1Pa-41

Proceedings of Symposium on Ultrasonic Electronics, Vol. 31 (2010) pp. 97-98
6-8 December, 2010

Sonophotocatalytic destruction of chloroform : Synergistic effect

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1. Introduction

Trihalomethanes (THMs) can be generated in chlorine disinfection process in water supply system due to various precursors such as natural organic matters (NOMs) and are quite harmful to human health. Among the THMs, chloroform is one of the compounds that in formed in large amounts. And this compound has been known a carcinogen in experimental animal such as rats [1].

For the removal of these pollutants, a variety of technologies including ozonation, air-stripping, activated carbon adsorption, and membrane separation are used. But, these technologies have some disadvantages for treatment of chloroform. The ozonation has to control a concentration of ozone in the aqueous phase because it is harmful to life. Air-stripping, activated carbon adsorption, and membrane separation process need further treatment because they just transfer the pollutant from aqueous phase to other phase [1].

Recently ultrasound (US) has emerged as one of innovative advanced oxidation processes. During cavitation events volatile compounds can be pyrolyzed inside the cavitation bubble and less volatile compounds can be oxidized by radical species in the interface and bulk phase. Moreover it was revealed that the removal of pollutants could be enhanced significantly when ultrasound, ultraviolet and catalyst (TiO_2) were used simultaneously [2,3].

Degradation chloroform by ultrasound has been studied in few research groups. But parameters related with only ultrasound and solution, such as power intensity, pH, and temperature, were investigated [1,4,7].

In this study a combination of ultrasound, ultraviolet and catalyst for degradation of chloroform were applied. And the synergistic effect was defined and the evaluation of synergistic effect was investigated at optimal condition in US/UV system.

2. Materials and Method

Chloroform (99%) was purchased from Sigma-Aldrich. A 10 mg/L of chloroform was used in the reaction system. The stainless- steel-rectangular reactor consisted of one transducer located at the bottom of reactor and four UVC lamps on the cap of reactor. The total volume of the reactor was 3L and the reactor was filled with 1.5 L of solution. The applied ultrasonic frequencies are 35, 283, 450, and 935 kHz and the input power of ultrasound and UVC lamps were 60 W and 40 W, respectively. The temperature of solution was maintained at 20±2 degree Celsius by using the cooling system. The concentration of chloroform was measured by a purge and trap (Teledyne Tekmar Velocity XPT) and a gas chromatography (Agilent 6890N) equipped with flame ionization detector (FID). Total organic carbon (TOC) was measured by TOC analyzer (SIevers 5310C).

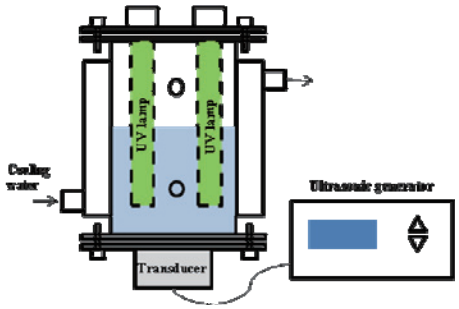

Fig. 1 Experimental setup.

3. Results and discussion

To evaluate a synergistic effect of ultrasound combined with photocatalytic system, the synergistic effect has to be defined. So in this study, a synergistic effect has been defined that the value of rate constant at optimal condition of combined system is divided by sum of rate constants of each independent system at optimal condition. The equation is shown as below [5].

$$Synergy(S) = \frac{k_{combined}}{k_1 + k_2} \qquad (1)$$

Where, $k_{combined}$ is the rate constant of combined process, k_1 is the rate constant of ultrasound based process, and k_2 is the rate constant of ultraviolet based process. For calculation of the synergistic effect, the rate constants were evaluated by experiments.

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Fig. 2 shows the rate constants of each process according to ultrasonic frequencies. The optimal frequency for sonophotocatalytic degradation of chloroform was 283 kHz and 450 kHz of ultrasonic frequency and results were similar with other researcher [6]. For comparison with ultraviolet based process, photolysis and photocatalysis were carried out and the results were 0 and 3.33×10^{-2} min^{-1}. A Significant enhancement was observed on sonophotocatalytic degradation, the rate constant of sonophotocatalysis was 2 times more than photocatalysis and 10 times more than the other processes.

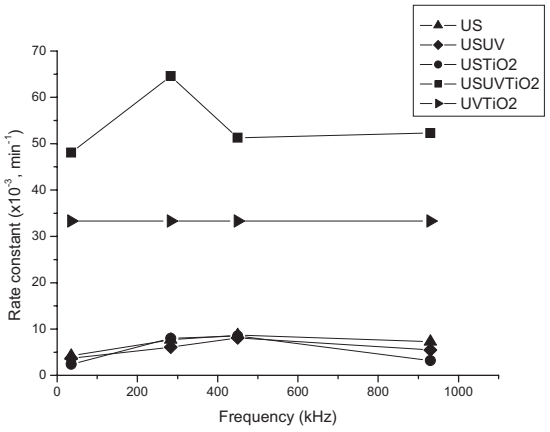

Fig. 2 Rate constants of each system according to ultrasonic frequency.

From these results, the values of synergistic effect were calculated by equation (1) and are shown in table 1. The synergistic effect which is only energy based process was 1.07 and it means only 9% of enhancement was observed comparing with sonolysis process (the rate constant on photolysis by UV was observed 0). But the synergistic effect of sonophotocatalysis of chloroform was 1.54 by addition of TiO_2 which works as catalyst.

Table I. The rate constants and values of synergistic effect

US Frequency (kHz)	Rate constant (x 10^{-3} ,min^{-1})		S	Rate constant (x 10^{-3} ,min^{-1})		S
	US	US/UV		US/TiO_2	US/UV/TiO_2	
35	4.2	3.7	1.14	2.4	48.1	1.35
283	7.7	7.7	1.26	8.0	64.6	1.56
450	8.7	8.1	1.07	8.5	51.3	1.23
935	7.3	5.5	1.33	3.2	52.3	1.43
optimum	**8.7**	**8.1**	**1.07**	**8.5**	**64.6**	**1.54**

The main degradation mechanism of chloroform by ultrasound was because of pyrolysis in the bubble inside and interfaces of bubble [7]. From the result of energy based process, almost of chloroform was destroyed by ultrasound. The ultraviolet cannot enhance the main mechanism (pyrolysis), so both energy sources acted independently.

Photocatalytic degradation of chloroform was very fast and the rate of degradation was enhanced by addition of ultrasound. It can be interpreted that the dispersion of catalyst was enhanced by the physical effect of ultrasound, because the catalyst was not work with ultrasound for a degradation of chloroform. And the ultrasound can enhance the mass transport of pollutants to surface of catalyst [8].

4. Conclusion

The synergistic effect was defined and a value of synergistic effect for sonophotolysis and sonophotocatalysis of chloroform was evaluated. The synergistic effect of sonophotolysis of chloroform was not significantly enhanced, because there were no reaction mechanisms relating to ultrasound and ultraviolet for degradation of chloroform. On the contrary, a significant enhancement was observed on sonophotocatalysis of chloroform. In this case, a main mechanism was photocatalysis. The ultrasound enhanced a dispersion of catalyst and mass transport of pollutants to surface of catalyst.

Acknowledgement

This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) grant funded by the Ministry of Education, Science and Technology (KRF-2009-0092799).

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