Ozonation of trichloroethylene in acetic acid solution with soluble and solid humic acid

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ABSTRACT

The combined flushing and oxidation process using acetic acid and ozone has been used successfully to remove trichloroethylene (TCE) completely from contaminated soil. In this study, the effects of humic acid, a fraction of the organic matter in soil, over the performance of TCE decomposition was evaluated. TCE decomposition by ozone was enhanced by the presence of humic acid at concentrations lower than $8\,mg\,C\,L^{-1}$ and then inhibited at higher concentrations. It is possible that the presence of the soluble humic acid fraction during the ozonation of TCE in acetic acid solutions produces hydroxyl radicals during the TCE ozonation which appears to be the reason for the enhanced TCE decomposition rate. Solid humic acid reduced TCE decomposition rate by acting as an ozone scavenger. Similarly, sorbed TCE reduced the amount of TCE available for decomposition by ozone in solution.

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1. Introduction

Trichloroethylene (TCE) has been used as a degreaser, a dry cleaning agent, an agent to remove caffeine from coffee, and an ingredient in the manufacture of some pesticides, resins, paints, and varnishes [1]. TCE is a priority toxic pollutant and has been found in at least 861 sites among 1428 of the most serious hazardous waste sites recognized by USEPA in the National Priorities List of the United States [2].

The injection of washing solutions into soil for its remediation using surface trenches, horizontal or vertical drains, is called *in situ* flushing. Different types of surfactants, solvents and cosolvents have been employed to dissolve and to remove contaminants from soil. Solvents can improve NAPLs (non-aqueous phase liquids) removal by enhancing their solubilization and mobilization [3,4]. *In situ* flushing with solvents reduces the time to remediate a site compared to the use of water alone. Additionally, the optimal mobilization significantly reduces the capillary forces trapping

the NAPLs, thereby allowing NAPLs to readily undergo partitioning into aqueous solution [5].

We proposed a new flushing technique utilizing an organic solvent with dissolved ozone where ozone decomposed the pollutant and further elution of the pollutant from soil was enhanced [6]. The remediation time and solvent volume applied were reduced compared to solvent itself. When acetic acid was used as a flushing solvent, the rate of TCE removal in the flushing process with ozone was from 1.5 to 2.5 times higher than the flushing process without ozone. Acetic acid was chosen for two reasons: high capacity for ozone dissolution ($225\,mg\,L^{-1}$ in 99% acetic acid, whereas $9.5\,mg\,L^{-1}$ in water at $20\,°C$), and high TCE oxidation rate compared to that in distilled water even at the same ozone concentration [7,8].

In the flushing process with ozone, soil organic matter would affect the efficiency of TCE decomposition. Part of soil organic matter can dissolve into the flushing solvent, where most of them remain as solid organic matter. Previous researchers [9–11] have shown that humic acids in soil had a complex behavior in ozone reaction because these compounds either enhance the decomposition of contaminants as an initiator and a promoter of hydroxyl radicals or inhibit that as an ozone scavenger [12–14]. The sorption of contaminants onto solid organic matter also reduced the reaction between contaminants and oxidants, decreasing the remediation speed [12,15]. Humic acids are known to bind hydrophobic compounds because their molecules are normally larger and contain more aromatic character than fulvic acids and humin [12]. In these studies humic acids were used as mixtures of

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both soluble and solid fractions and the effect of each fraction on the ozone reaction was not clear.

In the flushing process with ozone, applying acetic acid solution with ozone passing through a soil layer, ozone reaction would be affected by soluble and non-soluble (solid) soil organic matter in acetic acid solution. Therefore, we have to evaluate the effects of not only soluble but also solid organic matter on ozone reaction in acetic acid solution.

The objective of this study is to evaluate the effects of soluble and solid humic acids on TCE decomposition using ozone in acetic acid solution. In addition, the sorption of TCE into solid humic acid in the presence of acetic acid solutions was evaluated to determine the amount of TCE dissolved and available to react with ozone in solution. Although fulvic and humic acids are typical soil organic matter, fulvic acids would be dissolved due to their solubility in acetic acid solution with low pH and only humic acids would remain in soil [16]. We targeted humic acids as organic matters in this study because effects of dissolved fulvic acid on the ozone reaction have been well studied [17].

2. Experimental

2.1. Reagents

Trichloroethylene (Wako Pure Chemical Industries Ltd., 99.5%), acetic acid (Kanto Chemical, 99.5%), humic acid (Wako Pure Chemical Industries Ltd., 088-04622 [coal origin]), *t*-butanol (Wako Pure Chemical Industries Ltd., 99.0%) and other chemicals were used as obtained from the respective sources without further purification. The elemental analyses for the humic acid are summarized in Table 1. All solutions were prepared in ultra pure water.

Acetic acid concentrations used in the experiments were 0 (ultra pure water), 10 and 25%, and the humic acid concentrations ranged from 0 to $40 \, \text{mg C L}^{-1}$. Humic acid solutions were prepared by weighting solid humic acid in water or acetic acid solutions, and were mixed by shaking during 24 h at 80 rpm. The mixture was kept in refrigeration until it was used.

2.2. Humic acid dissolution

Fraction of soluble or solid humic acid was determined as a function of acetic acid concentration. In this case, ultra pure water, 10 and 25% acetic acid solutions without ozone were used as solvents. One hundred milliliters of ultra pure water or each of the acetic acid solution was placed in 150 mL vial. Humic acid was added to get a final concentration of $100 \, \text{mg C L}^{-1}$, sealed with a Teflon coated silicon septum, and mixed by shaking for 24 h at 80 rpm. The percentages of soluble and solid fractions were determined after filtration (0.7 μm glass microfiber filters) based on the Standard Methods 2540C and 2540 [18].

Solid and soluble fractions of humic acid were separated by filtering 500 mL of humic acid solution ($100 \, \text{mg C L}^{-1}$, in water or acetic acid solutions) with 0.7 μm glass microfiber filters (Whatman Trade Mark, GF/F) in order to determine their individual effects on TCE decomposition rate, ozone consumption and TCE sorption.

Table 1
Elemental analyses of humic acid sample (Wako)

Property	
C (%)	62.68
H (%)	2.85
N (%)	1.45
O (%)	19.54
Ash (%)	13.48

The filters were pre-washed to remove any impurity, placed in an oven overnight (103–105 °C), and kept into a desiccator until these were used. The soluble humic acid fraction was kept in the refrigerator. To eliminate any soluble products remaining, the solid fraction of humic acid was washed several times with the solution (ultra pure water or 10 or 25% acetic acid solution), filtered, dried and stored in a desiccator until it was used. All the experiments were performed at room temperature ($20 \pm 2 \, °\text{C}$).

2.3. TCE sorption onto humic acid

Sorption experiments were performed to determine the capacity of humic acid to sorbed TCE. Humic acid (10 mg) was weighted in a 150 mL vial, and 100 mL of ultra pure water or acetic acid solution (10 or 25%) without ozone was added into the vial. The vial was sealed with a Teflon coated silicon septum, and mixed by shaking for 24 h at 80 rpm. After this period, the vials were open and TCE was added to get a final concentration of $50 \, \text{mg L}^{-1}$. The vials were sealed again and shaken for 48 h at 80 rpm. After filtration with 0.7 μm glass microfiber filters, TCE concentration was determined.

2.4. Ozone consumption

Ozone consumption by humic acid and its soluble and solid fractions was determined in water, 10 and 25% acetic acid solutions using humic acid, as mixture and as soluble fraction, in concentrations from 0 to $8 \, \text{mg C L}^{-1}$. Ozone gas was generated from dried oxygen (99.99%) using an ozone generator (Fuji Electric, POX-1). Ozone gas was supplied into a washing bottle (300 mL) with an ozone dose of $1.37 \, \text{mg O}_3 \, \text{min}^{-1}$ through a porous glass gas sparger located above the bottom of the bottle. A magnetic stirrer was also used to provide sufficient mixing of the ozone and the solution, and to facilitate ozone gas transfer. Ozone gas was fed to have the initial concentration ($17 \pm 2 \, \text{mg O}_3 \, \text{L}^{-1}$) in ultra pure water or acetic acid solutions. Ozone concentration was determined every 10 min for 2 h using the iodometric method.

2.5. TCE decomposition

TCE decomposition rate ($K_{\text{TCE},\text{O}_3}$, min^{-1}) with ozone was evaluated with and without humic acid and each of its fractions (soluble and solid) in water and acetic acid solutions (10 and 25%) through batch experiments. After ozone was dissolved into the solution, TCE was added to have an initial concentration of $50 \, \text{mg L}^{-1}$ (0.38 mM). Humic acid was also added to have the initial concentration. Samples were taken to determine residual TCE concentration. Residual ozone concentration was determined before the addition of TCE and at the end of each experiment.

2.6. Radical production

To determine the production of hydroxyl radicals (•OH) by ozone in the presence of humic acid, *t*-butanol was added into the reactor to have a concentration of 10 mM. *t*-Butanol was chosen because is a well-known hydroxyl radical scavenger [19,20]. The concentration of *t*-butanol ([*t*-But]) to achieve >90% removal of hydroxyl radicals was determined using the next expression [19],

$$[t\text{-But}] = \frac{10 \times \sum k_{i,\text{OH}}[S_i]}{k_{t\text{-But},\text{OH}}} \tag{1}$$

where $k_{i,\text{OH}}$ and $k_{t\text{-But},\text{OH}}$ are second order rate constants for the reaction of hydroxyl radicals with a specific solute (S_i) and *t*-butanol, respectively. Rate constants were taken from the literature [21,22].
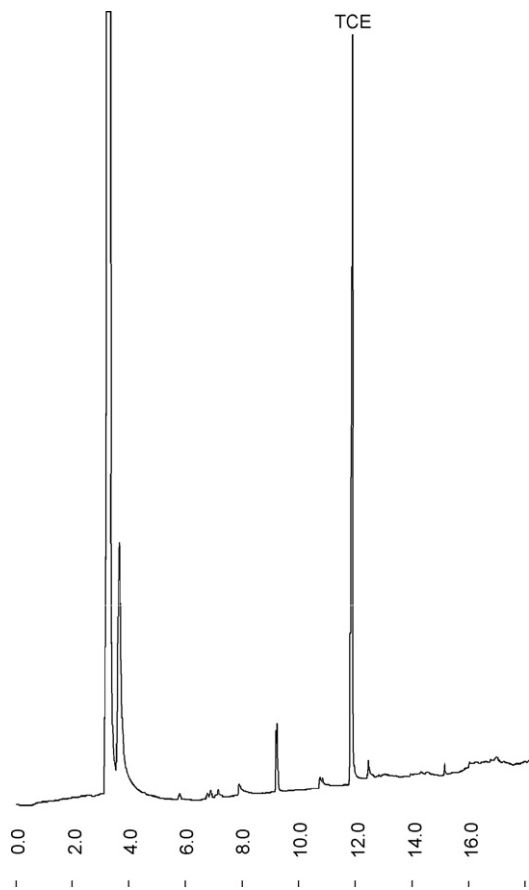
Fig. 1. GC-ECD spectrum variation of TCE with the reaction time.

Fig. 2. Distribution of soluble and solid fractions of humic acid in different acetic acid solutions. Total humic acid concentration = 100 mg C L^{-1}; 24 h agitation at 80 rpm.

25% acetic acid solution with ozone was used in these experiments, and initial TCE concentration was fixed at 50 mg L^{-1} (0.38 mM).

2.7. Analytical methods

TCE concentration was determined by headspace method using a gas chromatograph [23]. A 5 μL aliquot was taken from the reactor and added into a 20 mL vial containing 10 mL of ultra pure water and 5 μL of 0.1% Na$_2$SO$_3$ solution to quench residual ozone. The vial was sealed with a Teflon coated silicon septum, and the TCE was analyzed using a gas chromatograph with an electron capture detector (GC-ECD) (Shimadzu, GC-14B). The typical GC spectrum variation with the reaction time is shown in Fig. 1.

Humic acid concentration was determined as total organic carbon (TOC) with an automatic Carbon Analyzer (Shimadzu, TOC-5050A). Ozone concentrations in the solvent were determined using the standard iodometric method [18]. Acetic acid concentration was determined by titration with 1.0N NaOH using an automatic titrator (Kyoto Electronics, APB-410/AT-400). pH was measured using a glass electrode (Horiba, F-51).

3. Results and discussion

3.1. Distribution of soluble and solid humic acid fractions in acetic acid solutions

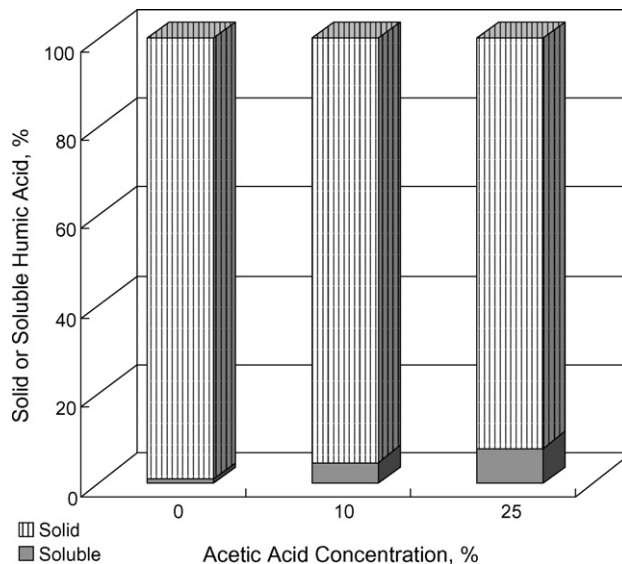Previous studies show that the increase in acetic acid concentration modifies the chemical properties of humic acids producing both soluble and solid fractions [24,25]. The distribution of soluble and solid humic acid fractions could affect the chemical reactions between humic acid and ozone, and then affect TCE decomposition rate due to the ozone in the solution. To determine the changes in the distribution of soluble and solid fractions, the percentage of each fraction was determined at different acetic acid concentrations.

Fig. 2 shows that the percentage of soluble humic acid fraction augmented with the increasing of acetic acid concentration. The soluble humic acid concentrations were 0.9, 4.5 and 7.7 mg C L^{-1} in ultra pure water, 10 and 25% acetic acid solutions, respectively, where pH values were 6.3, 2.5 and 1.9, correspondingly. Humic acid dissolution increased at higher acetic acid concentration because organic acid could denature proteins and produce dispersion by conformational changes in humic acids fragments [26]. Brigante et al. [27] pointed out that the attractive interactions (such as hydrogen bonding, cation bridging and hydrophobic interactions) which form associations with humic acids molecules could be disrupted by the presence of simple organic acids, such as acetic acid.

Although the dissolution of humic acid is strongly dependent on pH, that is, increased dissolution with increase in pH, the results in Fig. 2 showed that the aggregation effect of pH was strongly reduced by the presence of acetic acid.

3.2. TCE decomposition in the presence of humic acid

TCE decomposition by ozone in acetic acid followed a first order reaction kinetics with respect to TCE concentration [8,28]. TCE decomposition rate (K_{TCE,O_3}, min^{-1}) was determined by regression analysis using the normalized TCE remaining concentration ($-\ln[TCE]_t/[TCE]_0$) vs. reaction time (t); all the correlation coefficients (R^2) were larger than 0.9.

$$[TCE]_t = [TCE]_0 \exp^{-K_{TCE,O_3} t} \tag{2}$$

TCE decomposition rates (K_{TCE,O_3}, min^{-1}) calculated as first order reactions were evaluated as a function of humic acid concentrations as shown in Fig. 3. K_{TCE,O_3} augmented with the increasing of acetic acid concentration from 0 to 25% in the case of no humic acid. The addition of solvents, such as acetic acid, propionic acid, acetonitrile, among others, into water was reported to enhance degradation efficiency due to the increase in the solubility of the
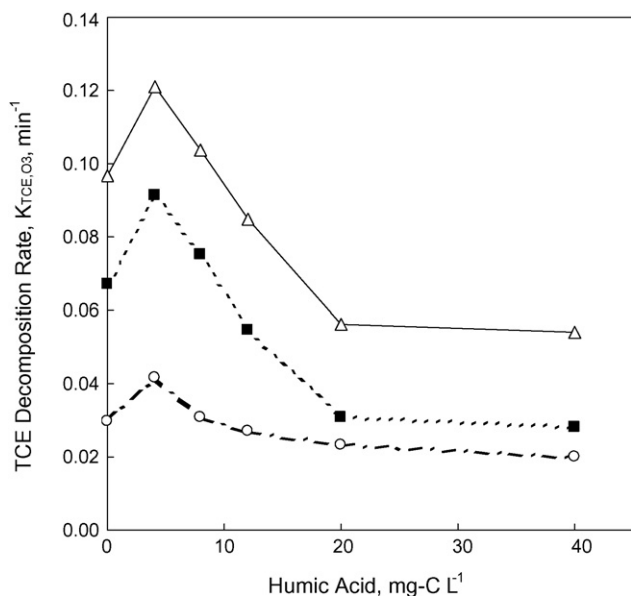
Fig. 3. Effects of acetic acid and humic acid concentrations on TCE decomposition rate constants (K_{TCE,O_3}). $[TCE]_0 = 50\,mg\,L^{-1}$; $[O_3]_0 = 17.5 \pm 0.5\,mg\,L^{-1}$. Acetic acid concentration, ($\triangle$) 25%; ($\blacksquare$) 10%; ($\bigcirc$) 0% (ultra pure water).

pollutant resulting in enhancement of mass transfer between the pollutant and the oxidant applied [28,29].

TCE decomposition was enhanced by small addition of humic acid (less than $8\,mg\,C\,L^{-1}$) for all solutions and then decreased with the increase in humic acid concentration. The higher humic acid concentration would work as an ozone scavenger [30,31].

3.3. TCE sorption into humic acid

It is known that TCE partition into solid humic acid reduces its reactivity with ozone, and as a consequence reduces TCE decomposition rate [15,32,33]. Therefore, TCE sorption into solid humic acid was determined at different acetic acid concentrations as shown in Fig. 4.
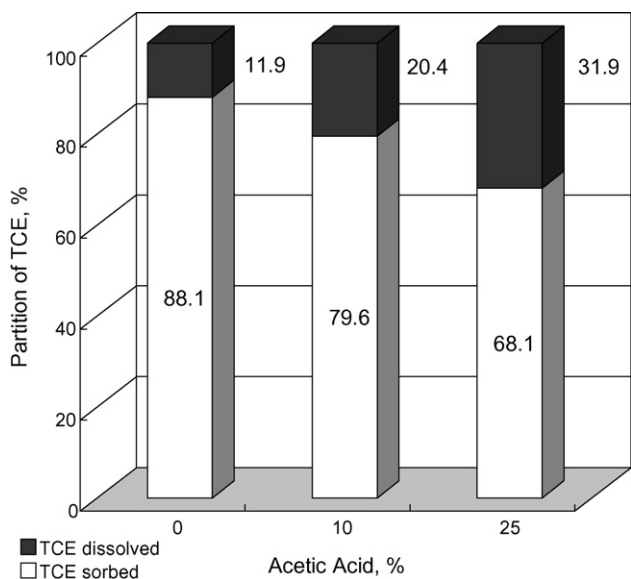

Fig. 4. TCE sorption onto solid humic acid in 0, 10 and 25% acetic acid solutions without ozone. $[TCE]_0 = 50\,mg\,L^{-1}$; $[Humic\,acid]_0 = 100\,mg\,C\,L^{-1}$.
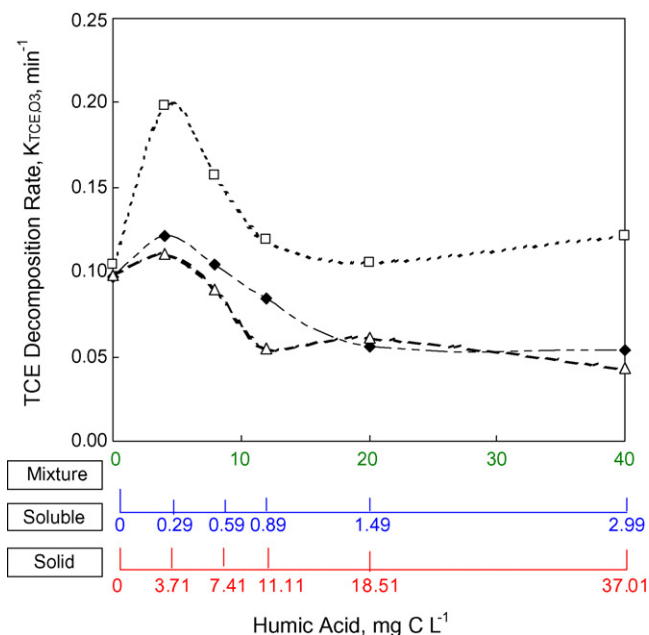

Fig. 5. TCE decomposition rate (K_{TCE,O_3}) in 25% acetic acid solution in the presence of humic acid (mixture, solid and soluble fractions). $[TCE]_0 = 50\,mg\,L^{-1}$; $[O_3]_0 = 17.5 \pm 2.0\,mg\,L^{-1}$. Humic acid as ($\square$) soluble fraction; ($\blacklozenge$) mixture; ($\triangle$) solid fraction.

The percentage of TCE sorbed into humic acid decreased with increasing acetic acid concentration. Sorption of TCE in 10 and 25% acetic acid solutions were 9.6 and 22.7% lower than that in ultra pure water, respectively. The solubility of TCE in acetic acid is much higher than that for ultra pure water; as a consequence, increase in acetic acid concentration reduced the amount of TCE sorption into solid humic acid. Additionally, previous studies showed an increase in the number of hydrophobic microsites on humic acid with decrease in pH [16,34]. Higher concentration of acetic acid in the solution produced lower pH. Consequently, the amount of TCE sorption into solid humic acid was lowest in 25% acetic acid solution. Therefore, availability of TCE for ozone would increase by the increase in acetic acid concentration. As a result, TCE decomposition was enhanced with the increasing in acetic acid concentration as shown in Fig. 3.

3.4. Contribution of solid and soluble fractions to the enhancement of TCE decomposition

The individual effects of solid and soluble fractions on TCE decomposition by ozone were evaluated in 25% acetic acid solution. Fig. 5 shows the effects of the total humic acid (mixture), the solid and the soluble fractions on K_{TCE,O_3}. To evaluate contributions of the solid and the soluble fractions in enhancing TCE decomposition by adding humic acid, its concentration as a mixture and the corresponding soluble and solid concentrations are shown in different x-axes. The values of soluble and solid humic acid concentrations on each axis were adapted with the values used in the mixture.

The soluble fraction was only 7.7% of the total humic acid in 25% acetic acid solution as shown Fig. 2. Although the soluble fraction was only $0.29\,mg\,C\,L^{-1}$ in $4\,mg\,C\,L^{-1}$ of humic acid, the addition of this amount enhanced TCE decomposition rate 2.0 times, while the enhancement was only 1.1 times by adding of $3.71\,mg\,C\,L^{-1}$ of the solid fraction. The addition of soluble humic acid until $2.99\,mg\,C\,L^{-1}$ enhanced TCE decomposition. However, the addition of more than $7.41\,mg\,C\,L^{-1}$ of solid humic acid worked as an ozone scavenger and inhibited TCE decomposition. These results suggested that the
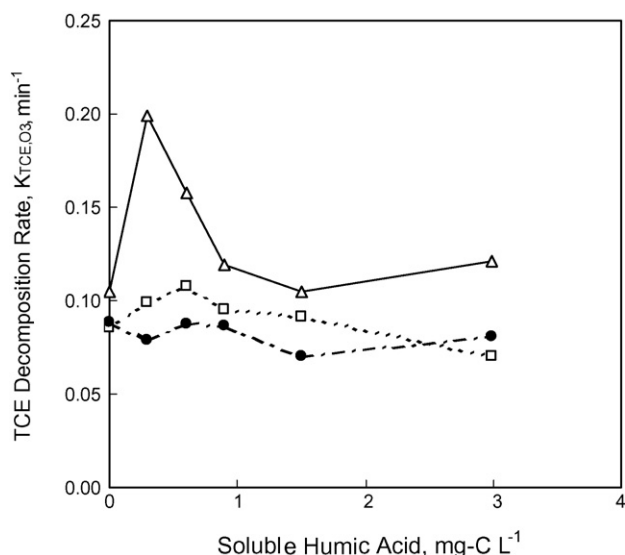
Fig. 6. TCE decomposition rate (K_{TCE,O_3}) in ($\triangle$) 25% acetic acid solution without *t*-butanol; ($\square$) 25% acetic acid solution with *t*-butanol; ($\bullet$) HCl solution, in the presence of soluble humic acid. $[TCE]_0 = 50\,mg\,L^{-1}$, $[O_3]_0 = 18.1 \pm 0.8\,mg\,O_3\,L^{-1}$, $[t\text{-butanol}]_0 = 10\,mM$, and pH 1.9.

enhancement of TCE decomposition by a smaller amount of humic acid (mixture) addition was mainly caused by the soluble fraction and the inhibition of TCE decomposition was mainly caused by the solid fraction.

3.5. Radical production

Previous studies carried out in water [10,13] suggested that humic substances act principally as initiators and promoters of radical species formation (e.g. hydroxyl radicals), if their concentrations are low. In our experiments, radical species may be produced by the addition of the soluble humic acid fraction as well. To confirm the production of hydroxyl radicals, TCE ozonation in 25% acetic acid solution with the soluble humic acid fraction was carried out in the presence of *t*-butanol, a well-known radical scavenger [20]. It is known that *t*-butanol is a strong hydroxyl radical scavenger which has the reaction rate constant of $6 \pm 2 \times 10^8\,M^{-1}\,s^{-1}$ with hydroxyl radicals [21,22] and $3 \times 10^{-3}\,M^{-1}\,s^{-1}$ with ozone [35]. Fig. 6 shows that the addition of the soluble fraction did not enhance TCE decomposition in the presence of *t*-butanol, indicating that enhancement of TCE decomposition by the addition of the soluble fraction was caused by radical production.

To evaluate the effects of low pH (1.9) produced by 25% acetic acid into radical production, HCl was used instead of 25% acetic acid solution to lower pH of the solution to 1.9. TCE decomposition rates were not enhanced at any humic acid concentration in the HCl solution, indicating that radicals were not produced by lower pH even if humic acid was present in water. Therefore, radicals were produced by ozonation only in the presence of both humic acid and acetic acid.

4. Conclusions

The objective of this study was to evaluate the effects of soluble and solid organic matter, specifically humic acid, on TCE decomposition by ozone in acetic acid solution. The specific conclusions derived from this study are as follows:

1. TCE decomposition by ozone in 0–25% acetic acid solutions was enhanced by the presence of humic acid in less than $8\,mg\,C\,L^{-1}$ and then was inhibited.
2. The enhancement of TCE decomposition by the addition of humic acid was mainly caused by the soluble fraction in humic acid and the inhibition when more than $8\,mg\,C\,L^{-1}$ was caused by the solid fraction which worked as an ozone scavenger.
3. The enhancement of TCE decomposition by adding the soluble fraction was explained by the production of hydroxyl radicals, which were produced by ozonation in the presence of both humic and acetic acid.
4. The increase in acetic acid concentration reduced TCE sorption into solid humic acid, and as a consequence it increased the availability of TCE for decomposition by ozone in solution.

Acknowledgement

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