The Influence of Soil and Organic Matter on Trichloroethylene Decomposition by Fenton Reaction

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Contamination of soil and ground water by trichloroethylene (TCE) has become a serious problem in recent times. Fenton reaction can be used for the chemical decomposition of polluting substances. In this study, Fenton reagent was used as an in situ oxidizing agent for soils contaminated with TCE. We investigated the kinetics of TCE decomposition by Fenton reaction involving Fe(II). The results of our experiments show that the rates of TCE decomposition in the presence of all soils except Toyoura sand are lower than that in the absence of soils. TCE decomposition by Fenton’s reaction with Fe(II) in the presence and absence of black soil was found to be of the first order to concentrations of TCE and Fe(II) and half-order to hydrogen peroxide concentration. The reaction rate constants in the presence and absence of black soil were determined to be 1.048 and 0.568 (L mol$^{-1}$)$^{1.5}$ s$^{-1}$, respectively. Assuming the reaction order to be 2.5, the reaction rate constants in the presence of humic acid, Kanuma soil, Toyoura sand, and akadama soil were determined to be 0.849, 0.725, 1.050, and 0.354 (L mol$^{-1}$)$^{1.5}$ s$^{-1}$, respectively. The decrease in the rate is speculated to be affected by both specific surface area and carbon content of the soil.

Introduction

The volatile organic chloride compound trichloroethylene (TCE) has excellent degreasing power. Hence, it has been often used as a solvent for dry cleaning. It is still used for purposes such as removing grease from metallic parts. However, its indiscriminate use has caused the contamination of soil and ground water. The toxicity of TCE for humans has drawn attention in recent times. TCE has been recognized as a carcinogen. Hence, it is essential to purify contaminated soils and groundwater.

Although an adsorption method is used to treat technology contaminated soils and groundwater, but its cost is high. In Japan, pumping and aeration method is normally used. But, it can’t be applied to widespread polluted soil. It is expected that in situ treatment technologies will be effective for site remediation of polluted soil even if the reactions involved are slow. However, the in situ treatment technologies for contaminated soils are limited to chemical methods involving oxidation, reduction, and catalysis reactions and biological methods involving the use of microorganisms (Chen et al., 2001).

In the United States of America, contaminated soils and groundwater are treated by the injection of Fenton reagents (Weeks et al., 2000). Fenton reaction has so far been studied by various research groups. In these researches, a great deal of effort has been made on kinetic study (Chen et al., 2001; Liou and Lu, 2008). Generally, treatment by Fenton reaction is carried out by injecting the oxidizing agent hydrogen peroxide with Fe(II) ions into the contaminated soil. This results in the formation of hydroxyl radicals which are powerful oxidizing agent (Barb et al., 1951). This method has been proven to be effective in the destruction of oils, benzene, and TCE (Tang and Huang, 1996). The kinetic equation of TCE decomposition by Fe(II) ions can be written as follows (Takuma et al., 2007).

$$\frac{dC_{TCE}}{dt} = -k^{*} \left(C_{TCE}\right)^{y} \times \left(C_{Fe(II)}\right)^{m} \times \left(C_{H_{2}O_{2}}\right)^{n}$$ (1)

Fenton reaction in soils has previously been studied (Silva et al., 2009). However, the effects of soil components such as organic compounds on the reaction kinetics have not been studied intensively. Takuma et al. (2007) reported that the reaction rate of TCE decomposition by Fenton reaction in the presence of humic acid differs from that in the absence of humic acid; however, this difference is not remarkable. Further investigation was not conducted.

In this study, Fenton reagent was used as an in situ oxidizing agent for different soils contaminated with TCE. We studied the kinetics of the TCE decomposition in the presence and absence of soils (e.g., black soil) and...
Table 1 Characteristics of soil samples

<table>
<thead>
<tr>
<th>Soil</th>
<th>Kanuma soil</th>
<th>Black soil</th>
<th>Akadama soil</th>
<th>Toyoura sand</th>
<th>Humic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content [wt%]</td>
<td>27.0</td>
<td>25.0</td>
<td>47.5</td>
<td>0.5</td>
<td>13.8</td>
</tr>
<tr>
<td>Specific surface area [m²/g]</td>
<td>231.3</td>
<td>24.8</td>
<td>160.7</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Equivalent diameter [µm]</td>
<td>0.013</td>
<td>0.12</td>
<td>0.019</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Amount of carbon [wt%]</td>
<td>0.07</td>
<td>9.10</td>
<td>1.14</td>
<td>*</td>
<td>50.0¹</td>
</tr>
<tr>
<td>Amount of nitrogen [wt%]</td>
<td>0.007</td>
<td>0.540</td>
<td>0.092</td>
<td>*</td>
<td>1.50¹</td>
</tr>
<tr>
<td>Soil classification</td>
<td>Granular soil</td>
<td>Volcanic ash soil</td>
<td>Clay soil</td>
<td>Sand</td>
<td>—</td>
</tr>
</tbody>
</table>

*Less than quantification limit of gas adsorption measurement or NC analyzer
¹Data from the homepage of Telnite Co.

1. Experimental

1.1 Soil samples

In this study, we used commercially available soil samples; Kanuma soil, akadama soil, black soil, and Toyoura sand. We also used humic acid, which was supplied by Wako Pure Chemical Industries Ltd. Humic acid is known as a typical constituent of soil organic matter.

Table 1 lists the characteristics of each soil sample. We determine the moisture content of the soil by using a moisture meter with an infrared ray dryer (FE-5 µm 1 µm 600, Kett Electric Laboratory), the specific surface area of soil particles by gas adsorption measurements (Brunauer-Emmett-Teller (BET) equation Gemini, Micrometrics Corporation Ltd.), and the carbon and nitrogen content of the soil by using a NC analyzer (SUMIGRAPH NC-22A, Shimadzu Science East, Corporation Ltd.). The equivalent diameter of soil particles is obtained by assuming that the primary particles are spheres with a density 2 × 10³ kg/m³.

Figures 1–3 show scanning electron microscopy (SEM) (JSM-5200, JEOL, Ltd.) images of soil surfaces. It is considered that the inside of the particles in Figures 1–3 mainly contributes to the BET surface area, especially in the case of Kanuma and akadama soils.

1.2 Decomposition rate of TCE in the absence of soils

All experiments were conducted at room temperature (298 K). 5 mL of various concentrations (1–20 mmol/L) of saturated solution of iron sulfate and TCE (8.37 mmol/L, 298 K) and 5 mL of various concentrations (0.176–1.76 mol/L) of hydrogen peroxide were mixed in a test tube. The instant of mixing was defined as the reaction start time. After a predetermined reaction time, 10 mL of n-hexane was poured to a 20 mL test tube and residual TCE was extracted. The concentration of the residual TCE in the n-hexane phase was quantified by gas chromatography with an electron capture detector (GC-ECD) (GC-14B, Shimadzu Science East, Corporation Ltd.).

In this paper, the word “concentration” refers to the concentration of a compound in its aqueous solution after the mixing, e.g., initial concentrations of iron sulfate...
and hydrogen peroxide are 5 mmol/L and 0.088 mol/L, respectively.

1.3 Decomposition rate of TCE with various soils
1 g of soil sample was placed in a test tube. Other experimental method is as well as the above.

1.4 Decomposition rate of TCE with humic acid
0.1 g of humic acid was used instead of 1 g of soil samples. Other experimental method is as well as the above.

2. Results and Discussion
2.1 Decomposition rate of TCE
In Sections 2.1 and 2.3, data obtained in a previous study (Takuma et al., 2007) were used in addition to the newly obtained data for reanalysis.

Figure 4 shows the time variation of the residual TCE concentration. In the figure, it is seen that TCE decomposes immediately after the start of the experiments. This decrease in TCE concentration is well correlated with the concentration of Fe(II) ions (Takuma et al., 2007). It is found that the logarithm of the residual TCE concentration decreases linearly with the elapsed time. Hence, the reactions are thought to be of the first order to TCE concentration for this period. The pseudo first-order reaction rate constants \( k \) \([s^{-1}]\) were calculated from the slopes in Figure 4.

The values of \( k \) were plotted against the concentrations of Fe (II), as shown in Figure 5. From the slopes, the reaction order was calculated, and it was again found to be of the first order to Fe(II) concentration. Further, the reaction rate constants \( k^* \) \([L/(mol\cdot s)]\) were calculated.

The values of \( k^* \) were plotted against the concentration of hydrogen peroxide, as shown in Figure 6. From the slopes, the reaction order was calculated, and it was found to be of half order to hydrogen peroxide concentration. Further, reaction rate constants \( k^{**} \) \([L\cdot mol^{-1}\cdot s^{-1}]\) were calculated from the slopes and were found to be \( k^{**} = 1.048 (L\cdot mol^{-1})^{1.5}\cdot s^{-1} \).

2.2 Decomposition rate of TCE with black soil
Figure 7 shows the time variation of the residual TCE concentration. From Figure 7, it is seen that TCE decomposes after a certain reaction time. It was found that the logarithm of residual TCE concentrations decreased linearly with the elapsed time. Hence, the reactions were...
thought to be of the first order to TCE concentration for this period. The pseudo first-order reaction rate constants \( k \ [s^{-1}] \) were calculated from the slopes.

The values of \( k \) were plotted against concentrations of Fe (II) (Figure 8). From the slopes, the reaction order was calculated, and it was found to be first order to Fe (II) concentration. Further, the reaction rate constants \( k^* \ [L/(mol \cdot s)] \) were calculated.

The values of \( k^* \) were plotted against the concentrations of hydrogen peroxide solution, as shown in Figure 9. From the slopes, the reaction order was calculated, and it was found to be of half order to hydrogen peroxide concentration. Further, the reaction rate constants \( k^{**} \ [L \cdot mol^{-1} \cdot s^{-1}] \) were calculated from the slope and were found to be \( k^{**} = 0.5679 \) (L·mol\(^{-1}\)·s\(^{-1}\)).

### 2.3 Decomposition rate of TCE with humic acid

Figure 10 shows the time variation of the residual TCE concentration obtained in a previous study (Takuma et al., 2007). The decomposition rate was proportional to the concentrations of TCE and Fe (II) (Figures 10 and 11). The obtained second–order reaction rate constants \( k^* \) are plotted against the concentrations of hydrogen peroxide solution in Figure 12. In the present study, the experiments were repeated, especially for low concentrations of hydrogen peroxide, and only the reliable data are shown and analyzed by considering the same reaction order as the data corresponding to the presence and absence of black soil. The reaction rate constants \( k^{**} \ [L \cdot mol^{-1} \cdot s^{-1}] \) was calculated from the slope. The value was found to be \( k^{**} = 0.8485 \) (L·mol\(^{-1}\)·s\(^{-1}\)).

#### 2.4 Assumption of reaction rate equation

From these results, the reaction rate equations for TCE decomposition by the Fenton reaction were determined to be as follows.

**Without soil**

\[
dC_{\text{TCE}}/dt = -k_0^{**} C_{\text{TCE}} \times C_{\text{Fe(II)}} \times (C_{\text{H}_2\text{O}_2})^{0.5} \\
k_0^{**} = 1.048 \text{ (L·mol}^{-1}\text{·s}^{-1}) \tag{2}
\]

**With black soil**

\[
dC_{\text{TCE}}/dt = -k_{B}^{**} C_{\text{TCE}} \times C_{\text{Fe(II)}} \times (C_{\text{H}_2\text{O}_2})^{0.5} \\
k_{B}^{**} = 0.568 \text{ (L·mol}^{-1}\text{·s}^{-1}) \tag{3}
\]
Table 2  Reaction rate constants in the presence and absence of soils

<table>
<thead>
<tr>
<th>Soil</th>
<th>Without soil</th>
<th>Kanuma soil</th>
<th>Black soil</th>
<th>Akadama soil</th>
<th>Toyoura sand</th>
<th>Humic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction rate constant</td>
<td>1.048</td>
<td>0.725</td>
<td>0.568</td>
<td>0.354</td>
<td>1.050</td>
<td>0.849</td>
</tr>
<tr>
<td>[(L·mol⁻¹)¹.⁵·s⁻¹]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

![Fig. 12](image_url)  
Relation between $C_{H_2O_2}$ and $k^*$ in the presence of humic acid

![Fig. 13](image_url)  
Influence of soil on residual TCE concentration

With humic acid

$$ \frac{dC_{TCE}}{dt} = -k_{H^*}C_{TCE} \times C_{Fe(II)} \times (C_{H_2O_2})^{0.5} \quad (k_{H^*} = 0.849 \text{ (L·mol}^{-1} \text{)¹.⁵·s}^{-1}) \quad (4) $$

The reaction rate constant in the presence of black soil is smaller than that in the absence of soil, which indicates that black soil obstructs TCE decomposition. The reaction rate constant in the presence of humic acid was only slightly lower than that in the absence of soil.

2.5 Influence of soil and organic matter on TCE decomposition by Fenton reaction

Figure 13 shows the time variation of the TCE residual concentration and the influence of various soils on it. It was found that the logarithm of the residual TCE concentration decreased linearly with the elapsed time for all soils. The TCE decomposition rate in the presence and absence of Toyoura sand was found to be almost identical. Hence, it was concluded that Toyoura sand does not retard TCE decomposition. On the other hand, in the presence of Kanuma, akadama, and black soils, the decomposition rate was found to be significantly lower than that in their absence.

The time variation of pH through the experiments is shown in Figure 14. It was found that the steady pH values obtained decreases in the absence of soil are different from those obtained in the presence of soils. However, the reaction rate constants in the absence of soil and in the presence of Toyoura sand did not differ considerably.

The reaction rate constants of various soils were cal-
culated assuming reaction rate equations with the same reaction orders as those obtained in the presence and absence of black soil. The reaction rate constants for Kanuma soil, Toyoura sand, and akadama soil were determined as 0.725, 1.050, and 0.354 (L·mol\(^{-1}\)·s\(^{-1}\)) \(^{1.5}\)·s\(^{-1}\), respectively. Table 2 lists the reaction rate constants in the presence and absence of soils. It was found that the reaction rate constant in the presence of akadama soil was significantly smaller than that in the absence of soil; this is similar to the case of TCE decomposition in the presence and absence of black soil. However, the reaction rate constant in the presence of Toyoura sand was almost equal to that in the absence of soil.

2.6 Mechanism of the retardant effect of soil on the rate

The retardant effect of soil on TCE decomposition rate may be due to the adsorption of TCE on the soil particles or the competition reaction of organic materials in the soil with Fenton reagents.

In the present study, the effect of the adsorption was confirmed to be negligible because there was almost no decrease in TCE concentration when TCE was mixed with soil in the absence of Fenton reagents.

In Figure 15, all the obtained reaction rate constants are plotted against the specific surface area of the soil particles on the abscissa and the carbon content in the aqueous solution on the ordinate. The carbon content is an indicator of the amount of soil organic compounds, which retard TCE decomposition. From Figure 15, it is seen that the effect of soil on reaction rate constant is remarkable only when the specific surface area and carbon content are sufficiently large. This is can be explained as follows. The Fenton reaction occurring at the surface of the soil organic matter is proportional to the surface area of the soil and the fraction of surface area containing organic matter; this fraction is considered to be proportional to the carbon content of the soil. The remarkable retardation of TCE decomposition in the presence of black and akadama soils is due to the relatively large values of the surface area and carbon content in these cases. On the other hand, the minor effects of humic acid and Kanuma soil on TCE decomposition are due to the extremely small surface area and low carbon content, respectively.

Conclusion

TCE decomposition by Fenton’s reaction with Fe(II) in the presence and absence of black soil was found to be first-order to concentrations of TCE and Fe(II) and half-order to hydrogen peroxide concentration. The reaction rate constants in the presence and absence black soil were determined to be 1.048 and 0.568 (L·mol\(^{-1}\)·s\(^{-1}\)) \(^{1.5}\)·s\(^{-1}\), respectively. Assuming the reaction order to be 2.5, the reaction rate constants in the presence of humic acid, Kanuma soil, Toyoura sand, and akadama soil were determined to be 0.849, 0.725, 1.050, and 0.354 (L·mol\(^{-1}\)·s\(^{-1}\)) \(^{1.5}\)·s\(^{-1}\), respectively. It was found that the reaction rate constants corresponding to akadama and black soils were significantly smaller than the reaction rate constant in the absence of soil. It was suggested that the effect of soil on TCE decomposition is remarkable only when both specific surface area of soil particles and the carbon content of the soil are sufficiently large.

Literature Cited


