



## Sonochemical degradation of chlorinated hydrocarbons using a batch and continuous flow system

Bongbeen Yim<sup>a,\*</sup>, Hiroshi Okuno<sup>a</sup>,  
Yoshio Nagata<sup>b</sup>, Yasuaki Maeda<sup>a</sup>

<sup>a</sup> Department of Applied Materials Science, College of Engineering, Osaka Prefecture University,  
Gakuen-cho 1-1, Sakai, Osaka 599-8531, Japan

<sup>b</sup> Research Institute for Advanced Science and Technology, Osaka Prefecture University,  
Gakuen-cho 1-2, Sakai, Osaka 599-8597, Japan

Received 29 April 2000; received in revised form 10 October 2000; accepted 11 October 2000

---

### Abstract

The sonochemical degradation of chlorinated hydrocarbons such as 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene in aqueous solution was carried out in the batch and continuous flow systems at an ultrasonic frequency of 100 kHz under an air atmosphere. In the batch experiment, the rate of degradation follows the order 1,1,1-trichloroethane > tetrachloroethylene > trichloroethylene, and the chlorinated hydrocarbon were readily degraded by ultrasonic irradiation. The experiments in the continuous flow system were performed in the range of volumetric flow rate from 7 to  $30 \times 10^{-3} \text{ l min}^{-1}$ . The conversion of the chlorinated hydrocarbons at a steady-state of reactor depended on the volumetric flow rate. The yield of  $\text{Cl}^-$  (as a measurement of mineralization of chlorinated hydrocarbons) was 70–90% of the chlorine atoms in the parent chlorinated hydrocarbon molecules. From the viewpoint of the scale-up process, the sonochemical degradation of trichloroethylene was simulated in a three stage reactor, and the conversion (>99%) in a third stage reactor was showed the good results that can be satisfied a desired water quality standard. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Continuous flow system; Sonochemical degradation; Trichloroethylene; 1,1,1-Trichloroethane; Tetrachloroethylene

---

\* Corresponding author. Tel.: +81-722-54-9321; fax: +81-722-54-9321.  
E-mail address: yim@ams.osakafu-u.ac.jp (B. Yim).

## 1. Introduction

The chlorinated hydrocarbons (CHs) such as 1,1,1-trichloroethane (MC), trichloroethylene (TCE), and tetrachloroethylene (PCE) have been commonly used as the prevalent industrial solvents for the metal degreasing, paint stripping, and dry cleaning industry. The CHs are known as persistent contaminants that remain in groundwater due to their poor reactivity under natural conditions. In addition, because they are classified as suspected carcinogens, the efficient treatment of wastewater and groundwater contaminated by the CHs is of great important.

The sonochemical effect by high power ultrasound is generally explained by the hot spot theory, which brings about high temperatures (several thousand degrees) and high pressures (hundreds of atmospheres) during the collapse of the cavity [1,2]. In aqueous sonochemistry, three possible reaction sites such as the cavity interior, bulk solution, and interfacial region between cavity and bulk solution have been postulated. In the cavity interior, hydroxyl radicals and hydrogen atoms are formed via pyrolysis of the water vapor, and decomposition of volatile compounds in the aqueous solution may occur by a gas phase pyrolysis or a combustion reaction. In the interfacial region, although, the temperature and pressure is lower than in the cavity interior, high temperature and pressure with a large gradient still exist in this region. In the bulk solution, solutes react with H atoms and OH radicals, which migrated from the cavity interior and interfacial region allowing escape from recombination [3,4].

Over the last several years, ultrasound has been adopted for the degradation of a variety of chemical contaminants in aqueous solutions, e.g. chlorinated compounds [5–8], chlorofluorocarbons [9–11], phenols [12,13], aromatic compounds [14–16], methyl *tert*-butyl ether [17] and hydroxybenzoic and humic acid [18], and the ultrasound has been found to be a promising tool for the degradation of contaminants in dilute aqueous solutions.

However, in a number of studies on the sonochemical degradation of environmental contaminants, a reactor with a batch system has so far been exclusively used for ultrasound irradiation. From the viewpoint of the scale-up process for a practical wastewater treatment, the use of the reactor with a continuous flow system is desirable.

In the present work, we report the results of the sonochemical degradation of the CHs in aqueous solutions using a batch and continuous flow system and discuss the practical use of sonolysis for wastewater treatment.

## 2. Experimental methods

All CHs (reagent grade) were purchased from Wako Pure Chemicals and were used without further purification. Water was purified with a Milli-Q system (resistivity > 18 M $\Omega$  cm).

The experimental set-up for a batch and continuous flow reactor was shown in Fig. 1. The ultrasound-generating system that consists of a frequency generator (NF Electric Instruments), broadband power amplifier (ENI), and transducers (30 mm $\phi$ ) oscillating at 100 kHz with an input power of 140 W was used for ultrasonic irradiation. The reactor was made of disk transducers fixed at the planar bottom of a rectangle vessel 100 mm(length)  $\times$  100 mm(width)  $\times$  130 mm(height) with stainless steel bottom and frames and glass win-

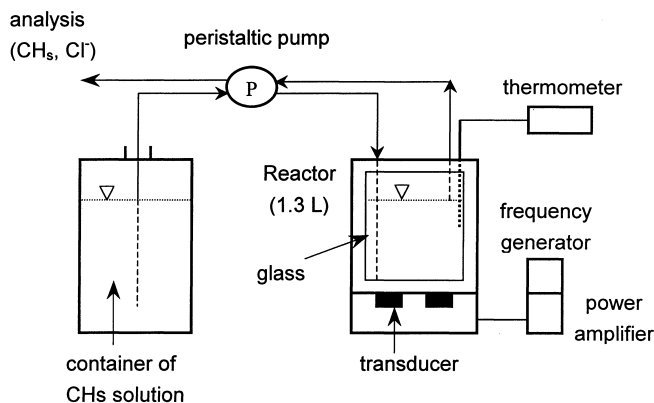


Fig. 1. The experimental set-up for a batch and continuous flow system.

dows. In the batch and flow experiments the reaction vessel was filled with each CHs aqueous solutions (1 l) before ultrasonic irradiation. All experiments were carried out under an air atmosphere. In the continuous flow system, the CHs aqueous solution was pumped through a PharMed tube (Cole-Parmer) using a peristaltic pump (Cole-Parmer) with two heads during sonochemical degradation.

All experiments for the sonochemical degradation of CHs were performed in duplicate. An aliquot of sonicated sample was extracted with hexane then analyzed using a Hewlett-Packard 5890 GC-ECD equipped with a DB-5 column, and carbon monoxide and carbon dioxide was analyzed using a Hewlett-Packard 6890 GC-TCD equipped with a GS-Molesive column. An ion chromatograph (IC-7000, Yokogawa) was used for the determination of the chloride ions ( $\text{Cl}^-$ ) formed from sonolysis of the CHs. The IC is equipped with a conductivity detector and ICS-A44 column (Yokogawa). The concentration of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) formed from the recombination of OH radicals released by sonolysis of water was determined by the KI calorimetric method [19,20]. In this method the sequence of iodide ions ( $\text{I}^-$ ) oxidation by  $\text{H}_2\text{O}_2$  in slightly acidic buffer conditions (pH 5.8) is as follows



The  $\text{I}_3^-$  was spectrophotometrically determined by its absorption at 350 nm (absorption coefficient:  $2.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) using an UV-VIS spectrophotometer (UV-3100, Shimadzu).

### 3. Results and discussion

Ultrasound powers actually delivered to the solution can be determined by the relationship temperature rise and irradiation time in a known mass of liquid [21]. This calorimetry has been widely used due to its simplicity in experimental procedure.

In the present work, the temperature of the liquid was measured at 10 s intervals using a thermometer (TR6824, Advantest). It was then confirmed that the temperature readings were independent of the measurement location in the liquid. From these experiments, the output power ( $P_{\text{output}}$ ) transferred to the solution was estimated to be 62 W (intensity is  $0.62 \text{ W cm}^{-2}$ ) that corresponds to 44.3% of the input power (140 W) read from an installed wattmeter.

Fig. 2 shows the concentration of  $\text{H}_2\text{O}_2$  formed from sonolysis of pure water in the batch and flow system under air. The concentrations of  $\text{H}_2\text{O}_2$  increased with irradiation time for 20 min. The initial formation rate of  $\text{H}_2\text{O}_2$  obtained from the batch experiment was  $1.8 \mu\text{M min}^{-1}$ . In flow experiment, the concentrations of  $\text{H}_2\text{O}_2$  accumulated in the reactor depended upon volumetric flow rate and were kept constant in the course of irradiation time. This results suggest that the performance of reactor in the batch and flow system may be dependent on the volumetric flow rate, when the ultrasonic power and the volume of solution in the reactor are maintained constant.

The sonochemical degradation of the CHs in the batch system was evaluated using first-order kinetics based on the linear relationship of  $\ln(C/C_0)$  versus irradiation time. Fig. 3 shows degradation profile of the CHs and first-order plots, and indicates a good fit to the first-order model. The rate of MC degradation was observed to be the fastest whereas, TCE was the slowest. The rate constants for MC and TCE are  $0.0821$  and  $0.0668 \text{ min}^{-1}$ , respectively. The CHs was rapidly degraded by ultrasonic irradiation and the half-lives for all the CHs was about 11 min. In addition, the degradation of CHs was not suppressed by the addition of 2-methyl-2-propanol, which is known as an effective scavenger of OH radicals

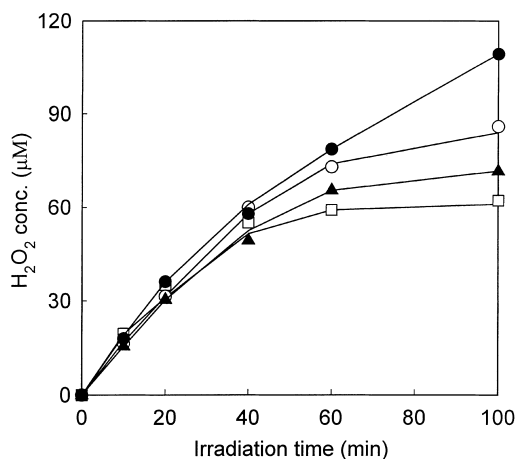


Fig. 2. Concentration of  $\text{H}_2\text{O}_2$  in the reactor as a function of irradiation time in various volumetric flow rates. (●) batch system; (○)  $7 \text{ ml min}^{-1}$ ; (▲)  $10 \text{ ml min}^{-1}$ ; (□)  $15 \text{ ml min}^{-1}$ .

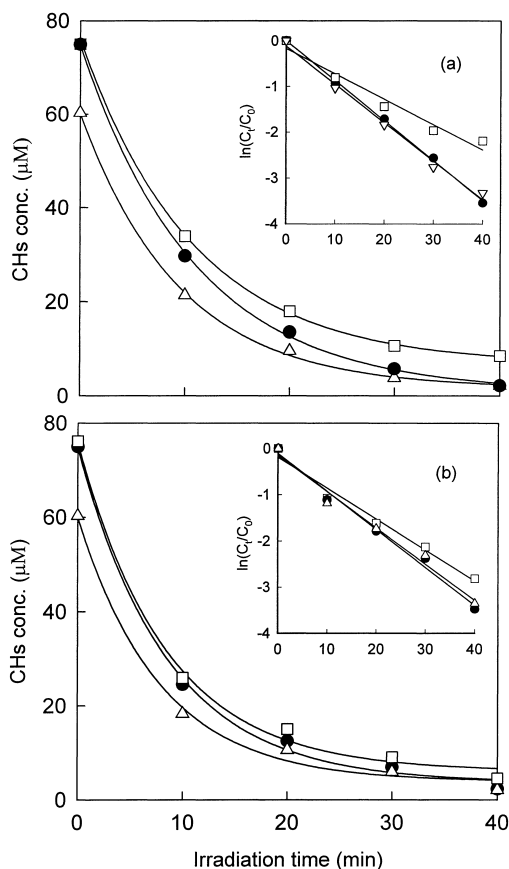


Fig. 3. Plots of observed first-order kinetic for CHs degradation in the batch system under air: (a) sonochemical degradation of individual CHs aqueous solution and (b) sonochemical degradation of CHs ternary mixture. (●) MC; (□) TCE; (△) PCE.

[8]. This indicates that the CHs were mainly degraded not by reaction with OH radicals, but by direct thermal reaction inside a collapsed cavitation bubbles.

Table 1 shows rates estimated from sonochemical degradation of individual and ternary mixture solution of each CHs. Compared with Table 1 shows that the rates of degradation for one chlorinated hydrocarbon were essentially unchanged by the presence of the other chlorinated hydrocarbon. It has been reported that the sonolysis of mixtures of two compounds having different physical property results in enhancement of the sonolysis by a direct reaction in the bulk solution with the byproduct [22] and by a reaction with the radicals produced during sonolysis [5]. Under the present sonolysis conditions, the sum of CHs concentration in the ternary mixture was about  $210 \mu\text{M}$ . In spite of the increase of the initial concentration of CHs with a low polytropic index ( $k = C_p/C_v$ ), the degradation of each chlorinated hydrocarbon would be independent of one another and the cavitation effects in ternary mixture would be not diminished.

Table 1  
Rate of sonochemical degradation of CHs using a batch system at 100 kHz<sup>a</sup>

	Rates ( $\mu\text{M min}^{-1} \text{W}^{-1}$ )		
	Individual	Mixture	Previous study <sup>b</sup>
MC	$0.073 \pm 0.003$	$0.081 \pm 0.004$	0.145
TCE	$0.068 \pm 0.005$	$0.081 \pm 0.007$	0.135
PCE	$0.063 \pm 0.002$	$0.068 \pm 0.002$	0.120

<sup>a</sup>  $[\text{MC}]_0 = [\text{TCE}]_0 = 75 \mu\text{M}$ ;  $[\text{PCE}]_0 = 60 \mu\text{M}$ ,  $\text{pH}_0 = 6.2\text{--}6.7$ ;  $T = 298 \text{ K}$

<sup>b</sup> Sonochemical degradation of CHs under argon at 293 K (frequency = 200 kHz, intensity =  $6 \text{ W cm}^{-2}$ ) [3].

The examination of the sonochemical degradation for the CHs using the continuous flow system, which could serve as the applicable means for treating an industrial wastewater was performed. Fig. 4 shows the sonochemical degradation of TCE versus irradiation time as a function of volumetric flow rate. In the beginning, the degradation of TCE appears tendency to degrade as in the unsteady-state of batch system, but the concentration of TCE after about 60 min from the beginning of the degradation became approximately constant for any volumetric flow rate. The degradation of TCE increased with decrease in volumetric flow rate, that is, with increase residence time (the time a given volume substance actually resides within the irradiation zone at the flow system) of TCE in the reactor.

To show the results of the sonochemical degradation in the continuous flow system, conversion as a function of volumetric flow rate was evaluated by the relationship of the initial concentration of CHs fed to reactor and the concentration of CHs resided in reactor after ultrasonic irradiation during a certain irradiation time as follows

$$\text{Conversion} = \frac{Q_f C_0 - Q_f C_t}{Q_f C_0} = 1 - \frac{C_t}{C_0} \quad (5)$$

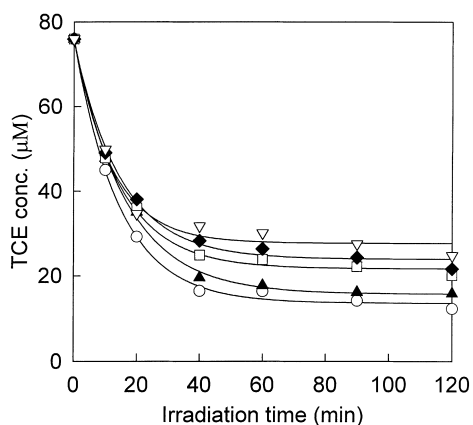


Fig. 4. Variation of TCE concentration vs. irradiation time for the sonochemical degradations in the continuous flow system: (○)  $7 \text{ ml min}^{-1}$ ; (▲)  $10 \text{ ml min}^{-1}$ ; (□)  $15 \text{ ml min}^{-1}$ ; (◆)  $20 \text{ ml min}^{-1}$ ; (▽)  $30 \text{ ml min}^{-1}$ .

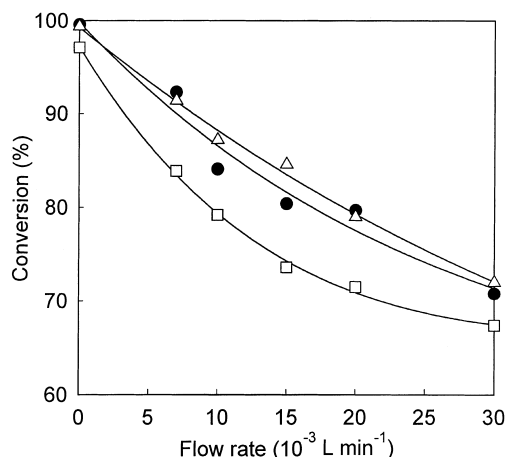


Fig. 5. Effect of volumetric flow rate on conversion of CHs in the continuous flow system (ultrasonic irradiation time: 120 min). (●) MC; (□) TCE; (△) PCE.

where  $Q_f$  is the feed volumetric flow rate to the reactor ( $\text{L min}^{-1}$ ),  $C_0$  is the initial concentration of the CHs aqueous solution fed ( $\mu\text{M}$ ) and  $C_t$  is the concentration of CHs in the reactor at irradiation time  $t$  ( $\mu\text{M}$ ).

The conversion as a function of volumetric flow rate after 120 min ultrasonic irradiation is shown in Fig. 5. The conversion obtained from sonochemical degradation in the batch system was over 97% against the initial concentration of the CHs, while the conversion of the CHs in the flow system was approximately 70–95% and was dependent on the volumetric flow rate. The increase of the volumetric flow rate results in a decrease of the conversion due to the reduction of residence time ( $\theta = V/Q_f$ ) of the CHs in the reactor.

It has been reported, that the main degradation products of the chlorinated compounds were hydrochloric acid (HCl) and carbon monoxide (CO) formed from direct thermal reaction in the cavitation bubbles under argon [22,23] and the CHs also were efficiently decomposed to inorganic carbons (CO and  $\text{CO}_2$ ) and  $\text{Cl}^-$  under air [8]. In the present work, the main product observed during the sonochemical degradation of the CHs was  $\text{Cl}^-$ . During the sonolysis under air, the pH of the aqueous solution continuously decreased, indicating the formation of HCl from the sonolysis of the CHs and the formation of nitrite and nitrate with time of ultrasonic irradiation [24]. Fig. 6 shows the total concentration of  $\text{Cl}^-$  measured quantitatively as a function of volumetric flow rate in sonochemical degradation of TCE. The total released chlorine was 70–90% of the chlorine present in the parent CHs molecules. The production of CO and  $\text{CO}_2$  was only qualitatively analyzed since it is difficult to collect the gaseous products under open systems. In the present experimental conditions, the high dechlorination and production of CO and  $\text{CO}_2$  indicates that the CHs was degraded mainly by a thermal reaction in the cavitation bubbles as well in such a lower ultrasound power.

Recently, it is reported the formation of reaction products during the sonolysis of chloroform at 900 kHz ( $0.17 \text{ W cm}^{-3}$ ). They observed the formation of carbontetrachloride ( $1.6 \mu\text{M}$ ), tetrachloroethane ( $0.6 \mu\text{M}$ ), and 1,1,2,2-tetrachloroethane ( $0.4 \mu\text{M}$ ) after 30 min

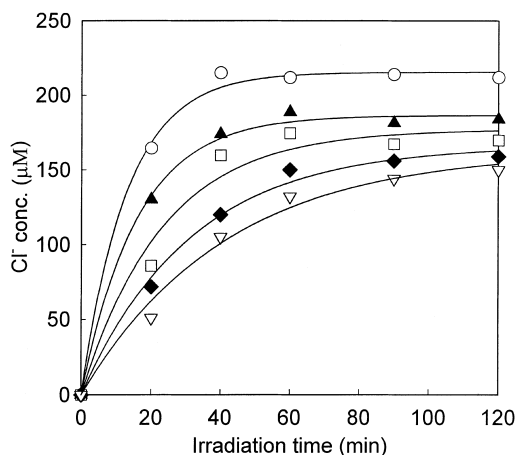


Fig. 6. Concentrations of chloride ion vs. irradiation time under the conditions of various volumetric flow rates in sonochemical degradation of TCE. (○) 7 ml min<sup>-1</sup>; (▲) 10 ml min<sup>-1</sup>; (□) 15 ml min<sup>-1</sup>; (◆) 160 ml min<sup>-1</sup>; (▽) 30 ml min<sup>-1</sup>.

sonolysis of chloroform (838 μM) [25]. These products, therefore, may be produced by ultrasonic irradiation although, these products are not identified in our experiment.

In continuous flow system, the reactor is treated as a continuously stirred tank reactor and the mass balance and recurrence equation for a series of continuous flow reactors can be written as Eqs. (6) and (7) [26]. Eq. (6) was postulated as the mass balance for the reactor operating in a transient unsteady-state. Eq. (7) can be solved from the differential equation (Eq. (6)) and be utilized as the recurrence equation for the calculation of the CHs concentration in a series of  $n$  number of reactors.

$$Q_f C_{n-1} = Q_f C_n + rV + V \left( \frac{dC_n}{dt} \right) \quad (6)$$

$$C_n = C_{n-1} \left\{ \frac{1}{\alpha^n} - \left[ \sum_{i=1}^n \frac{(1 - \alpha^i) \beta^{n-1}}{\alpha^i (n-i)!} \right] \exp(-\alpha\beta) \right\} \quad (7)$$

where  $C_n$  is the concentration of the CHs in the  $n$ th reactor (μM),  $r$  the degradation rate (μM min<sup>-1</sup>),  $V$  the volume of the reactor (l),  $\alpha$  and  $\beta$  are defined as  $1 + k\theta$  and  $t/\theta$ , respectively,  $k$  the degradation rate constant obtained from the batch experiment (min<sup>-1</sup>), and  $t$  the irradiation time (min).

Fig. 7 illustrates the plot for conversion calculated by Eq. (7) versus that obtained by experiment in a first reactor of the flow system. The calculated conversion tended to be slightly larger than the experimental conversion, and the experimental conversions of MC and PCE are in fair agreement with calculated conversion than that of TCE. However, the overall relationship between the calculated and experimental conversions shows a good correlation.

The one of the problem on the scale-up of reactor with a increasing of volume such as the large single reactor is a distribution and limitation of ultrasonic power [26,27]. On



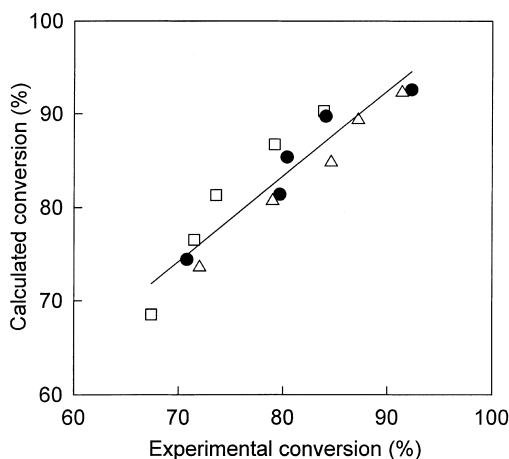


Fig. 7. Comparison between the conversion of CHs obtained by calculation and that obtained by experiment in the continuous flow system. (●) MC; (□) TCE; (△) PCE.

the other hand, the flow system for the multi stages provides several major advantages as follow: (1) the possibility of the coupling process with the traditional treatment plants; (2) the temperature controlling through the circulating reaction mixture; and (3) an additional control of system by varying the flow rate and by recycling a part of the flow [21]. In the present work, therefore, the reactor was hypothesized as a multi stages reactor consisting of a series of several smaller reactors in order to achieve to any desired water quality standard. Fig. 8 shows the variation of TCE concentration calculated throughout the three stages and that calculated in third stage was shown in inset of Fig. 8. It is postulated that the type of equipment, that is, the type of ultrasonic apparatus and transducer, and the ultrasound

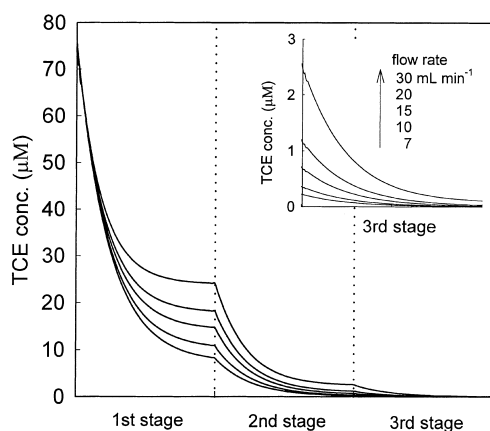


Fig. 8. Variation of the calculated concentration of TCE treated throughout the multi stages reactor. Inset is the calculation result in third stage:  $[TCE]_0$  is  $75 \mu\text{M}$ ; the period operated in one stage is 60 min.

$P_{\text{output}}$  was equivalent in each stage. Although, MC and PCE cases were not displayed in the figures, the results of their degradation in the multi stages reactor were similar to the case of TCE (Fig. 8). Under the given condition of volumetric flow rate and  $P_{\text{output}}$ , it can be thought that the steady-state in the each stage was reached at 60 min of sonolysis, and the concentration of TCE in the each stage was dependent on the volumetric flow rate. If the multi stages reactor is continuously operated, the concentration of the contaminant in each stage is kept constant at the concentration of the steady-state. In view of an environmental protection laws, the concentration of TCE (e.g. 0.11  $\mu\text{M}$ ) obtained from the degradation up to a third stage, should be enough to implement the water quality standard for the protection of a groundwater. Since the application of the continuous flow system with ultrasonic units results in good efficiency in the degradation of high concentration CHs, it is possible to treat the groundwater contaminated by CHs of low concentration.

In addition, the application of the sonochemical continuous flow system on the in situ can be helpful in the treatment for very much larger the volumes than those considered in the our flow system (minimum 43.21  $\text{day}^{-1}$ ) and in the coupling effect as the pre- or post-treatment process with the traditional treatment plants in order to degrade the hazardous materials among the wastewater.

### Acknowledgements

This study was supported by Special Coordination Funds from the Science and Technology Agency of the Japanese Government, and the Japan Steel Industry Foundation for the Advancement of Environmental Protection Technology.

### References

- [1] K.S. Suslick, D.A. Hammerton, R.E. Cline, *J. Am. Chem. Soc.* 108 (1986) 5641.
- [2] K.S. Suslick, *Science* 247 (1990) 1439.
- [3] K. Makino, M.M. Mossoba, P. Riesz, *J. Phys. Chem.* 87 (1983) 1369.
- [4] T. Kondo, L.J. Kirschenbaum, H. Kim, P. Riesz, *J. Phys. Chem.* 97 (1993) 522.
- [5] D. Drijvers, H. van Langenhove, L. Nguyen Thi Kim, L. Bray, *Ultrason. Sonochem.* 6 (1999) 115.
- [6] H. Hung, M. Hoffmann, *J. Phys. Chem. A* 103 (1999) 2734.
- [7] K. Inazu, Y. Nagata, Y. Maeda, *Chem. Lett.* (1993) 57.
- [8] I. Hua, M.R. Hoffmann, *Environ. Sci. Technol.* 30 (1996) 864.
- [9] Y. Nagata, K. Hirai, K. Okitus, Y. Maeda, *Chem. Lett.* (1995) 203.
- [10] K. Hirai, Y. Nagata, Y. Maeda, *Ultrason. Sonochem.* 3 (1996) S205.
- [11] H.M. Cheung, S. Kurup, *Environ. Sci. Technol.* 28 (1994) 1619.
- [12] C. Pétrier, M.F. Lamy, A. Francony, A. Benahcene, B. David, V. Renaudin, N. Gondrexon, *J. Phys. Chem.* 98 (1994) 10514.
- [13] A. Kotronarou, G. Mills, R. Hoffmann, *J. Phys. Chem.* 95 (1991) 3630.
- [14] C. Petrier, Y. Jiang, M.F. Lamy, *Environ. Sci. Technol.* 32 (1998) 1316.
- [15] L.K. Weavers, F.H. Ling, M.R. Hoffmann, *Environ. Sci. Technol.* 32 (1998) 2727.
- [16] A. Visscher, P. Eeno, D. Drijvers, H. Langenhove, *J. Phys. Chem.* 100 (1996) 11636.
- [17] J.W. Kang, M. Hoffmann, *Environ. Sci. Technol.* 32 (1998) 3194.
- [18] Y. Nagata, K. Hirai, H. Bandow, Y. Maeda, *Environ. Sci. Technol.* 30 (1996) 1133.
- [19] M. Gutiérrez, A. Henglein, F. Ibañez, *J. Phys. Chem.* 95 (1991) 6044.
- [20] A.E. Alegria, Y. Lion, T. Kondo, P. Riesz, *J. Phys. Chem.* 93 (1989) 4908.

- [21] T.J. Mason, *Practical Sonochemistry: User's Guide to Applications in Chemistry and Chemical Engineering*, Ellis Horwood, London, 1991, p. 45.
- [22] I. Hua, M. Hoffmann, *Environ. Sci. Technol.* 30 (1996) 864.
- [23] K. Yokoyama, G. Fujisawa, A. Yokoyama, *J. Chem. Phys.* 102 (1995) 7902.
- [24] Supeno, P. Kruus, *Ultrason. Sonochem.* 7 (2000) 109.
- [25] P. Kruus, L. Beutel, R. Aranda, J. Penchuk, R. Otson, *Chemosphere* 36 (1998) 1811.
- [26] N. Gondrexon, V. Renaudin, C. Petrier, P. Boldo, A. Bernis, Y. Gonthier, *Ultrason. Sonochem.* 5 (1999) 125.
- [27] O. Dahlem, J. Reisse, V. Halluin, *Chem. Eng. Sci.* 54 (1999) 2829.