



## Coupling of zero valent iron and biobarriers for remediation of trichloroethylene in groundwater

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### Abstract

This study attempted to construct a three series barrier system to treat high concentrations of trichloroethylene (TCE; 500 mg/L) in synthetic groundwater. The system consisted of three reactive barriers using iron fillings as an iron-based barrier in the first column, sugarcane bagasse mixed with anaerobic sludge as an anaerobic barrier in the second column, and a biofilm coated on oxygen carbon inducer releasing material as an aerobic barrier in the third column. In order to evaluate the extent of removal of TCE and its metabolites in the aquifer down gradient of the barrier system, a fourth column filled with sand was applied. Residence time of the system was investigated by a bromide tracer test. The results showed that residence time in the column system of the control set and experimental set were 23.62 and 29.99 days, respectively. The efficiency of the three series barrier system in removing TCE was approximately 84% in which the removal efficiency of TCE by the iron filling barrier, anaerobic barrier and aerobic barrier were 42%, 16% and 25%, respectively. *cis*-Dichloroethylene (*cis*-DCE), vinyl chloride (VC), ethylene and chloride ions were observed as metabolites following TCE degradation. The presence of chloride ions in the effluent from the column system indicated the degradation of TCE. However, *cis*-DCE and VC were not fully degraded by the proposed barrier system which suggested that another remediation technology after the barrier treatment such as air sparging and adsorption by activated carbon should be conducted.

**Key words:** iron filling; biobarrier; remediation; permeable reactive barriers; trichloroethylene

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### Introduction

Trichloroethylene (TCE) is a chlorinated solvent widely used as an industrial solvent and degreaser (Schnabel et al., 1996). It is considered a hazardous substance because of its toxicity and environmental persistence. When TCE is released into the environment, it will either evaporate or penetrate the soil into the groundwater and move downward by gravity through an aquifer until it reaches an impermeable layer. Therefore, it can become a long-term source of dissolved contaminant plumes at contaminated sites. Several methods are used to prevent TCE from contaminating groundwater including pump and treat, chemical oxidation, air stripping and thermal treatment. A system of permeable reactive barriers (PRBs) is one of the methods that have received attention as an alternative

technology to control TCE (Kao et al., 2001; Lee et al., 2007; Shin et al., 2007; Wang and Tseng, 2009).

The PRBs system is an *in situ* treatment technology for groundwater contamination. PRBs are designed to intercept a plume of contaminated groundwater moving under the natural gradient. PRBs have been found to be a cost-effective containment technology for groundwater remediation (Gavaskar et al., 1998; Kao and Lei, 2000; McNab and Ruiz, 2000). There are three types of PRBs: sorptive media, reactive media, and enhanced biodegradation media. Activated carbon and zeolite are the most frequently used sorptive media in PRBs. Among a variety of reactive materials, zero valent iron (ZVI) has shown the greatest efficiency for reducing chlorinated compounds in groundwater (US EPA, 1997, 2002). The previous findings by Teerakun et al. (2008) indicated that the concentration of TCE as high as 1000 mg/L did not reduce the efficiency of ZVI to remove TCE. Bioactive barriers

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filled with free or immobilized microorganisms capable of degrading target contaminants are used for enhancing biodegradation media. Since a high concentration of TCE (greater than 100 mg/L) could have adverse effects on the microorganisms in the biodegradation media, resulting in a reduction in the removal efficiency of the bioactive barrier (Teerakun et al., 2007), the combination of ZVI and a bioactive barrier to treat groundwater contaminated with high concentrations of TCE might increase the efficiency of PRBs. In this study, we proposed a PRBs series consisting of an iron filling base barrier followed by an anaerobic bioreactive barrier and an aerobic bioreactive barrier. The iron filling barrier was used as the source of ZVI to treat a high concentration of TCE. Residues of TCE and its metabolites after treatment with the iron filling barrier were further treated by the anaerobic then the aerobic bioreactive barrier. It was hoped that the proposed PRBs could to the great extent remove high concentrations of TCE as well as its metabolites.

## 1 Materials and methods

### 1.1 Chemicals

Trichloroethylene, TCE, 98%, was purchased from Riedel-deHaën, Germany. *cis*-1,2-Dichloroethylene, (*cis*-DCE, 97%) was purchased from Sigma Aldrich Chemical, USA. Vinyl chloride, VC, 2000 mg/L in methanol, was purchased from Chem Service, USA. Ethylene, 99.5%, was purchased from Supelco, USA. All other chemicals and reagents were analytical grade and purchased from BDH, England.

### 1.2 Synthetic groundwater

Synthetic groundwater consisted of (mg/L):  $\text{KH}_2\text{PO}_4$ , 326.4;  $\text{Na}_2\text{HPO}_4$ , 1263.8;  $\text{Mg}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ , 98.6;  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , 44.1;  $\text{NH}_4\text{Cl}$ , 10.7 and trace elements including  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , 1;  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ , 1;  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ , 0.25;  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , 0.25;  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , 0.25;  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , 0.25;  $\text{ZnCl}_2$ , 0.25; and  $\text{NH}_4\text{VO}_3$ , 0.1. The pH of the synthetic groundwater solution was adjust to 7.5 according to Kao et al. (2001).

### 1.3 Iron

Iron fillings, wastes from a machine shop located at Khon Kaen, Thailand, were collected and sieved to obtain particles ranging in size from 425 to 850  $\mu\text{m}$ . These iron fillings were pre-treated by soaking in 10% NaOH solution and periodically sonicated for 20 min to remove lipids from the surface, then washed with 3% HCl solution for 30 min to remove iron oxide from the surface. Finally, the fillings were rinsed with DI water for 30 min to remove residual HCl and  $\text{Fe}^{2+}$ . Following these procedures, the iron particles were then used to remove TCE and its intermediates in synthetic groundwater. Based on analysis by SEM-EDS, the surfaces of the pre-treated iron fillings were found to consist of 51% Fe (ZVI), 48% O, and 1% Si. The XRD pattern showed that the iron fillings were a mixture of iron, magnetite, maghemite and quartz (data not

shown).

### 1.4 Potential inducer

Orange peel, the waste from a shop selling orange juice, was used as a potential inducer of monooxygenase to co-metabolize TCE using an aerobic microorganism. The orange peel was dried at room temperature, chopped into small pieces, passed through a 2 mm sieve, and kept at  $-20^\circ\text{C}$  until use. One gram dry weight of orange peel contained approximately 13 mg of limonene determined by the method of Chotratanadilok et al. (2002).

### 1.5 Organic amendment

Sugarcane bagasse, the fibrous residue of sugarcane stalk remaining after the juice has been extracted, was collected from a sugar factory (Mitara Phoo Weang Co., Ltd., Thailand). Before use, the sugarcane bagasse was dried at  $60^\circ\text{C}$ , milled and sieved through a 2 mm sieve. The dry milled sugarcane bagasse consisted of 0.19% total N and 49.93% organic carbon.

### 1.6 Inoculum

Anaerobic sludge and aerobic activated sludge were collected from An-ping Municipal Wastewater Treatment Plant and An-ping Wastewater Treatment Plant, Taiwan, respectively. An-ping Wastewater Treatment Plant receives wastewater from the manufacturing processes of industries that use volatile organic compounds as solvents. The anaerobic and aerobic sludges were separately acclimatized with TCE at a concentration of 100 mg/L, and incubated at room temperature ( $27 \pm 3^\circ\text{C}$ ) for 21 days to enhance the TCE degradation ability of the microorganisms in the sludges. After acclimatization, the microorganisms in the anaerobic and aerobic sludges were harvested by centrifugation at 6000 r/min for 10 min and the pellets were re-suspended in synthetic groundwater before separately inoculated in their respective columns. Characteristics of raw sludge are shown in Table 1.

**Table 1** Characteristics of raw sludge

Properties	Aerobic sludge	Anaerobic sludge
pH	7.30	6.80
Total suspended solids (TSS) (g/L)	41.00	17.63
Volatile suspended solids (VSS) (g/L)	34.20	6.95

### 1.7 Biofilm

Aerobic activated sludge was coated on a 1.0-cm<sup>3</sup> cube of organic-carbon-inducer-releasing material (OCIRM) to develop the biofilm using the protocol of Tremoulet et al. (2002).

### 1.8 Organic-carbon-inducer-releasing material

A 1.0-cm<sup>3</sup> OCIRM cube was constructed to continuously supply dissolved oxygen (DO), carbon and inducer for biodegradation of TCE and its metabolites. OCIRM was comprised of binding cement, calcium peroxide ( $\text{CaO}_2$ ),

sand, sugarcane bagasse, fly ash and water at the ratio of 1.5:1.5:0.2:0.2:1.3:2 by weight. Sugarcane bagasse was used as the carbon source. Calcium peroxide was used to supply oxygen. Sand was used as a bulking material. Orange peel was added to the OCIRM to obtain a concentration ratio of the contaminant to limonene of 1:2.5.

### 1.9 Sorption of TCE, *cis*-DCE and VC on sand, sugarcane bagasse and OCIRM

The capacity of sand, sugarcane bagasse and OCIRM to adsorb TCE and its metabolites, i.e., *cis*-DCE and VC were determined by conducting a batch equilibrium experiment at TCE, *cis*-DCE or VC concentrations of 1.0, 5.0, 10.0, 15.0 and 20.0 mg/mL. All contaminant solutions were prepared in synthetic groundwater. Three grams sand or 1 g sugarcane bagasse or a 3 g cube of OCIRM was placed into a 50 mL serum bottle and mixed with 20 mL of synthetic groundwater. The serum bottles were sealed with Teflon-lined rubber septa and an aluminum cap to prevent leakage of the contaminants, shaken on a vertical rotary shaker at  $(25 \pm 2)^\circ\text{C}$ , for 24 hr, at 90 cycles per min. After 24 hr, the liquid in the serum bottle was taken and analyzed for TCE, *cis*-DCE and VC concentrations by a gas chromatography equipped with a flame ionization detector (GC-FID). The data were fitted to the Freundlich equation (Sposito, 1980) to describe the kinetics of the contaminants to each material.

### 1.10 Column study

A laboratory-scale three series barrier system was developed using a series of continuous flow glass columns (Fig. 1) to remediate TCE in synthetic groundwater. The first column was a chemical treatment consisting of sand and iron fillings at a weight ratio of 50:50. After packing, the column was flushed with nitrogen gas for 30 min to create anaerobic conditions. This column was used to remediate synthetic groundwater containing TCE at a high concentration of 500 mg/L. The second column was packed with 3500 g sand, 350 mL anaerobic sludge and 10 g sugarcane bagasse, and then flushed with nitrogen gas for 1 hr to

create anaerobic conditions. This column was used as the anaerobic bioreactive barrier to remove TCE residues and its metabolites in the effluent from the first column. The third column was filled with 3000 g sand and 800 g aerobic sludge biofilm coated on the OCIRM. This column was used as the aerobic bioreactive barrier to remove TCE and its metabolites in the effluent from the second column. In order to evaluate the extent of the removal of TCE and its metabolites in the aquifer down gradient of the barrier system, a fourth column packed with 250 g sand was applied. The first and fourth columns were 30 cm in length with an inside diameter of 5 cm. The second and third columns were 30 cm in length with an inside diameter of 10 cm. The contents of each column were well mixed by the rotary shaker at 100 r/min before being packed into the column. The column was saturated for 4 days, with the synthetic groundwater. The synthetic groundwater was then added to adjust the flow rate before switching to the synthetic groundwater containing 500 mg/L TCE and 100 mg/L bromide. Bromide was used as the tracer to determine the effect of the reactive materials, i.e., iron fillings, anaerobic sludge and the biofilm of aerobic sludge on the distribution of bromide in the column. TCE and bromide breakthrough curves (BTCs) were constructed by plotting the relative TCE or bromide concentration ( $C/C_0$ ).  $C_0$  is the initial concentration and  $C$  is the fraction concentration of TCE or bromide. The average flow rate in the column system was maintained at 64 mL/day to mimic the average groundwater flow. The barrier system was operated for 80 days in the dark at  $20^\circ\text{C}$ . The effluent from each column was sampled every 2 days until the concentration of TCE in the effluent of each column reached a steady state, i.e., the variation in TCE percentage was less than 10%. The concentrations of TCE, *cis*-DCE, VC and ethylene (ETH) in synthetic groundwater were determined using gas chromatography (GC). The concentration of chloride was analyzed using ion chromatography (IC). COD was analyzed by the dichromate reflux method described in standard methods (APHA, 1992).

In order to investigate the dissipation of TCE by the abiotic process, a control set of continuous glass flow columns was operated using the same methods as described above. However, the reactive materials, i.e., iron fillings, anaerobic sludge and the biofilm of aerobic sludge coated on the OCIRM were not added to the first, second, and third columns, respectively. Sodium azide (0.1% by weight) was added to the TCE solution before adding to the columns to ensure death of the microorganisms.

### 1.11 Analytical method

TCE, *cis*-DCE, VC and ETH concentrations in the synthetic groundwater were measured by analyzing 50  $\mu\text{L}$  headspace samples using Agilent 4820D GC-FID (Agilent Technologies, USA) and a Rtx-624 capillary column ( $30 \times 0.53$  mm ID; 3  $\mu\text{m}$ ) (Restek, USA). The GC oven temperature of  $60^\circ\text{C}$  was held for 6 min and then ramped at  $8^\circ\text{C}/\text{min}$  to  $200^\circ\text{C}$  where the oven was held for 1 min. Percentage of recovery for this method was 87%. The detection limit of GC-FID was 0.1 mg/L for TCE, *cis*-DCE

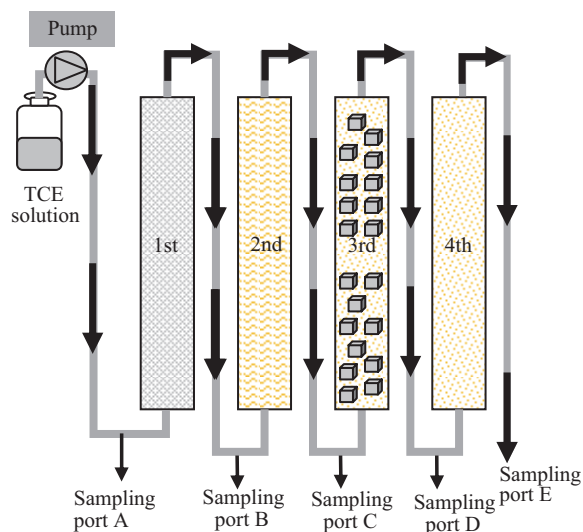


Fig. 1 Schematic diagram of column system (not subject to scale).

**Table 2** Freundlich isotherm constants for sorption of TCE and its metabolites

Materials	TCE			<i>cis</i> -DCE			VC		
	$K_f$ (L/kg)	$n$	$R^2$	$K_f$ (L/kg)	$n$	$R^2$	$K_f$ (L/kg)	$n$	$R^2$
Sand	0.07	1.07	0.99	0.07	0.96	0.99	0.02	1.10	0.98
Sugarcane bagasse	23.36	1.09	0.99	22.66	1.13	0.98	1.81	0.86	0.97
OCIRM	2.63	1.09	0.99	1.76	0.98	0.96	0.56	0.89	0.97

$K_f$ : Freundlich adsorption coefficient;  $n$ : the energy heterogeneity of the adsorption site (empirical constant);  $R^2$ : coefficient of determination from regression analysis.

and VC.

Anions i.e., bromide and chloride were determined using an IC (Dionex DX-120) equipped with RFC-30 EGII (KOH), Autosampler Thermo Finnigan Spectra SYSTEM model AS 1000 with 20  $\mu$ L injection volume, IonPac<sup>®</sup> AG11 guard column (4  $\times$  50 mm), IonPac<sup>®</sup> AS11 analytical column (4  $\times$  250 mm), ASRS<sup>®</sup>-ULTRA II (4 mm) suppressor and a conductivity detector. The column temperature was controlled at 30°C. IC was operated at a flow rate of 1.0 mL/min with a gradient of 0.5 mmol/L KOH 0–4 min, 0.5–35 mmol/L KOH 4–22 min, 18 mmol/L KOH 22–26 min and 0.5 mmol/L KOH 26–30 min.

## 2 Results and discussion

### 2.1 Sorption experiment

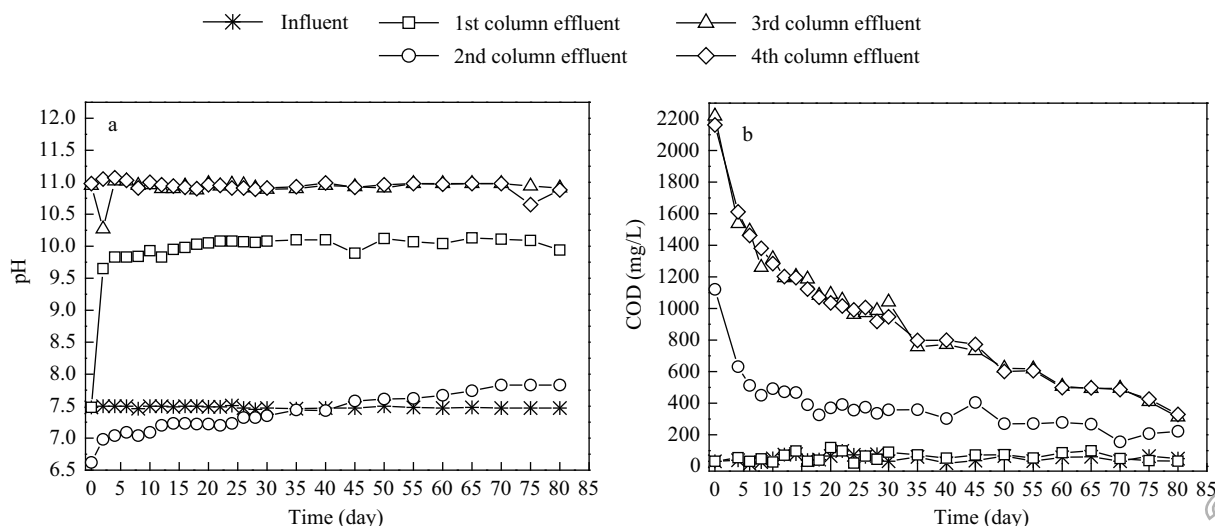
The values of the Freundlich isotherm constants for sorption of the contaminants to the solid media, i.e., sand and sugarcane bagasse are shown in Table 2. The regression,  $R^2$ , which ranged between 0.96 and 0.99 indicated a good fit of the data to the Freundlich isotherm in all treatments. Results indicated that the sorption isotherms were not linear ( $n \neq 1$ ). Higher  $n$  values indicated better adsorption and less effect of concentration change on the adsorptive capacity (Faust and Aly, 1987). The results suggested that sugarcane bagasse was a good sorbent for TCE, *cis*-DCE and VC giving the highest  $K_f$  values of 23.36, 22.66 and 1.81 L/kg, respectively.

### 2.2 Column experiment

#### 2.2.1 Bioprocess monitoring

The variations in pH, COD and DO in the effluent from the column system were monitored as the most important factors affecting the efficiency of TCE removal in the column system. Figure 2a shows the temporal pH variations in the effluent from each column. After treatment with iron fillings, the pH of the effluent from the first column rapidly increased from 7.5 to 10, which might be due to the release of hydroxide ions generated from the reaction between the iron fillings and TCE in the aqueous solution under anaerobic conditions (Baciacchi et al., 2003; Volpe et al., 2004). Further treatment of the effluent in the anaerobic biological column (the second column) resulted in a decrease in pH from 10 to approximately 7.2. This might have been the result of the metabolic products generated by anaerobic microorganisms in the system, i.e., volatile fatty acids such as acetic, propionic and/or butyric acids (Schöllhorn et al., 1997). Hydroxide ion released from cement used as binding material in the OCIRM contributed to the increase in effluent pH from the third and the fourth columns from 7.2 to 11. The pH in the fourth column remained unchanged due to the absence of reactive material.

The profiles of COD concentration in the effluent from the column system are shown in Fig. 2b. The initial COD in the influent was 51.49 mg/L. After treatment with iron fillings, the COD in the synthetic groundwater remained the same. The effluents from the second and third columns at day 0 contained high COD concentrations of 1100 and 2200 mg/L, respectively, due to the presence of organic materials, i.e., sugarcane bagasse (columns 2 and 3) and



**Fig. 2** pH (a) and COD (b) variations in the effluent from the column system over time.

limonene in the orange peel (column 3). After 7 days of column operation, COD values in the effluent from the second column rapidly decreased and then stabilized. In the third column, COD in the effluent rapidly decreased from day 0 to day 10 and then gradually decreased to 329 mg/L at the end of the experiment. This decrease in COD values during the column operation could be the result of a loss in the amount of sugarcane bagasse due to groundwater flow and the degradation of sugarcane bagasse by microbes. COD in the effluent from the fourth column at day 80 contained COD (312 mg/L) that was higher than the maximum standard level for industrial effluent (150 mg/L, Nasrullah et al., 2006), which suggested that the amount of sugarcane bagasse added to the second and third columns as a carbon source for the microorganisms should be reduced.

The overall DO level in the effluent from the column system (the fourth column) was above 5 mg/L (data not shown) ensuring that the OCIRM could sufficiently supply oxygen to the column system and degradation of TCE in the third column was under aerobic conditions.

It's worth noticing that although the sugarcane bagasse in the OCIRM can provide enough carbon source, the nitrogen can be a limited factor which inhibits the growth of microorganisms. Therefore, the appropriate amount of inorganic nitrogen should be added to the OCIRM, which may result in the enhancement of the removal efficiency of TCE by biological reaction.

## 2.2.2 Bromide tracer test

The tracer test in the column system was conducted in both the experimental and control sets to determine the effect of the reactive materials, i.e., iron fillings, anaerobic sludge and the biofilm of aerobic sludge on the distribution of bromide in the column. The normalized breakthrough curves for the bromide tracer in the column system are depicted in Fig. 3. An overall residence time (RT) of bromide determined by integration of the RT distribution curve in the column system of the control set was 23.62 days (Fig. 3a). A longer RT of 29.99 days was observed in the column system (Fig. 3b). The breakthrough curve of bromide in the control column indicated nearly ideal distribution without the retardation factor, in which all curves were not right shifted. The breakthrough curve of bromide in the third column of the experimental set was significantly shifted to the right which implied that the biofilm coated on the OCIRM affected the distribution of bromide in the column system by reducing the effective porosity resulting in a decrease in the diffusion ability of bromide in the column system (Charbonneau et al., 2006).

## 2.2.3 TCE breakthrough curves and degradation efficiency

In general, TCE transport through the column system in the control set was obviously retarded except in the first column. In the first column,  $C/C_0$  was equal to 1 implying that TCE was not dissipated (Fig. 3a). This column was

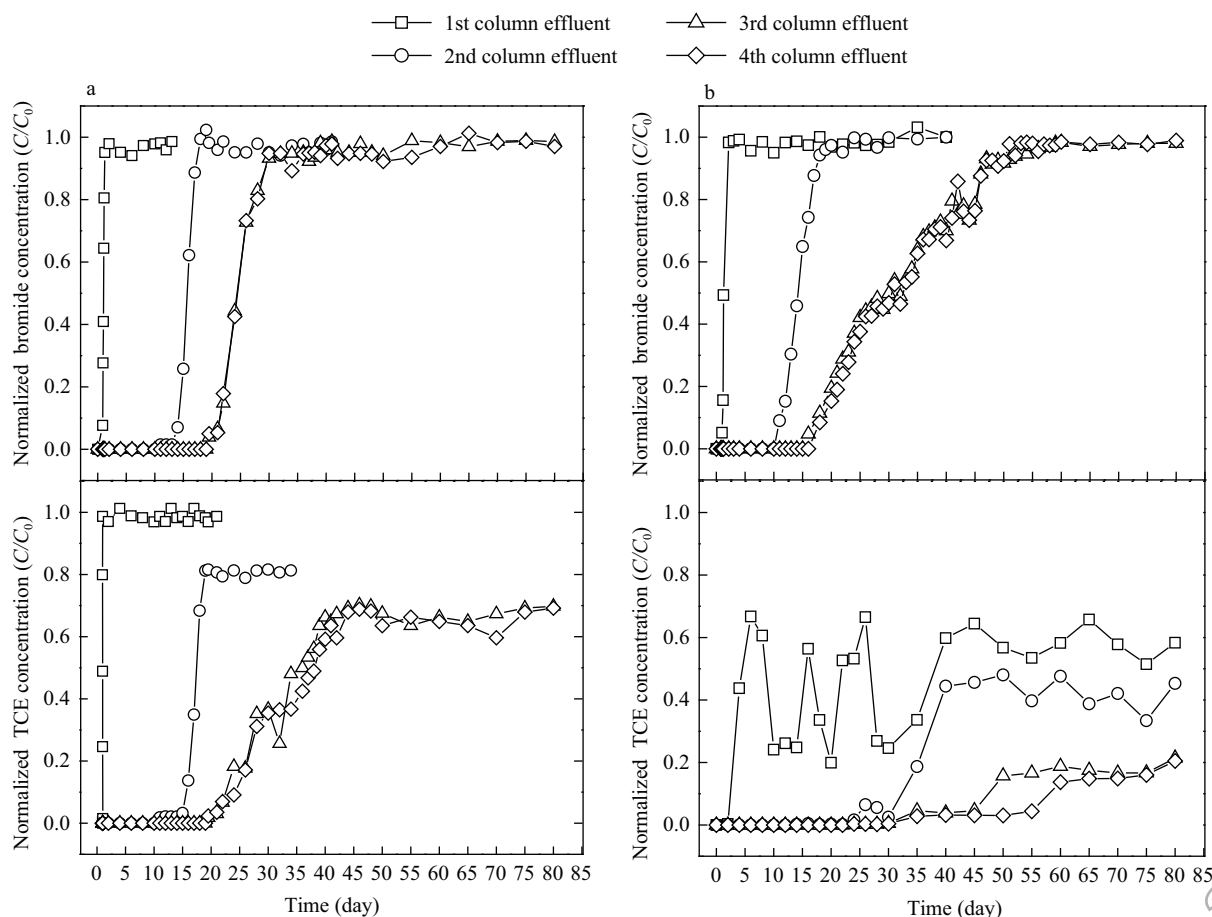


Fig. 3 Normalized concentrations of bromide and TCE during column operation. (a) control column; (b) experimental column.

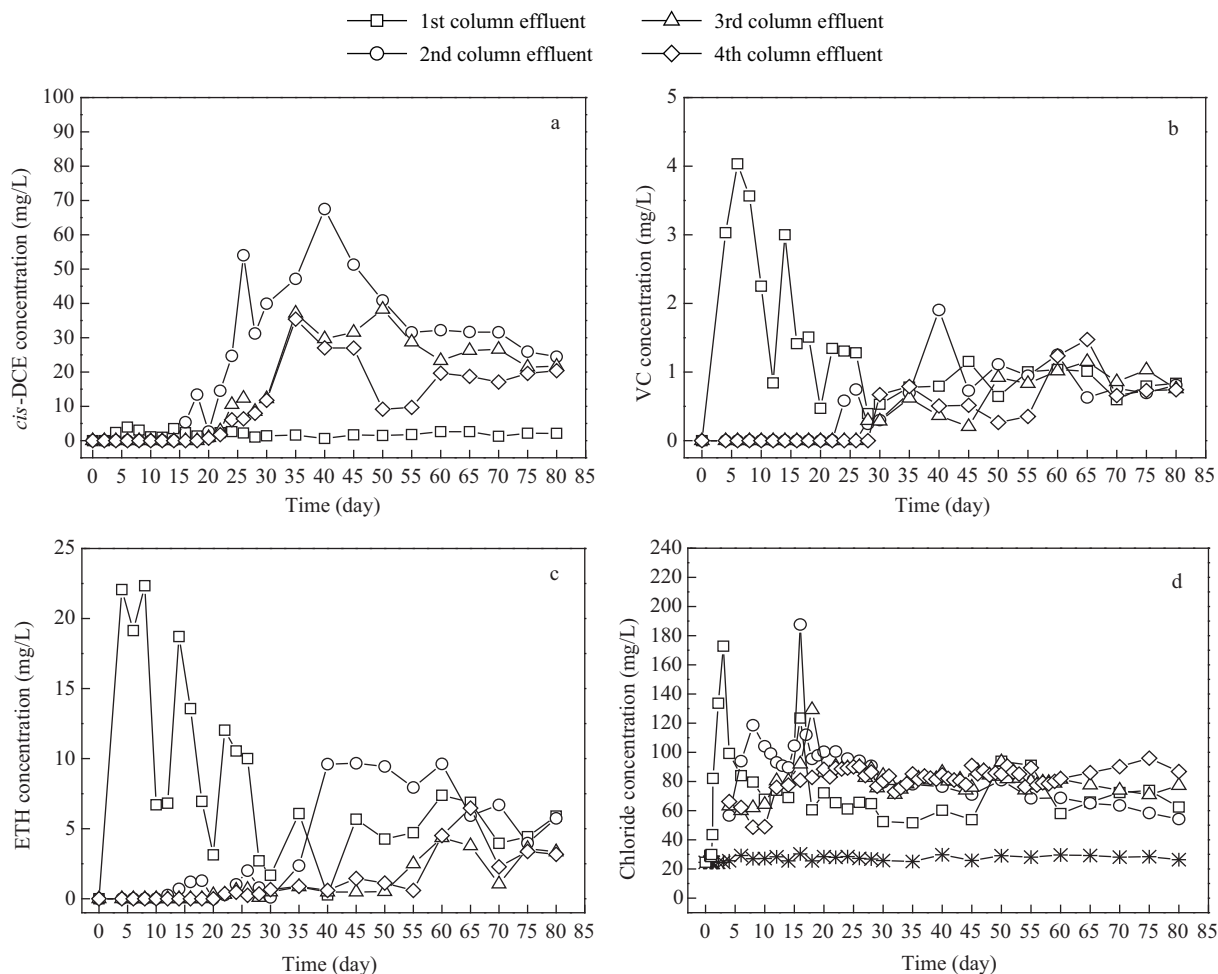


Fig. 4 TCE metabolite concentrations in the column effluent versus time. (a) *cis*-DCE, (b) VC, (c) ETH and (d) chloride.

packed with sand which has a low sorption capacity with a  $K_f$  value of 0.07 L/kg (Table 2), thus there was no sorption of TCE onto sand. These results also confirmed that TCE was removed in the first column, in the experimental set, by the reaction with iron fillings. In the second column,  $C/C_0$  was approximately 0.8, indicating that some TCE was dissipated by sorption onto the sugarcane bagasse which had a  $K_f$  value of 23.36 L/kg. In the third column,  $C/C_0$  was approximately 0.7, TCE may have been dissipated by sorption onto the OCIRM ( $K_f$  value of 2.63 L/kg) (Table 2). It was obvious that the  $C/C_0$  in the second column was higher than that in the third column, despite the fact that sugarcane bagasse has a much higher  $K_f$  value than the OCIRM. This might be due to the fact that the amount of sugarcane bagasse added to the second column was only 10 g while 800 g OCIRM was added to the third column. TCE dissipation in the control set was found to be 29.34% (Fig. 3a).

The breakthrough curves of TCE in the experimental set were due to TCE degradation. The degradation of TCE in the column system reached a steady state after 60 days of operation. The results indicated that 42% of TCE was removed by reductive dechlorination of the iron filling treatment in the first column (Fig. 3b). Previous research reported that the removal efficiency of TCE by ZVI was greater than 70% (Kang et al., 2006; Volpe et al., 2004). The relatively low percentage of TCE removal

in our column system could be due to the high pH value of groundwater itself (7.5) and the increase in pH to 10 in the first column during reductive dechlorination of TCE. Under high pH conditions, the oxide and hydroxide of iron are coated on the surface of iron, which could limit the access of TCE to the iron surface thus reducing the efficiency of TCE reductive dechlorination by ZVI (Dombek et al., 2001). The optimum pH for TCE removal using ZVI was found to be 4.9 (Chen et al., 2001).

The second column with the anaerobic biological process gave a percentage of TCE removal of 15% which was not obviously different from the abiotic control (20.2%) (Fig. 3b). This may be due to the fact that a high concentration of TCE (294 mg/L) in the effluent from the first column was still present. At this high concentration, the anaerobic sludge used as inoculum was not able to degrade TCE since it was acclimatized with TCE at 100 mg/L. An increase in TCE concentration at the acclimatization step could increase the ability of TCE degraders in the anaerobic sludge.

A relatively high TCE removal percentage of 25% was obtained in the third column containing the biofilm coated on the OCIRM, despite the fact that a high pH value of approximately 11 was observed and the TCE concentration entering this column was greater than 230 mg/L (Fig. 3b). These results implied that the microorganisms in the biofilm could survive in a stressful environment and play

an important role in degrading TCE. The polysaccharide coating around bacterial cells in the biofilm and the OCIRM as support material can act as a protective agent against the adverse effects of environmental conditions (Singh et al., 2006).

No significant TCE removal was observed in the fourth column indicating that TCE could not be degraded without the presence of reactive materials.

### 2.2.4 TCE metabolites

*cis*-DCE, VC, ETH and chloride ions were observed as the metabolites of TCE degradation in the column system (Fig. 4). High concentrations of VC, ETH and chloride ions were observed in the first column. The concentration of *cis*-DCE in the first column was negligible which implied that *cis*-DCE underwent reductive dechlorination by iron fillings which resulted in the daughter products, i.e., VC, ETH and chloride ions. A high concentration of *cis*-DCE was observed in the effluent from the second column which then decreased after it passed through the third column. These results are consistent with previous research which found that the degradation of *cis*-DCE was more effective by co-metabolism under aerobic conditions than under anaerobic conditions (Wang, 2006).

The presence of chloride ions in the effluent from the column system indicated the degradation of TCE. *cis*-DCE and VC which are more toxic than TCE, were not fully degraded by the proposed barrier system, which suggested that another remediation technology after the barrier treatment should be conducted.

## 3 Conclusions

The degradation of TCE following a three series barrier system was influenced by chemical and biological processes. The TCE removal efficiency of the three series barrier system was 84%. The removal of TCE by the iron fillings barrier, anaerobic barrier and aerobic barrier were 42%, 16% and 25%, respectively. *cis*-DCE, VC, ETH and chloride ions were observed as the metabolites of TCE degradation in the column system. The presence of chloride ions in the effluent from the column system indicated the degradation of TCE. Noxious metabolites of TCE, i.e., *cis*-DCE and VC were not fully degraded by the proposed barrier system, which suggested that another remediation technology after the barrier treatment such as air sparging following by adsorption using activated carbon should be conducted.

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