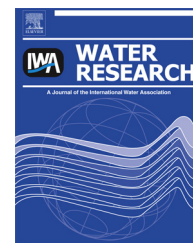


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Development of KMnO_4 -releasing composites for in situ chemical oxidation of TCE-contaminated groundwater

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ABSTRACT

The objective of this study was to develop a controlled-oxidant-release technology combining in situ chemical oxidation (ISCO) and permeable reactive barrier (PRB) concepts to remediate trichloroethene (TCE)-contaminated groundwater. In this study, a potassium permanganate (KMnO_4)-releasing composite (PRC) was designed for KMnO_4 release. The components of this PRC included polycaprolactone (PCL), KMnO_4 , and starch with a weight ratio of 1.14:2:0.96. Approximately 64% (w/w) of the KMnO_4 was released from the PRC after 76 days of operation in a batch system. The results indicate that the released KMnO_4 could oxidize TCE effectively. The results from a column study show that the KMnO_4 released from 200 g of PRC could effectively remediate 101 pore volumes (PV) of TCE-contaminated groundwater (initial TCE concentration = 0.5 mg/L) and achieve up to 95% TCE removal. The effectiveness of the PRC system was verified by the following characteristics of the effluents collected after the PRC columns (barrier): (1) decreased TCE concentrations, (2) increased ORP and pH values, and (3) increased MnO_2 and KMnO_4 concentrations. The results of environmental scanning electron microscope (ESEM) analysis show that the PCL and starch completely filled up the pore spaces of the PRC, creating a composite with low porosity. Secondary micro-scale capillary permeability causes the KMnO_4 release, mainly through a reaction–diffusion mechanism. The PRC developed could be used as an ISCO-based passive barrier system for plume control, and it has the potential to become a cost-effective alternative for the remediation of chlorinated solvent-contaminated groundwater.

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1. Introduction

Subsurface contamination by toxic chemicals is a widespread environmental problem at industrial and waste dumping sites

worldwide (Stroo et al., 2012), and organic chemicals are often the primary contaminants of concern (COCs). Chlorinated organic compounds are commonly found COCs at many contaminated sites, and trichloroethene (TCE) is among the most ubiquitous of chlorinated organic compounds found

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in contaminated groundwater (McCarty, 2010; Baek and Lee, 2011; Lee, 2011).

Chemical oxidation of contaminants is a technology that has been successfully applied to ex situ and in situ treatment of groundwater containing chlorinated organic solvents (West et al., 2008; Huang et al., 2012). Several oxidants, including hydrogen peroxide, Fenton's reagent (hydrogen peroxide combined with ferrous iron), permanganate (MnO_4^-), persulfate, and ozone, are currently used for environmental remediation (Yasunaga and Hirotsuji, 2008; Tsai et al., 2010; Liang et al., 2011; Ildiko et al., 2013). The advantages of applying potassium permanganate (KMnO_4) in the field also include its chemical stability, its cost effectiveness, and its byproducts being less hazardous than those of other oxidants (Woo et al., 2009; Loomer et al., 2011). Potassium permanganate has been used for in situ TCE oxidation in laboratory and field-scale studies (Loomer et al., 2011; Wu et al., 2013). When KMnO_4 is used as the oxidant, TCE breaks down to CO_2 and Cl^- , while MnO_4^- reduces to manganese dioxide (MnO_2) (a solid precipitate) or Mn^{2+} (Loomer et al., 2011).

Permeable reactive barriers (PRBs) have been employed as innovative and cost-effective tools for in situ remediation of contaminated groundwater (Christenson et al., 2012; Yuan et al., 2012). Various reactive materials have been developed and successfully used in PRBs for plume control and contaminant removal (Lee et al., 2009; Semkiw and Barcelona, 2011; Baric et al., 2012). Controlled-release techniques have attracted attention in diverse fields, such as the pharmaceutical and agrochemical industries (Wu, 2008; Lee et al., 2009; Chansanroj and Betz, 2010; Shibata et al., 2010). Biodegradable polymers have been used to make controlled-release materials. Among the commercialized polymers, polycaprolactone (PCL) [$(\text{C}_6\text{H}_{10}\text{O}_2)_n$] has received considerable attention due to its high flexibility and biodegradability, as well as its hydrophobic nature (Sabet and Katbab, 2009; del Valle et al., 2011; Gupta et al., 2012). However, the high production cost of PCL appears to limit its commercial applications. This limitation can be overcome by blending PCL with cost-effective biodegradable natural biopolymers, such as starch, cellulose, and chitin, to create new materials with the desired properties (Campos et al., 2012; Hassan et al., 2012; Ji et al., 2012). Starch is most often used because it is abundant, inexpensive, renewable, and fully biodegradable (Konsoula and Liakopoulou-Kyriakides, 2006). In this study, starch was blended with PCL to modify the physical properties of the controlled-oxidant-release material, including its biodegradability, permeability, and mechanical strength.

A well-based reactive barrier system using KMnO_4 -releasing materials has been developed as a passive scheme for treating a dissolved contaminant plume in groundwater (Kang et al., 2004; Ross et al., 2005; Schwartz, 2005; Lee and Schwartz, 2007; Lee et al., 2009; Christenson et al., 2012; Yuan et al., 2012, 2013). Researchers have used various materials in the design of controlled-oxidant-release systems (Lee et al., 2008a,b; Christenson et al., 2012; Shojaee et al., 2013; Song et al., 2013). The production of slowly released potassium permanganate materials for in situ chemical oxidation has been reported by several researchers (Kang et al., 2004; Lee et al., 2007; Lee and Schwartz, 2007; Lee et al., 2009; Christenson et al., 2012). The encapsulated or wrapping

materials used have included paraffin, polyester mesh bags, Boler wax, Piccolyte resin S115, Epolene C-16, and stearic acid (Kang et al., 2004; Ross et al., 2005; Schwartz, 2005; Lee et al., 2007, 2009; Yuan et al., 2012). However, some of these synthetic materials are restricted in their applicability because they are not highly biodegradable and might be harmful to organisms and the environment. In contrast, PCL materials are generally harmless, nontoxic, biodegradable, and preferable for environmental reasons.

This study examined aspects of using KMnO_4 as the active component of a well-based permeable reactive barrier system. In this system, KMnO_4 -releasing composites (PRCs) were used to create chemically active zones in the subsurface. The composites are PCL– KMnO_4 mixtures and are cylindrical in form. While the reaction kinetics for permanganate oxidation of chlorinated solvents are well documented (Waldemer and Tratnyek, 2006; Urynowicz, 2007), information on their degradation rates at low reagent levels, comparable to the rate of oxidation in treatment schemes using KMnO_4 -releasing materials, are not available in the literature. Thus, a PRC for KMnO_4 release was designed for use in the long-term control of a subsurface contaminant plume, in which contaminants are oxidized by the KMnO_4 released from the PRC.

The main objectives of this study were to design and develop the PRC and test its feasibility for TCE plume control. In this study, TCEs were used as the target compounds, and batch and column studies were conducted to evaluate the feasibility of using a PRC barrier for TCE plume control. In the batch experiments, the components of the PRC and the optimal KMnO_4 release rate were determined. In the column experiments, the effectiveness of the PRC developed in remediating TCE-contaminated groundwater was evaluated. The innovative aspects of the PRC developed and its application include the following. (1) Instead of using a single wrapping material, the PRC is a composite material made of biodegradable PCL and starch. These components can be biodegraded by indigenous microorganisms after use and will not accumulate in the subsurface and ecosystem. Thus, this composite material is more flexible and better suited to field application than systems containing less biodegradable materials. (2) Because the passive PRC barrier system can be employed in situ, it has lower operation and maintenance costs than conventional in situ chemical oxidation systems.

2. Materials and methods

All of the chemicals used in this study were of analytical grade. The TCEs (99.97%, TEDIA Company Inc., Fairfield, Ohio) and potassium permanganate (KMnO_4 , min. 99% Riedel-de Haen, Germany) were of reagent grade and were selected as the target compounds and the oxidant, respectively. Polycaprolactone (molar mass $80,000 \text{ g mol}^{-1}$) was supplied by Solvay Co. (Warrington, England). Starch (27% amylose and 73% amylopectin) was purchased from the Sigma Chemical Corp. (Steinheim, Germany).

In this study, a series of preliminary trial-and-error laboratory tests were conducted to identify an appropriate composition for the mixture (data not shown) (Wang, 2011). The PRC was prepared by blending KMnO_4 , PCL, and starch

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