Decomposition of Dichloromethane by Discharge inside Bubble in Water

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ABSTRACT

Decomposition of dichloromethane (DCM) by discharge inside bubble in water is investigated. A gas injected discharge reactor is employed to achieve degradation with high energy efficiency. The reactor consists of a glass tube and a tungsten wire inserted into the glass tube, which is immersed in the water. The nanosecond pulsed high voltage generated by an inductive energy storage system pulsed power generator is applied to the tungsten wire to generate streamer discharge. Argon gas is injected into the glass tube to generate bubbles in the water. The experimental result shows that total organic carbon (TOC) and pH value decrease and chloride ion concentration increases by the discharge treatment. DCM is volatilized into the bubble, which is decomposed by hydroxyl radical produced by the discharge.

Keywords

Key Words (Water purification, discharge in bubble, dichloromethane, hydroxyl radical)

1. Introduction

Dichloromethane (DCM) is widely used as an industrial solvent and is one of hazardous chlorinated volatile organic compounds (VOCs). Owing to its chemical stability, it is difficult to decompose with conventional methods such as chemical oxidation and ozone treatment. A pulsed discharge plasma for treating pollutants in water has attracted a significant amount of attention. The pulsed discharge makes it possible to instantaneously produce a non-thermal plasma in which various chemical species, such as hydroxyl radicals, exist [1]~[3]. In this study, the decomposition of DCM by discharge inside bubble in water is investigated. Argon (Ar) and oxygen (O_2) gases are injected to identify the dominant reactions of the degradation of organic contaminants. In order to investigate the process of DCM decomposition, the experiments are conducted with mixed solution of DCM and Indigo carmine (IC).

2. Experimental Setup

The DCM solution is prepared by adding 1~ 6 μL of DCM into 15 mL of purified water in a 30 mL glass vial (Nichiden-Rika Glass, LTD, SVG-30) with a micro-syringe (SGE Analytical Science, 1 μL Syringe). The vial is sealed with a rubber cap coated with the Teflon, and is shaken for 2 hours. The concentration of DCM is ranged from 0.51 mM to 5.8 mM. The mixed solution of DCM and IC is prepared with dissolving IC into the DCM solution. The concentrations of DCM and IC in the mixed solution are adjusted at 0~5 mM and 0~1 mM, respectively.

Figure 1 shows a schematic diagram of the reactor [4]. Two glass tubes, in which the electrode of stainless steel wire (0.2 mm in diameter) or tungsten wire (0.2 mm in diameter) is inserted, are vertically immersed in the solution in the vial used for the preparation of the solutions. The inner diameter of both of the glass tubes is 0.8 mm. The electrode of the stainless steel wire is used as grounded electrode, and immersed the water. The length between the tip of the stainless steel wire and the tip of the glass tube is 20 mm. The electrode of the tungsten wire in the glass tube is placed above the water. The gap length between the tip of tungsten wire and the tip of glass

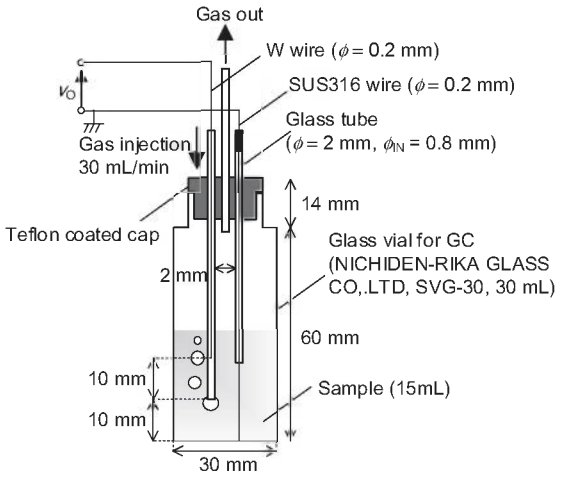

Fig. 1. Schematic diagram of the discharge reactor.

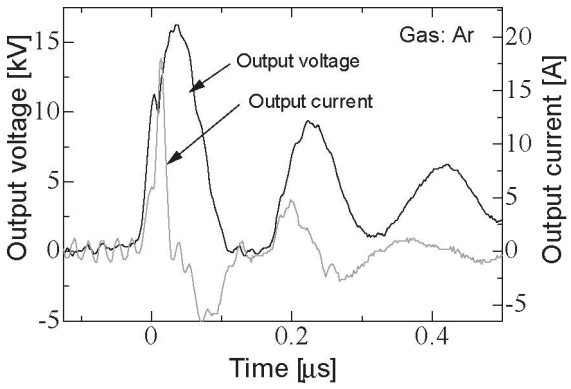

Fig. 2. Typical waveforms of output voltage and current.

tube is 10 mm. Argon gas is injected into the reactor through the glass tube with the tungsten wire. The gas flow rate is fixed at 30 mL/min. The injected gas is ejected through another glass tube placed in the center of the reactor. The pulsed voltage generated by The inductive energy storage system pulsed power generator [4] is applied to the tungsten wire to generate the streamer discharge in the tube and the bubble. Figure 2 shows the typical waveforms of output voltage and current. The peak value of the output voltage is 16 kV. The pulse repetition rate is fixed at 100 pulses per second.

The concentration of total organic carbon (TOC) of in the DCM solution is measured by a TOC analyzer (Shimadzu, TOC-VCSH), and DCM removal rate is obtained from the following equation:

$$\text{Amount of removed DCM} = \{\text{TOC (initial)} - \text{TOC (treated)}\} \times \frac{\text{MW of DCM (85)}}{\text{MW of Carbon (12)}} \times \frac{15}{1000}\,[\text{mg}] \quad (1)$$

The DCM removal rate is obtained by dividing the amount of removed DCM by the initial amount of DCM.

The concentration of chloride ion produced by decomposition of DCM [5] is determined using an ion chromatography (DIONEX, DX-320J). The DCM decomposition rate is obtained from the following equation:

$$\text{Amount of decomposed DCM} = \text{Concentration of } Cl^- \times \frac{\text{MW of DCM (85)}}{\text{MW of } Cl^- (35.5 \times 2)} \times \frac{15}{1000}\,[\text{mg}] \quad (2)$$

The DCM decomposition rate is obtained by dividing the amount of decomposed DCM by the initial amount of DCM.

The absorbance of the DCM-IC mixed solutions is measured by a spectrometer (Hitachi high technologies, U-1800) at a wavelength of 610 nm, and the decolorization rate is obtained from the following equation:

$$\text{Decolorization rate} = \frac{\text{(Absorbance (initial) – Absorbance (treated))}}{\text{Absorbance (initial)}} \times 100\% \quad (3)$$

3. Results and Discussion

3.1 Characteristics of DCM decomposition

Figure 3 shows DCM removal efficiency and DCM decomposition efficiency as a function of treatment time in the DCM solution in the case of Ar injection with and without discharges. The initial concentration of DCM is 0.87 mM. The DCM removal efficiency increases without discharges because of volatility of bubbling gas. The DCM removal efficiency and decomposition efficiency with discharges at treatment time of 25 min are 96% and 80%, respectively, which

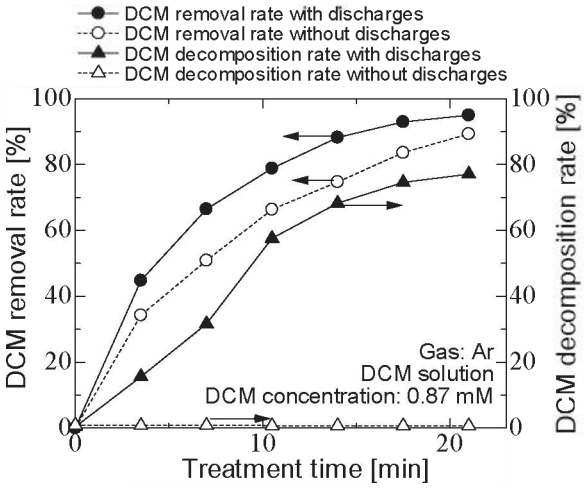

Fig. 3 DCM removal efficiency and decomposition efficiency as a function of treatment time with or without discharges.

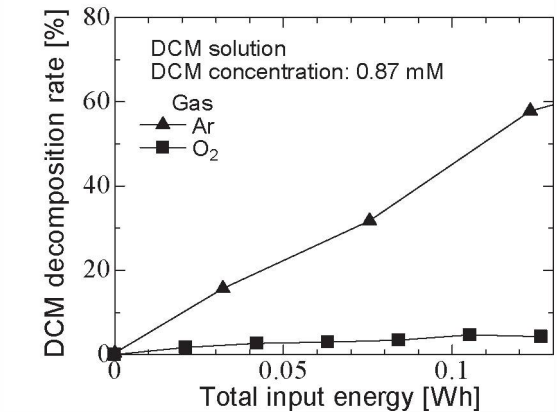

Fig. 4. DCM decomposition efficiency as function of total input energy into the reactor for Ar and O_2 injection.

indicates that approximately 83% of removed DCM is decomposed into hydrogen chloride (HCl) by discharges as following reactions [5]:

$$CH_2Cl_2 + \bullet OH \rightarrow \bullet CHCl_2 + H_2O \quad (5)$$

$$\bullet CHCl_2 + \bullet OH \rightarrow CHOCl + HCl \quad (6)$$

$$CHOCl + \bullet OH \rightarrow \bullet COCl + H_2O \quad (7)$$

$$\bullet COCl + \bullet OH \rightarrow CO_2 + HCl \quad (8)$$

Figure 4 shows the DCM decomposition efficiency as a function of total input energy for Ar and O_2 injection. DCM decomposition efficiency in the case of Ar injection is much higher than that of O_2 injection with same input energy. Energy efficiency for hydroxyl radical production in the case of O_2

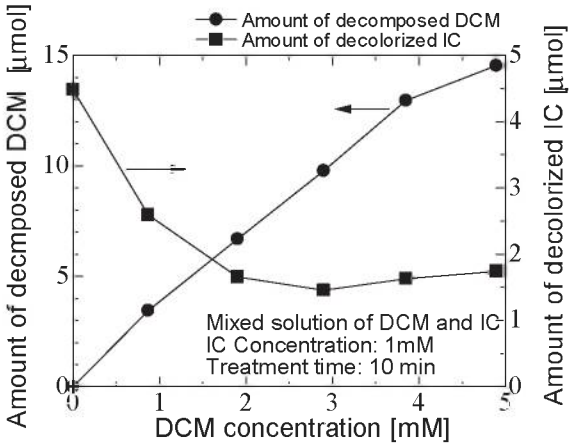

Fig.5 Amounts of decomposed DCM and decolorized IC as a function of IC concentration

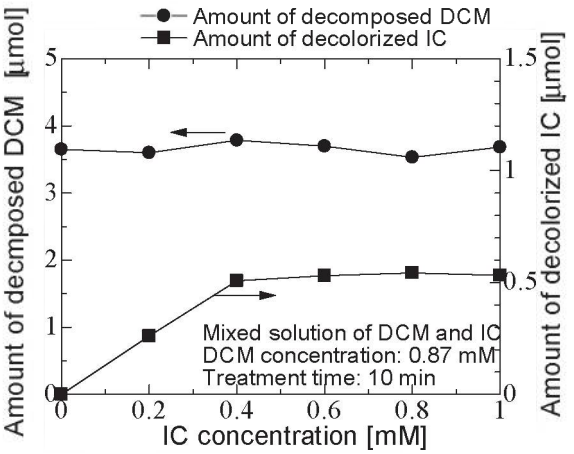

Fig.6. Amounts of decomposed DCM and decolorized IC as a function of DCM concentration

injection is lower than that of Ar injection, because ozone (O_3) produced by discharges reduces hydroxyl radical (•OH) [6]. These results show chemical species such as •OH produced by discharges mainly contributes to the decomposition of DCM.

3.2 Decomposition process of DCM

Figure 5 shows the amounts of DCM decomposed DCM and decolorized IC as a function of DCM concentration in mixed solution of DCM and IC. Ar gas is injected. The initial concentration of IC is 1 mM. The amount of decolorized IC decreases with increasing the DCM concentration. Figure 6 shows the amount of decomposed DCM and decolorized IC as a function of IC concentration. The initial

concentration of DCM is 0.87 mM. The amount of decomposed DCM is almost independent with IC concentration.

Although the reaction rate of •OH with DCM (2.2×10^7 $M^{-1}S^{-1}$ [7]) is much lower than that with IC (1.8×1010 $M^{-1}S^{-1}$) [8]), the amount of decomposed DCM is about 6 times higher than that of decolorized IC when the concentration of DCM equals that of IC as shown in Fig. 5. The contradictory results suggest the DCM decomposition process as follows. The DCM is volatilized into the bubble quickly because of its high volatility when the bubble is generated in the solution by the gas injection. •OH produced by discharges reacts with DCM inside bubble. •OH that not consumed in the reaction with DCM dissolves into the solution, and then reacts with IC in the solution. Since HCl has a high solubility, almost HCl is dissolved into the solution.

4. Conclusions

The decomposition of DCM by the discharge inside bubble is investigated experimentally. The DCM is only removed without discharges because of volatility of bubbling gas. The DCM is decomposed with discharges. DCM is volatilized into the bubble, which is decomposed by hydroxyl radical produced by the discharge.

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