

UV light-Induced Reductive Degradation of Haloaliphatic Compounds

*Sun Hee Yoon¹⁾, Dong Suk Han¹⁾, Ahmed Khodary¹⁾, Bill Batchelor²⁾ and
Ahmed Abdel-Wahab³⁾

¹ *Chemical Engineering Program, Texas A&M University at Qatar, Education City, PO
Box 23874, Doha, Qatar*

²⁾ *Zachry Department of Civil Engineering, Texas A&M University, College Station,
TX77840-3136, USA*

¹⁾ sun_hee.yoon@qatar.tamu.edu

ABSTRACT

Reductive degradation of 1,2-dichloroethane (1,2-DCA) and vinyl chloride (VC) occurred combination of ultraviolet (UV) and reducing agents in anaerobic environment. This is a new treatment process called advanced reduction process (ARP) that produces electron-rich radical anions exerted by UV radiation to break down chemical structure. In this study, different types of UV light (medium pressure mercury UV (UV-M), narrow-banded UV (UV-N), and low pressure mercury UV (UV-L)) emitting different light intensities and wavelengths have been employed as an energy source. Efficient degradations of 1,2-DCA was observed in reducing agents adsorbing light from UV-M lamp. Among the reducing agents investigated, specifically, sodium dithionite and sodium sulfite were found to be the best candidate to enhance the degradation of 1,2-

¹⁾ Postdoctoral research associate

²⁾ Professor

³⁾ Associated professor

DCA. Similar result was obtained in degradation of VC using UV-M/dithionite and UV-L/dithionite.

1. INTRODUCTION

1,2-dichloroethane (1,2-DCA) and vinyl chloride (VC) are among the national priority list (NPL) for environmental contaminants due to their serious effects on human health and the environment. They are more carcinogenic and recalcitrant in the water or air than other chlorinated aliphatic hydrocarbons (Scheutz et al., 2011). Due to their toxicity, a lot of remediation technologies have been increasingly emerged and developed. Many contamination sites has been being treated using biodegradation or biotransformation (Scheutz et al., 2011; Le and Coleman, 2011; Davis et al., 2009). As alternative technology to degrade chlorinated organic compounds, advanced oxidation process (AOP) has been widely employed, yielding hydroxyl radicals (OH^\bullet) from hydrogen peroxide when they are irradiated by a source of exerted energy such as UV light with catalyst (TiO_2) (Alnaizy and Akgerman, 2000; Wei et al., 2011). Although the use of AOP is populated in giving effective removal efficiency, reducing toxic intermediate products, and decreasing treatment time, the AOP has a limitation to reduce or transform oxidized compounds such as organic compounds containing C-H halogen groups (F, Cl, Br), and inorganic compounds (bromate, perchlorate, arsenate). In this study, the reductive degradations of 1,2-DCA and VC were investigated by a new treatment group of Advanced Reduction Process (ARP).

2. MATERIALS AND METHODS

2.1. Reagents and Apparatus

All chemical reagents were of analytical reagent grade. 1,2-dichloroethane ($\geq 99\%$, A.C.S reagent) and vinyl chloride were purchased from Sigma-Aldrich and Supelco. Sodium hydrosulfite ($\text{Na}_2\text{S}_2\text{O}_4$, Sigma-Aldrich), sodium sulfite (Na_2SO_3 , Mallinckrodt Chemicals), sodium sulfide nonhydrate ($\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, Sigma-Aldrich) and iron (II) sulfate heptahydrate ($\text{FeSO}_4\cdot 7\text{H}_2\text{O}$, Sigma-Aldrich) were used as reducing agents. Acetate (pH 4.5, HACH), phosphate buffer (pH 7.2, APHA), sodium phosphate dibasic anhydrous (Na_2HPO_4 , Mallinckrodt Co.) and sodium hydroxide (NaOH, Sigma-Aldrich) were used as buffer solutions. *n*-Hexane (HPLC grade, VWR) was used as a solvent to extract 1,2-DCA. All experiments were performed in anaerobic chamber (Coy Laboratory Products Inc.) with 99.99% N_2 gas. For all solutions, deoxygenated/deionized water (DDW) was prepared by purging 99.99% N_2 gas into 18 M Ω cm deionized water.

A medium pressure mercury ultraviolet (UV-M) lamp was purchased from UV-Consulting Peschl. The primary out of the lamp was 384nm and irradiated at approximately 2400 $\mu\text{watt}/\text{cm}^2$ of light intensity. As another type of UV lamp, a narrow banded UV (UV-N) lamp was purchased from Vilber Lourmat. The primary out of the lamp was at 312 nm and irradiated at 730 $\mu\text{watt}/\text{cm}^2$ of light intensity. A low pressure mercury ultraviolet (UV-L, 215nm) which has been popularly used in advanced oxidation process was purchased from Vilber Lourmat.

2.2. Analytical Methods

The analytic method for 1,2-DCA was carried out by gas chromatography (Agilent Technologies 7890A GC system) with micro-electron capture detector (μECD) in

splitless mode. The temperatures of the injector and the detector were set up to 200 and 280 °C, respectively. The oven temperature was programmed from 35 °C to 225 °C starting with hold at 35 °C for 15 min, then a ramp of 10 °C/min, a hold at 140 °C for 10 min, a ramp of 20 °C/min and a final hold of 1 min at 225 °C. Makeup flow of nitrogen gas was 15 mL/min and helium was used as a carrier gas. VC was analyzed using gas chromatography with flame ionization detector (FID) with headspace analyzer. For the operation of headspace analyzer, temperature of oven, loop, and transfer line were set to 85°C, 105°C, and 110°C, respectively. GC oven was programmed from 40°C at 3 min of a hold time, a hold of 8 min in 60 °C at 40°C/min, a hold of 5 min in 180 °C at 30°C/min, and then hold 6 min in 250 °C at 20 °C/min.

3. RESULTS AND DISCUSSION

Figure 1 shows that combination of reducing agents (RA) and UV light has a potential in degrading 1,2-DCA under anaerobic condition. It is evident that among four candidates chosen as a reducing agent, both dithionite and sulfite are capable of effectively decreasing initial concentration of aqueous 1,2-DCA as activated by UV-M or UV-N. Under UV irradiation, dithionite would be easily broken and transformed into sulfoxyl radical anions ($\text{SO}_2^{\cdot-}$) that yield abundant electrons because dithionite composes of long and week sulfur-sulfur bond. Sulfite anion that adsorbs wavelength of about 235 nm would become sulfite radical ions in a wide range of UV-M wavelength (200~600nm). However, under UV-N irradiation, sulfite anion would less adsorb UV-N light since UV-N has 312nm of wavelength. Based on the calculation of photon energy formulation, C-Cl bond in 1,2-DCA could be broken near 318 nm that is near the

primary output of UV-N wavelength. It would be postulated that the degradation efficiency was highly related to transference of electrons obtained from sulfite radical anions and wavelength in which UV absorbance for 1,2-DCA was the greatest. Conversely, Fe^{2+} and S^{2-} radiated by both types of UV light were not activated enough to give electron to rupture the chemical structure of 1,2-DCA. A batch experiment was conducted to degrade VC using dithionite/UV-M and their results were shown in Figure 1. The results showed the highest degradation efficiency of 1,2-DCA (Figure 2a). Figure 2b shows the reactivity of dithionite on degradation of VC as irradiated by UV-L. Aqueous dithionite could adsorb much energy from UV light in the range of wavelength from 200 to 400nm that is in good accordance with optimal irradiation of UV-M and UV-L lamps.

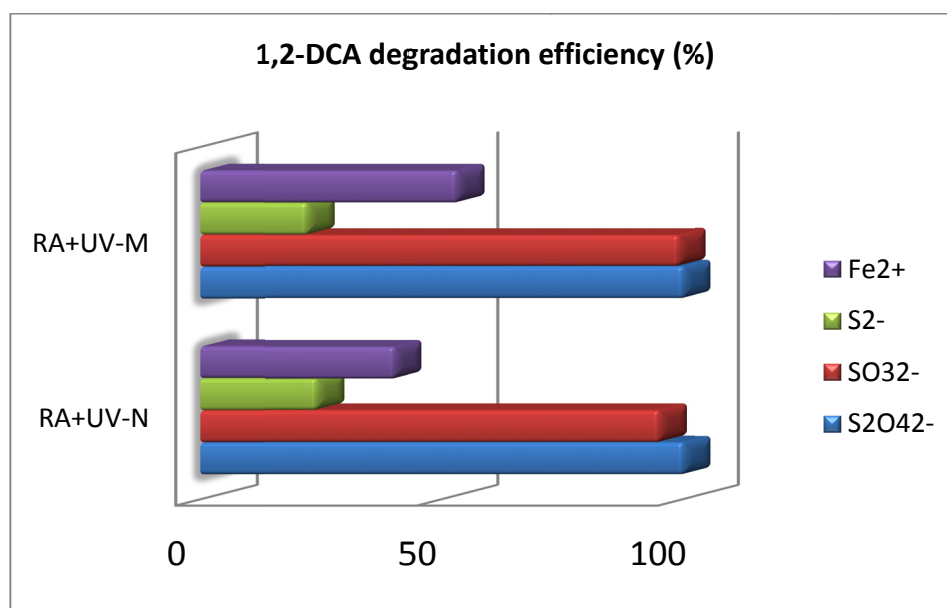


Figure 1. Degradation of 1,2-DCA by dithionite ($\text{S}_2\text{O}_4^{2-}$), sulfite (SO_3^{2-}), and sulfide (S^{2-}) and ferrous iron (Fe^{2+}) at pH = 7.2~7.4 and at reaction time = 60 min.; initial 1,2-DCA concentration = 0.25 mM; initial concentrations of reducing agents = 0.25 mM.

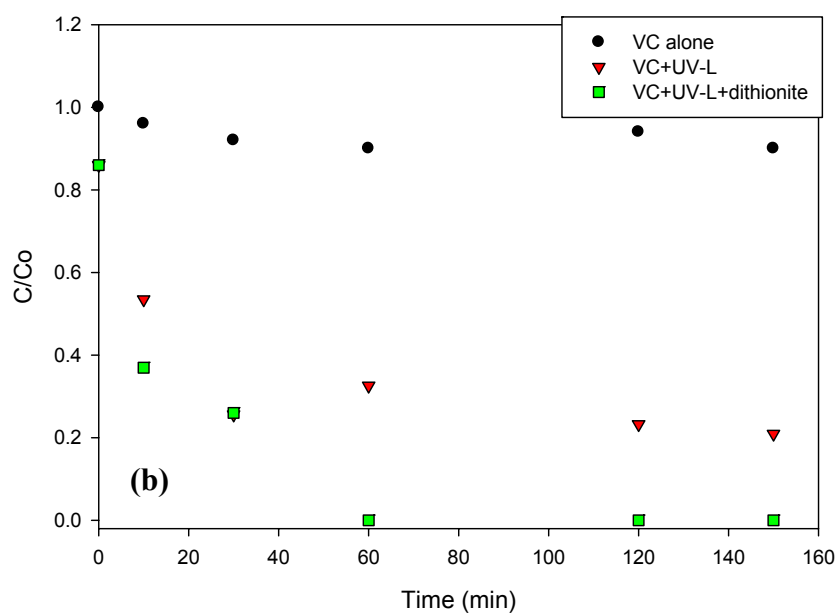
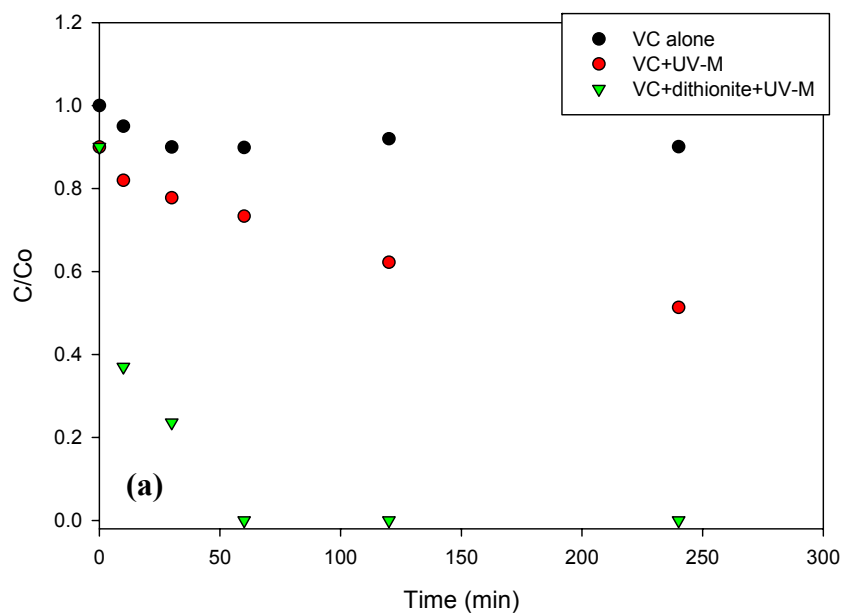


Figure 2. Comparison of source of UV light between the remaining fraction of DCA in aqueous dithionite solution at pH 7.01. Initial concentration of VC = 0.008mM; initial concentration of dithionite = 0.16mM.

4. CONCLUSION

A new treatment group of ARP efficiently enhanced degradation of aqueous 1,2-DCA and aqueous VC. Under UV-M irradiation, dithionite and sulfite became an abundant electron donor to completely degrade 1,2-DCA. Similar result was observed in the use of dithionite/UV-M. Dithionite was also well-activated by UV-L and its potential as a good electron donor was proved in decreasing aqueous VC.

REFERENCES

- Scheutz, C., Durant, N. D., Hansen, M. H. and Bjerg, P. L. (2011). "Natural and enhanced anaerobic degradation of 1,1,1-trichloroethane and its degradation products in the subsurface - A critical review." *Water Research* 45(9): 2701-2723.
- Le, N. B. and Coleman, N. V. (2011). "Biodegradation of vinyl chloride, cis-dichloroethene and 1,2-dichloroethane in the alkene/alkane-oxidising *Mycobacterium* strain NBB4." *Biodegradation* 22(6): 1095-1108.
- Davis, G. B., Patterson, B. M. and Johnston, C. D. (2009). "Aerobic bioremediation of 1,2 dichloroethane and vinyl chloride at field scale." *Journal of Contaminant Hydrology* 107(1-2): 91-100.
- Alnaizy, R. and Akgerman, A. (2000). "Advanced oxidation of phenolic compounds." *Advances in Environmental Research* 4(3): 233-244.
- Wei, M. C., Wang, K. S., Hsiao, T. E., Lin, I. C., Wu, H. J., Wu, Y. L., Liu, P. H. and Chang, S. H. (2011). "Effects of UV irradiation on humic acid removal by ozonation, Fenton and Fe-0/air treatment: THMFP and biotoxicity evaluation." *Journal of Hazardous Materials* 195: 324-331.