Reaction Mechanism and Kinetics of Degradation for Refractory Organic Pollutants in Water by Ultrasonic Irradiation

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Abstract

This experiment was performed to investigate the characteristics of sonolytic reaction as the basic data for development of the ultrasonic AOP(Advanced Oxidation Process) process from which the refractory organic compounds in aqueous solution which are not readily removed by the existing conventional wastewater treatment processes can be destructed and removed. Trichloroethylene (TCE), benzene, and 2,4-dichlorophenol(DCP) were used as the samples, and their destruction efficiency were measured in terms of experimental parameters of the initial solution concentration, initial solution pH, reaction temperature, acoustic frequencies and intensities. Results showed that the destruction efficiencies of all of the sample materials were above 80% within 120 minutes of sonolytic reaction in all reaction condition, The reaction order of these three compounds was verified as Pseudo first order.

From the fore-mentioned results, it can be concluded that the refractory organic compounds could be removed by the ultrasonic irradiation with radicals, such as H • and OH • causing the high increase of pressure and temperature. Finally, it appears that the new AOP technology using ultrasonic irradiation can be applied to the treatment of refractory substances which are difficult to be decomposed by the conventional methods.

1. Introduction

Trichloroethylene(TCE), benzene, and 2,4-Dichlorophenol(DCP) are the most common pollutants and can be to degrade by biological process. Therefore, a considerable interest has been devoted to developing new AOP process where TCE, benzene, and 2,4-DCP can be easily decomposed.

Ultrasonic irradation has been shown to be effective for advanced oxidation technology of the chemical contaminants in water. The chemical effects of ultrasound are due to the phenomenon of acoustic cavitation.Temperatures and pressures inside of cavitation bubble are on the order of 5000 K and 975 bar. In the homogeneous reactions, the destruction of organic compounds occurs inside the cavitation bubbles by a pyrolysis or radical reaction.

In this study, the efficiency of ultrasonic irradiation as AOP process for removal of the test pollutants has been evaluated.

2. Methods

A pilot plant was applied to obtain the performance data as a function of process parameter such as concentration, pH, reaction temperature, acoustic frequency and intensity. Ultrasonic irradadiation were performed with a Probe type Ultrasonic Transducer oprating 20 KHz,1000W and irradiated for 120 minutes at 20℃. The gas and solution was sampled every 10 minutes to be analysed. The products resulting from the ultrasonic irradiation of test compounds were analysed by GC and GC/MS.

3. Results

3.1. Reaction Mechanism

The ultrasonic reaction of benzene in the benzene aqueous solution differs from TCE in that it is a reaction in which HO · 와 H · radicals participate and the pyrolysis reaction due to the high temperature within the cavitation bubbles and near the bubble walls when the bubbles explode. Its reaction path can be shown as Figure 1 below.

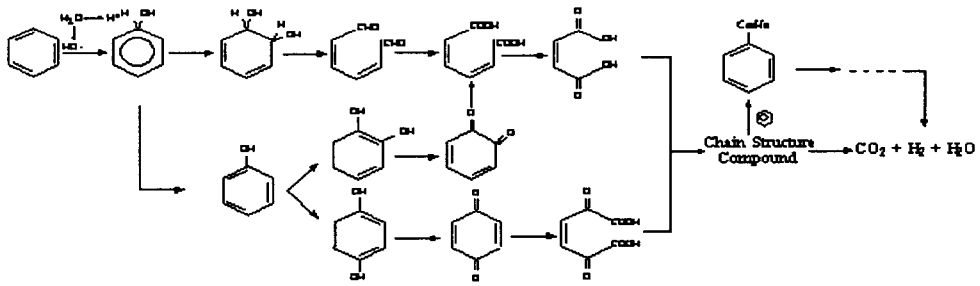

Fig. 1. Reaction pathway of the ultrasonic degradation of benzene in aqueous solution

When the benzene chain is continually broken, it is supposed to disintegrate into CO2 and water through the elimination of OH and the addition of hydrogen. Thus, also in the case of 2,4-DCP, two chlorine are substituted by OH due to HO · radicals and are converted to hydroquinone, benzoquinone, and catechol benzene, and can be predicted to follow the same reaction path as benzene afterwards(Figure 1).

3.2. Reaction kinetics

When irradiating ultrasonic waves in an aqueous solution containing organic compounds, the compounds become disintegrated due to the radical reaction resulting from the pyrolysis

within the cavitation bubbles and at the solution near the bubbles wall. During the various steps of the intermediate reaction stage, many middle products are produced and are finally disintegrated into CO_2와 H_2O. Thus, in order to derive a reaction rate equation which can be applied to all three sample chemicals, we simplified the reaction mechanism mentioned above as shown below.

(i) The initial reaction in which the sample chemical(RX) and water (H2O), H2, and O2 are disintegrated into radicals :

$$RX + h_{us} \xrightarrow{k_2} R\cdot + X\cdot \quad (1)$$

$$H_2O + h_{us} \xrightarrow{k_3} H\cdot + OH\cdot \quad (2)$$

$$O_2 + H\cdot \xrightarrow{k_4} HO_2 \quad (3)$$

$$H_2 + X\cdot \xrightarrow{k_5} H\cdot + HX \quad (4)$$

(ii) The reaction in which the sample chemicals are attacked by the radicals(M: middle product, P: final product) :

$$RX + H\cdot \xrightarrow{k_6} M \rightarrow P \quad (5)$$

$$RX + OH\cdot \xrightarrow{k_7} M \rightarrow P \quad (6)$$

$$RX + X\cdot \xrightarrow{k_8} R\cdot + X_2 \quad (7)$$

(iii) The reaction in which the radicals of the sample chemical combine with other radicals:

$$R\cdot + H\cdot \xrightarrow{k_9} M \rightarrow P \quad (8)$$

$$R\cdot + OH\cdot \xrightarrow{k_{10}} M \rightarrow P \quad (9)$$

$$R\cdot + X\cdot \xrightarrow{k_{11}} M \rightarrow P \quad (10)$$

(iv) The reaction in which the radicals recombine with each other:

$$H\cdot + H\cdot \xrightarrow{k_{12}} H_2 \quad (11)$$

$$HO_2\cdot + HO_2\cdot \xrightarrow{k_{13}} H_2O_2 + O_2 \quad (12)$$

$$X\cdot + X\cdot \xrightarrow{k_{14}} X_2 \quad (13)$$

$$OH\cdot + OH\cdot \xrightarrow{k_{15}} H_2O_2 \quad (14)$$

So, the sonochemical reaction of the sample chemicals can be shown with an equation that proves it to be a first reaction regarding the concentration of the chemical([RX]) as the following:

$$-\frac{d[RX]}{dt} = k[RX] \quad (15)$$

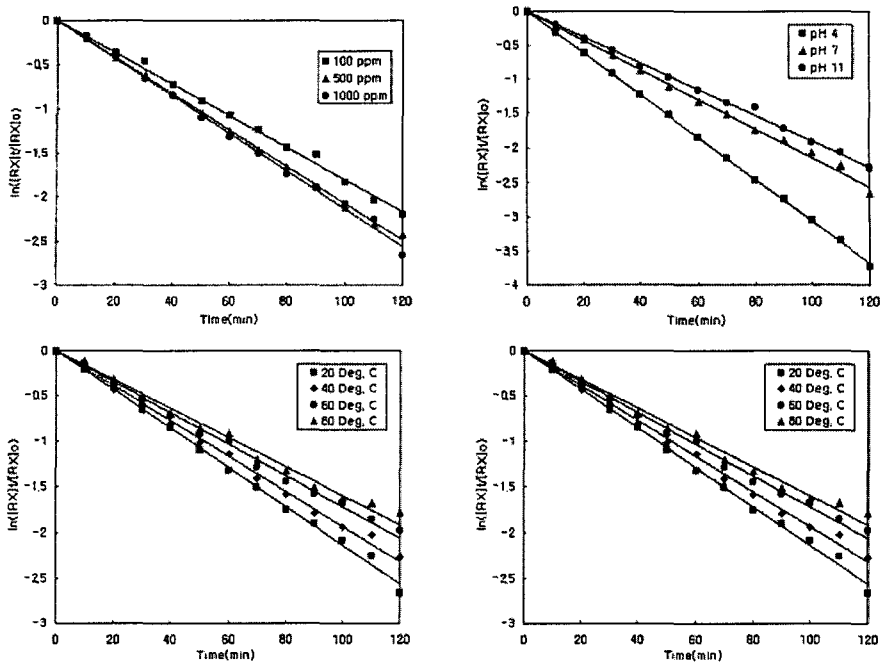

Fig. 2. Plots of the degradation rate of experimental compounds in different conditions by ultrasonic irradation.

In the Fig. 2 and Table 1, it was found that more than 80% of experimental compounds(TCE,benzene,2,4-DCP) were removed within 2 hours in all reaction conditions. The reaction order in degradation of these three compounds was verified as the pseudo-first order.

4. Conclusions

The decomposition of benzene produced toluene, phenol, and C1-C4 compounds, while the intermediates during the ultrasonic irradiation of 2,4-DCP were phenol, HCl, catechol, hydroquinone, and benzoquinone.

The rate of decomposition was found to be proportional to acoustic intensity. . All as the reaction temperature increased the decomposition rate of three reactants decreased.

Under batch reactor condition, more than 80% of TCE, benzene, and 2,4-DCP were removed within 2 hours at all reaction conditions. The degradation reaction was the pseudo-first order.

From the fore-mentioned results, it can be concluded that refractory organic compounds such as TCE, Benzene, 2,4-DCP could be removed by the ultrasonic irradiation radicals, radical causing the high increase of pressure and temperature. Finally it appeared that technology using ultrasonic irradiation can be applied to AOP process of refractory substances which are difficult to be decomposed by conventional methods.

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