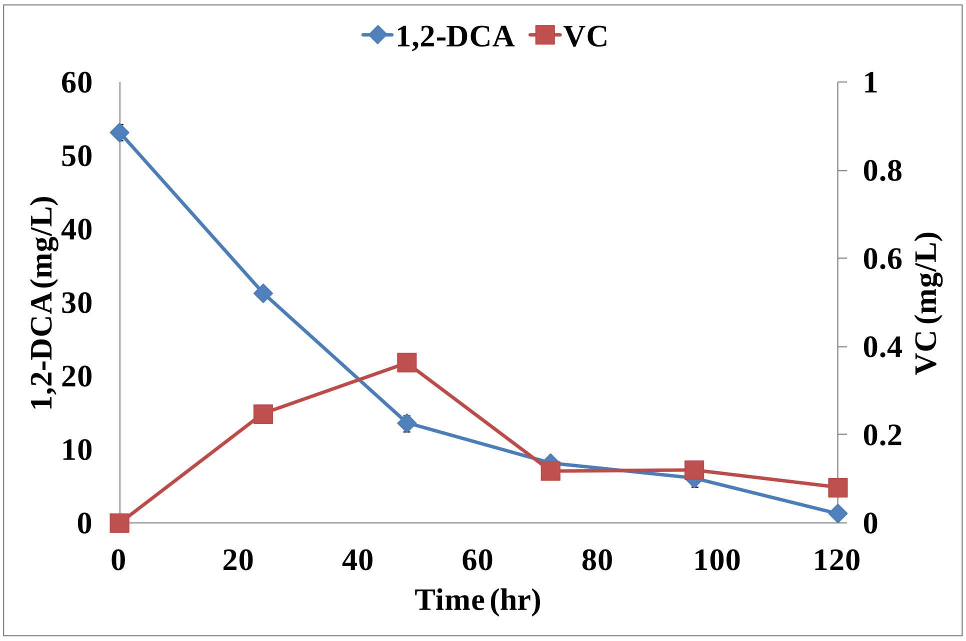


Fig. 1. 1,2-DCA removal by persulfate under different alkaline conditions.

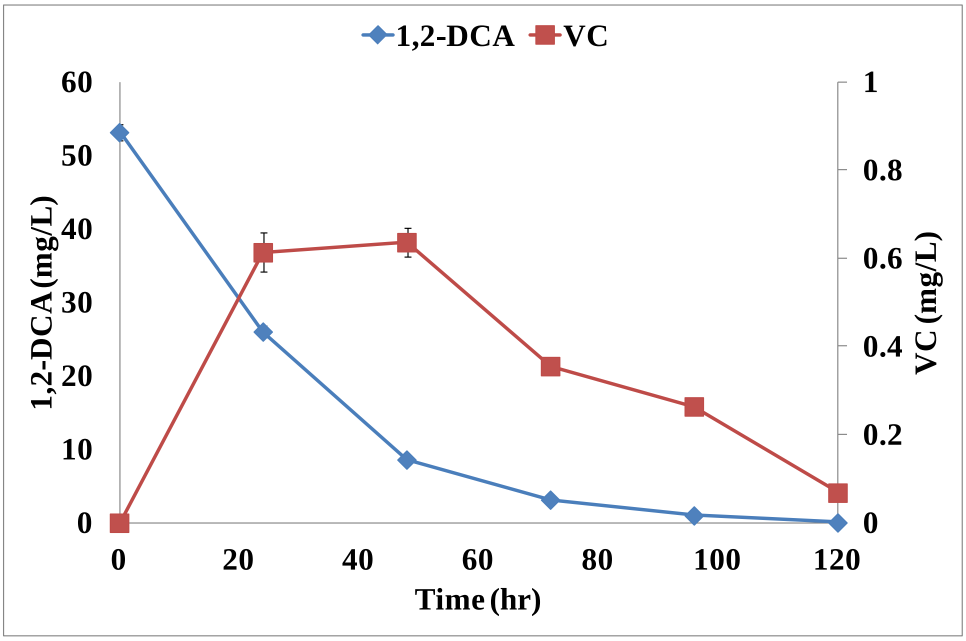
Table 3. Rate constants of 1,2-DCA degradation by persulfate under different alkaline conditions

1,2-DCA (mg/L)	Persulfate (%)	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

During 1,2-DCA oxidation, VC production was observed (Fig. 2). It is interesting because VC is a byproducts during the reductive dechlorination of 1,2-DCA, it might not be present in an oxidation system. Therefore, the VC production was reconfirmed by GC/MS (Fig. 3). The results show VC was indeed produced during alkaline-activated PS oxdiation.



(a)



(b)

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

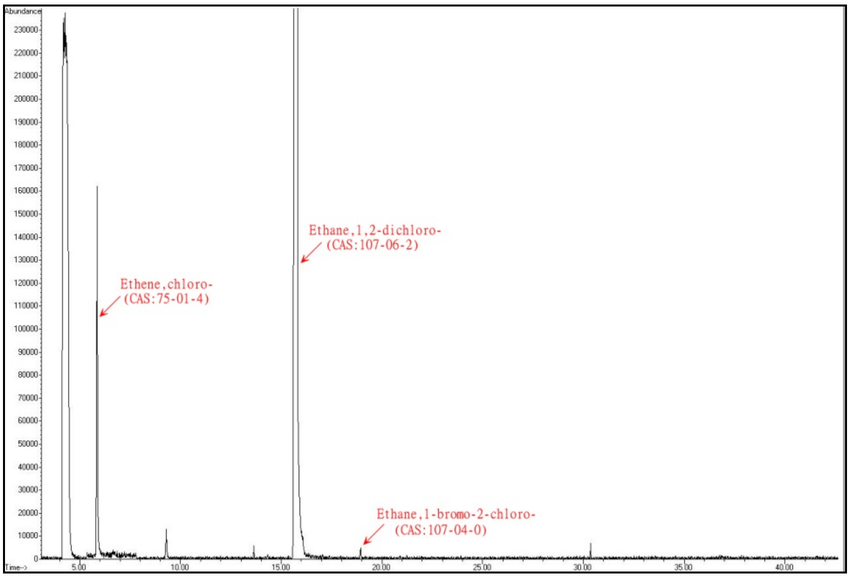


Fig. 3. Identification of VC production by GC-MS.

Two possible mechanisms of alkaline-activated persulfate have been proposed by Furman et al. (2010) and Watts (2011) (Eq. 6-11) and Corbin III (2008) (Eq. 12-17) as following.

$^{-}{}_{3}\mathrm{OS\text{-}O\text{-}O\text{-}SO_3}^{-} + \mathrm{H_2O} \xrightarrow{\mathrm{OH^-}} [^{-}{}_{3}\mathrm{OS\text{-}O\text{-}O}^{-}] + \mathrm{SO_4}^{2-} + 2\mathrm{H}^{+}$ Eq. 6

$[^{-}{}_{3}\mathrm{OS\text{-}O\text{-}O}^{-}] + \mathrm{H_2O} \xrightarrow{\mathrm{OH^-}} \mathrm{H\text{-}O\text{-}O}^{-} + \mathrm{SO_4}^{2-} + \mathrm{H}^{+}$ Eq. 7

$^{-}{}_{3}\mathrm{OS\text{-}O\text{-}O\text{-}SO_3}^{-} + 2\mathrm{H_2O} \xrightarrow{\mathrm{OH^-}} \mathrm{HO_2}^{-} + 2\mathrm{SO_4}^{2-} + 3\mathrm{H}^{+}$ Eq. 8

$\mathrm{H\text{-}O\text{-}O}^{-} + {}^{-}{}_{3}\mathrm{OS\text{-}O\text{-}O\text{-}SO_3}^{-} \rightarrow \mathrm{SO_4}\cdot^{-} + \mathrm{SO_4}^{2-} + \mathrm{H}^{+} + \mathrm{O_2}\cdot^{-}$ Eq. 9

$2\mathrm{S_2O_8}^{2-} + 2\mathrm{H_2O} \rightarrow 3\mathrm{SO_3}^{2-} + \mathrm{SO_4}\cdot^{-} + \mathrm{O_2}\cdot^{-} + 4\mathrm{H}^{+}$ Eq. 10

$\mathrm{SO_4}\cdot^{-} + \mathrm{OH}^{-} \rightarrow \mathrm{SO_4}^{2-} + \mathrm{OH}\cdot$ Eq. 11

$\mathrm{S_2O_8}^{2-} \rightarrow 2\mathrm{SO_4}\cdot^{-}$ Eq. 12

$\mathrm{SO_4}\cdot^{-} + \mathrm{OH}^{-} \rightarrow \mathrm{OH}\cdot + \mathrm{SO_4}^{2-}$ Eq. 13

$\mathrm{OH}\cdot + \mathrm{OH}\cdot \rightarrow \mathrm{H_2O_2}$ Eq. 14

$\mathrm{S_2O_8}^{2-} + 2\mathrm{H_2O} \rightarrow 2\mathrm{HSO_4}^{-} + \mathrm{H_2O_2}$ Eq. 15

$\mathrm{H_2O_2} + \mathrm{OH}^{-} \rightarrow \mathrm{HO_2}^{-} + \mathrm{H_2O}$ Eq. 16

$\mathrm{H_2O_2} + \mathrm{HO_2}^{-} \rightarrow \mathrm{O_2}\cdot^{-} + \mathrm{OH}\cdot + \mathrm{H_2O}$ Eq. 17

Under alkaline conditions, hydroxyl, sulfate, and superoxide radicals are all in the system. It has been reported that the reduced superoxide radical was predominant in alkaline-activated persulfate (Zhoa et al., 2013). Therefore, superoxide radical may contribute the production of VC via the reductive dechlorination of 1,2-DCA during alkaline-activated persulfate oxidation. Therefore, both oxidation and reductive dechlorination contributed the removal of 1,2-DCA, causing the enhancement of 1,2-DCA degradation.

Figure 4 show MTBE removal by persulfate under different alkaline conditions. MTBE degradation was stalled under alkaline conditions. Since superoxide radicals are ineffective in the degradation of MTBE, only sulfate and hydroxyl radicals contributed the removal of MTBE. This may be the reason that caused the retardation of MTBE removal. Table 4 shows the rate constants of MTBE degradation by persulfate under different alkaline conditions. The degradation of MTBE by persulfate also followed pseudo-first-order kinetics. The results show MTBE had a highest degradation rate constant under unactivated conditions.

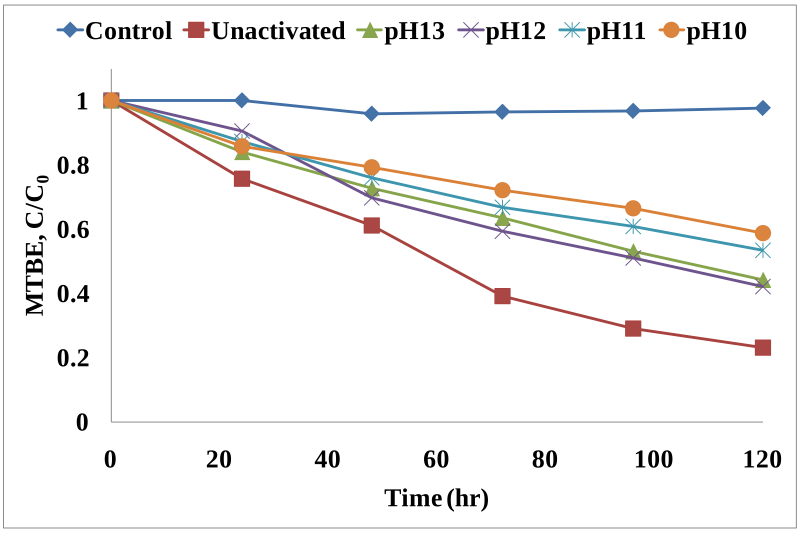
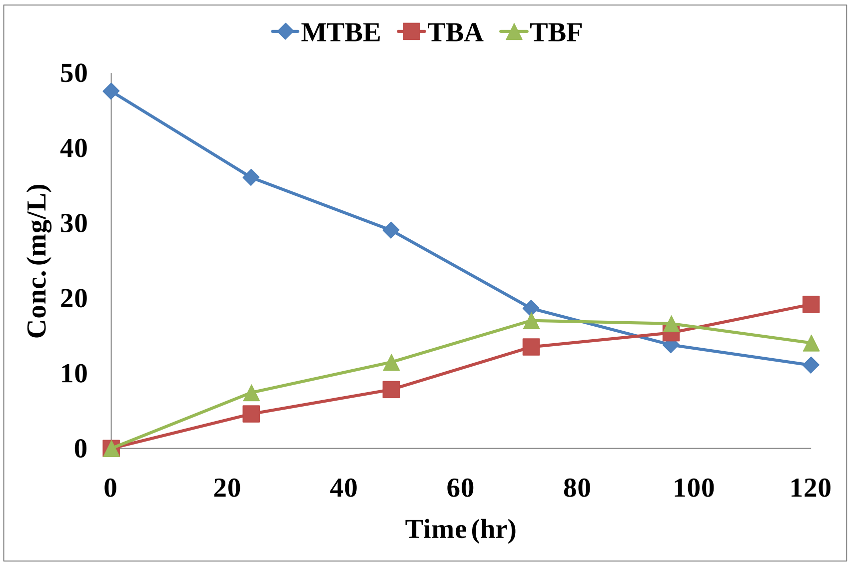


Fig. 4. MTBE removal by persulfate under different alkaline conditions.

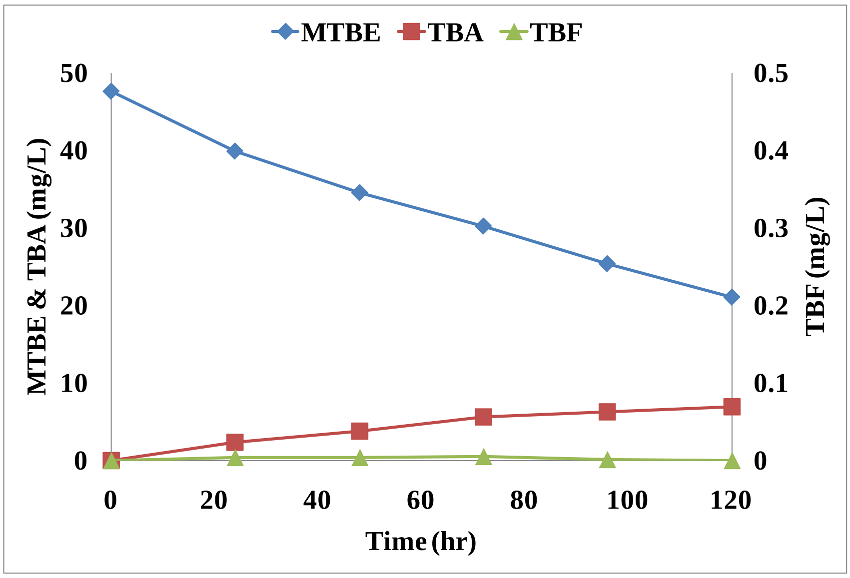
Table 4. Rate constants of MTBE degradation by persulfate under different alkaline conditions.

MTBE (mg/L)	Persulfate (%)	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

TBF and TBA were produced during MTBE oxidation. However, the production of TBF and TBA was inhibited under all alkaline conditions. Figure 6 presents the scheme of MTBE degradation with advanced oxidation processes (Huang et al., 2002). Acid-catalyzed hydrolysis is necessary to produce TBF during MTBE oxidation. Under high pH conditions, acid catalyzed hydrolysis was limited. Therefore, the production of TBF became limited. Since TBA is produced from the hydrolysis of TBF, TBA formation was also inhibited under high pH conditions.



(a)



(b)

Fig. 5. Degradation of 1,2-DCA and production of TBF and TBA during (a) unactivated and (b) alkaline-activated PS oxidation (pH 13).

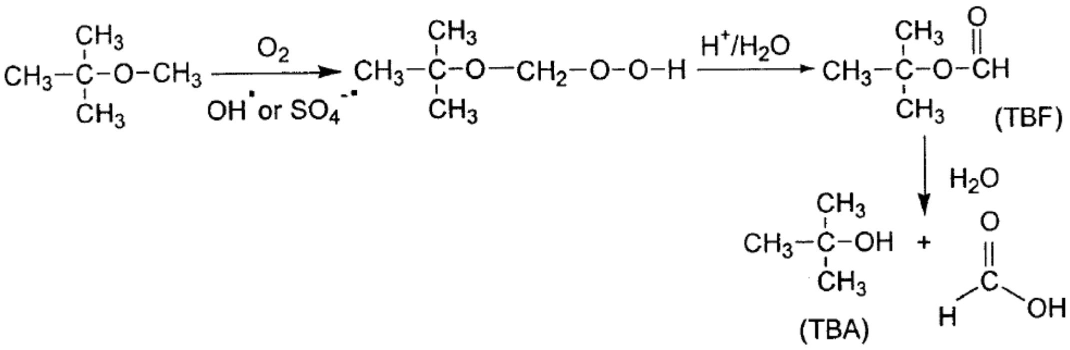
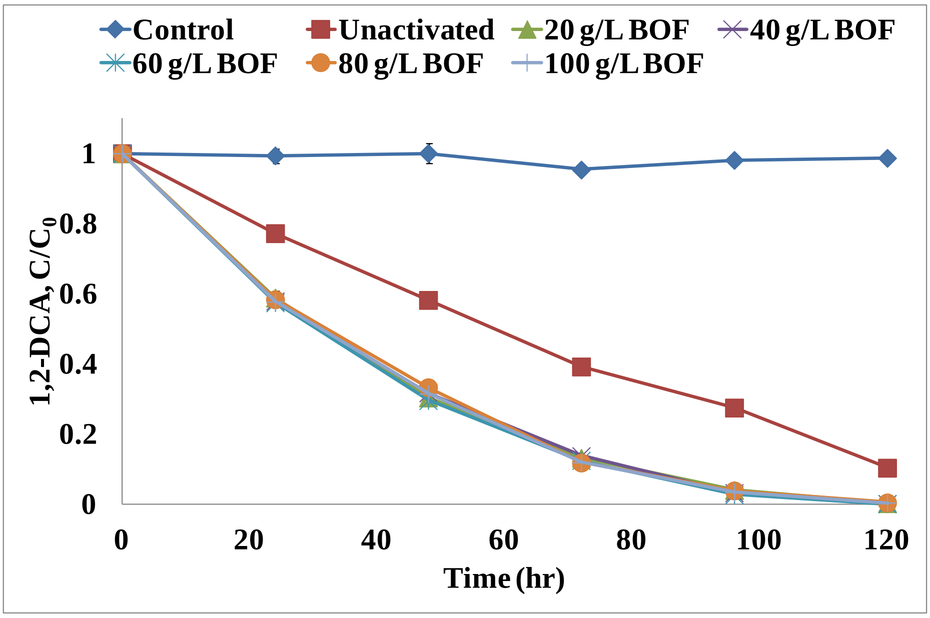


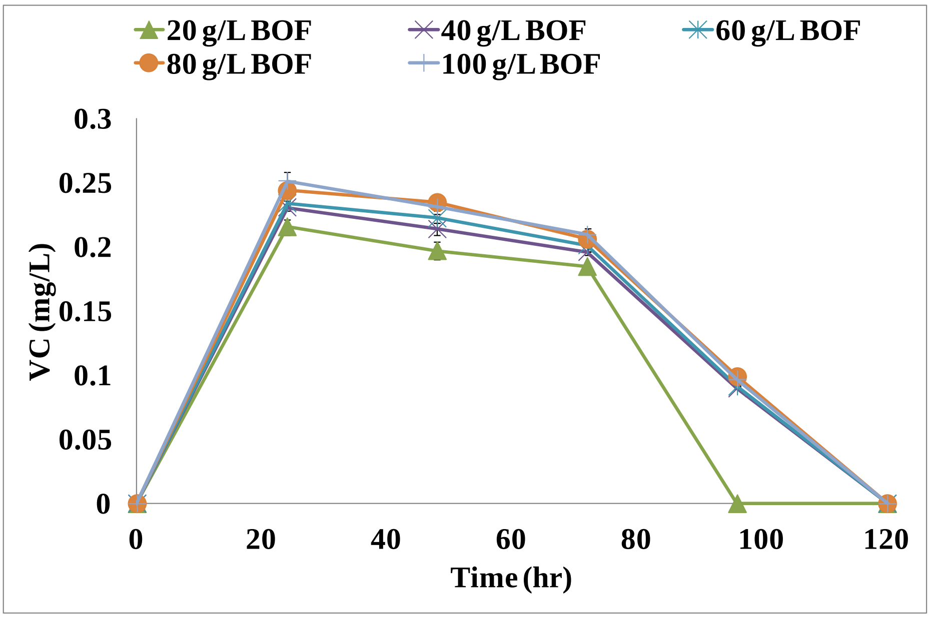
Fig. 6. Scheme of MTBE degradation with advanced oxidation processes (Huang et al., 2002).

Figure 7 shows the degradation of 1,2-DCA and the production of VC during PS oxidation with the addition of different dosages of BOF slag. After BOD slag was added, pH in the system rapidly increased to 12. The results show the removal of 1,2-DCA was enhanced with the addition of BOF slag. In addition, VC was also produced. The results reveal the addition of 20 g/L slag could effectively activated PS to enhance 1,2-DCA degradation. Results of heavy metal analysis show no heavy metals were released from the slag during the treatment. Therefore, slag seems to be a good alternative to activate PS.

Figure 8 show the degradation of MTBE and production of TBF and TBA during persulfate oxidation with the addition of different dosages of BOF slag. Results reveal MTBE degradation was stalled and the production of TBF and TBA was limited with BOF slag addition due to high pH conditions.

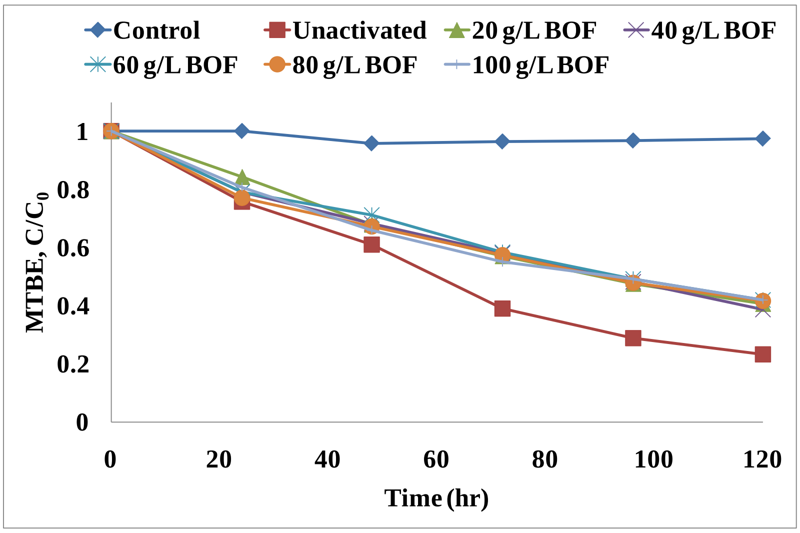


(a)

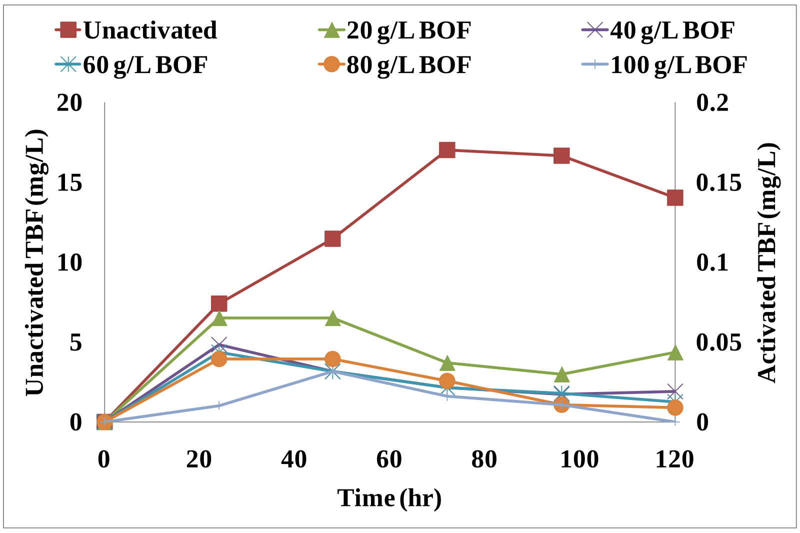


(b)

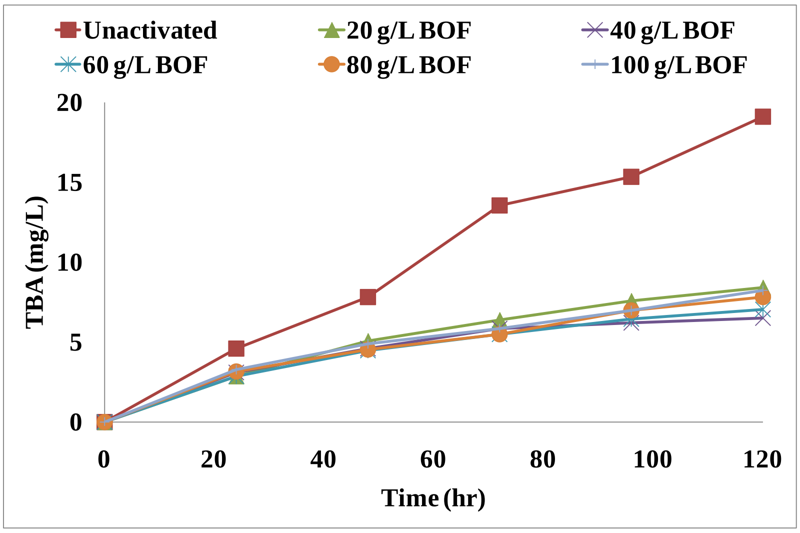
Figure 7. Degradation of 1,2-DCA (a) and the production of VC (b) during PS oxidation with the addition of different dosages of BOF slag.



(a)



(b)



(c)

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.

Conclusions

1. Superoxide radicals, hydroxyl radicals, and sulfate radicals may all exist in alkaline-activated persulfate.
2. Removal of 1,2-DCA could be enhanced by alkaline-activated PS with pH above 12.
3. 1,2-DCA might be dechlorinated by superoxide radicals to produce VC during alkaline-activated persulfate oxidation.
4. MTBE degradation was stalled under alkaline conditions, possibly due to the presence of superoxide radicals.
5. BOF slag could effectively increase the solution pH to derive alkaline-activated persulfate reaction.
6. EPR (electron paramagnetic resonance) analysis needs to be conducted to confirm the role of the reduced superoxide radicals in contaminant removal.

7. Since the mechanisms of contaminant removal by alkaline-activated persulfate are complicated, a feasibility study is necessary before alkaline-activated persulfate is applied to other target compounds to avoid the retardation of contaminant degradation.

Reference

Anipsitakis, G.P. and Dionysiou, D.D. Radical generation by the interaction of transition metals with common oxidants. Environ. Sci. Technol., 38, 3705-3712, 2004.

Block, P.A., Brown, R.A., Robinson, D. Novel activation technologies for sodium persulfate in situ chemical oxidation. Proceedings of the 4th International Conference on the Remediation of Chlorinated and Recalcitrant Compounds, 2004.

Constanza, J., Otano, G., Callaghan, J., Pennell, K.D. PCE oxidation by sodium persulfate in the presence of solids. Environ. Sci. Technol., 44, 9445-9450, 2010.

Furman, O.S., Teel, A.L., Watts, R.J. Mechanism of base activation of persulfate. Environ. Sci. Technol., 44, 6423–6428, 2010.

Gao, Y.Q., Gao, N.Y., Deng, Y., Yang, Y.Q., Ma, Y. Ultraviolet (UV) light-activated persulfate oxidation of sulfamethazine in water. Chem. Engine. J., 195–196, 248-253, 2012.

Huang, K. C., Couttenye, R. A., and Hoag, G. E. Kinetics of heat-assisted persulfate oxidation of methyl tert-butyl ether (MTBE). Chemosphere, 49, 413-420, 2002.

Hussain, I, Zhang, Y., Huang, S., Du, X. Degradation of p-chloroaniline by persulfate activated with zero-valent iron. Chem. Eng. J., 203, 269-276, 2012.

ITRC (Interstate Technology & Regulatory Council). Technical and Regulatory Guidance for In Situ Chemical Oxidation 2nd Ed, 2005.

Johnson R.L., Tratnyek, P.G., Johnson, R.O., Persulfate persistence under thermal activation conditions. Environ. Sci. Technol., 42, 9350-9356, 2008.

Liang, C., Bruell, C.J., Marley, M.C., and Sperry, K.L. Persulfate oxidation for in situ remendiation of TCE I- activated by ferrous ion with and without a ○persulfate-thiosulfate redox couple. Chemosphere, 55, 1213-1223, 2004a.

Liang, C., Bruell, C.J., Marley, M.C., and Sperry, K.L. Persulfate oxidation for in situ remendiation of TCE Ⅱ- activated by chelated ferrous ion. Chemosphere, 55, 1225-1233, 2004b.

Liang, C., Huang, C.F., Chen, Y.J. Potential for activated persulfate degradation of BTEX concentration. Water Res., 42, 4091-4100, 2008.

Liang, H.Y., Zhang, Y.Q., Huang, S.B., Hussain, I. Oxidative degradation of p-chloroaniline by copper oxidate activated persulfate. Chem. Eng. J., 218, 384-391, 2013.

Lin, Y.T., Liang, C., Chen, J.H. Feasibility study of ultraviolet activated persulfate oxidation of phenol. Chemosphere, 82, 1168-1172, 2011.

Oh, SY., Kim, H.W., Park, J.M., Park, H.S., Yoon, C. Oxidation of polyvinyl alcohol by persulfate activated with heat, Fe2+, and zero-valent iron. J. Hazard. Mater., 168, 346-351, 2009.

Watts, R.J. Enhanced reactant-contaminant contact through the use of persulfate in situ chemical oxidation (ISCO). SERDP Project ER-1489, 2011.

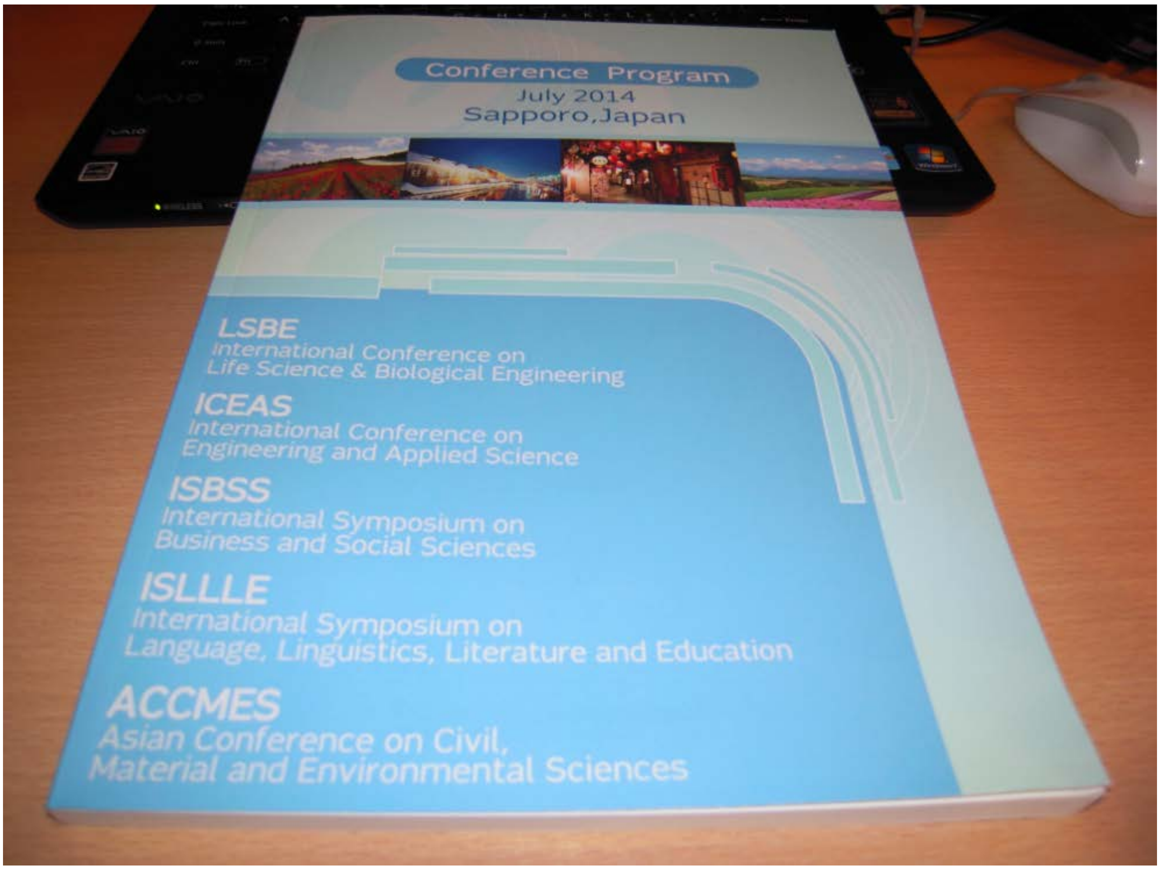
Yang, S., Yang, X., Shao, X., Niu, R., Wang, L. Activated carbon catalyzed persulfate oxidation of Azo dye acid orange 7 at ambient temperature. H. Hazard. Mater., 186, 695-666, 2011.

Zhao, D., Liao, X., Yan, X., Huling, S.G., Chai, T., Tao, H. Effect and mechanism of persulfate activated by different methods for PAHs removal in soil. Journal of Hazardous Materials, 254-255, 228-235, 2013.

三、活動照片


July 2014
Sapporo, Japan
The Joi onference of
LS , ICEAS,
IS , ISLLLE & ACCMES
札幌
Organ gher Education Forum

會場報到



Conference Program
July 2014
Sapporo,Japan

LSBE
International Conference on
Life Science & Biological Engineering

ICEAS
International Conference on
Engineering and Applied Science

ISBSS
International Symposium on
Business and Social Sciences

ISLLLE
International Symposium on
Language, Linguistics, Literature and Education

ACCMES
Asian Conference on Civil,
Material and Environmental Sciences

會議議程及摘要集

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)	$\boxed{3.77} \times 10^{-6}$	0.993
		10	1.43×10^{-6}	0.962
		11	2.51×10^{-6}	0.992
		12	$\boxed{6.57} \times 10^{-6}$	0.976
		13	$\boxed{11.7} \times 10^{-6}$	0.994

15

申請人於 7/23 日口頭發表情形