Sonophotolytic and sonophocatalytic degradation of THMs mixture in aqueous phase

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1. Introduction

During chlorine disinfection for inactivation of harmful microorganism to human health in water supply system, various disinfection byproducts (DBPs) are generated. These DBPs have possiblities to cause cancer when people drink such chlorine disinfected water. Among the DBPs, THMs are main compounds that in formed in large amount compared to others[1].

There are several physical and chemical treatment technologies for removing these THMs. However, the physical treatment technologies such as air-stripping, membrane filtration etc need further treatment because they just transfer those pollutants to other phasees. And ozonation is restricted to a degree due to the addition of ozone to treated water.

Application of ultrasound and ultraviolet provides mechanisms for oxidation of THMs in aqueous phase. By ultrasound, volatile pollutants can be pyrolyzed inside the bubbles and less volatiles can be oxidized by radical species interface or bulk phase according to volatility. By ultraviolet, a chemical bond which absorbs the light can be broken or hydroxyl radical from cleavage of water molecules oxidizes the pollutants.

A main degradation mechanism of THMs by ultrasound is pyrolysis due to its relatively high volatility. The order of degradation rate was $CHCl_3$ > $CHBrCl_2$ > $CHBr_2Cl$ > $CHBr_3$. However, application of ultraviolet shows opposite trend which is mainly due to C-Br band absorbing wavelength of 254nm. In this case, the order of degradation rate was $CHBr_3$ > $CHBr_2Cl$ > $CHBrCl_2$ > $CHCl_3$[2].

In this study, therefore, a comparison of rate constants between individual and combined system for degradation of THMs mixture was investigated. And evaluation of the synergistic effects was investigated in combined system.

2. Materials and Methods

Total concentration of THMs was 10 mg/L and each concentration was 2.5 mg/L. The stainless-steel- rectangular reactor consisted of one

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transducer located at the bottom of reactor and four UV lamps on the cap of reactor as shown **Fig. 1**. The UV lamp used generated UVC with a 200-280 nm wavelength for direct photolysis and photocatalysis. The total volume of the reactor was 3L and the reactor was filled with 1.5 L of solution. The applied ultrasonic frequency was 450 kHz and the input power of ultrasound and UVC lamps were 60 W and 40 W, respectively. A TiO_2 (Degusa P25) was used as catalyst and dose of TiO_2 was 0.3g/L. The temperature of solution was maintained at 20±2 degree Celsius by using the cooling system. The concentration of THMs was measured by a purge and trap (Teledyne Tekmar Velocity XPT) and a gas chromatography (Agilent 6890N) equipped with flame ionization detector (FID).
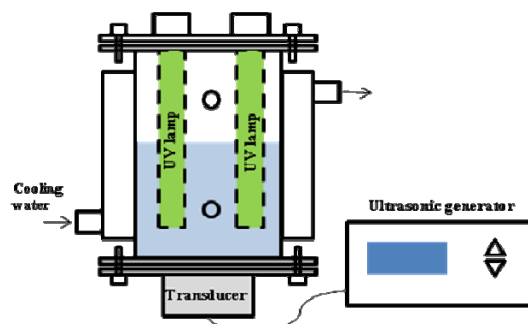

Fig. 1 Experimental setup

3. Results and Discussions

The observation rate constants of sonophotolysis were $2.03 \times 10^{-3} \sim 7.43 \times 10^{-1}$ min^{-1}. The degradation rate constant increased with the number of C-Br band as shown in **Fig. 2**. It is reported that the extinction coefficient of bromoform was 519 L mol^{-1} cm^{-1} and that of chloroform was 0.1 L mol^{-1} cm^{-1}. The ability for absorption of UVC light is 5190 times higher for bromoform which has 3 of C–Br band compared with chloroform which have 3 of C–Cl bands[3,4].

The enhancement of sonophotolysis is explained increased in concentration of hydroxyl radical produced b the dissociation of hydrogen peroxide which is formed by recombination of hydroxyl radicals. During sonication, hydroxyl radicals are

produced by the dissociation of water molecule in a cavitation bubble. These hydroxyl radicals can recombine to each other again forming hydrogen peroxides. Hydrogen peroxide can also be dissociated by UVC, therefore the enough hydroxyl radicals be maintained to oxidize compounds.
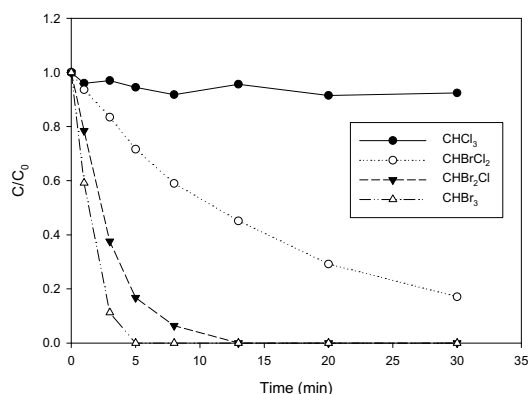

Fig. 2 Sonophotolytic degradation of THMs

In case of sonophotocatalysis, the observed degradation rate constants were $4.84 \times 10^{-3} \sim 1.71 \times 10^{-2}$ min^{-1} as shown in **Fig. 3**. It is 10 ~ 50 times smaller than sonophotolysis except chloroform. This is because an addition of catalyst inhibits the direct photolysis which is a strong dominant degradation mechanism for the removal of Br contained compound. On the contrary, the degradation mechanism for chloroform is not concentrated on direct photolysis, because of which little enhancement on the degradation was shown for chloroform.
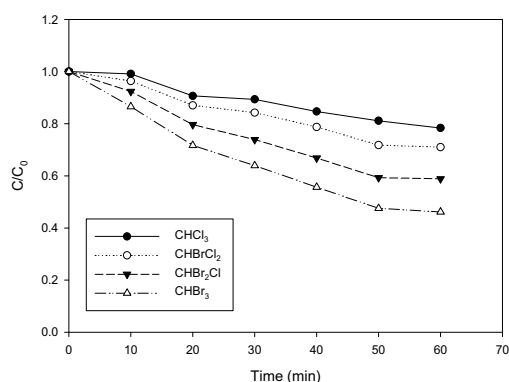

Fig. 3 Sonophotocatalytic degradation of THMs

In previous research, the observed rate constant for chloroform alone was 8.7×10^{-3} min^{-1} and mainly degraded by pyrolysis of ultrasound[5,6]. However, in the mixture, the rate is decreased because of a competition between THMs for

volatilizing into the cavitation bubble. In a case of photocatalysis, most of the ultraviolet energy was consumed by degradation of Br contained compounds which have high extinction coefficient. Therefore, addition of other oxidant or increase of energy intensity is required for treatment of THMs mixture, especially, chloroform.

Rate constants and synergistic effect of each process are shown **Table. I**. Even the degradation rate constant was the lowest; chloroform shows the highest synergistic effect in both sonophotolysis and sonophotocatalysis. A main mechanism for degradation of chloroform is pyrolysis by ultrasonic cavitation events, and radiation of ultraviolet provides additional mechanism which is radical oxidation. In a contrary, pollutants which have C–Br band were degraded by direct photolysis. The rate constants of degradation were increased with increase in the number of C–Br band. And the synergistic effect of Br contained compound was increased with increase of number in the Br in sonophotocatalysis.

Table. I Rate constants and synergistic effects.

THMs	Rate constant ($\times 10^{-3}$,min^{-1})			S	Rate constant ($\times 10^{-3}$,min^{-1})			S
	US	UV	US /UVC		US /TiO$_2$	UV /TiO$_2$	US/UVC /TiO$_2$	
CHCl$_3$	0.72	0.42	2.03	0.78	0.59	1.55	4.84	1.09
CHBrCl$_2$	0.66	50.25	59.2	0.16	0.52	3.23	6.70	0.77
CHBr$_2$Cl	0.64	276	353	0.28	0.45	6.62	11.0	0.56
CHBr$_3$	0.60	504	743	0.47	0.32	11.71	17.1	0.42

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