Simultaneous Decomposition of Phenol and Sodium Formate by Discharge Inside Bubble in Water

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We have investigated water purifications by a discharge propagating in a bubble in water containing two organic compounds, phenol and sodium formate. In order to evaluate decomposition rate of phenol and sodium formate, the mixed solution of them were employed. Oxygen gas was injected into the water through a vertically positioned glass tube, in which the high-voltage wire electrode was placed to generate plasmas at low applied voltage. The phenol in the mixed solution was easier to decompose than the phenol in the single ingredient solution. The pH value of the solution after the discharge treatment increased with increasing initial concentration of the sodium formate, which enhanced the decomposition of phenol in mixed solution. The amount of decomposed sodium formate decreased with increasing initial concentration of the phenol.

Key words: water purification, pulsed power, plasma, ozone

1. Introduction

Water pollution caused by industrial wastewater, domestic wastewater, and dumping waste is serious problem for human health and the global ecosystem. Water quality has been partially improved due to the recent various legal restrictions and the development of water purification technology. However, water pollution is still problem in local areas because the groundwater has been contaminated with previous illegally dumped industrial wastes and with the soil contamination by industrial wastewater. Although contaminants are treated with chemicals such as oxidants in these days, the method has various limitations [1]. Pulsed discharge plasma for decomposing contaminants in water have been attracted much attention as a new technology [2]. The pulsed discharge makes it possible to instantaneously produce non-thermal plasma which generates various chemical species such as hydroxyl radical, ozone and oxygen radical. These species play an important role in the decomposition of chemical organic compounds [2,3].

Although many studies have been conducted on the treatment of the wastewater including single contaminant with discharge plasma [4-6], almost wastewater includes multiple contaminants. In this study, water purification by discharge inside bubbles in water including multiple organic compounds is investigated. Contaminants in water are generally divided in two types; one has a benzene ring, and the other has no benzene ring. Then phenol and sodium formate are employed as specimens. The formic acid ion is known as a decomposition product of phenol [7]. In the experiment, influence of formic acid ion on decomposition rate of phenol by discharge in water is investigated. Influence of the initial concentration of the coexisting compound on the decomposition rate was also investigated.

2. Experimental setup and procedure

Figure 1 shows a schematic diagram of the reactor. 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 aqueous solution in a glass beaker (74 mm height, 30 mm diameter). 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 tube is 10 mm. Oxygen 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 \(V_{O} \) generated by a pulsed power generator is applied to the tungsten wire to generate the streamer discharge in the tube and the air bubble.

Figure 2 shows a schematic diagram of the magnetic pulse compression circuit (Suematsu Electronics Co., LTD., MPC3000S-SP). The capacitor \(C_0 \) is charged up to a charging voltage by the charger. The energy stored in \(C_0 \) is transferred to \(C_1 \) through the pulse transformer P.T. The pulsed voltage is generated at secondary side of the pulse transformer. The pulsed voltage is compressed by saturable inductors (SI1, SI2 and SI4) and capacitors (C2 and C3). A saturable inductor SI3 is connected in parallel with C3 to shorten the pulse width of the output voltage (\(V_{O} \)).

Figure 3 shows typical waveforms of output voltage and current when the reactor was connected. The peak value of the output voltage (\(V_{O} \)) is 20 kV. A pulse repetition rate is fixed at 250 pulses per second. Phenol solution or sodium formate solution is
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1. Introduction

The simultaneous decomposition of phenol and sodium formate in water was investigated using a discharge inside bubble reactor. The reactor was designed to mimic natural environments where reactions between pollutants and atmospheric oxygen occur.

2. Materials and Methods

2.1. Experimental Setup

The reactor consisted of a 30 mL/min gas injection system, a Teflon coated cap, and a gas out system. The reactor was immersed in a water bath maintained at ambient temperature.

2.2. Chemicals

The chemicals used were phenol and sodium formate, both of which were dissolved into 15 mL of purified water. The phenol concentration was 1 mM, and the sodium formate concentration was also 1 mM.

2.3. Measurement Techniques

Conductivity and pH value were measured using a conductivity meter (μSFS ASRS®-ULTRA) and a pH meter, respectively. The concentration of total organic carbon (TOC) was measured using a TOC analyzer (Shimadzu Corp., TOC-VCSH).

3. Results

3.1. Decomposition Rate

Figure 4 shows the ion chromatograms of (a) sodium formate solution and (b) phenol solution for various treatment times. The decomposition rate of phenol and sodium formate as a function of treatment time is shown in Figure 5.

The decrease in TOC was noted with an increase in treatment time. The TOC removal rate is obtained by the following equation:

\[
\text{TOC removal rate} = \frac{(\text{TOC (initial)} - \text{TOC (treated)}) \times 100}{\text{TOC (initial)}} \quad (1)
\]

3.2. Decomposition Process

Figure 6 shows the amount of formate in the phenol solution as a function of treatment time. The formate is decomposed by the active hydroxyl radical produced by discharge. The increase of pH value is caused by the production of formate. The decrease of pH value is caused by the production of formic acid such as formic acid and oxalic acid.

4. Discussion

The decomposition rate for sodium formate in the mixed solution is higher than that in the single solution. On the other hand, the decomposition rate for phenol in the mixed solution is lower than that in the single solution. This is attributed to the different reactivity of the two pollutants with ozone.

5. Conclusion

The simultaneous decomposition of phenol and sodium formate using a discharge inside bubble reactor has been successfully demonstrated. Further research is needed to optimize the reaction conditions for efficient pollutant degradation.

Fig. 1 Schematic diagram of the reactor.

Fig. 2 Schematic diagram of the magnetic pulse compression circuit.

Fig. 3 Waveforms of output voltage and output current.

dissolved into 15 mL of purified water at a concentration of 1 mM. The mixed solutions were prepared by dissolving phenol and sodium formate simultaneously into 15 mL of purified water. The concentration of phenol and sodium formate in the mixed solution was adjusted at 0-1 mM respectively. The initial conductivity of the sodium formate solution, phenol solution and mixed solution were 90.6, 0.6, 95 μS/cm, respectively.

The concentration of phenol was measured using PACKTEST (KYORITSU CHEMICAL-CHECK Lab., Co. WAK-PNL). There was no interference with measurement using PACKTEST by pH value under the present experimental conditions. The concentration of sodium formate is determined by measuring the formic acid ion using an ion chromatography (DIONEX DX-320F; IonPack AS14 / AG14) [8]. Eluent was 3.5 mM Na₂CO₃/1.0 mM NaHCO₃ with a flow rate of 1.2 mL/min. The conductivity was suppressed to 10 μSFS ASRS®-ULTRA. The concentration of total organic carbon and inorganic carbon were measured with a TOC analyzer (Shimadzu corp., TOC-VCSH).
formate increases with increasing treatment time [7,9,10]. The part of chromatogram between 10 to 16 minutes in figure 4 (b) shows by-products produced by decomposition of phenol. Further consideration will be needed to yield any findings byproduct except for formate.

Figure 5 shows the decomposition rate for phenol and sodium formate as a function of treatment time. Solid lines show the results with the single solutions and dashed lines show the results with the mixed solutions. The decomposition rate for phenol in the mixed solution is higher than that in the single solution. On the other hands, the decomposition rate for sodium formate in mixed solution is lower than that in the single solution. Reaction rate of ozone with phenol and formate are $1.3 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ (23°C, pH2-6) and $1.0 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$ (20°C, pH2-4), respectively [11]. Therefore, phenol is decomposed preferentially in the mixed solution because reaction rate of ozone with phenol is higher than ozone with formate. TOC removal rate for the sodium formate solution is 100% at treatment time of 30 minutes, which indicates that sodium formate is perfectly decomposed into CO$_2$ and H$_2$O. On the other hands, TOC removal rate of phenol solution and mixed solution at treatment time of 30 minutes are 17 and 34%, respectively.

3.2 Decomposition process
Formate is produced by decomposition of phenol as a by-product [7]. Figure 6 shows the amount of formate in the phenol solution as a function of treatment time. The amount of formate linearly increases with increasing treatment time. It is assumed that the decomposition rate of the sodium formate is saturated at treatment time of 20 minutes for the mixed solution (figure 5) because the formate increases with increasing decomposition of phenol.

Figure 7 shows the pH value as a function of treatment time. The pH value in the single ingredient solution of sodium formate increases with increasing treatment time. The formate is decomposed by the active species produced by the plasma through the reactions as shown in the following equations (2) ~ (4) [12,13],

$\text{HCOO}^- + \cdot \text{OH} \rightarrow \text{H}_2\text{O} + \cdot \text{COO}$ (2),

$\text{HCOO}^- + \text{O}^- \rightarrow \text{OH}^- + \text{COO}^-$ (3),

$\text{HCOO}^- + \text{O}_3 \rightarrow \text{CO}_2 + \cdot \text{OH} + \text{O}_2$ (4).

Hydroxyl radical produced by discharge has a high reactivity. However, in the case of oxygen injection, O$_3$ reduces $\cdot \text{OH}$ through the reaction (5) [14].

$\text{O}_3 + \cdot \text{OH} \rightarrow \text{HO}_2 + \text{O}_2$ (5).

Moreover, the lifetime of hydroxyl radical in water is on the order of nanoseconds. Therefore, O$_3$ produced by discharge mainly contributes to decompose chemical compounds in the case of O$_2$ injection [14]. Thus, it is assumed that the equations (3), (4) are main reaction. The increase of pH value is caused by the production of the hydroxide ion through the decomposition of formate. The pH value in the single ingredient solution of phenol decreases with increasing treatment time. It is assumed that the decrease of pH value is caused by the production of the organic acid such as formic acid and oxalic acid though the decomposition of phenol [15]. The decrease of pH value in the mixed solution is inhibited by decomposition of sodium formate. Reaction rate of ozone with phenoxide ion is $1.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ (23°C, pH2-6) [9], which is much higher than that with phenol ($1.3 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$). Concentration of the phenoxide ion increases with increasing the pH value. Therefore, the decomposition rate of phenol in the mixed solution is higher than that in the single solution due to the increase of the pH value. These results suggest that the decomposition rate of contaminant in water is enhanced with a combination of specific contaminants.

Figure 8 shows amount of sodium formate and inorganic carbon in the single ingredient solution of sodium formate as a function of treatment time. As shown in the figure, the amount of inorganic carbon
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3.3 Influence of initial concentration

Figure 9 shows the amount of decomposition of phenol and sodium formate as a function of the initial concentration of sodium formate. The initial concentration of phenol is 1 mM and that of sodium formate is varied from 0 to 1 mM. Treatment time is fixed at 5 minutes. As shown in the figure, the amount of decomposed phenol increases with increasing initial concentration of sodium formate. Moreover, the amount of decomposed sodium formate increases with increasing initial concentration of sodium formate. The amount of decomposed sodium formate is negative value in the case of the initial concentration of sodium formate of 0 and 0.25 mM. The result suggests that formic acid is generated by decomposition of phenol. Figure 10 shows the pH value before and after discharge treatment as a function of the initial concentration of sodium formate. As shown in the figure, the pH value after discharge treatment increased with increasing the initial concentration of sodium formate. The amount of decomposition of phenol increased with increasing the pH value by the addition of high concentration of sodium formate.

Figure 11 shows the amount of decomposed phenol and sodium formate as a function of the initial concentration of phenol. The initial concentration of sodium formate is 1 mM and phenol is varied from 0 to 1 mM. Treatment time is fixed at 5 minutes. As shown in the figure, the amount of decomposed phenol increases with increasing the initial concentration of phenol. Moreover, the amount of decomposed sodium formate decreases with increasing the initial concentration of phenol. The result suggests that active species preferentially react with phenol in the mixed solution.

4. Conclusion

Decomposition of phenol and sodium formate in the mixed solution using discharge inside bubble in water was investigated. The decomposition rate of phenol in the mixed solution is higher than phenol in the single solution. On the other hand, the decomposition rate of sodium formate in the mixed solution is lower than that of sodium formate. The amount of decomposition of phenol increases with increasing initial concentration of sodium formate. The amount of decomposition of sodium formate decreases with increasing initial concentration of phenol. The amount of decomposition of phenol increases with increasing pH value in the mixed solution caused by sodium formate decomposition.

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