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TCE reduction modeling in soil column: Effect of zero-valent iron, ferrous iron, and iron-reducing bacteria

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ABSTRACT

A model was developed to simulate the reduction of trichloroethylene (TCE) by permeable reactive barriers (PRBs). The model based on an axial transport model with chemical reaction terms was operated for a TCE solution, incorporating dispersion, convection, and reaction along the column flow-path and time. Reaction terms included TCE reduction by zero-valent iron (ZVI) or ferrous iron produced from ferric iron by iron-reducing bacteria (IRB). ZVI was oxidized by TCE to ferric iron which has no ability to reduce TCE. IRB reduced ferric iron to ferrous iron by transferring electrons from organic carbon sources such as lactate or glucose. Ferrous iron, thus produced, constantly reduced TCE although it had a relatively low reducing power compared to ZVI. The TCE concentration at the mid-port of the ZVI column was lower than one-tenth of the influent concentration until 200 h, but reached a 99% breakthrough at 1,390 h. The TCE reduction efficiency by the ZVI column was not recovered after the breakthrough. On the other hand, the life of ferrous iron column was prolonged in the presence of IRB. The TCE reduction efficiency was maintained at over 60% with 10,000 mg-IRB/L–pore volume of IRB. These results indicate that the application of IRB would be economical for a long-term operation of iron-based PRBs.

Keywords: Trichloroethylene; Modeling; Zero-valent iron; Ferrous iron; Iron-reducing bacteria

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1. Introduction

Trichloroethylene (TCE) is one of the most well-known halogenated hydrocarbon compounds, which is mainly used in the semi-conductor wiping or dry cleaning process. It is frequently detected in groundwater at industrialized areas. Zero-valent iron (ZVI) permeable reactive barriers (PRBs) have gained attention for the removal of various organic and inorganic contaminants including TCE, and it is estimated one of the most promising remediation techniques [1]. There were several studies related with the concept of TCE treatment applying ZVI [2]. ZVI oxidizes TCE to ethylene, a harmless organic matter. However, by reacting with TCE, ZVI itself is oxidized to ferric iron, which has no more reducing power to treat TCE. To extend its life, iron-reducing bacteria (IRB) can be applied to ferric iron. IRB uses ferric iron as electron acceptor by transferring electrons from electron donors, such as lactate, glucose, and other carbon sources, to ferrous iron. Although it has lower reducing power than ZVI, ferrous iron formed by IRB reduces TCE [2]. A ferrous iron column has constant TCE reduction ability when IRB exists in the column, because IRB constantly reduce ferric iron that is formed by TCE. In the present study, a numerical model for transport and reaction of

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TCE in the presence of the PRB medium was developed. One-dimensional finite differential method (FDM) equations were developed to model PRBs. The purpose of this modeling was to estimate the TCE reduction effect of ZVI or ferrous iron with IRB. The model incorporated the following variables: TCE, ZVI, ferrous iron, and IRB. The model could figure out the properties of each ZVI-packed column and ferrous iron-packed column supported by IRB. The proposed model provides a useful framework for predicting the TCE profiles in PRBs and shows the benefit of IRB.

2. Materials and methods

2.1. Model equations

A TCE transport equation incorporates dispersion, convection, and reaction of TCE by iron medium. Eq. (1) shows the TCE transport in a ZVI–packed column:

$$\frac{\partial C_T}{\partial t} = D\frac{\partial^2 C_T}{\partial x^2} - u\frac{\partial C_T}{\partial x} - k_{\mathrm{Fe(0)}} M_{\mathrm{Fe(0)}} C_T \qquad (1)$$

where C_T is the concentration of TCE in the column system (mg/L), D the hydrodynamic dispersion coefficient in the column system (cm^2/h), u the convection (cm/h), $k_{\mathrm{Fe(0)}}$ the second-order reaction constant by TCE concentration and ZVI medium weight per unit volume (L/mg/h), and $M_{\mathrm{Fe(0)}}$ the ZVI medium weight per unit volume in the column (mg/L).

The reaction between TCE and iron medium affected the iron medium weight per unit volume as well as the TCE concentration. Iron medium consumption by the reaction between TCE and iron medium is stoichiometrically proportional to the consumption of TCE reduction [3]. Therefore, an iron medium reaction equation can be described by multiplying the yield coefficient to the reaction term of Eq. (1). The ZVI profile by the reaction between ZVI and TCE is computed from

$$\frac{\mathrm{d}M_{\mathrm{Fe(0)}}}{\mathrm{d}t} = -Y_{\mathrm{Fe(0)}} k_{\mathrm{Fe(0)}} M_{\mathrm{Fe(0)}} C_T \qquad (2)$$

where $Y_{\mathrm{Fe(0)}}$ is the ZVI consumption coefficient per TCE reduction (iron medium weight per unit volume consumption per TCE concentration consumption).

ZVI is oxidized to ferric iron by the reaction with TCE. Ferric iron can be reduced to ferrous iron by the activity of IRB, and ferrous iron can reduce TCE. The ferrous iron production by IRB is shown in Eq. (3):

$$\frac{\mathrm{d}M_{\mathrm{Fe(II)}}}{\mathrm{d}t} = \frac{(\mu_{\mathrm{Fe}}/Y_{\mathrm{Fe}}) X_s M_{\mathrm{Fe(III)}}}{K_{\mathrm{Fe}} + M_{\mathrm{Fe(III)}}} \qquad (3)$$

where $M_{\mathrm{Fe(II)}}$ is the ferrous iron medium weight per unit volume in the column (mg/L), μ_{Fe} the maximum specific rate of ferrous iron reduction (h^{-1}), Y_{Fe} the ferrous iron yield coefficient per IRB growth (ferrous iron weight per unit volume production per biomass growth), X_s the concentration of biomass (mg/L), and $M_{\mathrm{Fe(III)}}$ the ferric iron weight per unit volume in the column (mg/L).

The TCE transport equation by the ferrous iron medium is written as follows:

$$\frac{\partial C_T}{\partial t} = D\frac{\partial^2 C_T}{\partial x^2} - u\frac{\partial C_T}{\partial x} - k_{\mathrm{Fe(II)}} M_{\mathrm{Fe(II)}} C_T \qquad (4)$$

where $k_{\mathrm{Fe(II)}}$ is the second-order reaction rate constant for ferrous iron.

The equations were solved using MATLAB to generate the transport and reaction of TCE, oxidation and reduction of iron medium, and IRB activity to iron medium.

2.2. Column set-up and parameter determination

The entire modeling was performed to represent a column system, shown in Fig. 1, and values of model parameters for the simulation are summarized in Table 1. The column was 50 cm long and 3 cm in diameter. In the model, samplings were performed at the inlet port, mid-port, and outlet port. The model was developed so that the column was packed with the mixture of 0.88–1.27 mm sized sand and ZVI medium. The weight ratio between

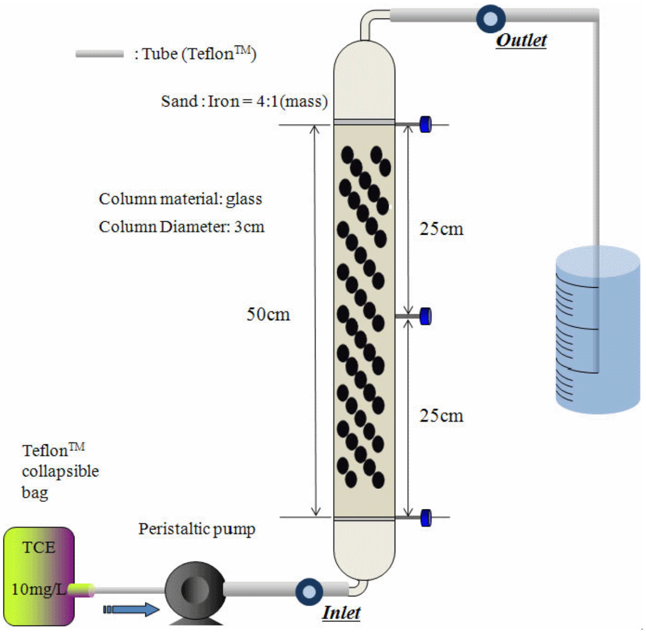

Fig. 1. Schematic diagram of column experiment applied in this modeling.

Table 1
Values of the model simulation parameters

Parameters	Description	Units	Values
D	Dispersion coefficient	$cm^2 h^{-1}$	1.15×10^{-3}
u	Velocity	$cm\ h^{-1}$	0.5
$k_{Fe(0)}$	Second reaction rate constant for Fe(0)	$L\ mg^{-1} h^{-1}$	7.539×10^{-5}
$k_{Fe(II)}$	Second reaction rate constant for Fe(II)	$L\ mg^{-1} h^{-1}$	1.885×10^{-5}
μ_{Fe}	Maximum specific rate of Fe(II) reduction	h^{-1}	0.32
K_{Fe}	Half iron reduction concentration rate	$mg\ L^{-1}$	1,619.65
Y_{Fe}	Fe(II) yield coefficient per IRB growth	—	9.382
$Y_{Fe(0)}$	Fe(0) consumption coefficient per TCE reduction	—	0.283
$Y_{Fe(II)}$	Fe(II) consumption coefficient per TCE reduction	—	0.849

the iron medium and sand was 1:4. The iron medium weight per unit volume in the column was obtained as 1,384.6 mg/L by considering the porosity, iron density, ratio of iron medium, and sand. The porosity of the packed media was estimated as 0.325 by volumetric analysis. The model assumed that a 10 mg/L concentration of TCE was injected into the column constantly and convection, u, of 0.5 cm/h was maintained in the column. Dispersion coefficient, D, was determined as 1.15×10^{-3} cm^2/h by considering the media packed in column and liquid velocity in the column [4]. Each ZVI and ferrous iron reaction rate constant, $k_{Fe(0)}$ and $k_{Fe(II)}$, was determined by pervious research as 7.539×10^{-5} L/mg/h and 1.885×10^{-5} L/mg/h, respectively [5]. Each ZVI and ferrous iron consumption coefficient per TCE reduction, $Y_{Fe(0)}$ and $Y_{Fe(II)}$, was determined by considering iron and TCE molecular weight, and the each value was 0.283 and 0.849, respectively.

The TCE reduction model by ferrous iron was developed so that the column was initially filled with ferric iron which was produced from the ZVI reacted with the TCE. This model initially settled the biomass concentrations and varied from 0 mg/L to 10,000 mg/L through the column systems. Generally, bacteria undergo several growth phases, such as the lag, log, stationary and death phase. Nevertheless, in this research, it was assumed that biomass is preserved constant to analyze the effect of a certain concentration of IRB. The ferrous iron yield coefficient per IRB growth, Y_{Fe}, was calculated quantitatively by considering chemical stoichiometry of reaction between ferrous iron and TCE, which was obtained as 9.382. The maximum specific rate, μ_{Fe}, and half iron reduction concentration rate, K_{Fe}, were found as 0.32 h^{-1} and 1,619.65 mg L^{-1}, respectively, by previous studies [5].

3. Results and discussion

3.1. TCE reduction in ZVI-packed column

The TCE reduction by the ZVI-packed column was modeled by Eq. (1). Fig. 2 shows the TCE reduction rate decreased continuously after the reaction had started. The TCE concentration was decreased more than 99% until 235 h. The TCE reduction rate dropped to less than 85% after 706 h, and the TCE reduction rate became less than 1% after 1,390 h. The continuous decrease of TCE reduction can be explained by Eq. (2). It indicates that the ZVI in the column was also decreased associated with the TCE reduction, coupled with the oxidation of ZVI.

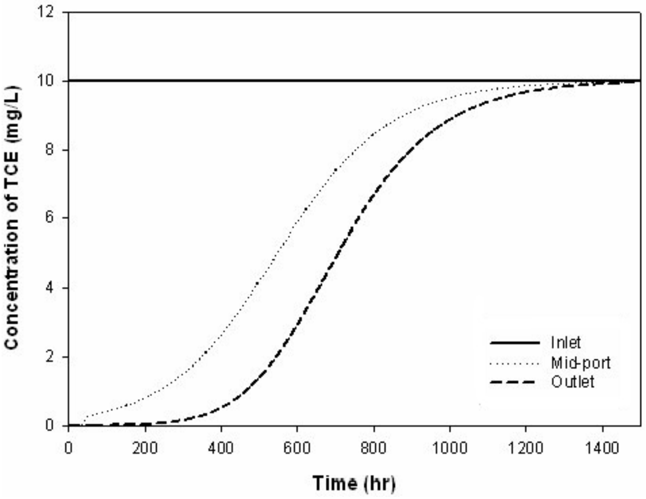

Fig. 2. Temporal change of the TCE concentrations in the ZVI-packed column.

Fig. 3 describes the TCE concentration profile through the column length. It shows that the profile proceeds toward the outlet with the reaction time. Approximately 99% of TCE was reduced within 9 cm distance from the column inlet at 10 h. TCE was completely reduced at 15 cm. More than 99% TCE was treated at 23 cm and 34 cm point distances from the inlet at the 500 h and 1,500 h conditions, respectively.

3.2. TCE reduction in ferrous iron and IRB mixed column

TCE reduction is approximately 1.3 mg/L, 5.4 mg/L, and 6.1 mg/L in the 100 mg/L, 1,000 mg/L, and

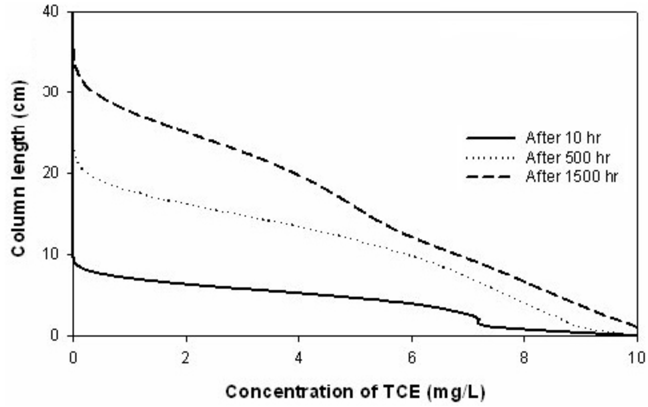

Fig. 3. Profiles of the TCE concentration in the ZVI-packed column.

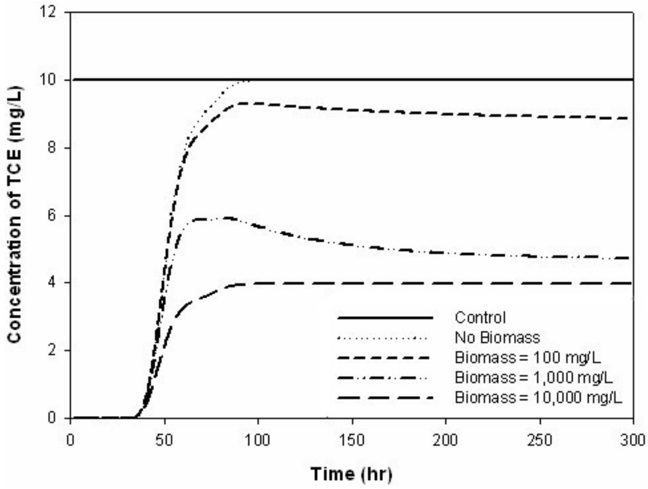

Fig. 4. Temporal changes of the TCE concentrations at the mid-port in the ferric iron packed column with IRB.

10,000 mg/L of biomass condition, respectively (Fig. 4). TCE reduction rate in each biomass condition reaches an equilibrium state. This can be explained that ferrous iron production by IRB and ferrous iron oxidation by TCE reaction became equilibrated. By numerical formula, this can be explained that IRB activity in Eq. (3) offsets TCE and the ferrous reaction term of Eq. (4).

No reaction occurs in the abiotic condition. However, the breakthrough of TCE appears after approximately 35 h. This can be explained by Fig. 5, the tracer test model of the column system. The breakthrough curves in both mid-port and outlet appeared approximately 35 h and 75 h time elapsed, respectively. This is because it requires time for TCE to reach at mid-port and outlet port sections by convection and dispersion. Thus, it can be explained that retardation of breakthrough appearance was due to TCE dispersion and convection. The tracer model can be useful tools for analyzing reaction excluding the effect of dispersion and convection in the TCE transport model.

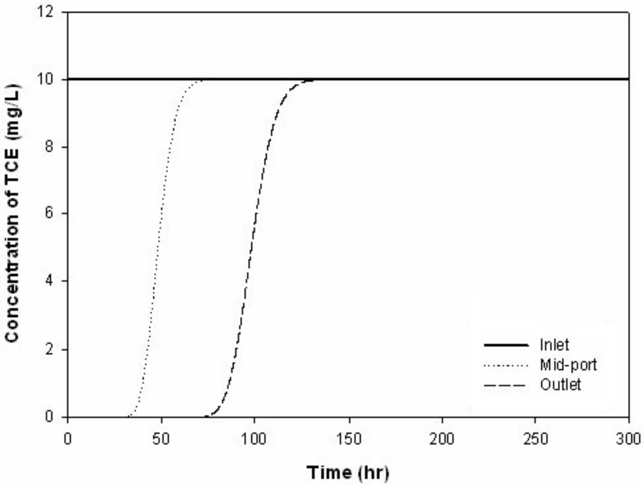

Fig. 5. Concentration of TCE in the column filled without ZVI media.

4. Conclusions

Reactive transport models for describing the TCE transport and reduction in the both ZVI and ferric iron with IRB columns were developed and simulated. The model results indicated that the TCE reduction efficiency in the ZVI column was highest at the initial phase, but non-reversibly decreased to zero with reaction time. On the other hand, TCE reduction rate in the ferric iron and IRB mixed column was lower than that in the ZVI column, but it could be sustained at certain level by the ferric iron reduction by IRB in the column. This indicated that the ferrous iron medium contributed by IRB was less effective than virgin ZVI, but could contribute to long-term groundwater treatment because it regenerated the reducing power continuously.

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