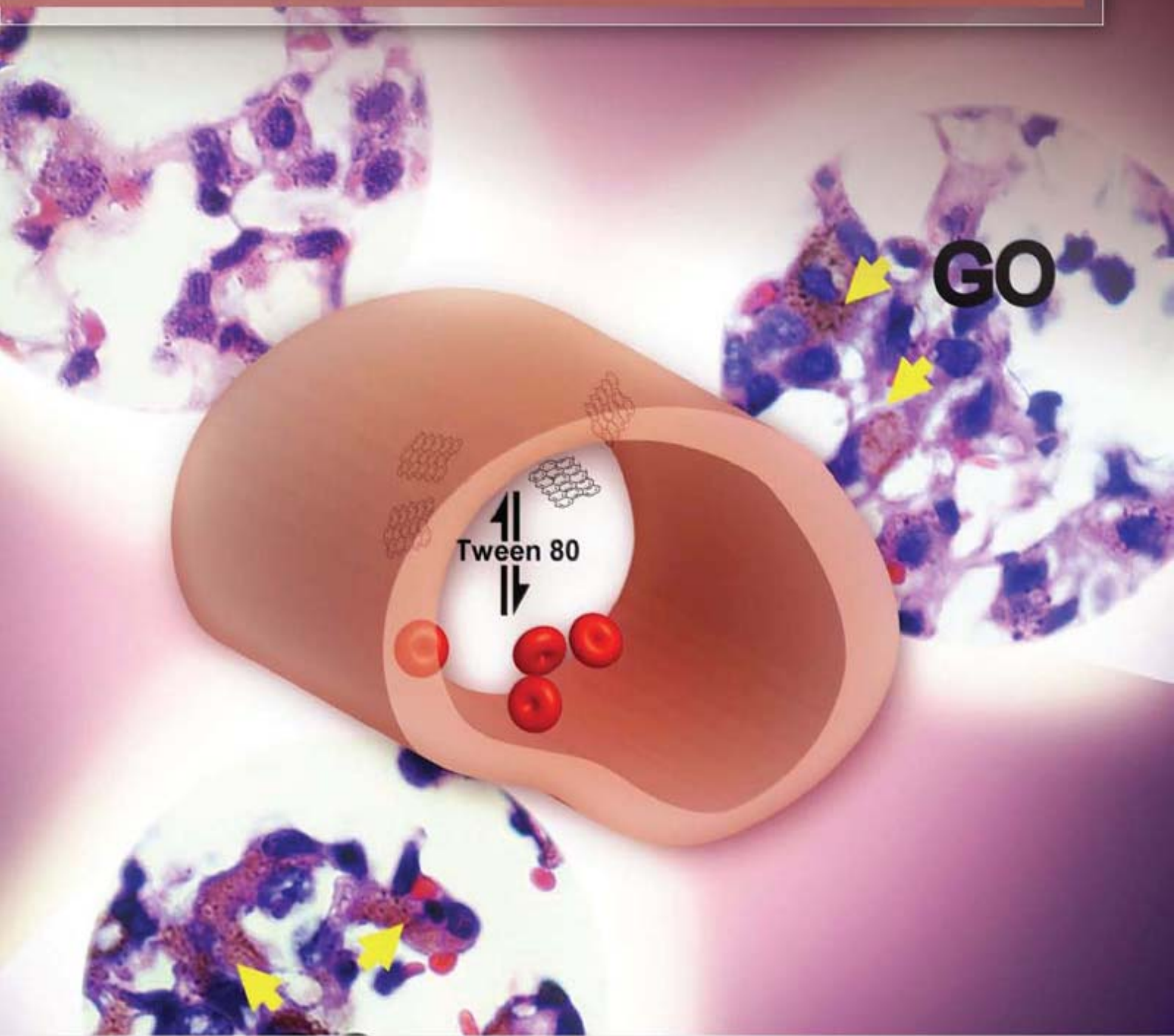


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## CONTENTS

### Environmental biology

Continuous live cell imaging of cellulose attachment by microbes under anaerobic and thermophilic conditions  
using confocal microscopy

Zhi-Wu Wang, Seung-Hwan Lee, James G. Elkins, Yongchao Li, Scott Hamilton-Brehm, Jennifer L. Morrell-Falvey ..... 849

Response of anaerobes to methyl fluoride, 2-bromoethanesulfonate and hydrogen during acetate degradation

Liping Hao, Fan Lü, Lei Li, Liming Shao, Pinjing He ..... 857

Effect of airflow on biodrying of gardening wastes in reactors

F. J. Colomer-Mendoza, L. Herrera-Prats, F. Robles-Martínez, A. Gallardo-Izquierdo, A. B. Piña-Guzmán ..... 865

### Environmental health and toxicology

The *ex vivo* and *in vivo* biological performances of graphene oxide and the impact of surfactant on graphene  
oxide's biocompatibility (Cover story)

Guangbo Qu, Xiaoyan Wang, Qian Liu, Rui Liu, Nuoya Yin, Juan Ma, Liqun Chen, Jiuyang He, Sijin Liu, Guibin Jiang ..... 873

Determination of the mechanism of photoinduced toxicity of selected metal oxide nanoparticles (ZnO, CuO, Co<sub>3</sub>O<sub>4</sub> and  
TiO<sub>2</sub>) to *E. coli* bacteria

Thabitha P. Dasari<sup>1</sup>, Kavitha Pathakoti<sup>2</sup>, Huey-Min Hwang ..... 882

Joint effects of heavy metal binary mixtures on seed germination, root and shoot growth, bacterial bioluminescence,  
and gene mutation

In Chul Kong ..... 889

### Atmospheric environment

An online monitoring system for atmospheric nitrous acid (HONO) based on stripping coil and ion chromatography

Peng Cheng, Yafang Cheng, Keding Lu, Hang Su, Qiang Yang, Yikan Zou, Yanran Zhao,

Huabing Dong, Limin Zeng, Yuanhang Zhang ..... 895

Formaldehyde concentration and its influencing factors in residential homes after decoration at Hangzhou, China

Min Guo, Xiaoqiang Pei, Feifei Mo, Jianlei Liu, Xueyou Shen ..... 908

### Aquatic environment

Flocculating characteristic of activated sludge flocs: Interaction between Al<sup>3+</sup> and extracellular polymeric substances

Xiaodong Ruan, Lin Li, Junxin Liu ..... 916

Speciation of organic phosphorus in a sediment profile of Lake Taihu II. Molecular species and their depth attenuation

Shiming Ding, Di Xu, Xiuling Bai, Shuchun Yao, Chengxin Fan, Chaosheng Zhang ..... 925

Adsorption of heavy metal ions from aqueous solution by carboxylated cellulose nanocrystals

Xiaolin Yu, Shengrui Tong, Maofa Ge, Lingyan Wu, Junchao Zuo, Changyan Cao, Weiguo Song ..... 933

Synthesis of mesoporous Cu/Mg/Fe layered double hydroxide and its adsorption performance for arsenate in aqueous solutions

Yanwei Guo, Zhiliang Zhu, Yanling Qiu, Jianfu Zhao ..... 944

Advanced regeneration and fixed-bed study of ammonium and potassium removal from anaerobic digested wastewater  
by natural zeolite

Xuejun Guo, Larry Zeng, Xin Jin ..... 954

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Eutrophication development and its key regulating factors in a water-supply reservoir in North China	
Liping Wang, Lusan Liu, Binghui Zheng .....	962
Laboratory-scale column study for remediation of TCE-contaminated aquifers using three-section controlled-release potassium permanganate barriers	
Baoling Yuan, Fei Li, Yanmei Chen, Ming-Lai Fu .....	971
Influence of Chironomid Larvae on oxygen and nitrogen fluxes across the sediment-water interface (Lake Taihu, China)	
Jingge Shang, Lu Zhang, Chengjun Shi, Chengxin Fan .....	978
Comparison of different phosphate species adsorption by ferric and alum water treatment residuals	
Sijia Gao, Changhui Wang, Yuansheng Pei .....	986
Removal efficiency of fluoride by novel Mg-Cr-Cl layered double hydroxide by batch process from water	
Sandip Mandal, Swagatika Tripathy, Tapswani Padhi, Manoj Kumar Sahu, Raj Kishore Patel .....	993
Determining reference conditions for TN, TP, SD and Chl- <i>a</i> in eastern plain ecoregion lakes, China	
Shouliang Huo, Beidou Xi, Jing Su, Fengyu Zan, Qi Chen, Danfeng Ji, Chunzi Ma .....	1001
Nitrate in shallow groundwater in typical agricultural and forest ecosystems in China, 2004–2010	
Xinyu Zhang, Zhiwei Xu, Xiaomin Sun, Wenyi Dong, Deborah Ballantine .....	1007
Influential factors of formation kinetics of flocs produced by water treatment coagulants	
Chunde Wu, Lin Wang, Bing Hu, Jian Ye .....	1015
 <b>Environmental catalysis and materials</b>	
Characterization and performance of Pt/SBA-15 for low-temperature SCR of NO by C <sub>3</sub> H <sub>6</sub>	
Xinyong Liu, Zhi Jiang, Mingxia Chen, Jianwei Shi, Wenfeng Shangguan, Yasutake Teraoka .....	1023
Photo-catalytic decolourisation of toxic dye with N-doped titania: A case study with Acid Blue 25	
Dhruba Chakraborty, Susmita Sen Gupta .....	1034
Pb(II) removal from water using Fe-coated bamboo charcoal with the assistance of microwaves	
Zengsheng Zhang, Xuejiang Wang, Yin Wang, Siqing Xia, Ling Chen, Yalei Zhang, Jianfu Zhao .....	1044
 Serial parameter: CN 11-2629/X*1989*m*205*en*P*24*2013-5	



## Laboratory-scale column study for remediation of TCE-contaminated aquifers using three-section controlled-release potassium permanganate barriers

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### Abstract

A laboratory-scale study with a sand column was designed to simulate trichloroethylene (TCE) pollution in the aquifer environment with three-section controlled-release potassium permanganate (CRP) barriers. The main objective of this study was to evaluate the feasibility of CRP barriers in remediation of TCE in aquifers in a long-term and controlled manner. CRP particles with a 1:3 molar ratio of  $\text{KMnO}_4$  to stearic acid showed the best controlled-release properties in pure water, and the theoretical release time was 138.5 days. The results of TCE removal in the test column indicated that complete removal efficiency of TCE in a sand column by three-section CRP barriers could be reached within 15 days. The molar ratio of  $\text{KMnO}_4$  to TCE in the three-section CRP barriers was 16:1, which was much lower than 82:1 as required when  $\text{KMnO}_4$  solution is used directly to achieve complete destruction of TCE. This result revealed that the efficiency of CRP for remediation of TCE was highly improved after encapsulation.

**Key words:** chlorinated solvent; encapsulation; groundwater;  $\text{KMnO}_4$ ; permeable reactive barrier; sand column

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### Introduction

Trichloroethylene (TCE) is a commonly used chlorinated solvent in industry. Once released into the subsurface environment, a great fraction of TCE tends to be retained in the solid phase, and then TCE adsorbed by soil can be slowly released back into groundwater, which causes a distribution of TCE between soil and water. Soil sorption may inhibit or limit the natural attenuation or bioavailability of TCE. However, TCE-contaminated groundwater can pose a threat to human health as a suspected carcinogen (Lavin et al., 2000; Moore et al., 2010). A variety of technologies have been widely studied for TCE-contaminated soil and groundwater remediation (Liang et al., 2004; Davie et al., 2008; Weyens et al., 2009; Kirschling et al., 2010). Among them, advanced oxidation technology has been considered an efficient method to transform most chlorinated solvents to short-lived intermediates, and further to the final innocuous by-products (Yan and Schwartz, 1999, 2000). As a low-cost and easily handled reagent, potassium permanganate ( $\text{KMnO}_4$ ) is often used for the *in-situ* chemical oxidation (ISCO) of TCE in groundwater (Mackinnon

and Thomson, 2002; Heiderscheidt et al., 2008). Studies have revealed that the remediation performance of ISCO strongly depends on how  $\text{KMnO}_4$  is delivered into the contaminated zone (Schnarr et al., 1998; Crimi and Siegrist, 2005). In practical applications, permanganate is typically injected as an aqueous solution, which causes losses due to heterogeneous distribution, non-selective oxidation, and also self-decomposition (Schnarr et al., 1998; Schroth et al., 2001; MacKinnon and Thomson, 2002; Lee et al., 2003). Hence, a large amount of  $\text{KMnO}_4$  is required for the complete degradation of TCE. For example, it has been reported that the required mass ratio of  $\text{KMnO}_4$  to TCE was 82:1 to destroy all of the TCE within 120 days during a 3-D flow tank study (Lee et al., 2003), which is much larger than the stoichiometric requirement of 2:1.

To enhance the effective usage of  $\text{KMnO}_4$ , controlled-release permanganate (CRP) technology has been recently developed as an improved, *in-situ* remedial option for treating dissolved contaminant plumes of TCE in groundwater (Kang et al., 2004; Ross et al., 2005; Lee and Schwartz, 2007a). It was reported that the microcapsules, comprising  $\text{KMnO}_4$  granule core and waxy polymeric coating, have an extended duration of permanganate release in the range of several days to years (Kang et al., 2004; Ross et al.,

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2005; Lee and Schwartz, 2007b; Lee et al., 2008a). These microcapsules have been used to study the kinetics and efficiency of TCE removal in bench-scale experiments (Lee and Schwartz, 2007a; Yuan et al., 2012). For the future field application of CRP, CRP particles have received a great deal of attention as reactive materials used in permeable reactive barriers (PRB) for TCE plume control and removal of TCE (Lee and Schwartz, 2007a; Lee et al., 2008b, 2009). Lee et al. (2009) reported that a CRP barrier system with  $\text{KMnO}_4$  granules in paraffin wax-silica sands matrix was able to remove 74% of TCE for a 87  $\mu\text{g/L}$  plume during the first 20 days and 65% for a 172  $\mu\text{g/L}$  plume during the next 33 days. However, the remediation efficiency of TCE and the delivery activity of the oxidant in PRB might be different due to the CRP particles having a different waxy polymeric coating, which presented its own controlled-release properties.

In this study, new CRP particles comprised of potassium permanganate and stearic acid were used to construct three-section CRP remedial barriers for remediation of a TCE-contaminated aquifer in a sand column. The main objectives of this study included: (1) assessment of the removal efficiency of TCE by three-section CRP barriers in a sand column, (2) evaluation of the effective usage of released permanganate by studying the molar ratio of permanganate to TCE after each section of the CRP barrier, (3) discussion of  $\text{MnO}_2$  precipitates formed during the remediation and the possibility of removal by oxalic acid.

## 1 Materials and methods

### 1.1 Materials

The column experiment was conducted using 40/70-mesh quartz sand as a porous medium (Hengsheng Silica Sand Company, China). The sand was pre-washed and desiccated prior to use. Analytical grade TCE (> 99% purity) was purchased from Sigma-Aldrich. HPLC-grade methanol and acetonitrile were obtained from CNW, Germany. Sodium thiosulfate was obtained from Tianjin FuChen

Chemical Reagent Factory (China). Purified water was used for all experiments. The diameters of CRP particles used in the column study ranged from 2–5 mm with mass ratio of solid  $\text{KMnO}_4$  to stearic acid of 1:3 (Yuan et al. 2012).

### 1.2 Release experiments

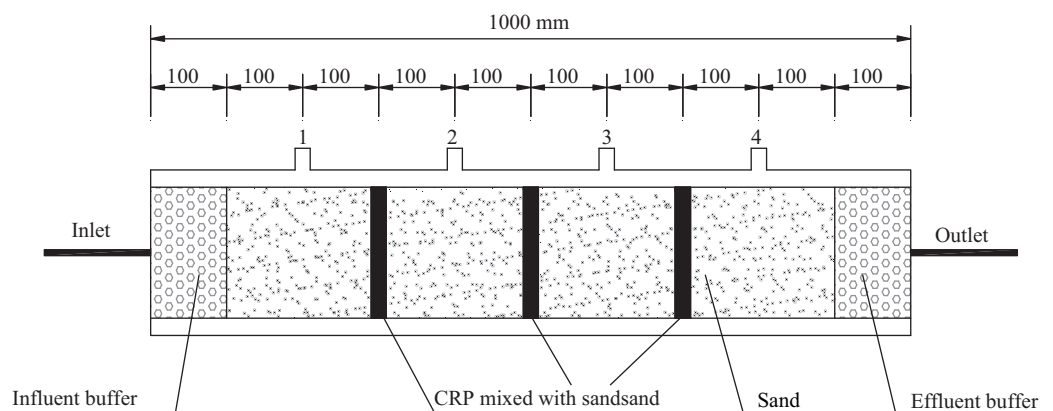
A 175-mg of encapsulated CRP with 1:3 mass ratio of solid  $\text{KMnO}_4$  to stearic acid was introduced into 200 mL deionized water at room temperature under constant stirring (200 r/min) with a mechanical stirrer to ensure a well-mixed solution. Aliquots of the aqueous solution were taken every 24 hr until 312 hr, and the released concentration of  $\text{KMnO}_4$  was measured with a UV spectrophotometer at 525 nm wavelength. The weight of released  $\text{KMnO}_4$  was calculated by multiplying the released concentration of  $\text{KMnO}_4$  with the 200 mL volume. Experiments were performed in triplicate, and the release rate ( $R$ , %) was calculated using Eq. (1).

$$R = \frac{\text{Weight of released } \text{KMnO}_4}{\text{Weight of } \text{KMnO}_4 \text{ in CRP}} \times 100\% \quad (1)$$

### 1.3 Column experimental outline

Two continuous-flow polymethyl methacrylate columns (ID = 142 mm, length = 1000 mm) were constructed. One as the control column was used to determine the variation of TCE concentration and the adsorption of TCE onto the silica sand without CRP applied. The other one as the test column was filled with CRP particles to simulate the oxidant release barrier and evaluate the effectiveness of released permanganate on TCE oxidation. **Figure 1** shows the layout of the laboratory-scale test column.

In the test column, approximately 24 g CRP (containing about 6.1 g  $\text{KMnO}_4$ ) mixed with silica sand at the mass ratio of 1:3 were divided into three equal parts and placed in the cross-section of the column 30, 50 and 70 cm away from the inlet to form three discrete controlled-release oxidation zones. The rest of the test column was filled with 40/70-mesh silica sand, which was packed to an approximate bulk density of 1.47 g/cm and porosity



**Fig. 1** Schematic diagram of column setup (ID = 142 mm, length = 1000 mm). Three controlled-release potassium permanganate (CRP) barriers are located at 300, 500 and 700 mm from the inlet. The peristaltic pumps were used for flow control and sample collection. 1–4: sample port.



of 0.51. Input and output chambers on both ends of the column were separated from the sand by rigid stainless steel screens to prevent sand from entering the chambers and also filled with glass beads to assure flow equalization for uniform distribution of TCE solution into and out of the column. The control column was constructed in the same manner without CRP particles.

Three pore volumes of water (pH 7.0) were flushed through the columns at the beginning of the experiment to ensure equilibration of the column. A TCE solution with initial concentration of 4.0–4.2 mg/L was continuously pumped into the columns under saturated conditions at the constant flow rate of 2 mL/min provided by peristaltic pumps (YZ1515, Lange Instrument Company, China). A 5-mL aliquot of reaction solution from ports 1, 2, 3, 4 and outlet was taken every 24 hr and then filtered through 0.2  $\mu\text{m}$  nylon syringe filters to separate the precipitated manganese dioxide. After filtration, a 1-mL aliquot of solution for TCE analysis was quickly withdrawn and then injected into a 2.0-mL vial with screw caps and Teflon-lined septa charged with solid sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ), which was used to terminate any further oxidation of TCE. The experiment in the control column was operated in the same manner as the test column except no CRP was applied in the column. TCE analysis was only done for the control column for 9 days and then the control column was stopped. Effluent from the column was collected in a waste container and treated to remove TCE and  $\text{MnO}_4^-$  before disposal. The excess  $\text{MnO}_4^-$  was removed from the effluent through reduction by  $\text{Na}_2\text{S}_2\text{O}_3$ .

When the test column stopped running after 17 days, 0.016 mmol/L of oxalic acid was pumped into the column at 10 mL/min flow rate to remove  $\text{MnO}_2$ , which is the product of the reaction of  $\text{KMnO}_4$  and TCE.

#### 1.4 Chemical analysis

The concentration of TCE was analyzed by high-performance liquid chromatography (HPLC, Hitachi L2000, Japan) equipped with a L2455 photodiode array detector at 214 nm and a L2200 autosampler. Separation was accomplished under a reversed-phase isocratic condition with a Regis ODS C18 column (5  $\mu\text{m}$ , 250 mm  $\times$  4.6 mm i.d., Rainin Instrument Company, Inc., USA). The mobile phase used for the analysis was acetonitrile and deionized water (70:30, V/V) at a flow rate of 1 mL/min. The  $\text{KMnO}_4$  concentration was measured at 525 nm by an UV-Vis spectrophotometer (GOLD S53/54, Shanghai, China).

## 2 Results and discussion

### 2.1 Release rate of CRP in water

The release profile of  $\text{KMnO}_4$  from CRP was measured in water as shown in Fig. 2. The release efficiency was well controlled and only 30.9%  $\text{KMnO}_4$  was released into water

from the CRP after 240 hr.

To simulate the release model of  $\text{MnO}_4^-$  from CRP, the release data obtained in Fig. 2 were fitted to the equation introduced by Sinclair and Peppas (1984) (Eq. (2)):

$$Q = kt^n \quad (2)$$

where,  $Q$  (%) is the percentage of  $\text{MnO}_4^-$  released at time  $t$  (hr),  $k$  is a rate constant incorporating the characteristics of  $\text{MnO}_4^-$  and the coating matrix system, and  $n$  is the diffusion exponent. This equation could simulate the release kinetics ( $R^2 > 0.98$ ) for the experimental data in Fig. 2. The theoretical  $t_{0.5}$  for released  $\text{MnO}_4^-$  at mass ratio of solid  $\text{KMnO}_4$  to stearic acid (1:3) is 138.5 days. These simulation data suggested that the CRP encapsulated with stearic acid could release  $\text{MnO}_4^-$  into water in a controlled manner over an extended period of time.

### 2.2 Breakthrough curve of TCE in the control column

The control column was filled with silica sand without CRP and then flushed with water to saturate the column. After being saturated by water, the TCE solution with initial concentration of 4.0–4.2 mg/L was continuously pumped into the control column at a flow rate of 2 mL/min for 9 days to evaluate the variation of TCE concentration in the sand column. The breakthrough curve of TCE is shown in Fig. 3.

On the first day, no TCE was detected because the pore water in the sand column was replaced by the TCE solution. The TCE concentration increased gradually with time after one day and reached 98% of the initial concentration on day 5 and thereafter remained constant, which indicated that the control column reached almost 100% breakthrough. In contrast to the influent, the approximately 2% loss could possibly be attributed to measurement error or the volatilization of TCE during sampling.

In order to verify this result, the flow velocity was calculated according to Eq. (3):

$$v = Q/A = (k/n_e)i \quad (3)$$

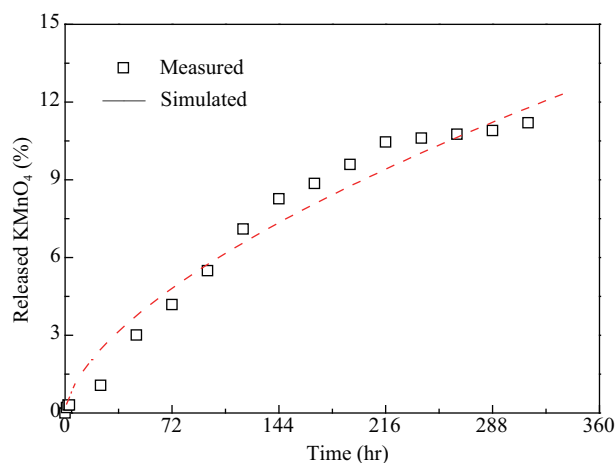
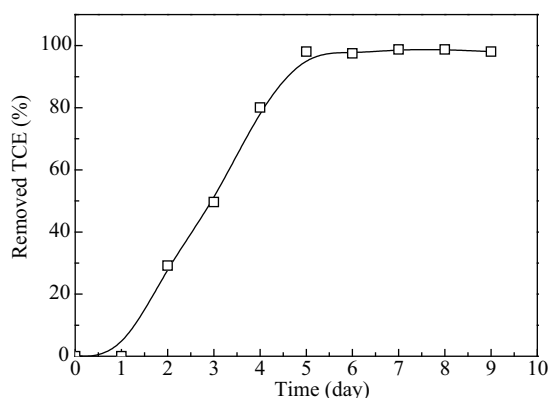


Fig. 2 Release curve of CRP in pure water. Experimental condition: 175 mg of CRP with 1:3 mass ratio of solid  $\text{KMnO}_4$  to stearic acid.



**Fig. 3** Breakthrough curve of TCE in control column. Experimental conditions: initial TCE concentration 4.2 mg/L, pH = 7.0.

where  $v$  (cm/day) is the flow velocity,  $Q$  (mL/min) is the flow rate of TCE solution,  $A$  (cm<sup>2</sup>) is the cross-sectional area of the column,  $k$  (cm/sec) is hydraulic conductivity,  $n_e$  is porosity of silica sand (0.51) and  $i$  is hydraulic gradient ( $dh/dl = 0.006$ ).

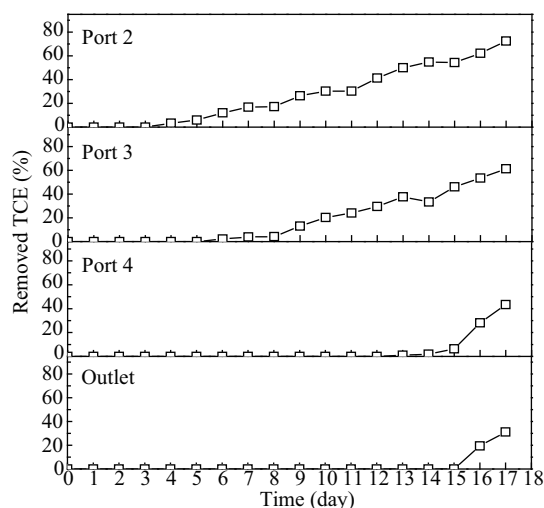
An inflow rate of 2 mL/min to the column provided a flow velocity of 18.2 cm/day in the sandy porous medium. At this velocity, it required 5.5 days for water to flow through the column, which is in agreement with the required equilibrium time obtained by the breakthrough curve. The hydraulic conductivity ( $k$ ) was calculated as  $1.79 \times 10^{-2}$  cm/sec, which is also in agreement with the associated parameter of silica sand ranging from  $5 \times 10^{-3}$ – $2 \times 10^{-2}$  cm/sec provided by the Silica Sand Company.

### 2.3 TCE removal in test column

The variation of TCE concentration in the test column at sample ports 2, 3, 4 and the outlet are presented in **Fig. 4**. Apparently, TCE was degraded by the three-section CRP barriers system for 16 days. During 15 days, removal efficiencies of TCE can reach 100% after three-section CRP barriers.

The sequential breakthrough of TCE was measured at sample port 2 on day 5 after the 1st CRP barrier, on day 9 at port 3 after the 2nd CRP barrier, and on day 14 at port 4 after the 3rd CRP barrier, and on day 16 at the outlet. Based on the control column data, at the velocity of 18.2 cm/day, the required times for TCE breakthrough were 2.2 days at port 2 (distance between inlet and port 2 is 40 cm), 3.3 days at port 3 (distance between inlet and port 3 is 60 cm), 4.4 days at port 4 (distance between inlet and port 4 is 80 cm) and 5.5 days at the outlet (distance between inlet and outlet is 100 cm). The difference in the breakthrough time between the calculated and experimental data can be attributed to the oxidation of the CRP.

At port 2, the TCE removal rate decreased by 75% (to 1.05 mg/L) after oxidation by the 1st CRP barrier on the 9th day and to 28% (to 3.02 mg/L) after 17 days, because excessive released  $\text{KMnO}_4$  flowed out of the column with the water flow, which caused a decrease in the



**Fig. 4** Removal efficiency of TCE after three-section CRP barriers in the column study. Experimental conditions: initial TCE concentration 4.2 mg/L, CRP = 24 g, pH = 7.0.

$\text{KMnO}_4$  concentration. Since TCE could not be removed completely by the 1st CRP barrier, increasing residual TCE flushed into the second CRP barrier from day 4 on. TCE residual concentration could be detected after day 6 at port 3, and the removal efficiency could always reach 87% on the 9th day after combined oxidation by the first and the second CRP barriers together, but decreased to 54% on day 15 and 49% on day 17. TCE continued to be removed in the third CRP barrier, although TCE could be detected in port 4 on day 13. Over 94% TCE removal rate was maintained after the three-section CRP barriers before 15 days and then the TCE residual concentration increased steadily. The TCE removal rate decreased to 57% after 17 days oxidation. After extending the reaction time, the removal efficiency of TCE could be further increased to 70% on the 17th day. This suggested that the removal efficiency can be improved by extending the contact time of released  $\text{KMnO}_4$  with TCE after the three-section CRP barriers.

In order to verify that insufficient reaction time caused the lack of longevity of the three-section CRP barriers, the molar ratios of  $\text{KMnO}_4$  to TCE at the sample port 3 were investigated as shown in **Table 1**. From **Table 1**, the  $\text{KMnO}_4$  concentration in solution was high for 5 days because some solid  $\text{KMnO}_4$  attached on the surface of the CRP caused the quick-release rate of  $\text{KMnO}_4$  from CRP in the early stage of the release period, according to the release mechanism of CRP in our previous study (Yuan et al., 2012). With increasing flushing time, the  $\text{KMnO}_4$  concentration decreased to 18.9 mg/L at day 15 and then remained constant due to the controlled-release property of the CRP. Before 15 days, TCE could be removed completely at molar ratios of  $\text{KMnO}_4$  to TCE ranging from 8.1 to 84. However, after 15 days, the removal efficiency for the 2.57 mg/L TCE plume decreased to 50% even if the molar ratio between released  $\text{KMnO}_4$  and TCE reached 6.4, which is still much higher than the stoichiometric

**Table 1** Molar ratios of KMnO<sub>4</sub> to TCE in sample port 3

Time (day)	5	9	11	13	15	16	17
C <sub>KMnO<sub>4</sub></sub> at port 3 (mg/L)	103.9	55.6	38.4	26.9	18.9	18.7	18.7
C <sub>TCE</sub> at port 3 (mg/L)	0	0.55	1.01	1.58	1.93	2.25	2.57
C <sub>TCE</sub> at the outlet (mg/L)	0	0	0	0	0	0.81	1.30
Observed molar ratio of KMnO <sub>4</sub> to TCE	–	84	31	14	8.1	6.9	6.4
Theoretical molar ratio of KMnO <sub>4</sub> to TCE	2						

–: not applicable.

requirement of 2. The same results could also be found in a previous publication (Lee et al., 2009), where the removal efficiency was 65% and 74% for TCE plumes of 172 µg/L and 87 µg/L after three discrete CRP barriers, although the molar ratios of KMnO<sub>4</sub> to TCE were 8.7 and 14.3, respectively.

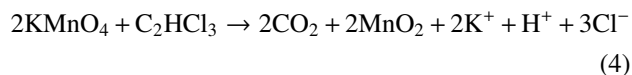
According to Lee et al. (2009), there are three possible reasons affecting the incomplete destruction of TCE by KMnO<sub>4</sub> such as insufficient supply of KMnO<sub>4</sub>, short reaction time, or incomplete mixing of MnO<sub>4</sub><sup>–</sup> with the TCE solution. In our previous batch-scale study (Yuan et al., 2012), 5.5 mg/L of TCE concentration could be completely removed by CRP after 12 hr of reaction time although the molar ratio between released KMnO<sub>4</sub> and TCE was only 2.98, which is slightly higher than the stoichiometric requirement of 2. According to the half-life of 17.8 min for TCE reacted with KMnO<sub>4</sub> reported by Yan and Schwartz (2000), it required about 9 half lives (about 178 min) to completely remove TCE with an initial concentration of 2.25–2.57 mg/L. In this column study, the supply of KMnO<sub>4</sub> ranging from 6.4–84 mg/L was enough to destroy TCE and the residence time for TCE removal from port 3 to the outlet was about 2.1 days based on Eq. (3), which was much longer than the time required for complete destruction of TCE. This suggested that complete mixing of KMnO<sub>4</sub> with TCE is a more important factor than the other two. Some researchers reported that lack of lateral dispersion of KMnO<sub>4</sub> in a well-based CRP barrier would have caused incomplete mixing with TCE, and reduced the overall removal efficiency (Lee et al., 2009; Lee and Schwartz, 2007a, 2007b). In this study, CRP barriers built by mixing CRP particles and sand aimed to create a well-distributed release of KMnO<sub>4</sub> to overcome the lack of lateral dispersion of oxidant. The three-section CRP barriers using a complete mixture of CRP particles with sand were better than the well-based CRP barriers (Lee et al., 2009) in the removal efficiency of higher concentrations of TCE. However, this approach also cannot solve this problem effectively and suggests that an advanced CRP system should be developed in future research.

#### 2.4 Effectiveness of released permanganate on TCE oxidation

In order to further study the effectiveness of released permanganate on TCE oxidation in the experimental column,

the molar ratio of KMnO<sub>4</sub> to TCE after the three-section CRP barriers was calculated (Table 2). The effectiveness of released permanganate on TCE oxidation decreased and the molar ratio of KMnO<sub>4</sub> to TCE increased after each of the three discrete CRP barriers. The molar ratio of KMnO<sub>4</sub> to TCE was 10:1 after the 1st, 20:1 after the 2nd and 42:1 after the 3rd CRP barrier. As noticed in Fig. 1, the TCE concentration at port 1, port 2 and port 3 could be regarded as the initial concentration for the 1st, 2nd and 3rd CRP barriers. It is reasonable that the initial TCE concentration of the first CRP barrier was greater than that of the second, and the second was greater than that of the third in turn. From our previous study (Yuan et al., 2012), the removal rate of TCE increased with the increase of initial TCE concentration, so the removal rate in the first CRP barrier was higher than the other two.

The mean molar ratio of KMnO<sub>4</sub> to TCE after the three-section CRP barriers was 16:1, which is still greater than the ideal stoichiometric ratio of 2:1 (Reaction (4)).



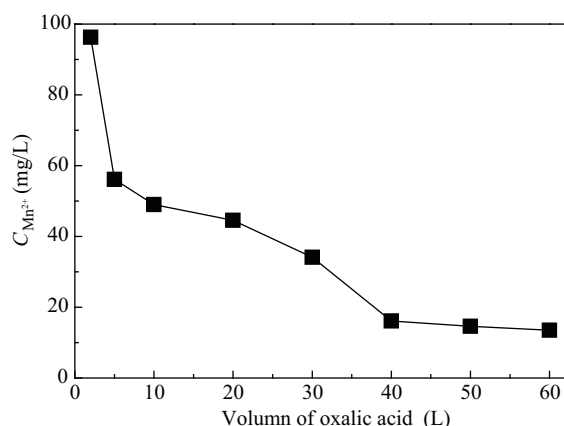
This low efficiency of reaction of KMnO<sub>4</sub> with TCE in the column experiment may be related to three factors. First, the low concentration of TCE after the three-section CRP barriers led to incomplete mixing between released MnO<sub>4</sub><sup>–</sup> and TCE. The second possibility is that the contact time of MnO<sub>4</sub><sup>–</sup> with TCE was not long enough because the column experiment was dynamic and the free water diffusion coefficient (*D*<sub>0</sub>) for TCE is approximately 40% less than that of KMnO<sub>4</sub> (Lide, 2004), which means that the permanganate ions migrate faster than TCE. Third, as we discussed before, lack of lateral spreading of KMnO<sub>4</sub> also contributed to the low usage of KMnO<sub>4</sub> in TCE oxidation. As a result, except for the portion of oxidant that reacted with TCE, the excessive KMnO<sub>4</sub> released from CRP flowed out of the column with the water flow, which

**Table 2** Ratio of the molar of KMnO<sub>4</sub> consumed per molar of TCE degraded in test column\*

Controlled-release oxidant zone	1st	2nd	3rd	3-Section
Consumption of KMnO <sub>4</sub> (mmol)	11.2	10.6	10.6	32.4
TCE removal quantity (mmol)	1.15	0.54	0.25	1.94
The molar ratio of KMnO <sub>4</sub> to TCE	10:1	20:1	42:1	16:1

\* 24 g of CRP with 1:3 of the mass ratio of solid KMnO<sub>4</sub> to stearic acid, 4.2 mg/L of TCE solution.





**Fig. 5** Variation of  $\text{Mn}^{2+}$  concentration after flushing with oxalic acid. Experimental condition:  $C_{\text{oxalic acid}} = 0.016 \text{ mmol/L}$ .

caused loss of oxidant.

In contrast to the direct use of pure  $\text{KMnO}_4$  solution (where the molar ratio of  $\text{KMnO}_4$  to TCE necessary to achieve complete destruction of TCE was 82:1 (Lee et al., 2003)), the efficiency of the oxidant was still highly improved after being encapsulated. Thus, the results from the column study suggested that three-section CRP barriers with encapsulated  $\text{KMnO}_4$  could be a promising technology for partially destroying TCE contaminants in a long-term and controlled manner.

### 2.5 Removal of $\text{MnO}_2$ in test column

With respect to TCE and  $\text{KMnO}_4$  systems, the reaction product  $\text{MnO}_2$  is immobile in non-acidic groundwater and has been found to significantly reduce the soil permeability and oxidation efficiency of TCE (Li and Schwartz, 2004a; Schnarr et al., 1998; West et al., 2008; Loomer et al., 2011). **Figure 5** shows that incomplete destruction of TCE occurred after 15 days and the excess of  $\text{KMnO}_4$  was flushed out of the test column. The experiment was stopped on day 18 due to the lower efficiency of TCE removal and the  $\text{MnO}_2$  precipitates found in the sand medium.

Some literature results reported that  $\text{Na}_2\text{HPO}_4$  and acidic solutions such as oxalic acid or citric acid are commonly used for inhibition or dissolution of produced  $\text{MnO}_2$ . Kao et al. (2008) found that up to 81.5% of  $\text{MnO}_2$  production can be effectively inhibited by the addition of  $\text{Na}_2\text{HPO}_4$  without decreasing the TCE oxidation rate. Li and Schwartz (2004b) found that the dissolution efficiency of  $\text{MnO}_2$  was low when of acidic solution was used to remove  $\text{MnO}_2$ , requiring 20–45 times more acid than that calculated from stoichiometry. The reaction between oxalic acid and  $\text{MnO}_2$  may be written as:



As a cheap and environmentally friendly chemical, oxalic acid was used to remove the reaction product  $\text{MnO}_2$  in this experiment. When the test column stopped running, 0.016 mmol/L oxalic acid was pumped into the column at

10 mL/min flow rate to remove  $\text{MnO}_2$ . As shown in **Fig. 5**, the concentration of  $\text{Mn}^{2+}$  ions decreased to 13.5 mg/L after being flushed by 60 L 0.016 mmol/L of oxalic acid, which was approximately 11 times the pore volume of the column. At 10 mL/min flow rate, it took 100 hr to flush the  $\text{MnO}_2$  precipitates. The result indicated that  $\text{MnO}_2$  could be removed by oxalic acid, but the efficiency was low, which may be due to the heterogeneity and insufficient contact time caused by flow bypassing and poor sweep efficiency (Li and Schwartz, 2004a). In order to minimize the cleanup time and the oxalic acid consumption, the optimum concentration of acid solution and flushing rate should be considered carefully in further study.

### 3 Conclusions

In this study, three-section permeable reactive barriers were built up using CRP particles with 1:3 molar ratio of  $\text{KMnO}_4$  to stearic acid as reactive materials for *in-situ* remediation of a TCE-contaminated aquifer. TCE could be removed completely after flowing through the three-section CRP barriers system for 15 days. The molar ratio of  $\text{KMnO}_4$  to TCE of the three-section oxidant zone was 16:1, which was much lower than that required when using  $\text{KMnO}_4$  solution directly (where the molar ratio of  $\text{KMnO}_4$  to TCE to achieve complete destruction of TCE was 82:1). The efficiency of the oxidant was highly improved after encapsulation due to its controlled release. This suggested that three-section CRP barriers with encapsulated  $\text{KMnO}_4$  would be a promising technology for destroying TCE contaminants in a long-term and controlled manner. After 15 days of reaction time, the efficiency of TCE destruction decreased due to the incomplete mixing and insufficient contact time between released  $\text{KMnO}_4$  and dissolved TCE, and the lack of lateral spreading of released  $\text{KMnO}_4$  into the pore water in the laboratory-scale test column. The advanced CRP barrier should be improved through a series of field applications in further study. Pumping an oxalic acid solution into the column could remove precipitates of  $\text{MnO}_2$ , to some extent.

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