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Reductive dechlorination and biodegradation of 2,4,6-trichlorophenol using sequential permeable reactive barriers: Laboratory studies

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Abstract

The reductive dechlorination and biodegradation of 2,4,6-trichlorophenol (2,4,6-TCP) was investigated in a laboratory-scale sequential barrier system consisting of a chemical and biological reactive barrier. Palladium coated iron (Pd/Fe) was used as a reactive barrier medium for the chemical degradation of 2,4,6-TCP, and a sand column seeded with anaerobic microbes was used as a biobarrier following the chemical reactive barrier in this study. Only phenol was detected in the effluent from the Pd/Fe column reactor, indicating that the complete dechlorination of 2,4,6-TCP was achieved. The residence time of 30.2–21.2 h was required for the complete dechlorination of 2,4,6-TCP of 100 $\mathrm{mg\,l^{-1}}$ in the column reactor. The surface area-normalized rate constant (k_{SA}) is 3.84 (± 0.48) $\times 10^{-5}\,\mathrm{l\,m^{-2}\,h^{-1}}$. The reaction rate in the column tests was one order of magnitude slower than that in the batch test. In the operation of the biobarrier, about 100 μM of phenol was completely removed with a residence time of 7–8 d. Consequently, the dechlorination prior to biodegradation turns out to increase the overall treatability. Moreover, the sequential permeable reactive barriers, consisting of iron barrier and biobarrier, could be recommended for groundwater contaminated with toxic organic compounds such as chlorophenols.

Keywords: 2,4,6-TCP; Zero-valent iron (ZVI); Palladium coated iron (Pd/Fe); Reductive dechlorination; Biodegradation; Sequential PRBs

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1. Introduction

The groundwater at many industrial sites and disposal areas is contaminated by halogenated aliphatics and aromatics. The chlorinated compounds, more specifically the chlorinated aromatic compounds, are noteworthy for their toxicity and recalcitrant nature in the environment (Ye and Shen, 2004). Chlorophenols are extensively used as wood preservers, pesticides, herbicides, biocides, and dyes.

Several physical, chemical, and biological methods including activated carbon adsorption, incineration, and biological degradation have been proposed for the treatment of chlorinated phenols (Wang et al., 2000). Generally, biological treatment is superior to physicochemical methods because the latter have high treatment costs and possibilities of causing a secondary pollution. However, microorganisms may easily be inhibited by toxic chlorophenols to be treated when conventional biological treatment methods are used (Wang et al., 2000).

One cost-effective approach for the remediation of contaminated soil and groundwater that is attracting increased attention is the installation of permeable reactive zones or barriers within aquifers. As contaminated groundwater moves under natural or induced hydraulic gradients through a permeable reactive zone, the contaminants are scavenged or degraded, and the decontaminated

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groundwater emerges from the downgradient side of the reactive zone (Starr and Cherry, 1994). The passive or semi-passive barrier concept has several advantages over other remediation technologies currently in use (e.g., pump and treat, air sparging, and so on), including lower maintenance costs, treatment *in situ*, and absence of above ground facilities and groundwater reinjection (Kao and Lei, 2000; Scherer et al., 2000).

Zero-valent iron (ZVI) is a readily available permeable reactive barrier (PRB) medium that is cost effective over a long term and has shown encouraging results in the remediation of contaminants from the groundwater (Benner et al., 1999; Phillips et al., 2000). However, ZVI has shown low reactivity for some contaminants including chlorinated aromatics. Chlorophenols and polychlorinated biphenyls have not been as facilely dechlorinated as trichloroethylene (TCE) and perchloroethylene (PCE) by ZVI (Chuang et al., 1995; Morales et al., 2002; Choi, 2004). Palladium-catalyzed iron (Pd/Fe) was used to enhance reactivity, and the dechlorination rate of chlorophenols could be increased by Pd/Fe (Liu et al., 2001; Morales et al., 2002; Choi, 2004; Xu et al., 2005). Another limitation of ZVI for PBR is incomplete clean-up in the case of halogenated aromatics. Although ZVI dechlorinates the halogenated aromatic compounds, the aromatic structure is not destroyed and is still toxic.

In this study, simulated sequential PRBs including chemical and biological reactive barriers were operated for the dechlorination and biodegradation of 2,4,6-trichlorophenol (2,4,6-TCP). Modified ZVI, Pd/Fe, was used as chemical barrier medium, and a sand column seeded with anaerobic microorganisms was used as a biobarrier following the chemical barrier. The main objectives of this study are to evaluate the dechlorination and biodegradation potential of the simulated sequential PRBs on 2,4,6-TCP and to confirm that the dechlorination prior to biodegradation can enhance the overall treatability of chlorophenols.

2. Materials and methods

2.1. Chemicals

Ethyl acetate (99.8%, HPLC grade), methyl alcohol (99.93%, HPLC grade), *p*-xylene (Anhydrous, 99+%), and phenol (loose crystals, 99+%, ACS reagent) were obtained from Sigma–Aldrich, (St. Louis, MO). Hydrochloric acid (37%, ACS grade), sulfuric acid (95–98%, ACS grade), palladium(II) chloride (5 wt.% solution in 10 wt.% HCl), 2,4,6-TCP (98%), 2,6-dichlorophenol (2,6-DCP, 99%), 2,4-dichlorophenol (2,4-DCP, 99%), 4-chlorophenol (4-CP, 99+%), and 2-chlorophenol (2-CP, 99+%) were supplied by Aldrich (Milwaukee, WI). Iron metal powder (electrolytic, finer than 150 μm) was supplied by Fisher Scientific (Fair Lawn, NJ). All chemicals were used as received without further purification. Sand (300–600 μm) obtained from Joomoonjin Silica Sand (Joomoonjin, Korea) was used as the medium of the column reactor. The received sand was washed with deionized water and was oxidized in a muffle oven (550 ± 50 °C) for about 30 min to eliminate organic fraction from the sand before use. The N_2-BET specific surface area of the sand was 0.1537 (±0.0032) $m^2\ g^{-1}$. Deionized water was generated by a Barnstead water purification system (resistivity $\geqslant 17.5\ M\Omega\ cm^{-1}$ and total organic carbon $< 1.0\ mg\ l^{-1}$) and was used in all experiments.

2.2. Biodegradation of 2,4,6-TCP and phenol

To compare the biodegradability of 2,4,6-TCP and phenol, biodegradation experiments were performed in batch bioreactors using mixed cultures. The anaerobic mixed cultures used were the anaerobic digested sludge obtained from the Shincheon municipal wastewater treatment plant in Taegu, Korea. Reagent-grade chemicals were used in nutrient medium preparation (Carr and Hughes, 1998).

The 2,4,6-TCP solution (106, 316, and 706 μM in the nutrient medium) and the phenol solution (119, 303, and 635 μM in the nutrient medium) were prepared. Each prepared solution (95 ml) was transferred to a serum bottle (120 ml), and an anaerobic mixed culture (5 ml) was added to each bottle. After sealing with a Teflon-lined butyl rubber septum and aluminum crimp cap, the solution was vigorously shaken for 30 s and then was allowed to sit quiescently at room temperature (25 °C). Three reaction bottles were prepared for each concentration, and two control bottles excluding the anaerobic mixed culture were also prepared. All the bottles and apparatus were autoclaved before use, and all the experiments were performed in a glove bag (Cole-Parmer Instrument Company) filled with N_2 gas. At each sampling time, 10 ml of the solution was removed from each reaction and control bottle for extraction and quantitative analysis.

2.3. Preparation of palladium-coated iron for column tests

Palladium deposits were spontaneously formed on the iron surface (Grittini et al., 1995; Muftikian et al., 1995). For the preparation of the Pd/Fe, 8.0 ml of the Pd stock solution (5.0 wt.% of Pd in 10% of hydrochloric acid) was diluted to 100 ml with deionized water and then added to 100.0 g of acid-washed iron powder. The contents were placed on a shaking table and were shaken at 180 rpm for 20 min. After that, the mixtures were rinsed with purified water and acetone, and were completely dried in a drying oven (60–65 °C) for 6–7 h and stored in nitrogen atmosphere.

2.4. Column reactor system

The schematic diagram of the column reactor system is shown in Fig. 1. Spectrum chromatography glass columns (2.64 cm i.d. × 30 cm long, Cole-Parmer Instrument