

## Effect of Ultrasonic Frequency on Chlorinated Compounds Degradation

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### 1. Introduction

The application of ultrasound to an aqueous solution produces cavitation bubbles, with extremely high temperature and pressure. The collapse of a bubble transfers the high energy to the interfacial region, where the dissolved organic pollutants in the aqueous phase can undergo a transformational reaction via pyrolysis and a radical reaction. The volatile species directly diffuse into the cavitation bubbles, which are then decomposed inside the bubble due mainly to pyrolysis. Conversely, non-volatile compounds are mainly degraded at the interfacial region by their reaction with radicals generated from the cavitation.

In previous studies with frequency which describe the ultrasonic destruction of many organic pollutants in water (phenol [1-3], atrazine and pentachlorophenol [4], carbon tetrachloride [2,5], 4-chlorophenol [6], trichloroethylene [5], chlorobenzene [7], 1,4-dioxane [8,9]). Most of work is performed with the help of the commercially available probe system working at 20 kHz, but it has not been demonstrated that for the same acoustical power the high frequency. Therefore, more researches with frequency under the same experimental conditions (same calorimetric power and reaction volume) were needed.

In this study, the effects of frequency on the chlorobenzene, chloroform were examined on the sonochemical degradation. The reaction rates of compounds were evaluated by frequencies. The formation of chloride ion (Cl<sup>-</sup>) from the chlorinated compounds and degradation of total organic carbon (TOC) concentration was measured.

### 2. Experimental Procedures

The highly pure compounds that were used in this experiment were as follows: chloroform (CF, Samchun); chlorobenzene (CB), potassium iodide (KI, Junsei), potassium biphthalate (Junsei), ammonium molybdate (Junsei), hydrogen peroxide (34.5%, Junsei).

The initial concentrations of chlorobenzene, and chloroform were 0.05 mM. 1 L of the aqueous solution was placed in a pyrex reactor. For the sonochemical degradation, the cup horn type reactor was placed in a constant temperature water bath (16±2 °C), with ultrasound then applied. The schematic of the reactors is presented in Fig. 1.

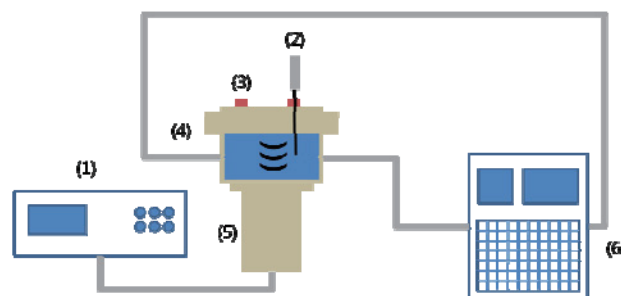


Fig. 1 Schematic of batch reactor (cup horn type): (1) Ultrasound generator, (2) Thermometer, (3) Liquid Sampling port, (4) Reactor, (5) transducer, (6) Cooling system

The 35, 74, 170 kHz frequencies were emitted from the Frexonic (Mirae Ultrasonics Tech., Korea) which consisted of single piezoelectric transducer (PZT, Tamura corp.). The 300 kHz and 1 MHz were individually irradiated by the MX-300 and Megasonic (Mirae Ultrasonics Tech., Korea) with single PZT (Tamura corp.). The diameter of the transducer is 10cm and it is the same for all frequencies. For each frequency, the same calorimetric power was applied. A 2mL aliquot was sampled at every 30 min, with the concentrations of chlorobenzene and chloroform analyzed using a gas chromatograph (series 6890N, Agilent, USA), with a flame ionization detector and a purge & trap unit (Tekmar Dohrmann, Velocity XPT, USA). In order to measure chloride ion, the by-product from the degradation of chlorinated pollutants was measured by ion chromatography (Dionex, DX 500). The TOC concentration was measured using a TOC analyzer (SEIVERS 5310C laboratory analyzer, GE) every 60 min.

### 3. Result and discussion

The concentration change of chlorinated compounds is shown in Fig. 2. A more rapid

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degradation of CB and CF occurred during sonolysis at 300 kHz than other frequencies. The order of degradation rate in each compound is 300>1,000>35>74>170 kHz. It is same with two chlorinated compounds.

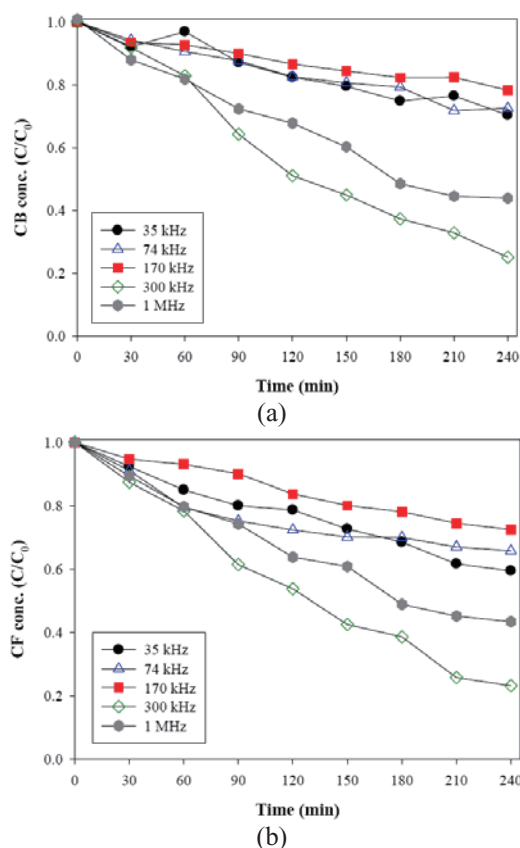
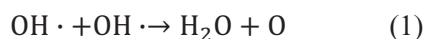
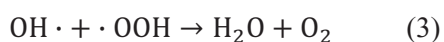


Fig. 2 Effect of frequency on the ultrasonic degradation of chlorinated compounds (a) chlorobenzene, (b) chloroform

At a higher frequency, the power of the cavitation effect decreased. Therefore, the cavitation event occurring at a low frequency is more violent and efficient on the inside of the cavitation bubble. However, at a low frequency the acoustic period is shorter than a high frequency. Following reaction pathways to those found in chemistry, in particular those leading to oxygen generation (Eq. [1,2]).



Consequently, most of the formed radicals have sufficient time to recombine. More hydroxyl radicals are available if they escape from the bubble (high frequency) in the medium. At low frequency, in the long-lived bubble, OH· can be scavenged by reaction with the hydroperoxyl radical (Eq. [3]).



In most cases, there exists an optimum frequency which the rate of radical production and the duration of cavity collapse provide the best conditions for the destruction of the target chemical [3,6]. Previous research has shown that the degradation rate of non-volatile compounds at higher frequencies (200, 500, 800 kHz) is faster than at lower frequencies (20 kHz) [2]. In case of the tendency at different frequencies for the degradation rate of volatile compounds is same. The degradation rate constants at high frequencies (500, 800 kHz) are higher than low frequencies (20 kHz) [2,7]. But those results showed only comparing single low and high frequency. In this research, two chlorinated compounds have optimum frequency (300 kHz). And the existence of optimum frequency for degradation of chlorinated compounds was confirmed.

Chlorine ion was detected by degradation of chlorinated compounds as a result of the cleavage of carbon-chlorine bond by high temperature and pressure inside of cavitation bubble [10]. In the case of TOC concentration was remained after 4 hours sonication (over 50 % of initial TOC). Hydrogen peroxide or some catalysts (Fe<sub>2</sub>SO<sub>4</sub>) and a combination of AOPs are required for the degradation of TOC.

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