A Comparison of the Experiment Results and the Radical Degradation Pathways in PCE through Atomic Charge Calculation

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Abstract : The intermediate product resulting from the radical degradation experiment of PCE and the atomic charge gained through Gaussian03W were compared against each other. The result was that the ratio of PCE radical degradation was almost 98% or higher after the 9 hr point in reaction time. The reaction speed constant was 0.16 hr^{-1} and it followed the first reaction. We could see that at each location of the PCE molecule, dechlorination happened at a point where the negative atomic charge was the greatest. Moreover, the intermediate product of PCE radical degradation that was confirmed in the experiment and literature coincided exactly with the intermediate product in the atomic charge calculation. Therefore, when the atomic charge is calculated, the radical degradation pathway of the organic chlorine compound could be forecast.

Keywords : PCE, radical reaction, degradation products, charge, reaction position

1. Introduction

Recently, pollution of the soil or underground water caused by chlorinated volatile organic coumpounds such as Perchloroethylene (PCE) is emerging as a big issue [1-3]. Purification policies to date have used aeration by drawing on polluted underground water [4] or using suction of the soil gas [5]. However, such methods use adsorption of the polluted gas by active coal[6] and therefore the active coal needs to be reprocessed. Meanwhile, as a way of directly degrading PCE or trichloroethylene

(TCE), biotreatment is considered but this takes a long time and a stable efficiency is hard to achieve. Moreover, unlike TCE, PCE is impossible to dechlorinize in the early stages using just aerobic microbial decomposition. Because of this, chemical or physical treatments are used for PCE. Therefore, in this study, Fenton treatment is focused on as a quick treatment for PCE. This is a reaction generating OH radical through hydrogen peroxide and ferrous chloride. Transition metal generates from the hydrogen peroxide ·OH[7-8]. The Fenton treatment method that uses a powerful oxidant which is ·OH is used for high concentration PCE, TCE-polluted water or DNAPL(Dense Non-Aqueous Phase Liquid). There are many papers on the Fenton treatment of PCE and TCE. Leung et al.

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completely turns the asorbed PCE on the sand into inorganic matter, leading to dichloroacetic acid being the only intermediate product[9]. Moreover, Sawyer et al. also reported that 98% of PCE was turned into inorganic matter through Fenton treatment using ferrous porous materials[10]. Another example is that Sims et al. reported that when the ratio of H_2O_2/PCE was in the range of 10-25 and the ratio of Fe/H_2O_2 was higher than 0.2, it was possible to turn almost 100% of the PCE into inorganic matter [11]. Meanwhile, as for the intermediate product, Several degradation pathway through dichloroacetic acid were reported[12-15]. Ollis   et   al.   used photocatalyst to degrade PCE but reported that   no   dichloroacetic   acid   was   not generated[16]. Glaze   et al. reported the pathway of generating TCAC and DCAA in the photocatalyst degradation of PCE through the reaction of ·OH and PCE[17]. Despite reports that through Fenton treatment PCE can be turned to inorganic matter, there is hardly any reports on the theoretical analysis of the reaction product. [18-20]. Therefore, this study verified the possibility of turning PCE into   inorganic   matter   through   Fenton treatment, identify the intermediate product and calculate the charge using the DFT method to compare with the intermediate product.

2. Materials and Methods

2.1. Materials

The following materials were used in PCE degradation   experiment: PCE   (98%, AccuStandard); TCAA (95%, Waco); DCAA (99%,   Waco); H_2O_2 (30%,   Waco); $FeSO_4.7H_2O$(97%,   Aldrich); Na_2SO_3 (99%, Aldrich); Na_2SO_4 (99%, Aldrich); NaOH (97%, Aldrich); MTBE (98%, Aldrich); H_2SO_4 (98%, Aldrich); ethylacetate (99%, Waco).

2.2. Methods

2.2.1 PCE degradation experiment

Since pH condition is the most important parameter   in   Fenton   treatment,   as   a preliminary   experiment,   a   PCE   solution   of initial concentration of 162 mg/L(1 mmol/L) and H_2O_2 solution   with   an   initial concentration of 1,000 mg/L were made. After adjuting them for pH 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, and 6.0, $FeSO_4.7H_2O$ was added so that   the   concentration   would   become 1,000mg/L, and left at room temperature for 24 hours for reaction. The result was that at each pH level, the PCE degradation ratio was, respectively, 33, 67, 98, 97, 9%, 82%, 71, and 55%. So the initial pH was set at 3-4 . H_2SO_4 was used to adjust the initial pH to 3.5, and into a 100 mL vial, was added so that the concentration of PCE, $FeSO_4.7H_2O$, and H_2O_2 would be 162 mg/L, 1,000 mg/L, and 500-2,000 mg/L, respectively.

2.2.2 PCE concentration measurement

After a certain amount of reaction time, in order to prevent the volatility of PCE, the reaction   container   was   dipped   into   liquid nitrogen to rapidly freeze it. Na_2SO_3 was added to stop the reaction. Then ethylacetate 10 mL was added for a 24 hour agitation to extract PCE.

2.2.3 Measurement of ratio of inorganic matter conversion

Before starting the reaction, the gas within the   reaction   container   was   exchanged   for nitrogen to remove CO_2. After a certain amount of time has passed for reaction, a syringe was used to insert 1N NaOH so that CO_2 was absorbed into the solution.   Next, a total   organic   carbon   meter   (TOC5000A: Shimazu) was used to measure the organic carbon amount.

2.2.4 Identification of the reaction product

In order to terminate reaction, H_2SO_4 was

added, MTBE 5 mL was added and the solvent was collected two times. After Na_2SO_4 was added to the solvent and dehydrated, 2 mL of it was taken to be added with diazomethanen-MTBE to methylize the solvent. This solution was analyzed qualitatively using GC/MS(589-2 Hewlett Packard) (For the column, HP-1 was used). For quantitative analysis, GC-ECD was used.

3. Results and Discussion

3.1. The ratio of PCE degradation and conversion of into inorganic matter with the addition of H_2O_2

The Fenton reaction differs in degradation efficiency dpending on how much H_2O_2 or $FeSO_4 \cdot 7H_2O$ were added. Therefore, the concentration of PCE and $FeSO_4 \cdot 7H_2O$ were maintained at a certain level, while the concentration of H_2O_2 was changed within the range of 500-2,000 mg/L to evaluate the degradation ratio of PCE. The result was that when the concentration of H_2O_2 was 1,000 mg/L, the PCE degradation rate was the highest at 98%. The removal rate of PCE is shown in Fig. 1. PCE radical degradation rate was almost more than 98% after the 9 hr. The reaction speed constant was 0.16 hr^{-1} and it seemed to follow the primary reaction. At reaction time 12 hr, the PCE concentration temporarily increases, but this seems to be an
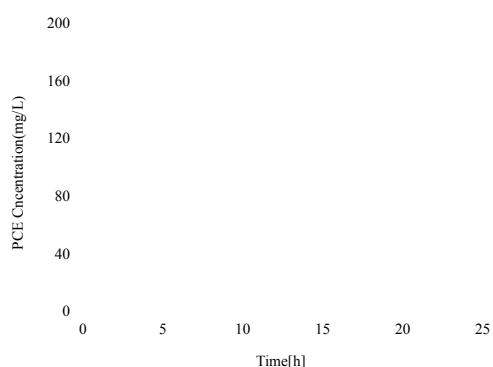

Fig. 1 Removal PCE by Fenton treatment.

error in the experiment. However after reaction time 24 hr, approximately 1.6% of the PCE was found to remain, indicating that the PCE degradation occurs rpaidly but it takes a long time for it to degrade 100%.

3.2. Identification of the degradation product and DCAA degradation rate

The solution that had completed the Fenton reaction was methylized and using GC-MS, the product of PCE Fenton reaction was investigated. The result found TCAA but DCAA which was reported in other literature, was not found. Since there is a high likelihood that DCAA would also be an intermediate product of PCE, the result of treating DCAA with an initial concentration of 126 mg/L(1 mmol/L) is shown in Fig. 2.
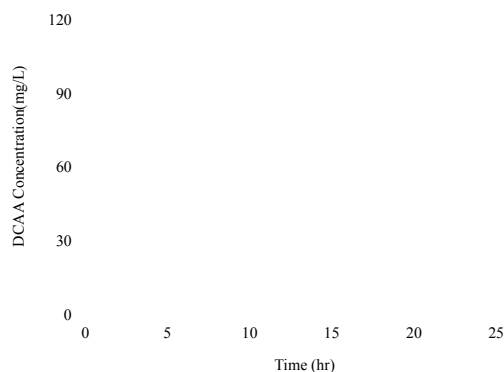

Fig. 2. Removal of DCAA by Fenton treatment.

Fig. 2 shows that 80% of the DCAA at the initial concentration degrades within 5hr. This result follows a similar pattern to the PCE degradation rate shown in Fig. 1, indicating that for PCE and DCAA, Fenton treatment is an effective method.

3.3 Comparison of the Charge values

This study confirmed TCAA as a degradation product of PCE. According to preceding studies, DCAA has been reported as a degradation product. Gaussian03W program

was applied on the reaction products confirmed through these experiments to calculate the atomic charges and compare them to one another. Table 1 shows that the Mulliken and CHelpG values of the number 1 or number 2 carbon of PCE are the same, indicating that the dechlorization reactivity is the same at carbon number 1 or 2. The atomic charge values were calculated for TCAA where one chlorine was separated from the number 1 or 2 carbon of PCE, and the other chlorine that had been combined with the carbon on one side moved. The result was that the number 1 carbon had a higher value than the number 2 carbon. This indicates that the number 1 carbon has a stronger ion-friendly reaction. This calculation result coincides with what was reported in preceding studies. Meanwhile, the atomic charge value was calculated for DCAA. The result was that for both the Mulliken and
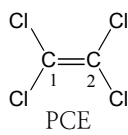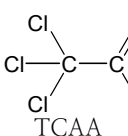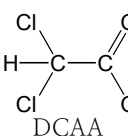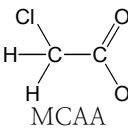
CHelpG values, number 1 carbon had a higher value than the number 2 carbon. Therefore, MCAA can be extrapolated to be a Fenton reaction product of DCAA. Lastly, the atomic charge value was calculated for DCAA. The result was that for both the Mulliken and ChelpG values, carbon number 1 was higher than number 2. Therefore, acetic acid can be extrapolated to be a product of Fenton reaction.

4. Conclusions

Fenton treatment was conducted on PCE to review the degradation products, and Gaussian03W program was used to calculate the results. The results were compared to reach the following conclusions.

1. A Fenton treatment on a PCE solution with an initial concentration of 162 mg/L and under conditions of H_2O_2 1,000 mg/L and $FeSO_4 \cdot 7H_2O$ 1,000 mg/L, the degradation ratio and conversion ratio to inorganic matter after 24 hr of reaction were both higher than 98%.

2. As a degradation product from the Fenton treatment of PCE, TCAA was found but DCAA was not found.

3. A Fenton treatment of DCAA showed a similar result to the Fenton treatment of PCE in terms of the removal rate and conversion rate to inorganic matter.

4. The atomic charge value was calculated for TCAA and DCAA which are known to be Fenton treatment products of PCE, and it was found that dechlorinization happes in the location of the carbon with the highest negative ion value. This corresponds with the findings of the reaction products in preceding studies. Therefore, once the atomic charge value is known, then the radical degradation

Table 1. Atomic charge in each radical reaction position of PCE

Compounds	Position	Charges	
		Mulliken	CHelpG
PCE	1	−1.021	0.036
	2	−1.021	0.093
TCAA	1	0.866	−0.188
	2	−0.550	0.739
DCAA	1	−0.345	−0.097
	2	−0.093	0.664
MCAA	1	−0.417	−0.149
	2	−0.042	0.723

pathway of organic chlorinated compounds including PCE can be extrapolated.

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