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TRICHLOROETHYLENE DECOMPOSITION BY FENTON REACTION AND ULTRASONIC IRRADIATION

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ABSTRACT

Trichloroethylene (TCE) is known as one of the persistent pollutants of soil and groundwater. TCE has carcinogenicity and should urgently be decontaminated. In this research, Fenton reaction and ultrasonic (US) irradiation were used for TCE decomposition as low cost and widely targetable advanced oxidation processes. First of all, our previous results related to the TCE decomposition is reviewed. Then the recent results are reported. Reaction temperature was set at 15℃ in order to prevent TCE volatilization. By the ultrasonic irradiation method, it was confirmed that the distribution of the US strength is also most flat inside the reaction vesssel, except the vicinity of the bottom, and TCE was slowly decomposed at constant rate irrespective of the fluctuation of power of the transducer. For the Fenton reaction, TCE-saturated solution (1.0 g/L) added with Fe ion was mixed with hydrogen peroxide solution. The decomposition rate of TCE by the Fenton reaction was measured and compared using both of ferrous ion (Fe^{2+}) and ferric ion (Fe^{3+}). Fairly amount of TCE was immediately decomposed after a reaction start (mixing of solutions) when Fe^{2+} was used.

Keywords: TCE; Fenton reaction; ultrasonic wave; composition reaction; decomposition.

1. INTRODUCTION

Volatile organic compounds (VOCs) such as trichloroethylene (TCE) are known as contaminants in soil and groundwater. TCE has carcinogenicity and should urgently be decontaminated. As a result, various decontamination processes for polluted soil and groundwater have been developed. So far, we have used Fenton reaction and ultrasound radiation for the decomposition of volatile organic compounds (VOCs), especially TCE.

OH radicals have a powerful oxidizing potential which is produced from hydrogen peroxide in the process of TCE decomposition by Fenton reaction. This happens by the oxidation-reduction of the ferrous and ferric irons contained in reaction solution. Therefore the difference in the reaction rate of TCE decomposition between with ferrous and ferric irons is our concern.

Ultrasonic irradiation has previously been reported as a promising method for the decomposition of organic compounds. When ultrasonic wave is irradiated into water, hotspots

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(reaction fields exhibiting high temperatures and pressures) are generated and organic compounds would likely be decomposed in the hotspots. In this research, Fenton reaction and ultrasonic irradiation were used for TCE decomposition as low cost and widely targetable advanced oxidation process. First of all, our previous results related to the TCE decomposition by Fenton reaction and ultrasonic irradiation are reviewed (Takuma, Kato and Kojima 2007; Takuma et al., 2008; Kojima et al., 2009a, b; Saito et al., 2012). Then the recent results are reported.

2. MATERIALS AND METHOD

2.1 Effect of Valence of Iron Ion on the Decomposition Rate of TCE by Fenton Reaction

Reaction temperature was set at 15^{o}C in order to prevent TCE volatilization in the present experiment. The TCE-saturated solution (1.0 g/L, around 8 mmol/L, 50 mL) added with Fe ion (1 mmol/L) was mixed with hydrogen peroxide solution (0.5 mol/L, 50 mL). At some period after mixing (reaction start), the residual TCE in the 1 mL of the sample was extracted into 3 mL and then 2 mL of hexane. After dehydration of the mixture of 5 mL of hexane solution by anhydrous sodium sulfate 1 mL was taken and 1 mL chloroform and 8 mL of hexane was added. The TCE concentration was measured by a ECD gaschromatograph (Shimadzu GC-14B) with ULBON HR-1 (I.D. = 0.53 mm、Length = 30 cm、Film = 2.0 μm) column under the condition of injection temperature of 200^{o}C. detection temp:200^{o}C column TENP:40^{o}C under the nitrogen flow with sprit ratio of 1:12.5. The decomposition rate of TCE by the Fenton reaction was measured and compared using both of ferrous ion (Fe^{2+}) and ferric ion (Fe^{3+}).

2.2 Ultrasonic Strength Distribution

The ultrasonic device (a water bath kept at 15^{o}C) with four transducers of 4 cm diameter is shown in Figure 1. The distribution of ultrasonic strength in it was measured by piezoelectric receiver as the voltage amplitude on the oscilloscope. At first, an ultrasonic receiver was placed in the water bath with a water depth of 80 mm. The height of the receiver end with the sensing part was kept at 30 mm from the bottom of water. Next, the depth profiles inside the reaction glass vessels (conical flask and three-necked round flask) were measured by changing their locations in the ultrasonic device.

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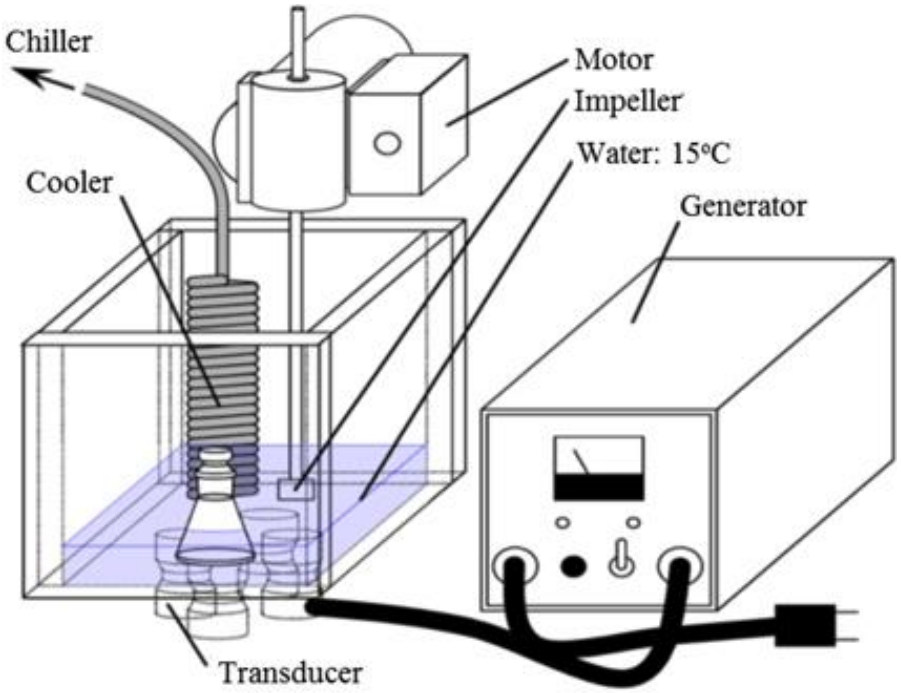

Figure 1: Ultrasonic irradiation device (water bath) and set-up.

2.3 Effect on the Decomposition Rate of TCE by Ultrasonic Irradiation

The TCE aqueous solution (0.5 g/L, around 4 mmol/L, 100 mL) in a three-necked round flask was placed at the middle center of the water bath (Figure 1) and irradiated of the ultrasonic wave was started. Solution was periodically sampled and the TCE concentration was measured as in the Fenton reaction experiments.

3. RESULT AND DISCUSSION

3.1 Rate of Equation Trichloroethylene Decomposition by Fenton Reaction

Rate equation of the trichloroethylene decomposition by Fenton reaction was proposed (Takuma et al., 2007). The rate was found to be first order to TCE concentration, first order to ferrous ion concentration and 0.5^{th} order to the hydrogen peroxide concentration. It was also found that the TCE concentration was drastically decreased by Fenton reaction at the first stage of the decomposition, when using ferrous ion. It was explained by the very rapid formation of hydroxyl radical and its reaction with TCE by the reactions of 1 and 3 in Table 1. Furthermore, it was suggested that the coexistence of other organic compounds might have inhibited the TCE decomposition rate.

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Table 1: Equation of Fenton reaction

1	$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^{\cdot}$
2	$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + HO^-$
3	$HO^{\cdot} + TCE \rightarrow DOCs$
4	$H_2O_2 + HO^{\cdot} \rightarrow H_2O + HO_2^{\cdot}$
5	$HO^{\cdot} + DOCs \rightarrow$ products
6	$Fe^{2+} + HO_2^{\cdot} \rightarrow Fe^{3+} + HO_2^-$
7	$Fe^{3+} + HO_2^{\cdot} \rightarrow Fe^{2+} + H^+ + O_2$
8	$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+$
9	$HO^{\cdot} + HO^{\cdot} \rightarrow H_2O_2$
10	$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2$

3.2 Influence of Soil and Organic Matters on Decomposition of Trichloroethylene with Fenton Reaction

Based on our results on the effect of coexistence of other compounds on the kinetics of decomposition of TCE by the Fenton's reaction with Fe^{2+}, effects of soil types on the decomposition rate of TCE was examined (Kojima et al., 2009b). The rate with soil except Toyoura sand was found to be lower than that in the case without soils. The rates of decomposition of TCE with and without black soil was found to be first-order to both concentrations of TCE and Fe^{2+}, and half-order to hydrogen peroxide concentration by the Fenton's reaction with Fe^{2+}. The decrease in the rate was suggested to be affected by both of the surface area and carbon content of the soil.

3.3 Effect of Valence of Iron Ion on the Decomposition Rate of TCE by Fenton Reaction

In Fenton reaction, when ferrous ion (Fe^{2+}) is used, it turns out that the rapid decomposition of TCE occurs at the first stage, as reported in our previous study (Takuma et al. 2007). According to the reaction mechanism in Table 1, OH radical is produced when ferrous ion is oxidized with hydrogen peroxide to produce ferric ion (Fe^{3+}) and it promotes the decomposition of TCE, while the ferrous ion is reproduced from ferric ion by equations 7, and 8. Thus, the OH radical is directly produced from ferrous ion while ferrous ion is also produced from ferric ion in the Fenton reaction. In the present paper, recent results on the effect of valence of iron ion are reported.

The result of the Fenton reaction using the ferrous ion (Fe^{2+}) and ferric ion (Fe^{3+}) are shown in Figure 2 where TCE concentration was plotted against the reaction time on a semi-log scale paper according to the first order reaction kinetics. First of all, the reproducibility was confirmed. Fairly amount of TCE was immediately decomposed after a reaction start (mixing of solutions) when Fe^{2+} was used. Moreover, even after the initial immediate decomposition, relatively fast decomposition of TCE was observed.

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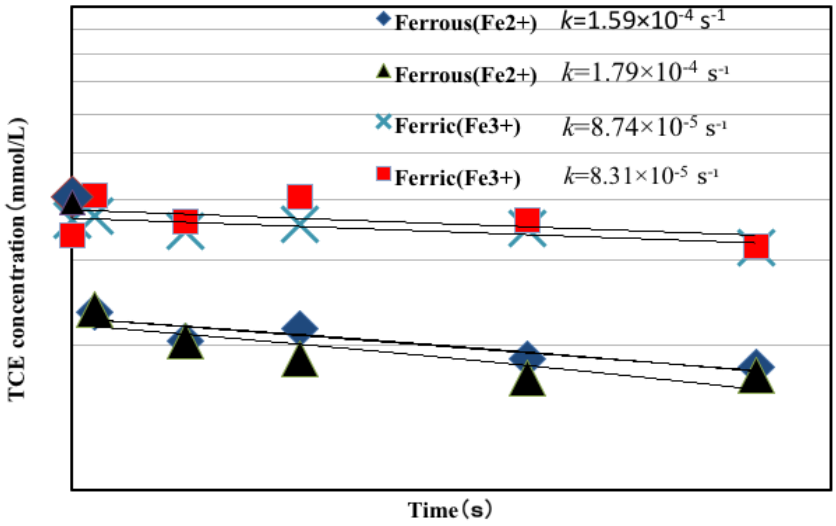

Figure 2: Result of Fenton reaction.

3.4 Decomposition Rate of TCE Using Iron Powder

The decomposition of TCE with iron powder was found to occur after some introduction period, which is not observed for that with ferrous iron. Regardless of the period, the decomposition rate was found to be analyzed as the first order reaction. The obtained first reaction rate constants were found to be proportional to the ion powder concentration, but the reaction order to hydrogen peroxide was changed with the range of its concentration. At relatively high concentration of hydrogen peroxide, the reaction order for the concentration of hydrogen peroxide became negative (Takuma et al., 2008; Saito et al., 2012).

3.5 Decomposition Rate of Various Organic Compounds by Ultrasonic Irradiation

We focused on sonochemistry which is a method of decomposing and removing these pollutants. In this study, the relationship between reaction rate of sonochemistry and operational parameters (sound pressure, initial concentration, and hydrophilicity of organic compounds) was investigated. The reaction rate was found to be increased with increasing sound pressure. The decomposition rates of compounds were found to increase but their pseudo first order rate constants were found to decrease with their increasing initial concentration, which suggests around half order kinetics. Finally, their reaction rates were found to increase when the smaller the hydrophilicity of decomposed compound (the greater the hydrophobicity of compound) becomes (Kojima et al., 2009a).

3.6 Ultrasonic Strength Distribution

The measured results of horizontal profiles inside the water bath are shown in Figure 3. The locations of the center of the four transducers are expressed as (x, y) = (55, 90), (125, 90), (90, 55), (90, 125) in mm. From this result, it turned out that there was hardly large difference in the ultrasonic strength among horizontally different measured points in the ultrasonic device though small difference in the strength is found depending on the relative location to the transducers.

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Next, the results of depth profile inside the reaction conical flask, placing at the center of the transducers (①-④), and at the middle center of the four transducers (⑤) are shown in Figure 4. The vertical location of the glass vessel, namely the space between the reaction vessel and the bottom of the water bath also changed from 0 mm (without space) to 30 mm. Almost flat ultrasonic strength profile is observed excepting the vicinity of the glass flask bottom when the flask is placed near the water bath bottom.

Almost similar results are shown in Figure 5, when a three-necked round flask is used instead of a conical flask. Almost no difference is found between Figure 4 and Figure 5, which suggests the effects of reaction grass vessel type is small except the vicinity of the water bath/ vessel bottom. It is suggested that the present results are explained by that the diffusion of the ultrasonic wave might be rapid after being released from the transducer.

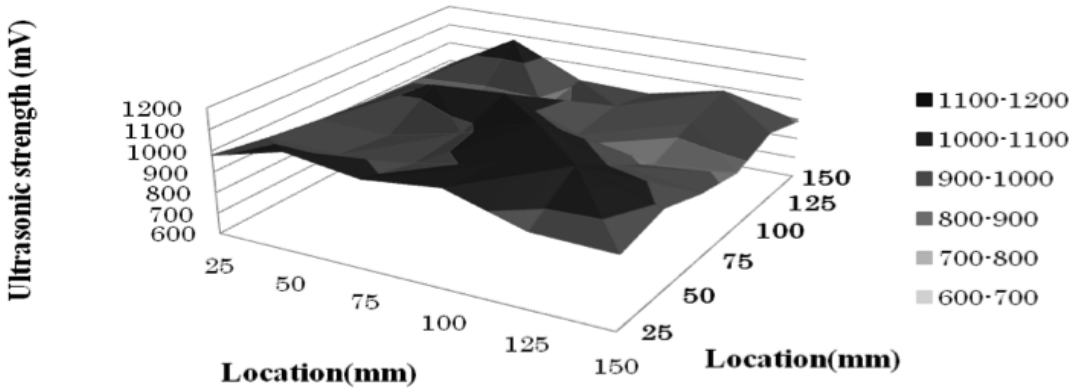

Figure 3: Distribution of ultrasonic strength.

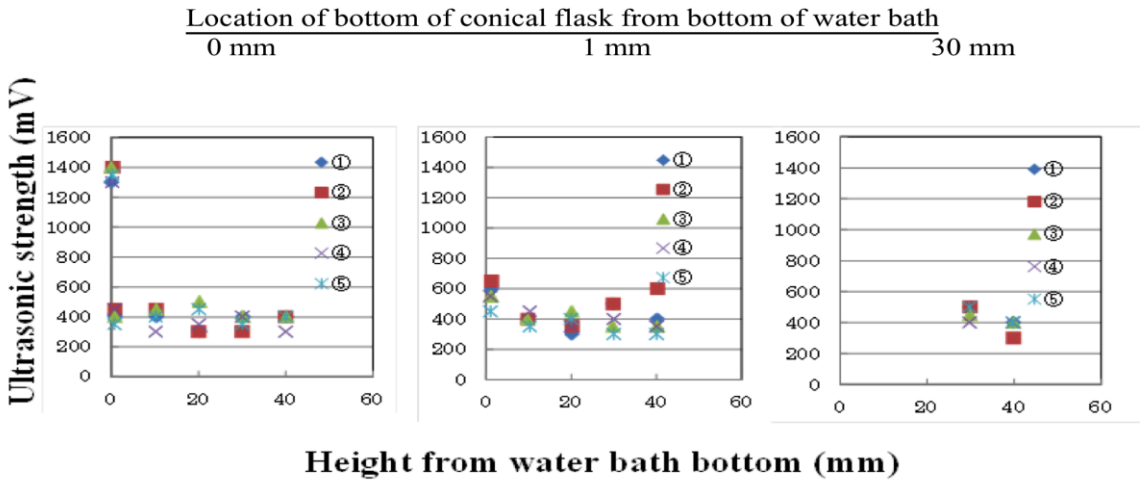

Figure 4: Ultrasonic strength at the center inside the conical flask with water amount of 100mL (water level of 45mm, ①-④: just above transducers, ⑤: center of four transducers).

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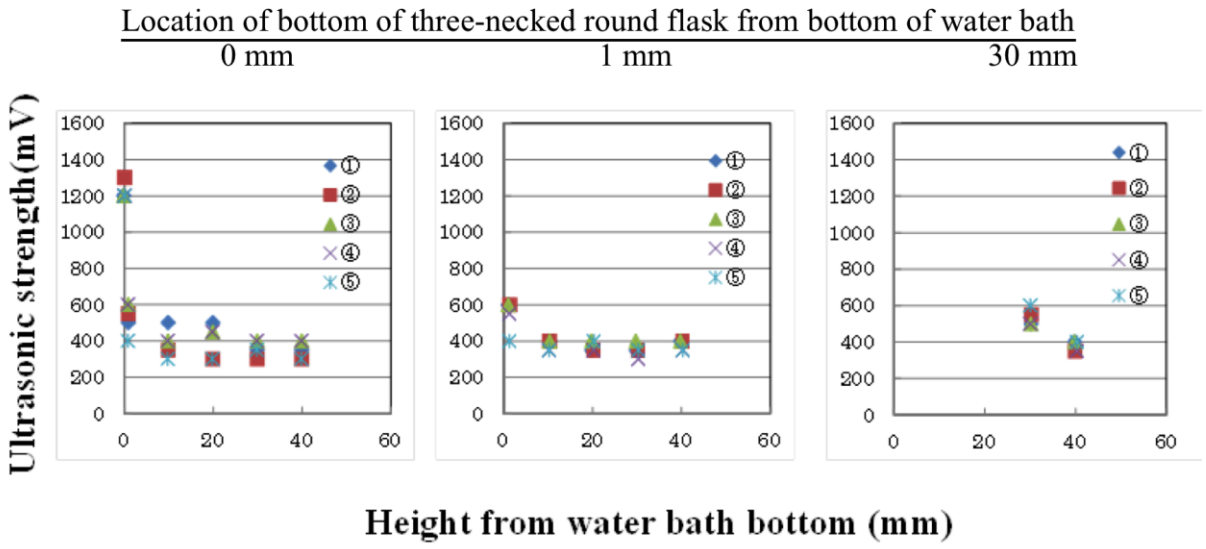

Figure 5: Ultrasonic strength at the center inside the three-necked flask with water amount of 100mL (water level of 45mm, ①-④: just above transducers, ⑤: center of four transducers).

3.7 Effect on the Decomposition Rate of TCE by Ultrasonic Irradiation

The results of TCE decomposition by ultrasonic irradiation are shown in Figure 6. Though the values of applied voltage was oscillated and averaged value for each experiment is different among experimental runs, almost same decomposition rate of TCE are observed which is consistent with the results of ultrasound strength. TCE decomposition rate by ultrasonic irradiation was slower than that by Fenton reaction of using ferrous ion.

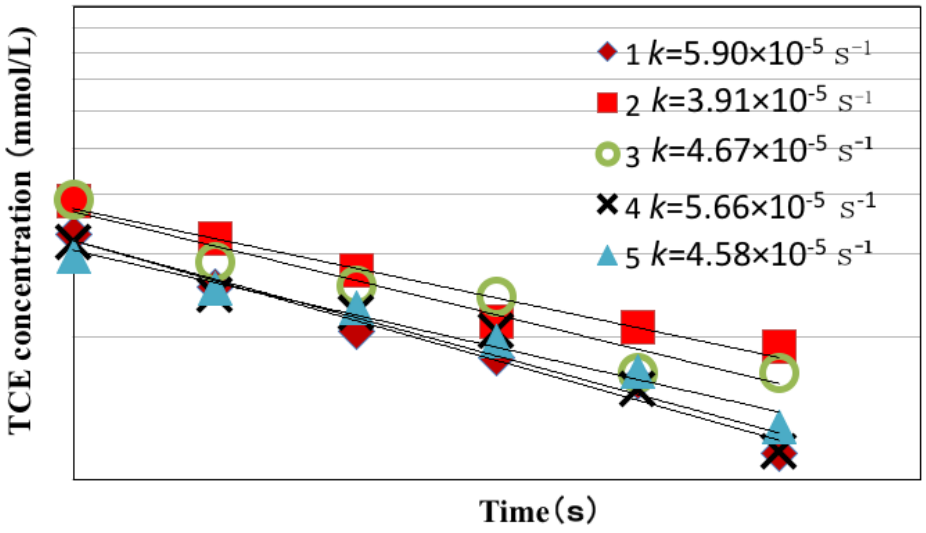

Figure 6: Reproducibility of TCE decomposition by Ultrasonic irradiation.

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4. CONCLUSION

Initial rapid decomposition of TCE followed by fast first order decomposition reaction kinetics was observed in case when ferrous ion was used for Fenton reaction. In the case of ferric ion, the initial decomposition was not observed and the rate constant for the first order rate regime was smaller than for ferrous ion. While stable ultrasonic strength and decomposition rate of TCE were observed by ultrasonic radiation, the decomposition rate was smaller than that by Fenton reaction.

REFERENCES

Kojima, T., Nakae, T., Takuma, Y., Kato, S., & Satokawa, S. (2009a). Decomposition of harmful organic compounds with ultrasound wave. *J. Chem. Eng. Japan,* 42 (Supplement 1), s56-s60.

Kojima, T., Saito, H., Fukuda, K., Takuma, Y., Kato, S., & Satokawa, S. (2009b). The influence of soil and organic matters on decomposition of trichloroethylene with Fenton's reaction, *J. Chem. Eng. Japan,* 42 (Supplement 1), s23–s28.

Saito, H., Tanaka, S., Fukuda, K., Takuma, Y., Kato, S., Satokawa, S., Yamazaki, A., & Kojima, T, (2012). Influence of pH and dissolved Fe ion concentration on decomposition of trichloroethylene with Fenton's reaction using iron powder. *Kagaku Kougaku Ronbunsyu*, 38 (5), 312-317.

Takuma, Y., Fukuda, K., Kawata, K., Kato, S., Satokawa, S., & Kojima, T. (2008). Decomposition reaction rate of trichloroethylene by Fenton reaction using iron powder. *Kagaku Kougaku Ronbunsyu*, 34 (2), 309-312.

Takuma, Y., Kato, S., & Kojima, T. (2007). Rate equation of trichloroethylene decomposition by the Fenton reaction. *Environmental technology* (in Japanese), 36(3), 198-204.

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