

## Degradation of Polychlorinated Dibenzo-*p*-Dioxins/Furans Using Heat-Activated Persulfate

Ji-hun Kim, Jae-min Lee, Ho-seok Lee, Jae-hwan Kim, Jin-wook Lee, and  
**Yoon-seok Chang** (yschang@postech.ac.kr) (POSTECH, South Korea)  
James T. Nurmi and Paul G. Tratnyek (tratnyek@ogi.ohsu.edu)  
(Oregon Health and Science University, Beaverton, Oregon)

**ABSTRACT:** Heat-activated persulfate was tested for destruction of polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs) in the laboratory. Combined technology of in situ chemical oxidation (ISCO) and in situ thermal remediation (ISTR) using heat-activated persulfate can be applied for destruction of the PCDD/Fs polluted soil and the PCDD/Fs containing fly ash from incineration process. To explore the treatability of PCDD/Fs, we determined the kinetics and products of the various congeners of PCDD/Fs oxidation using heat-activated persulfate. To simulate the soil environments, PCDD/Fs were absorbed to various sizes of glass beads as the absorbent. As a results, the kinetics of lower chlorinated (0~3 chlorines) congeners disappearance were followed to pseudo-first-order, but higher chlorinated congeners (4~8 Chlorines) were inhibited and not followed to pseudo-first-order. As a general, the kinetics of PCDD/Fs decreased as the numbers of chlorines increased. The effects of the size of medium and the dosage of persulfate are discussed.

### INTRODUCTION

Polychlorinated aromatic compounds are among the most problematic pollutants due to their chemical inertness, lipid solubility and toxicity. In particular, polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are known to be most toxic because they induce developmental toxicity, cancers and endocrine disruption, and are known recalcitrant pollutants. PCDDs/Fs are essentially planar chlorinated tricyclic aromatic compounds that are characterized by extremely low water solubility (19.3 ng/L) and low vapor pressure ( $7.4 \times 10^{-10}$  Torr at 25°C) (Shiu et al., 1988). These ubiquitous pollutants are released into the environment as by-products from sources such as waste incinerators and chlorinated chemical industries or forest fires (Kim et al., 2003). The fate of PCDD/Fs is finally to the particle e.g. soil or sediments, because they are strongly bound to the surface due to their low solubility.

There are extensive studies to treat PCDD/Fs on particulate matter, such as thermal destruction, Fenton process for AOP, bioremediation including anaerobic and aerobic microorganisms. Fenton oxidation process to the degradation of PCDDs/Fs showed that pretreatment with Fenton's reagent before biological degradation is more effective than direct biodegradation of PCDD contaminated soils (Kao et al., 2000).

The persulfate free radical ( $\text{SO}_4^{\cdot-}$ , ORP = 2.6 V), which can be generated from boiling persulfate, is roughly equivalent to the hydroxyl free radical in reactivity. Heat activated persulfate (HAP) using combined technology of in situ chemical oxidation (ISCO) and in situ thermal remediation (ISTR) was applied for destruction of PCE, TCE and the other toxic organics (Liang et al., 2004; Waldemer et al., 2007). The majors of

HAP process are (1) direct transport of HAP to PCDD/Fs contaminated site through water, (2) HAP doesn't need any catalyst for activation compared to Fenton oxidation process.

To explore the treatability of PCDD/Fs on particulate matter, several PCDD/Fs congeners were tested to examine the degradation kinetics by HAP. To simulate the particulate matters containing PCDD/Fs, various size of glass beads were used as the absorbent for PCDD/Fs. Also the dosages of persulfate to treat PCDD/Fs were examined.

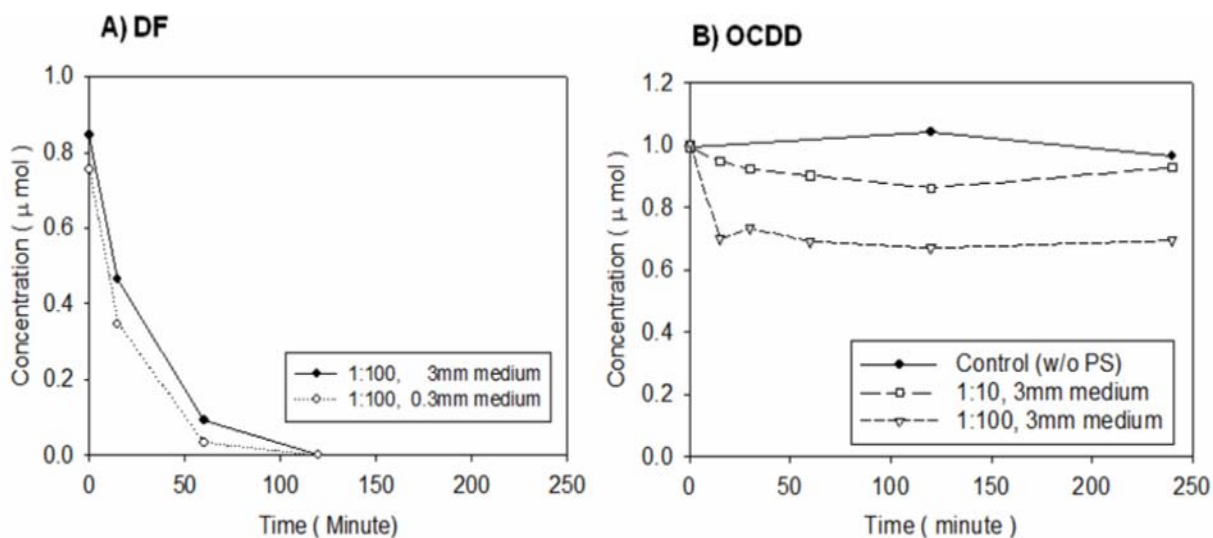
## MATERIALS AND METHODS

**Batch Experiments.** Glass beads (3.0mm and 0.15 mm size, Biospec Products, Inc.) were washed with 0.1 N HCl before experiments. 10 g of the washed beads were put into the 40mL reaction vials and 1  $\mu$  mol of PCDD/Fs native congeners (dibenzofuran(DF), dibenzo-p-dioxin(DD), 1-monochlorinated dibenzo-p-dioxin (1-MCDD), 1,2-DiCDD, 1,2,3-Trichlorinated dibenzo-p-dioxin (1,2,3-TriCDD), 1,2,3,4-tetrachlorinated dibenzo-p-dioxin (1,2,3,4-TCDD) and octachlorinated dibenzo-p-dioxin (OCDD), Accustandard) in acetone were spiked to the surface of glass bead. Then 2mL of acetone were added to the vials and was removed under N<sub>2</sub> stream to dope the PCDD/Fs on glass bead homogeneously and to remove the effect of solvent on reaction of PCDD/Fs. Then 10mL of distilled water to the vials and the vials were heated to 70°C. After temperature equilibration time 10 ~ 100  $\mu$  mol of persulfate (Sigma, >98%, prepared at 0°C) was added to the vials to initiated the reaction. The vials were mixed on the orbital mixer (150 rpm) operated at 70°C. At designed sampling time, the vials were cooled in ice to quench the reaction.

**Extraction and Analysis.** After cooling, the solution and the glass bead were separated and extracted respectively. 1,2,3,4-tetrachlorinated naphthalene was spiked as recovery standard. The solution was extracted by 3mL of toluene and the glass bead was separated by 3mL acetone at first and by 3mL of toluene at second. All extracts was kept in refrigerator before analysis to prevent the sulfate radical generation. The identification of each congeners was performed by gas chromatography (Column: DB5-MS, 30 m  $\times$  0.25 mm, 0.25 m) with ion-trap mass spectrometry (IT-MS; Finnigan, Model: Polaris Q). The quantification was performed by GC-FID (HP6890N, DB5, 30 m  $\times$  0.25 mm, 0.25 m). The approximate detection limits were 10 picomoles with IT-MS and 100 picomoles with GC-FID.

## RESULTS AND DISCUSSION

Figure 1 shows the degradation results of DF and OCDD by HAP. Non-chlorinated compounds, DF was degraded fast within 2 hours, however, fully chlorinated compounds, OCDD was degraded slowly and only about 33% of OCDD was removed when OCDD was adsorbed on 3mm glass bead medium and 100 times persulfate dosage. The kinetics of lower chlorinated (0~3 chlorines) congeners disappearance were followed to pseudo-first-order, but higher chlorinated congeners (4~8 Chlorines) were inhibited and not followed to pseudo-first-order. All experimental results of persulfate reaction for each PCDD/Fs congeners, each type of glass beads medium and persulfate dosages are listed on Table 1.

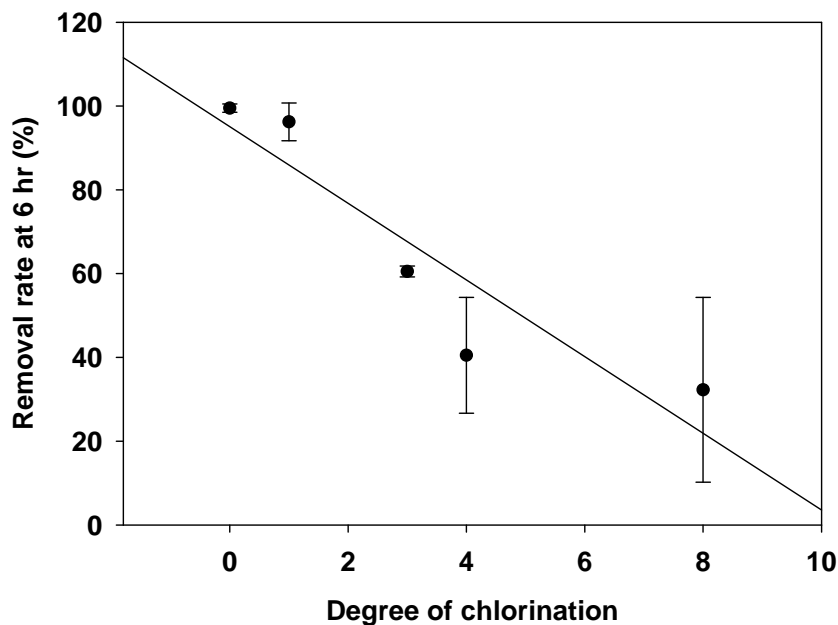


**FIGURE 1. Degradation profiles of A) DF and B) OCDD by persulfate injection.**

**TABLE 1. PCDD/Fs removal rates after 1 hr and 6 hr reaction.**

Congeners	1:10 (PCDD/Fs : persulfate)				1:100 (PCDD/Fs : persulfate)			
	3 mm		0.15 mm		3 mm		0.15 mm	
	Removal @ 1H (%)	Removal @ 6H (%)	Removal @ 1H (%)	Removal @ 6H (%)	Removal @ 1H (%)	Removal @ 6H (%)	Removal @ 1H (%)	Removal @ 1H (%)
DF	85	100	87	100	91	100	96	100
DD	78	98	84	100	88	100	90	100
1-MCDD	61	91	74	94	62	100	78	100
1,2,3- TriCDD	48	60	45	62	46	61	43	59
1,2,3,4- TCDD	21	36	33	34	29	31	62	61
OCDD	6	5	31	32	31	33	48	59

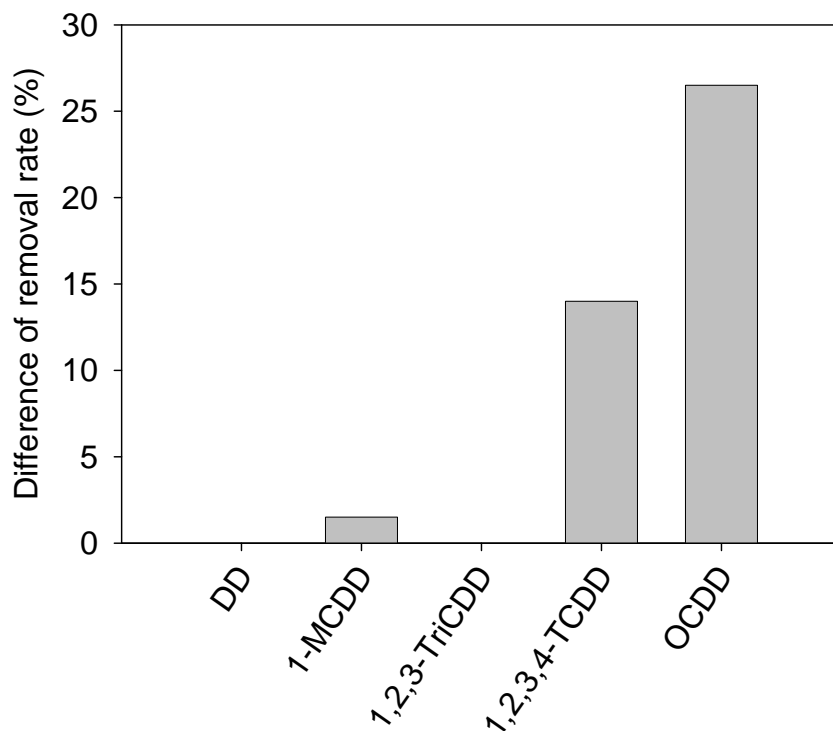
**Effect of Chlorination.** Figure 2 shows the relationship between the degrees of chlorination of the selected PCDDs and their removal rate by HAP. As a general, the kinetics of PCDD/Fs decreased as the numbers of chlorines increased. One possible reason for the effects of chlorination may be steric hindrance between the sulfate free radical and chlorines in PCDD/Fs molecules. This phenomenon is also observed in microorganism and advanced oxidation process such as Fenton's reaction, which are utilizing hydroxyl free radical as oxidant (Kao et al., 2000; Nam et al, 2006).



**FIGURE 2. Relationship between the degrees of chlorination of the selected PCDDs and their removal rate by heat-activated persulfate.**

**Effects of Medium Size.** The removal rate of PCDD/Fs on 0.15 mm glass bead was about 8% higher than that on 3 mm glass bead as Table 1 shown. Experiments for various sized medium of absorbents should be carried out further to elucidate the relationship between the reaction area and removal rate. However we can postulate that the increased area of reaction site might be the reason for the PCDD/Fs removal enhancement. On the analogy of this finding, treatment of PCDD/Fs polluted soil or sediment by HAP could have the advantage, because the levels of PCDD/Fs in environmental particulate matrices tends to increase as the particle sized decreased (Lee et al., 2006).

**Effects of Persulfate Dosage.** In case of lower chlorinated compounds (0~3), the removal rate was not enhanced by the increase of persulfate dosage. However, the removal rate of higher chlorinated compounds increased as persulfate dosage increased as Figure 3 shown. With this finding, the dosage of persulfate should be determined from not only the total concentration of PCDD/Fs, but also from the homologue pattern of PCDD/Fs in HAP application.



**FIGURE 3. Difference of removal rate between 1:10 and 1:100 persulfate dosage.**

## CONCLUSION

Results of the laboratory experiments presented that PCDD/Fs on particulate can be treated by HAP. Furthermore we found that (1) the removal rates of PCDD/Fs decreased as the numbers of chlorines increased by HAP, (2) the PCDD/Fs on the fine particle were removed better than on the coarse particle, (3) to treat the high chlorinated compounds, more persulfate should be consumed.

Still, the limitation of HAP on PCDD/Fs treatments is remained, that is the difficulty of treatments of the higher chlorinated compounds. Combined treatment with dechlorination by zerovalent iron could be the solutions for the limitation of HAP on PCDD/Fs treatment, and our groups are trying to combining the iron activated persulfate and zero valent iron to treat the PCDD/Fs.

## ACKNOWLEDGMENTS

This work was supported by BK 21 Project, POSCO and Korea Research Foundation grant funded by the Korean Government (MOEHRD) (KRF-2006-612- D00052).

## REFERENCES

Kao, C.M., and M.J. Wu. 2000. "Enhanced TCDD degradation by Fenton's reagent preoxidation." *Journal of Hazardous Materials*. 74: 197-211.

- Kim, E.J., J.E. Oh, and Y.S. Chang. 2003. "Effects of forest fire on the level and distribution of PCDD/Fs and PAHs in soil." *Science of the Total Environment*. 311: 177-189.
- Lee, S.J., J.H. Kim, Y.S. Chang, and M.H. Moon. 2006. "Characterization of polychlorinated dibenzo-p-dioxins and dibenzofurans in different particle size fractions of marine sediments." *Environmental Pollution*. 144: 554-561.
- Liang, C., C.J. Bruell, M.C. Marley, and K. L. Sperry. 2004. "Persulfate oxidation for in situ remediation of TCE. I. Activated by ferrous ion with and without a persulfate-thiosulfate redox couple." *Chemosphere*. 55: 1213-1223.
- Nam, I.H., Y.M. Kim, S. Schmidt, and Y.S. Chang. 2006. "Biotransformation of 1,2,3-tri- and 1,2,3,4,7,8-hexachlorodibenzo-p-dioxin by *Sphingomonas wittichii* strain RW1." *Applied and Environmental Microbiology*. 72: 112-116.
- Shiu, W.Y., W. Doucette, F.A.P.C. Gobas, A. Andren, and D. Mackay. 1988. "Physical-chemical properties of chlorinated dibenzo-p-dioxins." *Environmental Science & Technology*. 22: 651-658.
- Waldemer, R.H., P.G. Tratnyek, R.L. Johnson, and J.T. Nurmi. 2007. "Oxidation of chlorinated ethenes by heat-activated persulfate: Kinetics and products." *Environmental Science and Technology*. 41: 1010-1015.