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# Ex-situ Reductive Dechlorination of Carbon Tetrachloride by Iron Sulfide in Batch Reactor

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## Abstract

Ex-situ reductive dechlorination of carbon tetrachloride (CT) by iron sulfide in a batch reactor was characterized in this study. Reactor scaled-up by 3.5 L was used to investigate the effect of reductant concentration on removal efficiency and process optimization for ex-situ degradation. The experiment was conducted by using both liquid-phase and gas-phase volume at pH 8.5 in anaerobic condition. For 1 mM of initial CT concentration, the removal of the target compound was 98.9% at 6.0 g/L iron sulfide. Process optimization for ex-situ treatment was performed by checking the effect of transition metal and mixing time on synthesizing iron sulfide solution, and by determining of the regeneration time. The effect of Co(II) as transition metal was shown that the reaction rate was slightly improved but the improvement was not that outstanding. The result of determination on the regeneration time indicated that regenerating reductant capacity after 1st treatment of target compound was needed. Due to the high removal rates of CT, ex-situ reductive dechlorination in batch reactor can be used for basic treatment for the chlorinated compounds.

*Keywords*: Iron sulfide, Transition metal, Mixing time, Reductive dechlorination, Regeneration

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## 1. Introduction

Chlorinated organic compounds are commonly used in the dry cleaning and degreasing industries as a solvent while most of those chemicals have high toxicity and are known as recalcitrant materials. These chemicals are heavier than water and the contamination of soil or groundwater by those compounds has been an issue which was associated with risks to both human health and the environment.[1] Among these compounds, carbon tetrachloride (CT) was widely used until 1970s and in spite of its toxicity as well as ozone concerns, due to its increased use as a fire extinguisher and grain fumigation, the production of CT, in 1988, was 761 million lbs in USA.[2,3] Since 2000, its use was completely banned due to the 1992 amendment to the Montreal Protocol. CT is, however, still used for the detection of neutrinos and evaluation of hepatoprotective agents for the scientific research. As a probable human carcinogen (B2), CT has also high toxicity and is not easily biodegradable. In addition, because CT can be easily bioaccumulated in air, water, and soil environment, it can cause significant risk to human health. As a contamination episode, in 2005, CT had been detected in groundwater in Kyeonggi province, Korea. The groundwater contamination by CT may come from leakage from the underground storage tank which was located previously. Based on groundwater monitoring results of Korean Ministry of Environment, chlorinated organic compounds such as tetrachloroethylene (PCE) are dominant.[4] Therefore it is essential to develop and apply technologies to minimize environmental damages from these kinds of pollutants.

Reductive dehalogenations are important processes that influence the fate and transport of organic pollutants such as chlorinated aliphatic compounds in sediment-water system and aqueous environments. Several studies have been conducted to remove this toxic chlorinated compound by using reactive soil minerals under reducing conditions.[5-8] Recently, research related to abiotic transformation of contaminants using naturally occurring iron-bearing minerals such as iron sulfide is focused on investigating reaction mechanisms to identify the processes and to optimize their efficacy.[9-14] Based on the idea that iron sulfide can play an important role in transforming chlorinated organic compounds to less chlorinated hydrocarbon in soil and sediment systems, research has shown good degradation results by using the reductants and various contaminants and the improved degradation rates by mixing various additives.[10,15]

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There are some treatment technologies including the dehalogenation process that already was mentioned above to remove chlorinated organic compounds in groundwater; pump-and-treat with air stripping, in-situ thermal treatment, in-situ chemical oxidation, and surfactant/co-solvent flushing.[16] These technologies can be categorized by physical, chemical and biological treatments.[17-20] Almost of these technologies and research, however, are limited to focus on in-situ remediation or lab experiments using small batch reactors. Moreover, little research has been performed to apply iron sulfide to ex-situ remediation or a scale-up reactor.[21,22] In fact, to use the iron sulfide suspension in reactor, one should make the suspension either outside or inside of reactor before starting reductive dechlorination. In short, mixing time is the time taken right before the initiation of reductive dechlorination (i.e., right before spiking of CT). On the other hand, after a kinetic experiment, the reductive capacity of iron sulfide decreased. It could be regenerated by adding reducing agents in the regeneration time. Regeneration time is the time needed to recover the reactivity of reductants. However, even there is rare effort to examine the effect of mixing time to synthesize iron sulfide solution and regeneration time to recover the reactivity of reductants so that it could be used as treatment technology for chlorinated compounds in wastewater. This may be due to difficulties in extrapolating small scale experiments to real system that has little been reported to date. Therefore the effect of mixing time and using transition metal on synthesizing iron sulfide suspension and the proper time to regenerate the expensive reductants should be studied. This research presented here was conducted to describe a possibility of using ex-situ reductive dechlorination system for chlorinated compounds. The goals of this research were: (1) to characterize the effects of transition metal in iron sulfide solution and mixing time on ex-situ reductive dechlorination in batch reactor and (2) to determine the appropriate regeneration time of the reductant. In this study, we used CT as a contaminant, iron sulfide as a reductant, and 3.5 L batch reactor to attain our objectives.

## 2. Materials and Methods

### 2.1. Maintenance of Anaerobic Conditions

If there is no mention for the system used in this study, all experiments were carried out inside an anaerobic chamber (Coy Laboratory Products Inc., Grass Lake, MI) filled with 95% $N_2$/5% $H_2$. For the preparation of all aqueous solutions, solid suspensions, and chemical reagents, deaerated deionized water (DDW) was prepared by purging 18 MΩ·cm deionized water (Barnstead) with nitrogen for 2 hrs and with the anaerobic atmosphere for 12 hrs in the anaerobic chamber and used.

### 2.2. Materials

The following chemicals were used: Carbon tetrachloride (CT, 99.5%, Sigma-Aldrich), chloroform (CF, 99%, Junsei), 1,2-dibromopropane (1,2-DBP, 97%, Aldrich). $FeCl_2 \cdot 4H_2O$ (99%, Kanto) and $Na_2S \cdot 9H_2O$ (98+%, J.T. Baker) were used to synthesize FeS. $CoCl_2$ (97%, Junsei) was used as a source of transition metals. For keeping constant pH in aqueous solutions and FeS suspensions during reaction time, tris(hydroxymethyl) aminomethane (99.8%, Sigma-Aldrich) and tris(hydroxymethyl) aminomethane hydrochloride (99%, Sigma) (Tris buffer) were used.

Preparation of iron sulfide solution was conducted in the anaerobic chamber by adding 1.236 M of $Na_2S \cdot 9H_2O$ to the same amount of 1.068 M $FeCl_2 \cdot 4H_2O$ and mixing the slurry with the same amount of Tris buffer solution using a magnetic stirrer for 3 days to keep the suspension pH of concern constant.[11]

### 2.3. Experimental Procedures

A transparent cylinder type of acryl reactor was used for the experiments. The reactor was sealed by a cap with rubber ring, which successfully maintained anaerobic condition (Fig. 1). As shown in Table 1, the total reactor volume was 3.5 L, which was consisted of 3 L of liquid-phase and 0.5 L of gas-phase. The reason why the reactor designed to have gas-phase is to facilitate the kinetic experiments, although some significant portion of CT can be volatilized. The concentrations of target and intermediates in gas-phase and liquid-phases were measured for every experimental run.

On the other hand, because initial pH has a strong influence on reaction rate,[11] subsequent experiments were conducted by keeping the pH 8.5 constant using Tris buffer solution (0.1 M total). 3 L of FeS suspension of a certain concentration was transferred to reactor in which the slurry was mixed by a magnetic stirrer.

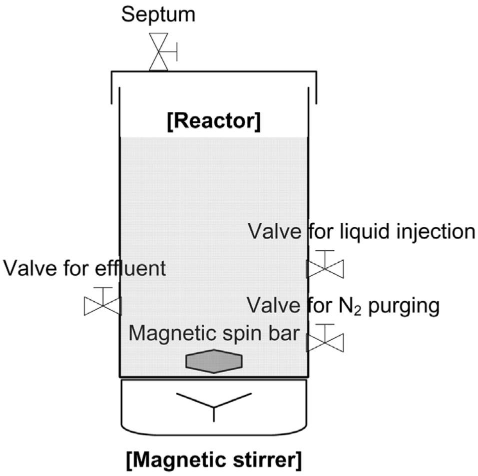

Fig. 1. Schematic diagram of batch reactor.

Table 1. Experimental condition for ex-situ reductive dechlorination system

| Target compounds | Initial conc. | pH | Liquid-phase volume | Gas-phase volume | Remarks |
|---|---|---|---|---|---|
| CT | 1.0 mM | 8.5 | 3.0 L | 0.5 L | Anaerobic condition |

To characterize the effects of reductant concentration on removal efficiency, each target concentration of FeS was prepared by diluting 33 g/L of FeS and to evaluate the effect of transition metal and mixing time on reductive dechlorination of CT, an exact amount of stock transition metal solution (1,200 mM) was added to FeS solution and this resulted in 2 mM of the concentration of transition metal in the suspension. The suspension was mixed for 1 hr to reach a chemical equilibrium and then the experiment to characterize the effect of transition metal and mixing time was performed. The reaction was initiated by spiking 5 mL of stock target compound solution resulting in 1 mM of CT in 3,000 mL suspension.

In addition, to determine the appropriate regeneration time of reductant, CT stock solution was spiked into the reactor containing FeS suspension and this made the each initial concentration of total system 1mM. The same FeS suspension was also used to degrade each 1 mM of CT during each three times with no regeneration of the suspension and the reactor was purged by using $N_2$ gas to remove CT remaining as both liquid-phase and gas-phase after finishing each one cycle. Each time to takes one cycle to degrade 1 mM of CT was 6 hrs. A control test containing Tris buffer and the target compound was conducted to check the loss of target compound due to sorption and volatilization during the reaction. All samples from the control test and the main reaction experiment were prepared in duplicate and were taken from reactor with respect to sampling time schedule. To evaluate the degradation kinetics of CT by FeS for each case, the concentrations of the target compound at each sampling point were monitored by liquid-liquid extraction with n-hexane (Merck).

### 2.4. Analytical Methods

After reacting with CT for scheduled time, one-hundred microlitre of mineral suspension was extracted with 1.4 mL of n-hexane, which contained 247 µM of 1,2-DBP as an internal standard. The samples were shaken for 1 hr using an orbital shaker at 200 rpm to transfer the CT into the extractant from liquid and suspension. Samples and standards were analyzed by a gas chromatograph with electron capture detector (GC/ECD, Hewlett Packard (HP) 5890 with a Ni-63 source) equipped with HP-5 column (30 m length, 0.32 mm i.d., 0.25 µm thickness). The temperatures of injector and detector were 175 and 300ºC, respectively. The oven temperature was programmed to be isothermal at 100°C for 5 min and the split ratio was 5:1.

### 2.5. Data Treatment

The concentration of CT rapidly decreased at first and then decreased slowly more and more. This reaction kinetics for the reductive dechlorination of CT was followed by a pseudo-first-order rate law as shown in Eq. (1).

$$\frac{dC_{aq,CT}}{dt} = -\frac{k \cdot C^0_{aq,CT}}{p_{CT}} = -k_{app} \cdot C^0_{aq,CT} \qquad (1)$$

where $C_{aq,CT}$ is the aqueous concentration of CT, k is the rate constant for degradation of target compound at the reactive surface, $C^0_{aq,CT}$ is the initial concentration of CT in aqueous-phase, $p_{CT}$ is the partitioning factor defined as $(1 + H_i \times (V_g / V_{aq}))$ to explain the effect of transferring of CT on aqueous-phase and gas-phases, H is the dimensionless Henry's law constant (1.20) for the CT,[23)] $V_{aq}$ and $V_L$ are volumes of the gas-phase and aqueous-phases, respectively, and $k_{app}$ is the apparent pseudo-first-order rate constant. The calculated $p_{CT}$ for CT in this study was 1.20. $k_{app}$ was estimated by using MATLAB® (MathWorks Inc.) that applies a Gauss-Newton algorithm to conduct a nonlinear regression of aqueous-phase target compound concentrations. $k_{app}$ was multiplied by $p_{CT}$ to calculate k and the k value was used to account for the rate for the decay of target compound.

## 3. Results and Discussion

### 3.1. Ex-situ Reductive Dechlorination by Iron Sulfide in 3.5 L Batch Reactor

Prior to conduct the experiment on removal efficiency, a control test was done by using 3.5 L batch reactor to check the effect of sorption and volatilization on the reactor inside. For this test, only Tris buffer solution and CT were used to check whether the sealing of the reactor system was well done or not. Fig. 2 shows the results of control test at pH 8.5 which indicate there was no significant sorption and volatilization inside the reactor. The concentration of CT in the gas-phase increased initially and reached at equilibrium, while that of CT in liquid-phase decreased and reached at equilibrium. Overall the gas-phase concentration of CT reached at the equilibrium in 10 hrs and so did the liquid-phase concentration of CT (Fig. 2(a) and Fig. 2(b)). Total concentrations of CT at 10 hrs in both gas-phase and liquid-phase were 96.1% of initial CT concentration.

In reductive dechlorination, the results of kinetic test have an important role to find rate constants which indicate overall rate of reaction in that system. Fig. 3 shows the reductive dechlorination of CT by FeS (6.0 g/L) at pH 8.5 which was expressed as both gas-phase and liquid-phase of target compound. From this result, concentration change of liquid-phase in CT with respect to time could be described by a pseudo-first-order rate law reasonably. 98.9% of 1mM CT in liquid-phase was reductively degraded in 6 hrs and the reaction rate constant of FeS for degrading CT in liquid-phase was 0.88 $hr^{-1}$ ($R^2 = 0.941$). Liquid-phase concentration of CT decreased gradually while gas-phase concentration of that increased and then decreased a little bit with respect to time. In case of CT concentration in gas-phase, initial concentration was not detected because of no partitioning between gas-phase and liquid-phase but as the CT in liquid-phase was transferred to gas-phase gradually, the concentration in gas-phase increased. The concentration increased was decreased a little bit due to degradation resulted from the reductive capacity of FeS solution,[10,11)] and then the concentration of CT in both gas-phase and liquid-phase reached the equilibrium state.

### 3.2. Effects of Reductant Concentration on Removal Efficiency

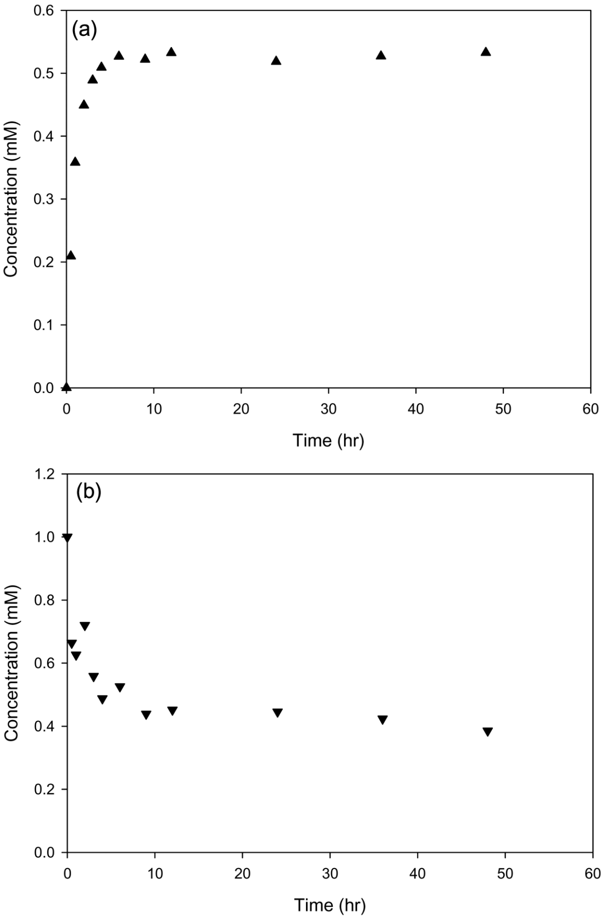

Fig. 2. Control test for 1 mM CT at pH 8.5 and 25ºC. a) concentration of CT in gas-phase for control test and b) concentration of CT in liquid-phase for control test.

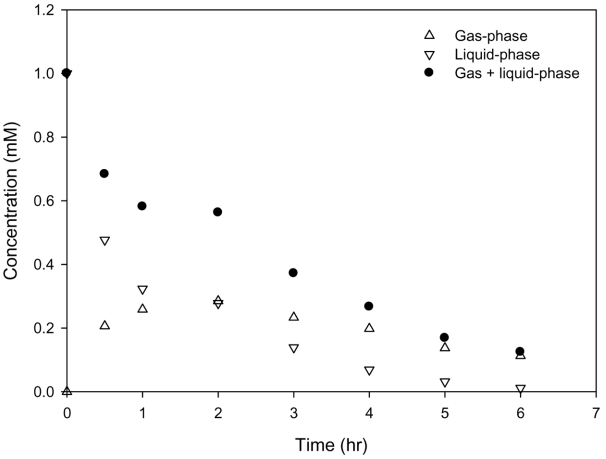

Fig. 3. Kinetic test for 1 mM CT at pH 8.5 and 25ºC (in both gas-phase and liquid-phase).

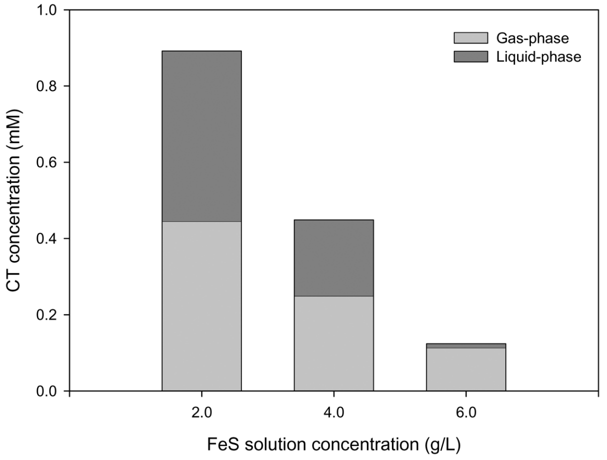

Fig. 4. The concentrations of target compound at 6 hrs later after reacting with different concentrations of reductant suspensions.

This experiment was conducted to investigate the removal efficiency of target compound (CT) by reductant (FeS) and the concentration of FeS suspension was 2.0, 4.0, and 6.0 g/L. This concentration range was determined from a preliminary experiment which was done by using 6.0 g/L of FeS and the experiment showed the removal rate of over 90% (for the liquid-phase sample) in 6 hrs. Based on the preliminary results (data not shown), final CT concentrations at 6 hrs after injecting target compound were observed when different concentrations of FeS solutions were applied in the system (Fig. 4). We have measured the initial and final concentrations of target compound at each experimental run so that we could use the removal efficiencies instead of rate constants. More kinetic data should be measured to obtain kinetic rate constants. When 2.0, 4.0, and 6.0 g/L of FeS suspension concentration were applied to scrutinize the effect of reductant concentration on CT removal efficiency, CT concentrations of liquid-phase after completing the reaction of 6 hrs were 0.447, 0.200, and 0.011 mM, respectively. If the gas-phase concentrations were considered, total initial concentrations of CT, at each different concentration of FeS suspensions (2.0, 4.0, and 6.0 g/L), were reduced to 10.8%, 55.1%, and 87.6%. The final concentration of target compound in reactor showed tendencies to decrease with increasing the concentrations of FeS suspensions. This may be resulted from the increased amount of $Fe^{2+}$ as well as $S^{2-}$ in the same volume of solution which has higher concentration of reductant. The increased $Fe^{2+}$ can be acted as electron donor when this ionized form is oxidized to $Fe^{3+}$ and the increased $S^{2-}$ can facilitate the reductive dissolution of $Fe^{3+}$ oxide to $Fe^{2+}$.11,14,24) Thus, the reductive capacity of the batch reactor having higher concentration of reductant can be increased and the increased concentration of reductant suspension can affect on removal efficiency for target chlorinated compound.

### *3.3. Process Optimization - (1) Effect of Mixing Time and Transition Metal on Ex-situ Reductive Dechlorination in Batch Reactor*

Determination on regeneration time of reductant is very important because the price of reductant is not cheap in most cases. It is desirable if we can minimize the additional expenditures which need to operate the system and if we are able to know the appropriate time to regenerate the expensive reductants. Additional expenditures may include an electric power which is required to mix the reductant suspension. Thus, reducing mixing time can make the process cost effective. Another way to cut down the expenses is to facilitate the reaction which we have an interest

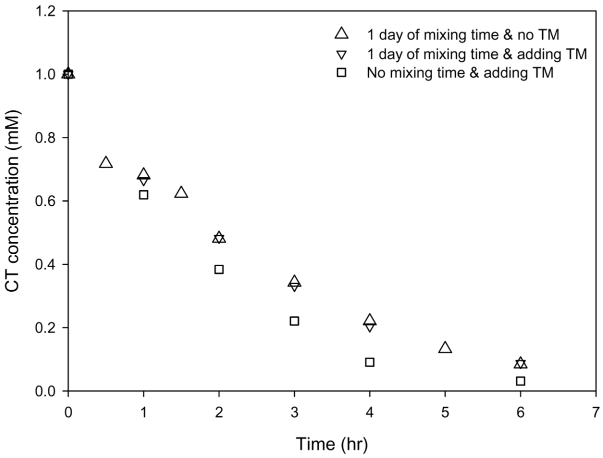

Fig. 5. Effect of mixing time and transition metal on reductive dechlorination.

by adding transition metal to iron sulfide suspension. A lot of attempts to enhance the reactivity of reactants used for the reductive dehalogenation of chlorinated compounds have been performed to date. For this purpose, researchers have mixed transition metals to zero-valent metals[25,26] and they reported improvements on reductive capacity in accordance with experimental conditions.

Fig. 5 shows the effect of mixing time and transition metal on reductive dechlorination of CT. The rate constant (0.5114) for CT degradation on gas-phase and liquid-phases by the suspension which was given no mixing time but adding transition metal (Co(II)) was bigger than those by two other suspensions (1 day mixing and adding transition metal, 0.3820; 1 day mixing and no transition metal, 0.3609). Similarly, if the rate constants for CT degradation on liquid-phase only by the different suspensions, although the rate constant (1.0621) for the suspension applying 1 day mixing and adding transition metal was not much different from that (1.0699) for the suspension applying 1 day mixing and no transition metal, the rate constant (1.1893) for the suspension applying no mixing but adding transition metal was still bigger than those for two other suspensions.

To evaluate the effect of mixing time on rate constant more in detail, another experiment was conducted and the results were expressed in Fig. 6. The rate constant (0.0853) for applying the suspension which was given no mixing time (0 day) was compared with that ($8.5984\times10^{-13}$) for 3 days mixing. When the suspension was given no mixing time (Fig. 6(a)), the concentration of CT decreased gradually, CF, a by-product, was formed and then the concentration of CF was kept in about 0.54 mM. While on the other, when the suspension was given 3 days mixing (Fig. 6(b)), the concentration of CT decreased similarly with the result of the suspension of no mixing time, but the concentration of CF increased within conducted experiment time. This may come from the reason why the aged suspension may have low reductive capacity if the suspension had the time to get aged even in anaerobic condition. Thus, from this result, reductive capacity of the suspension of no mixing time can be considered as higher than that of the suspension which was mixed for 3 days.

In summary, the results imply that as reductant suspension is mixed more and more in the reactor, it has an adverse effect on reductive dechlorination. In addition, adding transition metal to iron sulfide suspension shows a positive result on degrading the target compound although the improvement is just slightly increased.

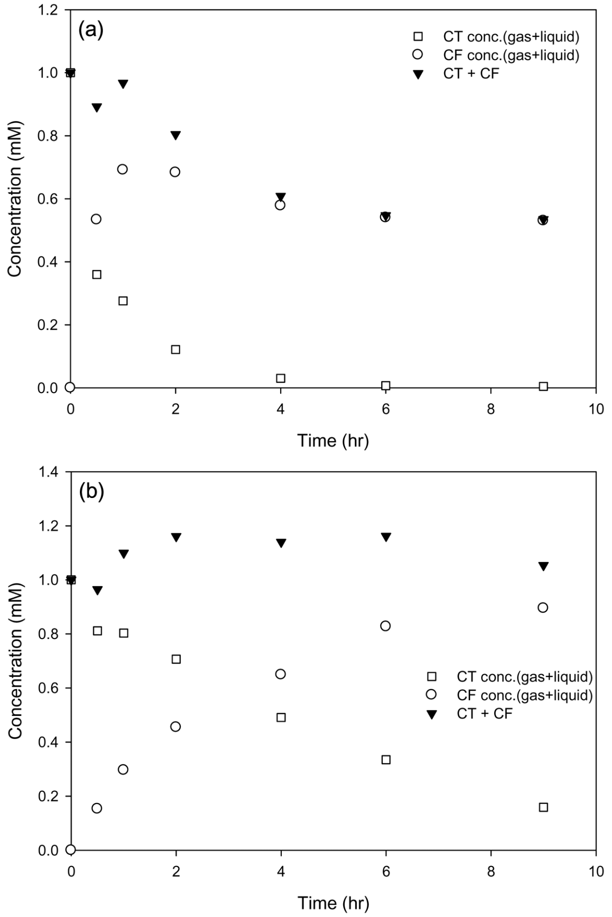

Fig. 6. Comparison of the result of 0 day mixing time with that of 3 days mixing time. a) variation of CT & CF concentration in applying 0 day of mixing time and b) variation of CT & CF concentration in applying 3 days of mixing time.

On the other hand, to evaluate the difference in between iron sulfide suspension without excess ions such as $S^{2-}$ by washing and iron sulfide suspension with excess ions in designated place there the reductive reaction will be occurred, two sets of experiments were done. When the reductive dechlorination process using iron sulfide suspension is applied in ex-situ treatment plant, the decision for which process is more proper is needed. In this research, the removal efficiency for each case about which excess ions in the reductive dechlorination are exist or not was identified. As a result, iron sulfide suspension with excess ions indicated better efficiency (iron sulfide without ions: 0.8840 $hr^{-1}$ ($R^2 = 0.9406$), iron sulfide with ions: 1.2785 $hr^{-1}$ ($R^2 = 0.9131$)). This result shows the way to form and use the iron sulfide suspension at the very place to operate reductive dechlorination process is better than the other way. Other researchers reported that existing of sulfide may contribute the formation of ferrous sulfide itself by combining ferrous ion with sulfide[12] or improve the reactivity of iron sulfide by coating other Fe(II) species.[13]

### *3.4. Process Optimization - (2) Determination on Regeneration Time of Reductant*

To decide what kinds of factors are important to operate a system, economical aspects as well as technical part should be considered thoroughly. In particular, determination on regeneration time of reductant was investigated in this section. To elucidate the time when injection of reducing materials such as hydrosulfide ($HS^-$) is needed, the system which has the same condition on every repeated operation including making the same condition with no degradation by-product as well as the contaminant and setting the same initial concentration of contaminant by spiking the contaminant again before starting next operation was used. For the aspect of facilitation as well as that of future application, both liquid-phase and gas-phase in the reactor system were applied because modified soil or activated carbon may be used as a material to treat the by-passed gas-phase which happens when raw wastewater flow into reactor. Moreover, by using gas-phase as well as liquid-phase, this system can be, surely, employed as one of the alternatives for soil and groundwater contaminated with chlorinated organic compounds by combining an air sparging treatment.

The problem which we may encounter whenever we handle toxic substances related to treatment is the environmental standards. The concentration of target compound was set by 1 mM which may be considered as a very high concentration that we cannot experience in our ambient environment (Fig. 7). However, this concentration was decided to focus on the determination on regeneration time of reductant so that we can predict the final concentration at any condition by using reaction rate constant. From the graph, after 1st, 2nd, and 3rd spiking the removal rates were 98.8%, 88.8%, and 75.8%, respectively. In Korea, there is no effluent water quality standard for CT. However, if we consider 0.004 mg/L of environmental standards for water quality and aquatic ecosystem as ambient water quality standard for CT, 0.04 mg/L of CT concentration will be an established value as an effluent water quality standard when dilution factor of 10 is applied to water quality standards. In addition, when the maximum possible exposure concentration is assumed as about 30 mg/L,[27] we can predict the final concentration at 6 hrs later after spiking target compound in the system by using a pseudo-first-order rate constant. The results of rate constants yielded from this method were 0.8348 $hr^{-1}$ ($R^2 = 0.9988$), 0.4502 $hr^{-1}$ ($R^2 = 0.9881$), and 0.3109 $hr^{-1}$ ($R^2 = 0.9580$) for the 1st, 2nd, and 3rd spiking, respectively, at initial concentration of 1 mM. If we apply the rate constant at 1st spiking, 1 mM of initial CT concentration, and 6 hrs of operation time, we can estimate the effluent concentration treated as 0.200 mg/L. Thus if we apply the initial concentration, a pseudo-first-order rate constant, and reaction time as 30 mg/L, 0.8348 $hr^{-1}$, and 9 hrs, respectively, the final concentration will result in 0.016 mg/L. This value is quite under the estimated effluent water quality standards. Therefore when we use 30 mg/L as an initial contaminant concentration, the iron sulfide suspension with excess ions as reductant, and about 6 hrs as reaction time, we can decide the regeneration time as after 1st spiking.

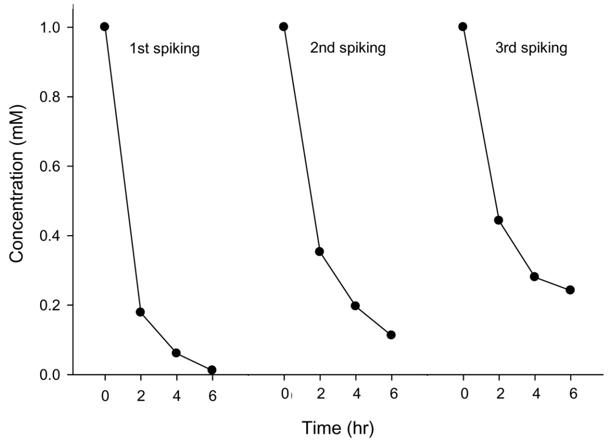

Fig. 7. The results of each spiking target compound in the same FeS solution without regeneration.

## 4. Conclusions

We investigated the effect of mixing time and transition metal on reductive dechlorination as well as how to determine the regeneration time of reductant as a tool of process optimization. In addition, the study to apply more effective reductant between the two of using iron sulfide suspension without excess ions and using iron sulfide suspension with excess ions also was conducted.

Although the ex-situ reductive dechlorination of CT and some factors such as the effect of mixing time may be used to treat this kind of chemicals, little research was conducted until now. From the evaluation of the effect of mixing time and transition metal, it was ascertained that decreasing mixing time and adding transition metal can increase the removal efficiency, and from the experimental results of determination on regeneration time of reductant, it was concluded that after 1st spiking, conducting a regeneration can make the attainment of effluent water quality standard for CT clear. In this part, a pseudo-first-order rate constant was used to predict the final concentration at the concerned time later. In addition, we elucidated the way to synthesizing iron sulfide in the practical place can be more efficient than using pure iron sulfide suspension already made from other places due to the contribution of excess sulfide. The results from this study can be used to apply this system to prototype of processes, and the research for more detailed optimization of reductant amount (or condition) should be performed hereafter.

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