

Kinetic correlation between degradation and dechlorination of perchloroethylene in the Fenton reaction

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Abstract—In the Fenton reaction, degradation and dechlorination are directly affected by the concentrations of hydrogen peroxide and Fe^{3+} . Although there is considerable research on the biodegradation of chlorinated compounds combined with the Fenton reaction, the kinetics of degradation and dechlorination of the reaction, with various concentrations of hydrogen peroxide and Fe^{3+} , have been rarely investigated. Therefore, we investigated the degradation and dechlorination of PCE with various concentrations of hydrogen peroxide and Fe^{3+} . The initial concentration of PCE (10 μM) decreased from a value of 8.9 μM (with 0.1 mM of hydrogen peroxide and 5 mM of Fe^{3+}) to 1.1 μM (with 10 mM of hydrogen peroxide and 5 mM of Fe^{3+}); the respective values for chloride ions produced were 0.9 and 21.6 μM . Also, the initial 10 μM of PCE decreased from 8.9 (with 0.1 mM of Fe^{3+} and 5 mM of hydrogen peroxide) to 2.2 μM (with 10 mM of Fe^{3+} and 5 mM of hydrogen peroxide); the respective chloride ions produced were 0.7 and 14.5 μM . The logarithmic correlations between the degradation and dechlorination coefficients were 0.7682 and 0.7834 for concentrations of hydrogen peroxide and Fe^{3+} , respectively. Both coefficients were used, from all possible cases, to derive six models which displayed both the ratio of degradation and dechlorination and the hydrogen peroxide and Fe^{3+} concentrations. The dechlorination of PCE could then be predicted with the model obtained by the coefficient with the concentration of hydrogen peroxide and Fe^{3+} . The models could be applied to various Fenton reactions for optimization of degradation or dechlorination, such as biodegradation of PCE which is scarcely degraded by aerobic bacteria.

Key words: Dechlorination Value, Degradation, Fenton Reaction, Kinetic Correlation, Perchloroethylene (PCE)

INTRODUCTION

Perchloroethylene (PCE) is a widely used chlorinated solvent and a common contaminant in groundwater. Aquifers containing PCE-contaminated water may be used as a source for municipal water supplies [1]. PCE is also a suspected carcinogen; therefore, the fate of PCE in the environment has become a fundamental health concern [2].

Since the Fenton reaction is a well-known potent oxidative reaction, many researchers have investigated the application of the Fenton reaction for degradation of various organic compounds [3-6]. For the treatment of these recalcitrant compounds, a number of chemical processes have been investigated, including oxidation by Fenton's reagent. The advantage of Fenton's reaction, compound degradation by Fenton's reagent, may yield (i) partial mineralization [7], (ii) lowered toxicity [8], and (iii) increased susceptibility to biodegradation [9]. Fenton's reagent (a mixture of hydrogen peroxide and ferrous salt) has gained a great amount of attention, due to its strong oxidation capabilities and low environmental impacts [10]. A Fenton system requiring aqueous $\text{Fe}(\text{II})$ for the formation of OH^- has been properly operated at the pH range of 2-4 by avoiding the formation of $\text{Fe}(\text{OH})_{3(s)}$ [11,12].

Several studies have also reported that PCE was dechlorinated by a Fenton reaction [13,14]. Individual kinetic models and reaction pathways of the Fenton reaction have also been proposed by

many [15-18]. PCE, which has four chloride ions, is not easily degraded by aerobic bacteria [2]. For biodegradation of PCE in wastewater, PCE has to be transformed to a more easily biodegradable form by other treatments. Various chemical methods, which could be used in conjunction with biological methods, have been studied to degrade PCE [19]. Among these methods, the Fenton reaction was one of the most frequently used for the dechlorination of PCE, because this reaction converts recalcitrant toxic compounds into biodegradable and less toxic [8,9].

In the Fenton reaction, degradation and dechlorination are directly affected by the concentrations of hydrogen peroxide and Fe^{3+} . Therefore, the absolute and relative concentrations of hydrogen peroxide and Fe^{3+} are very important in the overall process, including the Fenton reaction. Although there is considerable research on the biodegradation of chlorinated compounds combined with the Fenton reaction, the kinetics of degradation and dechlorination of the reaction, with various concentrations of hydrogen peroxide and Fe^{3+} , have been rarely investigated.

In this study, we investigated the conditions of the degradation and dechlorination of PCE. Kinetic experiments were conducted to investigate the effect of various concentrations of hydrogen peroxide and Fe^{3+} on the degradation and dechlorination of PCE and to draw the optimal operation conditions. We analyzed the coefficients of degradation and dechlorination, and expressed the correlations with the slopes, which were the coefficients in the first-order degree with degradation and dechlorination. Finally, we attempted to classify all possible examples into a series of models to show not only the most important factors affecting dechlorination, but also the opti-

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mal concentrations of hydrogen peroxide and Fe^{3+} .

EXPERIMENTAL

1. Chemicals

PCE and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were purchased from Sigma (Milwaukee, USA). Hydrogen peroxide was purchased from Wako (Tokyo, Japan).

2. Degradation of PCE

In the Fenton reaction, deionized water (5 ml) containing $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and PCE was dispensed into 60-ml headspace vials. PCE was added with a syringe, as an aqueous stock solution, through the septum of each vial, resulting in a final concentration of $10 \mu\text{M}$ ($=1.66 \text{ mg/L}$), which is similar to the PCE concentrations detected in the contaminated sites in Switzerland and the USA [20]. The concentrations of hydrogen peroxide and iron were modified, based on the previous study [19]. Hydrogen peroxide was added to the vials to initiate the Fenton reaction.

pH was adjusted to 5.0, and the vials were incubated in a shaker (120 rpm) for 90 min at 30°C . PCE degradation was quantitatively investigated, based on the reduction of PCE, using a gas chromatograph (Varian 3400 CX, Walnut Creek, CA, USA). The samples ($2 \mu\text{l}$) were injected with a $25\text{-}\mu\text{l}$ gas-tight syringe into a gas chromatograph equipped with a flame ionization detector and Supelco SPB-5 (Supelco Dark, Bellefonte, PA, USA) on a $30 \text{ m} \times 250 \mu\text{m}$ capillary column (column temperature: 70°C ; injector temperature:

150°C ; detector temperature: 250°C ; 30 ml/min ; N_2 as the carrier gas).

3. Dechlorination of PCE

The dechlorination of PCE was investigated during the Fenton reaction from the concentration of chloride ion, which was analyzed by ion chromatography (IC). The IC system (Waters, Milford, MA, USA) consisted of a pump (HP 526; Waters), a column heater (HP 530; Waters), and a conductivity detector (HP 550; Waters). The recently developed autosuppressor (Eris 1000HP; Alltech, Nicholasville, KY, USA) was used in suppressor analyses. The analytical columns for anion separation were Ion Pac AG 14 and AS 14 (Dionex, San Francisco, CA, USA).

RESULTS AND DISCUSSION

1. Degradation and Dechlorination of PCE by the Fenton Reaction

The degradation of PCE by the Fenton reaction was investigated at various concentrations of hydrogen peroxide. The initial concentration ($10 \mu\text{M}$) of PCE decreased to 8.9, 7.45, 7.0, 4.8 and $1.1 \mu\text{M}$ with 0.1, 0.5, 1.0, 5 and 10 mM of hydrogen peroxide and 5 mM of Fe^{3+} after 90 min, respectively (Fig. 1(a)). The concentration of chloride ions, which were produced from PCE by the Fenton reaction, increased to 0.9, 3.1, 7.6, 15.2 and $21.6 \mu\text{M}$ after 90 min, with the same concentrations of hydrogen peroxide and Fe^{3+} , respectively (Fig. 1(b)). Furthermore, the initial concentration of PCE decreased

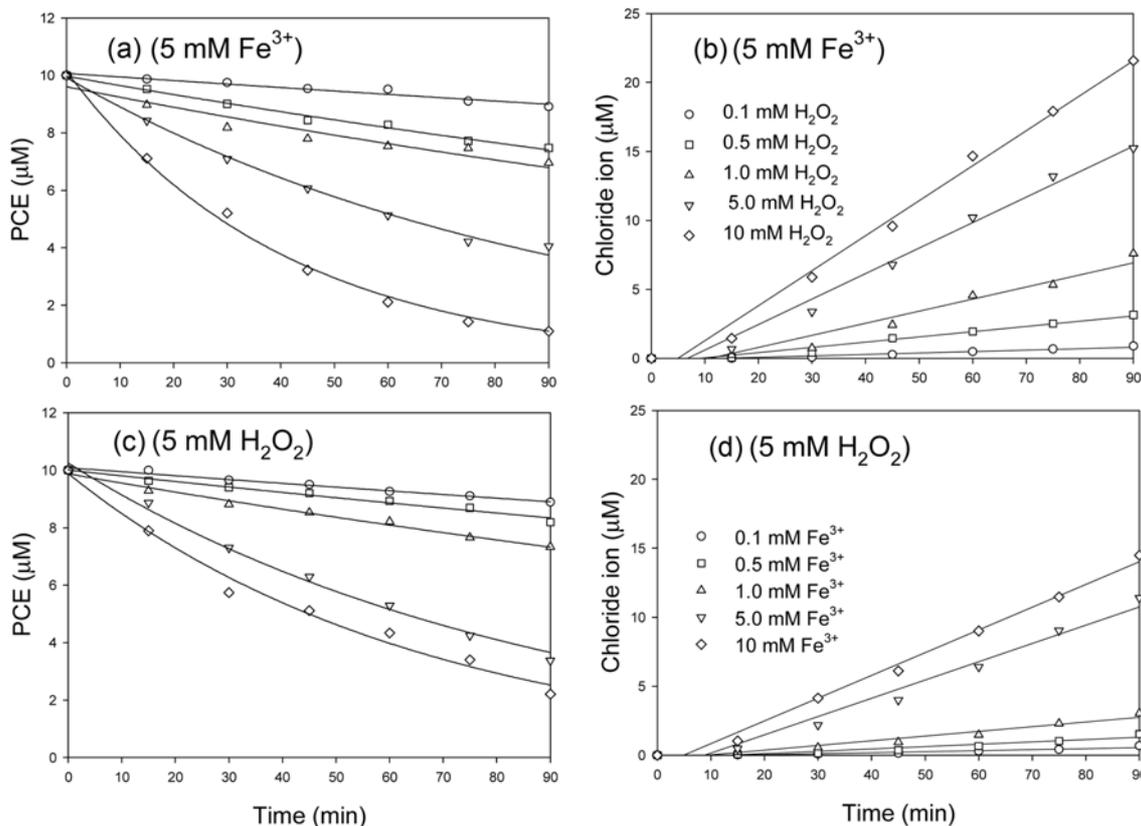


Fig. 1. Effects of various concentrations of hydrogen peroxide and Fe^{3+} on the degradation and dechlorination of PCE in the Fenton reaction. Hydrogen peroxide was added at a concentration of 0.1, 0.5, 1.0, 5.0 and 10 mM to a Fenton reagent containing 5 mM of Fe^{3+} ((a), (b)). In a similar manner, Fe^{3+} was added to a Fenton reagent containing 5 mM of hydrogen peroxide ((c), (d)).

to 8.9, 8.2, 7.3, 3.4 and 2.2 μM with 0.1, 0.5, 1.0, 5 and 10 mM of Fe^{3+} and 5 mM of hydrogen peroxide, respectively (Fig. 1(c)). The concentration of chloride ions increased to 0.7, 1.5, 3.0, 11.4 and 14.5 μM , respectively (Fig. 1(d)). These results show that the concentration of PCE decreased with the increasing hydrogen peroxide and Fe^{3+} concentrations. It seemed that the concentrations of hydrogen peroxide and Fe^{3+} are important factors which could determine the efficiency of the Fenton reaction. According to Leung et al. [16], an increase of hydrogen peroxide and Fe^{3+} could increase the degradation of PCE in the Fenton reaction. The Fenton reaction is caused by a hydroxyl radical from hydrogen peroxide and Fe^{3+} . Therefore, the fact that PCE decreased with increasing hydrogen peroxide and Fe^{3+} was due to an increased concentration of hydroxyl radical.

While PCE is degraded by the Fenton reaction, chloride ions are produced from PCE. When 8.9 μM of PCE was degraded by 10 mM of hydrogen peroxide and 5 mM of Fe^{3+} , 21.6 μM of chloride ion was produced. While 14.5 μM of chloride ion was released from 7.8 μM of PCE by 10 mM of hydrogen peroxide and 5 mM of Fe^{3+} . Therefore, the concentration of chloride ion increased with increasing hydrogen peroxide and Fe^{3+} . It seems that the number of hydroxyl radicals yielded by high concentrations of hydrogen peroxide is larger than the number yielded by high concentration of Fe^{3+} . Many researchers have reported that the Fenton reaction yielded hydroxyl radicals which were able to oxidize various organic compounds [10, 14,21-24].

The dechlorination value (D_m), calculated from ΔCl^- mol/DPCE

Table 1. Effects of hydrogen peroxide and Fe^{3+} concentrations on dechlorination of PCE

Concentration (mM)	Dechlorination value (D_m) ^a	
	H_2O_2 ^b	Fe^{3+} ^c
0.1	0.8	0.6
0.5	1.2	0.8
1.0	1.7	1.1
5.0	1.9	1.7
10	2.5	1.9

^aBased on Cl^- mol/DPCE mol

^bReacted with 5 mM of Fe^{3+}

^cReacted with 5 mM of hydrogen peroxide

mol, elucidated the dechlorination of PCE. When PCE was degraded by 10 mM of hydrogen peroxide and 10 mM of Fe^{3+} , the values were 2.5 and 1.9, respectively (Table 1). In other words, about 2.5 chloride ions per one molecule of PCE were released by 10 mM of hydrogen peroxide and 5 mM of Fe^{3+} ; 1.9 chloride ions per one molecule of PCE were released by 10 mM of hydrogen peroxide and 5 mM of Fe^{3+} . Therefore, hydrogen peroxide was more effective for dechlorination in the Fenton reaction. Dec and Bollag [25] predicted the dechlorination of chlorinated phenols and anilines in coupling reactions with the dechlorination number (DN), which was calculated from DPCE mol per one Cl^- mol. DN is useful in finding the reaction position, but is not suitable for PCE since all substitu-

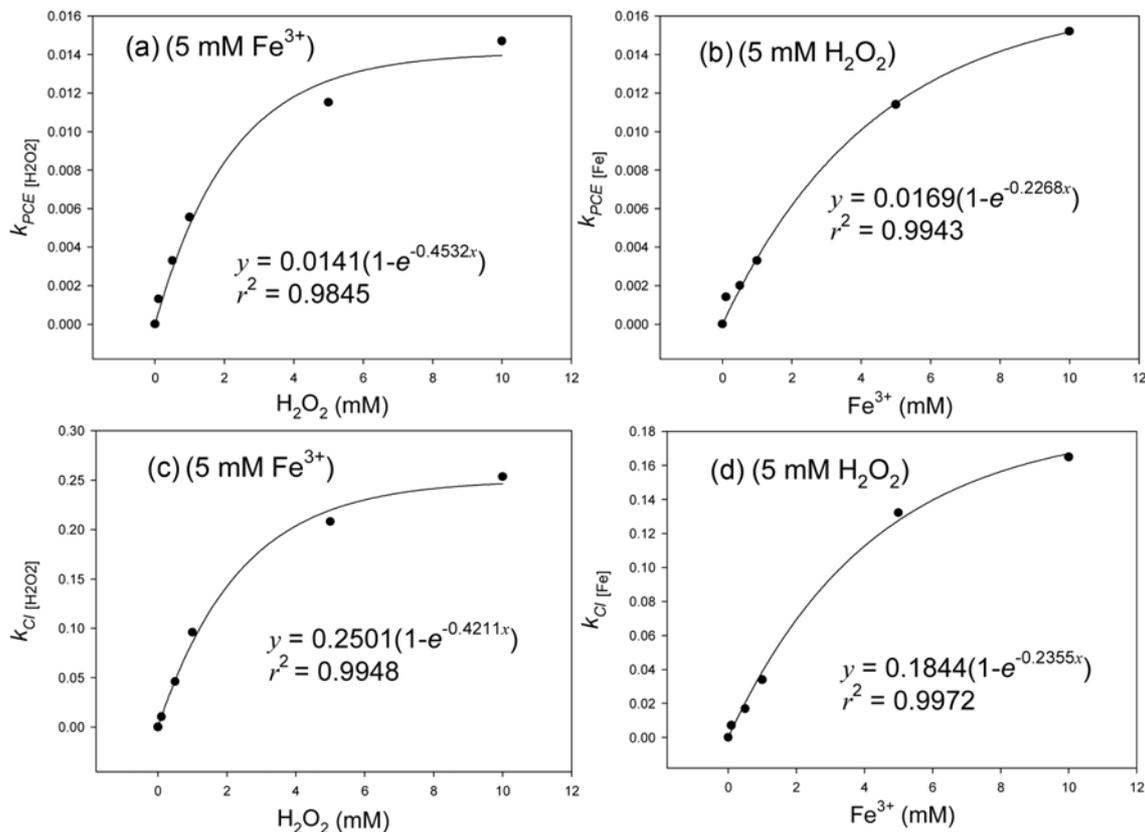


Fig. 2. Relationship between degradation coefficient (k_{PCE}) and concentration of hydrogen peroxide (a) and Fe^{3+} (c). Relationship between dechlorination coefficient (k_{Cl}) and concentration of hydrogen peroxide (b) and Fe^{3+} (d).

tion positions of PCE are occupied with chlorines in ethene. Therefore, we obtain D_m to obtain the theoretical number of chlorine ions released from one molecule of PCE.

2. Correlation between k_{PCE} and k_{Cl}

The relationship between degradation coefficient (k_{PCE}) and concentration of hydrogen peroxide and Fe^{3+} was investigated. Fig. 2 shows that the non-linear coefficient for the concentration of hydrogen peroxide was 0.4532. The $k_{PCE[H_2O_2]}$ increased with increasing hydrogen peroxide. The non-linear coefficient for the concentration of Fe^{3+} ($k_{PCE[Fe]}$) was 0.2268. The $k_{PCE[Fe]}$ also increased with increasing Fe^{3+} .

The relationship between dechlorination coefficient (k_{Cl}) on the concentrations of concentration of hydrogen peroxide and Fe^{3+} was investigated. Fig. 2(a) shows that the non-linear coefficient for the concentration of hydrogen peroxide was 0.4211. The $k_{Cl[H_2O_2]}$ increased logarithmically with increasing hydrogen peroxide. The non-linear coefficient for the concentration of Fe^{3+} ($k_{Cl[Fe]}$) was 0.2355. The $k_{Cl[Fe]}$ also increased with increasing Fe^{3+} . Weeks et al. [26] found that the first-order model provided the best fit for change of concentrations of H_2O_2 and TCE as a function of time in their experimental studies. They also noted that the actual processes involved in the degradation of H_2O_2 and TCE are more complex than first-order model predictions. Degradation rate constants of TCE obtained in the batch experiments depended on the experimental conditions, such as the initial $[H_2O_2]/[Fe^{2+}]$ ratio and the initial H_2O_2 and Fe^{2+} concentrations. Reactions in the later stages may have been catalyzed by regenerated Fe^{2+} and possibly Fe^{3+} .

The coefficients (slope) in the linear equations were transformed by natural log transformation from the degradation and dechlorination rate constants. The logarithmic equations, obtained by linear regression, between degradation and concentrations of hydrogen peroxide and Fe^{3+} were expressed as:

$$\ln k_{PCE[Fe]} = a_F + b_F \ln C_{Fe} \quad (1)$$

$$\ln k_{PCE[H_2O_2]} = a_H + b_H \ln C_{H_2O_2} \quad (2)$$

The equations between dechlorination and concentrations of hydrogen peroxide and Fe^{3+} were expressed as:

$$\ln k_{Cl[Fe]} = m_F + n_F \ln C_{Fe} \quad (3)$$

$$\ln k_{Cl[H_2O_2]} = m_H + n_H \ln C_{H_2O_2} \quad (4)$$

Eqs. (1)-(4) were obtained by logarithmic transform of results in Fig. 2. Substituting Eq. (1) in Eq. (3), we obtain:

$$\ln k_{PCE[Fe]} = a_F + b_F (\ln k_{Cl[Fe]} - m_F) / n_F = q_F + p_F \ln k_{Cl[Fe]} \quad (5)$$

And substituting Eq. (2) in Eq. (4), we obtain:

$$\ln k_{PCE[H_2O_2]} = a_H + b_H (\ln k_{Cl[H_2O_2]} - m_H) / n_H = q_H + p_H \ln k_{Cl[H_2O_2]} \quad (6)$$

According to Eqs. (5) and (6), the first-order equations versus k_{Cl} must constitute a straight line. In the equations, k_{PCE} is expressed by constants, coefficients and k_{Cl} . The coefficients, p_F and p_H , provide a great deal of information. (i) If p_F and p_H are higher than 1, k_{PCE} will change more effectively rather than k_{Cl} (Fig. 3(a)). In other words, the mol number for PCE degradation was larger than that for dechlorination. Therefore, the degradation of PCE could occur in the Fenton reaction without dechlorination. (ii) If p_F and p_H are lower than 1, k_{Cl} would change more effectively rather than k_{PCE}

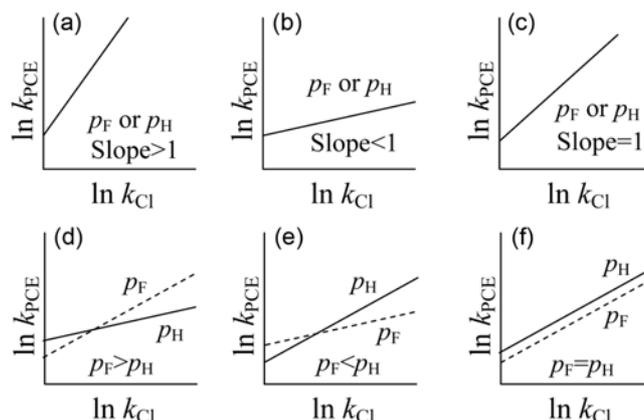


Fig. 3. Slopes for six possible models in the kinetic correlation between degradation and dechlorination. p_H and p_F are coefficients of the equations which expressed degradation and dechlorination with various concentrations of hydrogen peroxide and Fe^{3+} .

(Fig. 3(b)). In other words, the degradation rate is lower than the dechlorination rate. Therefore, over one chloride ion was released during degradation of one molecule of PCE. (iii) If p_F and p_H are equal to 1, k_{Cl} is directly proportional to k_{PCE} (Fig. 3(c)). This means that one chloride ion is released during degradation of one molecule of PCE. (iv) If p_F is higher than p_H , the concentration of hydrogen peroxide will have more effect on dechlorination than Fe^{3+} (Fig. 3(d)). (v) If p_H is higher than p_F , the concentration of Fe^{3+} will have more effect on dechlorination than the hydrogen peroxide (Fig. 3(e)). (vi) If p_H is equal to p_F , the effect of hydrogen peroxide on dechlorination will be the same as Fe^{3+} (Fig. 3(f)).

Substituting values for the constants and coefficients in the equations, we obtain:

$$\ln k_{PCE[Fe]} = -2.9193 + 0.7734 \ln k_{Cl[Fe]} \quad (7)$$

$$\ln k_{PCE[H_2O_2]} = -3.2637 + 0.7682 \ln k_{Cl[H_2O_2]} \quad (8)$$

Table 2 shows the slopes of the logarithmic equations. The slopes of Eqs. (1) and (2), which expressed $\ln k_{PCE}$ for the concentration of Fe^{3+} and hydrogen peroxide, were 0.5307 and 0.5609, respectively, while the slopes Eqs. (3) and (4), which expressed $\ln k_{Cl}$ for the concentration of Fe^{3+} and hydrogen peroxide, were 0.6908 and 0.7252, respectively. The slopes (p_F and p_H) of Eqs. (5) and (6) were

Table 2. Coefficients of dechlorination and degradation with concentrations of hydrogen peroxide and Fe^{3+} in the logarithmic equation

Coefficients	Slope
$k_{PCE[H_2O_2]}$	0.5307
$k_{PCE[Fe]}$	0.5609
$k_{Cl[H_2O_2]}$	0.6908
$k_{Cl[Fe]}$	0.7252
$k_{Cl[H_2O_2]}$ on $k_{PCE[H_2O_2]}^a$	0.7682
$k_{Cl[Fe]}$ on $k_{PCE[Fe]}^b$	0.7734

^aCoefficient (p_H) of the next equation, $\ln k_{PCE[H_2O_2]} = q_H + p_H \ln k_{Cl[H_2O_2]}$

^bCoefficient (p_F) of the next equation, $\ln k_{PCE[Fe]} = q_F + p_F \ln k_{Cl[Fe]}$

0.7682 and 0.7734, respectively. Fig. 3 shows the models of degradation and dechlorination occurring in the Fenton reaction with various concentrations of hydrogen peroxide and Fe^{3+} . Since both linear regression coefficients (slope) were lower than 1 in Fig. 3(b), the dechlorination reaction occurred more often than the degradation reaction. In other words, over one chloride ion was produced by the Fenton reaction during the degradation of one molecule of PCE. Since p_F was higher than p_H in Fig. 3(d), the concentration of hydrogen peroxide was more effective in dechlorination of PCE than Fe^{3+} . De Laat and Gallard [22] reported that the production rate of hydroxyl radicals increased with the ratio of hydrogen peroxide to Fe^{3+} ($\text{H}_2\text{O}_2/\text{Fe}^{3+}$). They could not explain how the hydrogen peroxide/ Fe^{3+} ratio affected degradation and dechlorination. In our experiments, however, the models show that the hydrogen peroxide/ Fe^{3+} ratio could affect degradation and dechlorination.

CONCLUSIONS

In the equations, when both coefficients, expressed by degradation and dechlorination rate constants, were below 1 and the Fe^{3+} coefficient was greater than that of hydrogen peroxide, the dechlorination coefficient was higher than the degradation coefficient of PCE, and hydrogen peroxide was a more effective dechlorination factor than Fe^{3+} in the Fenton reaction. We formulated six possible models for the correlation between degradation/dechlorination and various factors in the Fenton reaction. The dechlorination of PCE could then be predicted with the model obtained by the coefficient with the concentration of hydrogen peroxide and Fe^{3+} . In the Fenton reaction, dechlorination of PCE could be regulated by the model coefficients. In addition, the optimum concentration of hydrogen peroxide and Fe^{3+} could be obtained from the models. Therefore, the models could be applied to various Fenton reactions for optimization of degradation or dechlorination, such as biodegradation of PCE which is scarcely degraded by aerobic bacteria.

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NOMENCLATURE

DN : dechlorination number
 k_{Cl} : dechlorination coefficient
 k_{PCE} : PCE degradation coefficient

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