

## Degradation of dichloroacetonitrile by sonolytic ozonation

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### 1. Introduction

Dichloroacetonitrile (DCAN) is one of haloacetonitriles (HANs) mainly found in drinking water after chlorine disinfection. According to the World Health Organization (WHO), DCAN is amended to 0.09mg/l in drinking water. its regulation in South Korea is 0.09mg/l. According to the International Agency for Research on Cancer (IARC) and the United States Environmental Protection Agency (USEPA), DCAN is fetal and can cause malformations, and lung cancer<sup>[1]</sup>. Therefore an intensive study on development and demonstration of degradation system has to be considered to overcome the toxicity.

Advanced oxidation processes (AOPs) using ozonolysis, sonolysis and sonolytic ozonolysis are used to remove various pollutants such as phenolic compounds, organic dyes and hormones<sup>[2]</sup>. Sonolytic ozonolysis can produce more additional hydroxyl radicals which are strong oxidizing agent than sonolysis and ozonolysis. However, there are a few researches for treatment of the chlorine disinfection byproducts in drinking water treatment plant by sonolytic ozonolysis.

Therefore, the comparison of degradation rate constants between ozonolysis, sonolysis, and sonolytic ozonolysis of DCAN was investigated. And the mineralization rate of DCAN was studied.

### 2. Experimental methods

Dichloroacetonitrile (DCAN) was purchased from Sigma Aldrich (99.5% pure grade) and Methyl tert-butyl ether (MTBE) was purchased from JTBaker. A cylindrical pyrex vessel sonoreactor (Mirae Ultrasonic Tech. Inc.) equipped with one transducer (cup horn type) was placed under the reactor was used. Ozone from ozone generator (LAB 2B model) was injected into the reactor. The gas phase ozone analyzer (IN USA, Inc.) is installed on the top of the reactor. Liquid phase ozone analyzer (Analytical technology, Inc.) was installed with pump and sampling port. Reactor was closed by cork on the top. The concentration of dichloroacetonitrile was measured using GC-MS (Agilent 7890A & Agilent 5975C). Total Organic

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Carbon (TOC) of samples was measured using a TOC analyzer (GE Sievers 5310C Laboratory TOC analyzer and a Sievers 900 Autosampler) and pH was measured by pH analyzer (Thermo orion, Inc.). 5 mg/L of DCAN solution on 2L and the temperature was maintained at 20°C and initial pH was 6.5. Ultrasonic frequency was set at 283 kHz, and 20 W/L of power density and 3.7 g/hr of ozone dose were applied. Experimental set up was shown in Fig.1.

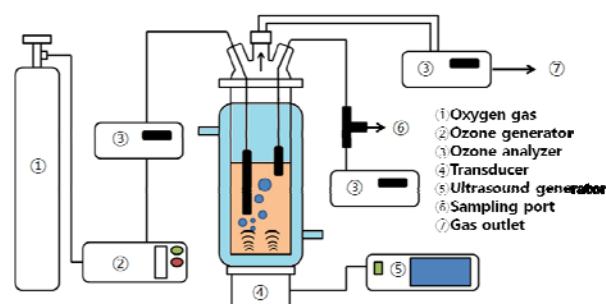


Fig. 1 Experimental set up.

### 3. Results and discussion

Advanced oxidation processes using ozone and ultrasound to oxidize organic matter and sonolytic ozonolysis process to remove the DCAN were studied. Fig. 2 shows the results from kinetic of Sonolysis, ozonolysis and sonolytic ozonolysis. And the pseudo first order rate constants were  $1.4 \times 10^{-3} \text{ min}^{-1}$ ,  $2.5 \times 10^{-3} \text{ min}^{-1}$  and  $8.4 \times 10^{-3} \text{ min}^{-1}$  for sonolysis, ozonolysis, and sonolytic ozonolysis, respectively. The rate constant for sonolytic ozonolysis was 2.15 times larger than sum of rate constants for the other processes. This result is suggested that ozone is decomposed by cavitation bubble collapse making in the addition of hydroxyl radicals.

Degradation mechanisms by ultrasound are pyrolysis and radical oxidation by hydroxyl radicals<sup>[3]</sup>. Hydroxyl radicals by ultrasound are generated during a cavitation event. For degradation of DCAN, the radical oxidation is main degradation mechanism because of its relatively low volatility. Ozonolysis provides the direct and indirect reactions to oxidize organic compounds<sup>[4]</sup>. Indirect reactions are produced by ozone and hydroxide ions with increasing pH<sup>[5,6]</sup>.

Sonolytic ozonolysis can produce more hydroxyl radical by thermal decomposition of ozone in collapse of cavitation bubble and reaction with water molecules as given below (eq 1-2)<sup>[7]</sup>.



Other mechanism for enhancement of sonolytic ozonolysis is high mass transfer of ozone from gas phase to liquid phase by physical effect of ultrasound. The ultrasound can produce mechanical effects such as mixing and breaking up of gas bubbles<sup>[8]</sup>.

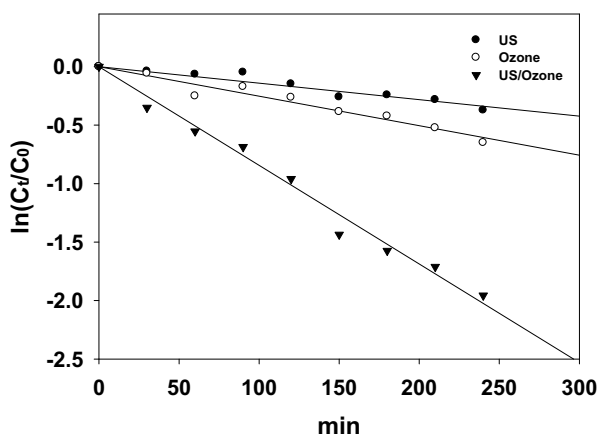


Fig. 2 Pseudo first order kinetics of DCAN (T: 20°C, initial pH: 6.5, ultrasound frequency: 283 kHz, power density: 20 W/L, ozone dose: 3.7g/L).

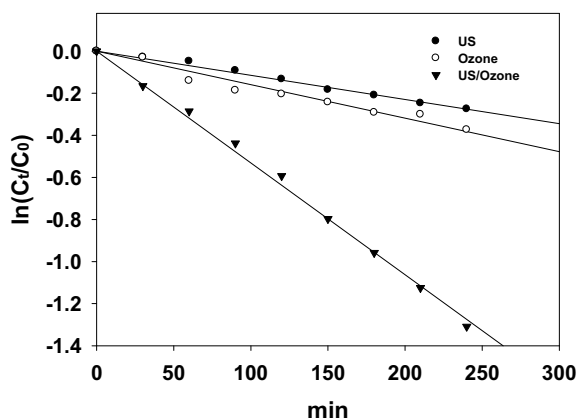


Fig. 3 Pseudo first order TOC of DCAN (T: 20°C, initial pH: 6.5, ultrasound frequency: 283 kHz, power density: 20 W/L, ozone dose: 3.7g/L).

Sonolysis, ozonolysis and sonolytic ozonolysis graph for removing TOC is shown in Fig. 3. The pseudo first order rate constants were  $1.15 \times 10^{-3} \text{min}^{-1}$ ,  $1.60 \times 10^{-3} \text{min}^{-1}$ ,  $5.31 \times 10^{-3} \text{min}^{-1}$  for sonolysis, ozonolysis, and sonolytic ozonolysis, respectively. Synergistic effect of sonolytic ozonolysis was approximately 1.93 times.

Applied ultrasonic frequency was 283 kHz in this study, however, there is an argument regarding the optimal frequency. L. weaver and M. Hoffmann reported that a low frequency (20 kHz) was more effective than high frequency (500 kHz) to degrade organics compound<sup>[8]</sup>. And Kang et al. reported the existence of the optimal frequency between 205 to 1078 kHz<sup>[9]</sup>. However, the input energy and the reactor shape were not the same in each experiment. Therefore, more investigation are needed for determining optimal frequency for sonolytic ozonolysis.

#### Acknowledgment

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