

ORC-GAC-Fe⁰ system for the remediation of trichloroethylene and monochlorobenzene contaminated aquifer: 1. Adsorption and degradation

LIN Qi¹, CHEN Ying-xu¹, Plagentz V.², Schäfer D.², Dahmke A.²

(1. Department of Environmental Engineering, Zhejiang University, Hangzhou 310029, China. E-mail: linqi@zju.edu.cn; 2. Institute für Geowissenschaften, Universität Kiel, Olshausenstrasse 40, D-24098 Kiel, Germany)

Abstract: Activities at a former Chemistry Triangle in Bitterfeld, Germany, resulted in contamination of groundwater with a mixture of trichloroethylene (TCE) and monochlorobenzene (MCB). The objective of this study was to develop a barrier system, which includes an ORC (oxygen release compounds) and GAC (granular activated carbon) layer for adsorption of MCB and bioregeneration of GAC, a Fe⁰ layer for chemical reductive dechlorination of TCE and other chlorinated hydrocarbon *in situ*. A laboratory-scale column experiment was conducted to evaluate the feasibility of this proposed system. This experiment was performed using a series of continuous flow Teflon columns including an ORC column, a GAC column, and a Fe⁰ column. Simulated MCB and TCE contaminated groundwater was pumped upflow into this system at a flow rate of 1.1 ml/min. Results showed that 17%—50% of TCE and 28%—50% of MCB were dissipated in ORC column. Chloride ion, however, was not released, which suggest the dechlorination do not happen in ORC column. In GAC column, the adsorption of contaminants on activated carbon and their induced degradation by adapted microorganisms attached to the carbon surface were observed. Due to competitive exchange processes, TCE can be desorbed by MCB in GAC column and further degraded in iron column. The completely dechlorination rate of TCE was 0.16—0.18 cm⁻¹, 1—4 magnitudes more than the formation rate of three dichloroethene isomers. Cis-DCE is the main chlorinated product, which can be cumulated in the system, not only depending on the formation rate and its decaying rate, but also the initial concentration of TCE.

Keywords: groundwater remediation; permeable reactive barriers; trichloroethylene; monochlorobenzene

Introduction

In Germany it is not necessary to explain what Bitterfeld means. Bitterfeld has become a symbol for any kind of pollution and destruction of landscape in the New States. The Bitterfeld district belongs to the federal state Saxon-Anhalt. It is the northern edge of the so called Chemistry Triangle, a large industrial region in East Germany dominated by chemical industry during the last century. The other two edges are Halle an der Saale and the better known Leipzig, the starting point of the political turn in the GDR and the reunification. In 1994, the Federal Government and the New States signed the Contaminated Site Remediation Agreement providing the money for all measures that must be executed. The goal of SAFIRA (Sanierungs-Forschung in regional kontaminierten Aquiferen), a joint project of several research partners is to develop and to provide the necessary technologies and methodologies to demonstrate the successful implementation of *in situ* reactive barriers in regionally contaminated aquifers. In this paper, ORC-GAC-Fe⁰ system for the remediation of trichloroethylene and monochlorobenzene contaminated aquifer was studied.

It is well known that permeable reactive barriers (PRBs) are suitable treatment technologies (Kao, 1997; Starr, 1994; Burris, 1995; Meggyes, 2000). Zero-valent iron is the most popular filling material and proved to be an effective way for the treatment of aliphatic halocarbons (Gillham, 1992; 1994; Weber, 1996; O' Hannesin, 1998). But, groundwater contaminated by a complex mixture of substances, e. g. MCB, CP, DCB, TCE, in the Bitterfeld aquifer cannot be treated only by iron filling.

Activated carbon is widely used to remove the contaminants from the water by sorption. But the carbon has to be replaced if its sorption

capacity is exceeded. A promising way seems to be the stimulation of microorganisms capable to mineralize the pollutants. The microorganisms covering the activated carbon as a biofilm degrade the adsorbed pollutants resulting in a continuous biological regeneration of the adsorbant. Furthermore, MCB, CP is the predominant contaminant in the Bitterfeld aquifer, thus, aerobic condition might be suggested. ORC is a kind of oxygen releasing compound. This material reacts with water and releases oxygen. Due to a special stabilization process the oxygen release is slow and constant. We expect an improved microbial aerobic degradation.

The principal objective of this study was to determine the possibility of ORC-GAC-Fe⁰ system in remediation of MCB and TCE polluted groundwater and illustrate the adsorption and degradation process in this system.

1 Experiments

1.1 Column set up

Three columns (d:10 cm) were combined sequently in this experiment (Fig.1). The first one (L:112.1 cm) was packed with 9.5 cm thick coarse sand filter at the bottom, 102 cm ORC at a rate of 1% by weight of the fine sand at the top. The effective porosity was determined to be 36%. The second one (L:112.1 cm) was packed with 9.5 cm thick coarse sand filter at the bottom, 98.1 cm GAC (granular activated carbon) at a rate of 0.68% by weight of the fine sand in the middle (40% effective porosity), and a 4.5 cm thick coarse sand filter at the top. The third one (L:112.1 cm) was packed with a 9.1 cm thick coarse sand filter at the bottom, 100 cm granular commercial iron in the middle (62% effective porosity), a 3 cm coarse sand filter at the top. Nine sampling needles with Luer Lock fittings, permanently installed along each column, served for sampling. The water used consisted of

NaHCO₃ (3 mmol/L), CaSO₄ (3 mmol/L), TCE (20 mg/L), MCB (20 mg/L). It was pumped upflow into the column by a peristaltic pump. A flow rate of 1.1 ml/min was chosen. This experiment was operated in a temperature controlled room (18°C).

Before the full system began to run, the third column (Fe⁰) had already run for 28 d. The medium percolated into column consisted of NaHCO₃ (3 mmol/L), CaSO₄ (3 mmol/L), and TCE (20 mg/L) only.

The GAC in the second column was also treated with 10 L saturated TCE before filled. The content of TCE was estimated to be 86–100 mg per gram dry GAC.

A small column, which was already enriched with microorganism, was connected with the first column at the beginning and run for 5 d in order to inoculate microorganism.

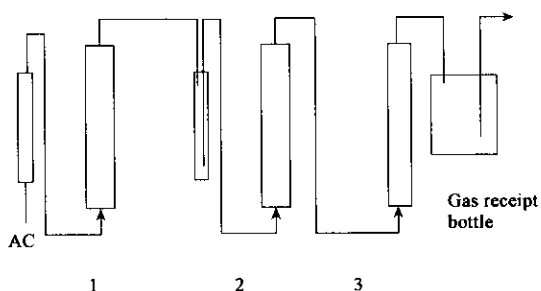


Fig.1 Scheme of ORC-GAC-Fe⁰ system.

1. 1% ORC + fine sand; 2. granular activated carbon + fine sand; 3. Fe(0)

1.2 Enrichment of microorganism

Two of glass column (35 cm length, 3.6 cm inner diameter) was performed for the enrichment of microorganism (Fig.2). One was packed with sand sampled from contaminated sites at Bitterfeld, Germany. The other was packed with GAC. The water medium, also sampled from contaminated sites, was added with saturated MCB to obtain the concentration of approximately 20 mg MCB/L, and percolated into column at an up-flow rate of 0.722 ml/min. This system was running for 21 d and the column filled with GAC was used as inocula.

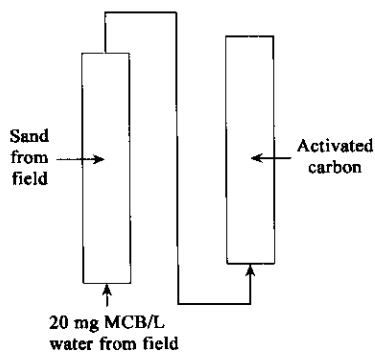


Fig.2 Set up for enrichment of microorganism

1.3 Chemical analysis

For analysis of concentrations of reactants and products, samples were passed through a 0.22 μm membrane filter. The concentrations of MCB, TCE, PCE, DCE isomers, VC, CH₄, C₂H₄, and C₂H₆ were determined by the headspace method using gas chromatography with a hydrogen flame ionization detector or electron captured detector (FID for high concentration of reactants and products, ECD for low concentration

of reactants and products). Chloride ion was performed using DX-100 ion chromatography.

2 Results and discussion

2.1 Dissipation in ORC column

After inoculated microorganism into system, the small column which act as inocula was disconnected with full system. The medium consisted of TCE and MCB was percolated into ORC column. The variance of chlorinated hydrocarbons, dissolved oxygen, anion ion, cation ion and TIC in solution was monitored over a period of approximately 100 d.

In ORC column, both MCB and TCE concentration decreased greatly, around 50%–83%, 46%–72% of initial TCE, MCB at the inflow of ORC column, respectively (Figs. 3, 4). Chloride ion, however, did not change significantly along the column (Fig.5). Since by-products from TCE and MCB biodegradation under aerobic condition have not been fully identified yet in this experiment, it was not clear whether biodegradation mechanism is prevalent in its removal. Further research in ORC column was done and the results were discussed in another paper.

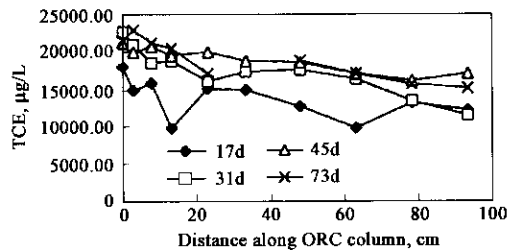


Fig.3 Dissipation of TCE along ORC column

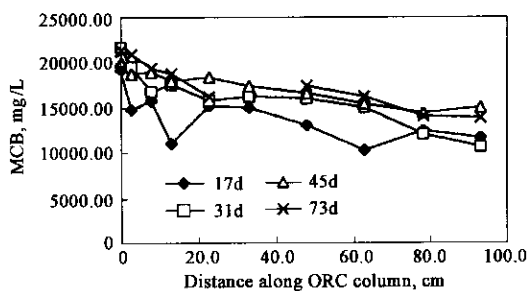


Fig.4 Dissipation of MCB along ORC column

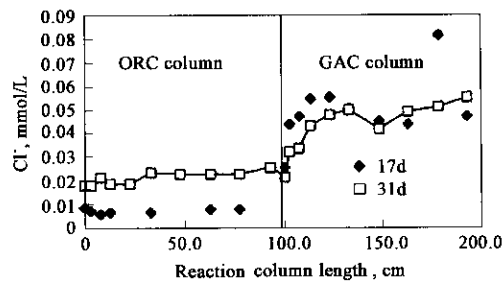


Fig.5 Variance of Cl⁻ along reaction length

2.2 Adsorption and regeneration in GAC column

In GAC column, MCB concentration rapidly declined as expected (Fig. 6). Since MCB has a high adsorption potential by GAC, it was not clear yet whether microbial activities were involved in its removal.

Further research should be done to distinguish between biological and adsorption processes. According to the results of Cl^- , TIC, pH(Figs.5, 7), the mineralization of chlorinated hydrocarbon under aerobic condition probably had happened. The decrease of pH along GAC column could be attributed to either the product of acid intermediate during biodegradation or the acidification of sand. However, the content of chloride in the outflow of GAC increased by 20–30 $\mu\text{mol/L}$ as compared with that in the inflow, which was most likely due to the mineralization of chlorinated hydrocarbon in GAC column. Since TCE could not serve as a sole carbon source for aerobic microorganisms (Segar, 1995), MCB should be degraded as source of carbon and energy if aerobic biodegradation occurs in this system.

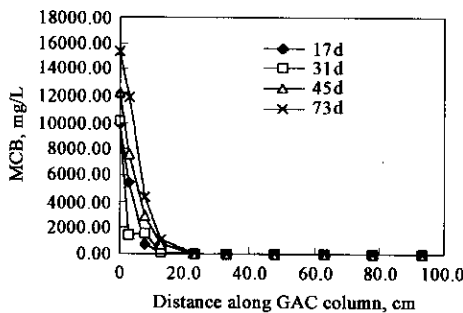


Fig. 6 Variance of MCB along GAC column

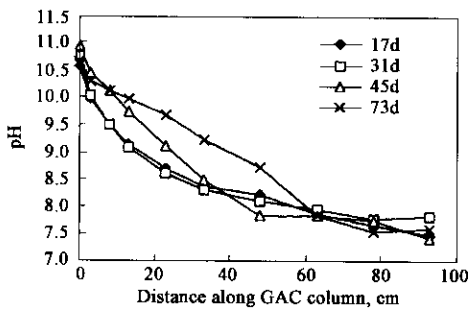


Fig. 7 Variance of pH along GAC column

Fig. 8 shows the variation of TCE along GAC column. TCE declined relatively slowly from 14.4 mg/L to about 3 mg/L , then changed less due to the pretreatment of GAC with saturated TCE. On day 45, the sorption capacity of TCE was already reached at the first 3 cm. When the moving MCB sorption front reaches the GAC section saturated by TCE, new sorption equilibrium would be established at the GAC surfaces and TCE would be partially removed by MCB due to competitive exchange processes. The water solubility of TCE and MCB are 7.7×10^{-3} (20°C), 4.3×10^{-3} mol/L (30°C), respectively. The relative low water solubility might be related to the more adsorption.

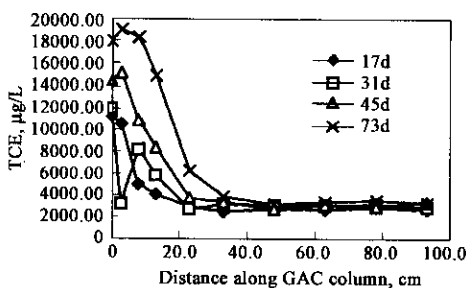


Fig. 8 Variance of TCE along GAC column

Besides, the production of ethane and ethene further suggested the biodegradation mechanism were occurring in this system (Fig. 9). Not only MCB was able to degraded, but also TCE might also be aerobic cometabolized. According to the research of Kao and Prosser (Kao, 1999), chlorobenzene can serve as the primary substrate (electron donor), and enhance TCE biodegradation to less-chlorinated compounds e.g. *cis*-DCE, VC.

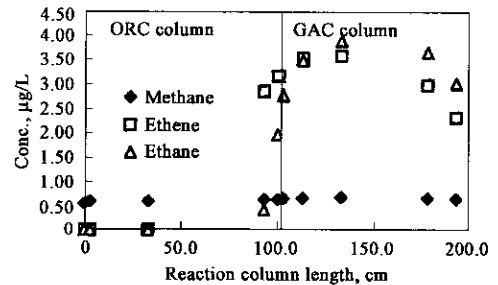
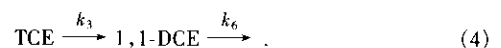
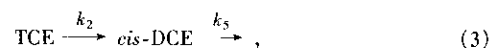
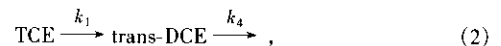
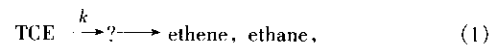


Fig.9 Variance of methane, ethane and ethane along reaction length

2.3 Degradation process in Fe^0 column

Prior to start-up of the full system (ORC-GAC- Fe^0), the third column, which was filled with zero-valent iron (Fe^0), had been running for 28 d. Samples for TCE, DCE isomers, VC, dissolved metal (Fe, Mn, Na, Ca), and anion (Cl^- , SO_4^{2-}) along the column were collected on day 13 and 24. The reduction of TCE and production of *cis*-DCE, *trans*-DCE, 1,1-DCE were observed and which is in agreement with the results of Arnold and Roberts (Arnold, 2000). VC production, however, was not observed in our experiments. According to the by-products observed in this experiment and the hypothetical reaction pathways suggested by Arnold and Roberts (Arnold, 2000), we assume that the degradation mechanism of TCE was adopted as follows:



The following rate equations were obtained based on the Reactions (1) to (4):

$$\frac{dC_{TCE}}{dX} = - (k + k_1 + k_2 + k_3) C_{TCE}, \quad (5)$$

$$\frac{dC_{\text{trans-DCE}}}{dX} = k_1 C_{TCE} - k_4 C_{\text{trans-DCE}}, \quad (6)$$

$$\frac{dC_{\text{cis-DCE}}}{dX} = k_2 C_{TCE} - k_5 C_{\text{cis-DCE}}, \quad (7)$$

$$\frac{dC_{1,1\text{-DCE}}}{dX} = k_3 C_{TCE} - k_6 C_{1,1\text{-DCE}}. \quad (8)$$

Thus, the variation of TCE, *trans*-DCE, *cis*-DCE and 1, 1-DCE concentrations along $Fe(0)$ column can be expressed by

$$C_{TCE} = C_{TCE0} \exp[-(k + k_1 + k_2 + k_3)X], \quad (9)$$

$$C_{\text{trans-DCE}} = \frac{k_1 C_{TCE0}}{k_4 - (k + k_1 + k_2 + k_3)} \{ \exp[-(k + k_1 + k_2 + k_3)X] - \exp(-k_4 X) \}, \quad (10)$$

$$C_{\text{cis-DCE}} = \frac{k_2 C_{TCE0}}{k_5 - (k + k_1 + k_2 + k_3)} \{ \exp[-(k + k_1 + k_2 + k_3)X] - \exp(-k_5 X) \} -$$

$$\exp(-k_5 X) \}, \quad (11)$$

$$C_{1,1-DCE} = \frac{k_5 C_{TCE}}{k_6 - (k + k_1 + k_2 + k_3)} \left[\exp[-(k + k_1 + k_2 + k_3)X] - \exp(-k_6 X) \right], \quad (12)$$

where C_{TCE} , $C_{trans-DCE}$, $C_{cis-DCE}$, $C_{1,1-DCE}$ are the concentrations of TCE, trans-DCE, *cis*-DCE, 1,1-DCE at reaction length X (in centimeter) in

Fe(0) column, respectively, and C_{TCE0} is the concentration of TCE at the inflow. k_1 , k_2 , k_3 are the pseudo first-order formation rate constant of trans-DCE, *cis*-DCE, 1,1-DCE, respectively, and k_4 , k_5 , k_6 , k decay rate constants of trans-DCE, *cis*-DCE, 1,1-DCE, and completely dechlorination rate of TCE, respectively.

According to the experimental data, the observed pseudo-first order rate constants were estimated (Table 1).

Table 1 Formation and decay rate of chlorinated hydrocarbon in zero-valent iron column (cm⁻¹)

Sampling time, d	k	k_1	k_2	k_3	k_4	k_5	k_6	k_T	R^2
13	0.185	10E-5	1.6 × 10E-2	10E-3	2.5 × 10E-2	10E-2	4 × 10E-2	0.2022	0.987
24	0.169	≪ k ₄	1.3 × 10E-2	8 × 10E-4		3 × 10E-2	8 × 10E-2	0.1828	0.984

Notes: $k_T = k + k_1 + k_2 + k_3$; k_T is the pseudo first-order decay rate constant of TCE.

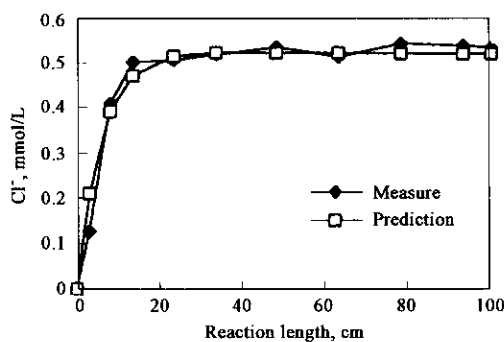
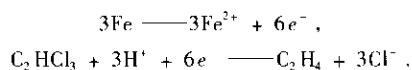


Fig. 10 Measured and predicted concentration profile of Cl⁻

The formation rates of three dichloroethene isomers were 1—4 orders lower than the decay rate of TCE, suggesting that the reaction mechanism in Eq. (1) is the primary reaction pathway. In addition, the results from the Cl⁻ analysis also supported this conclusion that TCE can be completely dechlorinated into nonchlorinated reaction by-products, though the exact mechanism can not illustrated yet (Fig. 10). Roberts *et al.* (Roberts, 1996) proposed β-elimination mechanism for TCE reduction by Fe⁰. It involves a two-electron transfer to produce chloroacetylene from TCE. The resulting chloroacetylene then undergoes hydrogenolysis to form acetylene which then undergoes another two-electron transfer to form ethene. Others suggested reduction reaction take place in one step as follows:



Given the low probability of an instantaneous transfer of this magnitude, Orth and Gillham (Orth, 1996) suggested that the TCE molecule must remain attached to the metal surface long enough for the six-electron transfer to occur. The TCE molecular remains attached to the metal surface either through the inherent hydrophobicity of TCE or, as Sivavec and Horney (Sivavec, 1995) suggested, by the formation of a strong chloroethene-iron pi bond. The reactive sites of the iron surface, thus, contribute much to the system and strongly influence the rate of reductive transformation of contaminants. Competing reactions occur during the degradation, since TCE and its degradation products adsorb onto the same reactive iron surface on which they are dechlorinated. Especially, *cis*-DCE, whose formation rate is relatively higher, would probably affect the adsorption of TCE. In single iron column system, the accumulation of *cis*-DCE was observed and the concentration of *cis*-DCE in outlet exceeded the maximum contaminant level (MCL) (the

concentration established under the Safe Drinking Water Act as being protective of human health and the environment).

Table 2 shows the formation and decay rate of chlorinated hydrocarbon in the zero-valent iron column of the ORC-GAC-Fe⁰ system. The decrease in the TCE concentration in the inflow of Fe⁰ column did not affect the decay rate constant of TCE, since k_T is determined by the term of $\ln(C_s/C_0)$. The formation rate of *cis*-DCE, however, was slightly decreased probably due to the decrease in the initial concentration of TCE. As the formation rate of *cis*-DCE was one magnitude less than its decomposition rate, relative low accumulation of *cis*-DCE was observed (Fig. 11).

Table 2 Formation and decay rate of chlorinated hydrocarbon in zero valence iron column of full system (cm⁻¹)

Sampling time, d	k_2	k_5	k_T	R^2
45	8.5 × 10E-3	3.5 × 10E-2	0.1802	0.9736
59	5 × 10E-3	7 × 10E-2	0.2066	0.9356
73	6.5 × 10E-3	8 × 10E-2	0.1891	0.9421
101	4 × 10E-3	8 × 10E-2	0.1894	0.9502

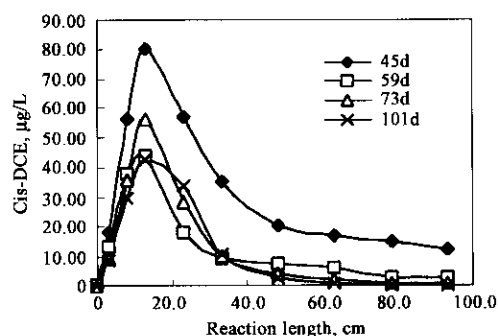


Fig. 11 Variance of *cis*-DCE in iron column

3 Conclusions

In ORC-GAC-Fe⁰ system, 17%—50% of TCE and 28%—50% of MCB were dissipated in ORC column. Chloride ion, however, was not released, suggesting the dechlorination did not happen. In GAC column, the adsorption of contaminants on activated carbon and the induced degradation by the adapted microorganisms attached to the carbon surface were observed. Due to competitive adsorption processes, TCE may be desorbed by MCB in GAC column and can be further degraded in iron column. The completely dechlorination rate of TCE was 0.16—0.18

cm^{-1} , 1—4 orders more than the formation rate of three dichloroethene isomers. *cis*-DCE is the major chlorinated product. It was observed that the formation rate of *cis*-DCE was one order less than the decomposition rate, resulting in relative low accumulation of *cis*-DCE in the outflow of the Fe^0 column.

Acknowledgements: This work is part of the SAFIRA project (Remediation research in regionally contaminated aquifers) sponsored by the German Federal Ministry of Education and Research (BMBF).

References:

- Arnold W A, Roberts A L, 2000. Pathways and kinetics of chlorinated acetylene reaction with $\text{Fe}(0)$ particles[J]. *Environ Sci & Tech.* 34: 1794—1805.
- Burris D R, 1995. Sorption of trichloroethylene and tetrachloroethylene in a batch reactive metallic iron-water system[J]. *Environ Sci Technol.* 29: 2850—2855.
- Gillham R W, Burris D R, 1992. *In situ* treatment walls—chemical dehalogenation, denitrification, and bioaugmentation[C]. Proceedings of the third international subsurface restoration conference. Dallas, TX, USA. 66—68.
- Gillham R W, Stephanie F H, 1994. Enhanced degradation of halogenated aliphatics by zero-valent iron[J]. *Ground Water*, 32: 958—967.
- Kao C M, Borden R C, 1997. Enhanced biodegradation of BTEX in a nutrient briquet-peat barrier system[J]. *J of Environ Engi.* 123: 18—24.
- Kao C M, Prosser J, 1999. Intrinsic bioremediation of trichloroethylene and chlorobenzen: field and laboratory studies [J]. *Journal of Hazardous Materials*, B, 69: 67—79.
- Meggyes T, Simon F G, 2000. Removal of organic and inorganic pollutants from groundwater using permeable reactive barriers. Part 2. Engineering of permeable reactive barriers[J]. *Land Contamination and Reclamation*, 8(3): 175—187.
- Orth W S, Gillham R W, 1996. Dechlorination of trichloroethene in aqueous solution using Fe^0 [J]. *Environ Sci Technol.* 30: 66—71.
- O'Hannesin S F, Gillham R W, 1998. Long-term performance of an *in situ* "iron wall" for remediation of VOCs[J]. *Ground Water*, 36: 164—170.
- Robert A L, Totten L A, Arnold W A *et al.*, 1996. Reductive elimination of chlorinated ethylenes by zero-valent metals[J]. *Environ Sci Technol.* 30: 2654—2659.
- Segar R L, Wys S L D, Speitel G E, 1995. Sustained trichloroethylene cometabolism by phenol-degrading bacteria in sequencing biofilm reactors[J]. *Water Environ Res.* 67: 764—774.
- Sivavec T M, Horney D P, 1995. Reductive dechlorination of chlorinated ethenes by iron metal[J]. *Natl Meet-Am Chem Soc Div Environ Chem*, 35: 695—698.
- Starr R C, Cherry J A, 1994. *In situ* remediation of contaminated groundwater: the funnel and gate system[J]. *Ground Water*, 32: 465—467.
- Weber E J, 1996. Iron-mediated reductive transformations: investigation of reaction mechanism[J]. *Environ Sci Technol.* 30: 716—719.

(Received for review September 9, 2002. Accepted November 7, 2002)