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Remediation of TCE-contaminated aquifer by an in situ three-stage treatment train system

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ABSTRACT

The industrial solvent trichloroethylene (TCE) is among the most ubiquitous chlorinated organic compounds found in groundwater contamination. The developed treatment train system included the first stage of groundwater and surfactant flushing followed by the second stage of potassium permanganate ($KMnO_4$) oxidation. The third stage was the application of enhanced bioremediation stage for the removal of residual TCE after the first two treatment processes. The objectives of this bench-scale study were to (1) assess the applicability of treatment train system for the remediation of TCE-contaminated aquifer, (2) determine the optimal operational conditions of the three-stage treatment system, and (3) evaluate the effects of residual surfactant Simple Green^{TM} (SG) after chemical oxidation stage on the efficiency of bioremediation process. In this study, three different surfactants [SG, Triton X-100, and Tween 80] were evaluated in batch experiments for their feasibility on TCE removal. Results from the surfactant biodegradation and microbial enumeration study indicate that SG was more biodegradable and was able to enhance the microbial activity of the intrinsic microorganisms. Thus, SG was applied in the following batch experiments of the treatment train system. Results from this study indicate that approximately 87.6% of TCE in the system (with initial concentration of 40 mg L^{-1}) could be removed from the simulated dense non-aqueous-phase liquids (DNAPLs) system after groundwater flushing followed by biodegradable surfactant (1 g L^{-1} of SG) flushing, while the TCE concentrations dropped from 40 to 4.96 mg L^{-1} at the end of the flushing experiment. Moreover, approximately 10.7% of the remaining TCE could be removed from the system after the oxidation process using $KMnO_4$ as the oxidant. Results from the oxidation process show that TCE was reduced from 4.96 to 0.69 mg L^{-1}, and chloride concentration was increased from 0 to 0.88 mg L^{-1} with the presence of 1 g L^{-1} of SG. The residual 1.7% of the TCE could be further remediated via the enhanced bioremediation stage, and the TCE concentrations dropped from 0.69 mg L^{-1} to below detection limit at the end of the bioremediation experiment. Results also indicate that the remaining $KMnO_4$ had no significant inhibition on bacterial growth and TCE biodegradation. Thus, SG flushing and $KMnO_4$ oxidation would not cause adverse effect on subsequent bioremediation process using intrinsic bacteria. Thus, complete TCE remediation was observed in this study using the three-stage treatment scheme. The proposed treatment train system would be expected to provide a more efficient and cost-effective alternative to remediate chlorinated solvent contaminated sites.

1. Introduction

Groundwater at many existing and former industrial sites and disposal areas is contaminated by chlorinated organic compounds that were released into the environment. Trichloroethylene (TCE), which is characterized as dense non-aqueous-phase liquids (DNAPLs), is one of the common pollutants in groundwater, and could be significant component of hazardous waste streams [1,2]. The toxic and persistent nature of TCE poses a serious health threat to humans and ecological receptors [3].

Among the various treatment technologies, treatment train system is becoming increasingly popular alternative for the treatment of organic-contaminated soils and groundwater. Two or more innovative and established technologies may be used together in treatment trains, which are either integrated processes or a series of treatments that are combined in sequence to provide the necessary treatment. Some treatment trains are employed when no single technology is capable of treating all the contaminants in a particular medium [4]. In addition, a treatment train might be used to render a medium more easily treatable by a subsequent technology, reduce the amount of waste that requires further treatment

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by a subsequent and more expensive technology, or minimize the overall cost of the treatment [5]. When in situ technologies are used in a treatment train, a more aggressive technology may be applied to remediate areas with high contaminant concentrations or NAPLs (hot spots), followed by application of a less aggressive technology to remediate a larger area that includes the former hot spot area [4]. Among these treatment methods, surfactant flushing, potassium permanganate ($KMnO_4$) oxidation, and enhanced bioremediation have been considered as promising remedial technologies due to their potential for treating TCE-contaminated groundwater [6–10].

Surfactants can increase the solubility of TCE by partitioning them into the hydrophobic cores of surfactant micelles above the critical micelle concentration (CMC). Thus, surfactants are able to improve the mass-transfer of TCE from solid into aqueous phases and the microbial remediation of TCE in groundwater [11–14]. Soil flushing is less time-consuming compared with bioremediation and natural treatment systems (e.g., phytoremediation), which are largely affected by climatic factors. Furthermore, surfactants are useful for the biodegradation of contaminates because they are able to enhance desorption and solubility of hydrophobic compounds. Many studies have been conducted to enhance biodegradation of TCE employing surfactant in contaminated soil and groundwater [15,16]. However, little information is available concerning the effects of surfactants on the enhancement of TCE cometabolism and inhibition of intrinsic bacteria growth [17,18].

Various studies have been conducted to investigate in situ chemical oxidation to remediate TCE within the source zone in subsurface environment. In situ chemical oxidation schemes using $KMnO_4$ have been demonstrated as an effective approach to degrade TCE via an oxidative dechlorination process in contaminated groundwater [19,20]. There is increasing interest in in situ treatment of TCE to utilize oxidant $KMnO_4$ due to the oxidant might migrate by diffusion and degrade TCE within a low permeability media [21]. Chemical oxidation (e.g., $KMnO_4$ oxidation) methods that are used to treat TCE are usually most effective when contaminants are present in the dissolved phase. Therefore, effective oxidation of TCE in DNAPL phases are highly dependent on the mass-transfer mechanism between aqueous and DNAPL phases. Accelerated oxidation of a contaminant in the aqueous phase (e.g., reducing the aqueous contaminant concentration) could lead to an increase in the concentration gradient for the contaminant (e.g., DNAPL dissolving into the aqueous phase). Hence, treatment of the contaminants where DNAPLs are present would be limited by low solubilities of target contaminants [22]. The ability of applying surfactant to enhance dissolution and desorption of organic compounds is well known. Surfactant-enhanced solubility has led to the development and use of surfactant flushing as a chlorinated organic compounds source remediation technology. However, contaminants are not destroyed during flushing, thus requiring $KMnO_4$ oxidation. The merits of surfactant addition during the remediation of chlorinated organic compounds contaminated groundwater might include enhancing $KMnO_4$ mass transfer, augmenting oxidation efficiency, and preventing MnO_2 clogging problem [16,19].

The term "enhanced bioremediation" encompasses a broad continuum of technologies that differ with respect to their inputs [23]. These technologies may involve the addition of electron acceptors, inorganic nutrients, carbon supplementation such as biodegradable surfactant to stimulate naturally occurring microbial populations (biostimulation) or could introduction of specific microorganisms to enhance the biodegradation of the target compound (bioaugmentation) [10,24,25].

In this study, an in situ three-stage remedial system consisting of groundwater and surfactant flushing followed by $KMnO_4$ oxidation process and enhanced bioremediation has been investigated to treat TCE-contaminated aquifer. The main objectives of this study included the following: (1) assessment of the applicability of combining surfactant flushing, $KMnO_4$ oxidation, and enhanced bioremediation for the remediation of TCE-contaminated aquifer, (2) determination of the optimal operational conditions of the three-stage treatment system, and (3) evaluation of the effects of residual surfactant SG after $KMnO_4$ oxidation stage on the efficiency of bioremediation process.

2. Materials and methods

2.1. Characteristics of soil and groundwater

The tested soil and groundwater were sampled from a background and uncontaminated area of a TCE-spill site in Taiwan. The soil sample was air-dried, passed through a 2-mm sieve and stored in closed containers at room temperature prior to use. The pH was measured using a mixture of soil and deionized water (1:1, w/v) with a glass electrode of a pH meter (Tow MP120 pH meter, Mettler-Toledo). Other analytical procedures of the site groundwater were described in Standard Methods [25]. Results reveal that the tested soils had a sandy loam texture (50% sand, 40% silt, and 10% clay). The soil organic matter content and pH (1:1 H_2O) were approximately 1.1% and 5.4, respectively. The groundwater contained the following components at the specified concentrations (units are in mg per liter of water): H_2PO_4, 326.4; Na_2HPO_4, 1263.8; $Mg_2SO_4 \cdot 7H_2O$, 98.6; $CaCl_2 \cdot 2H_2O$, 44.1; NH_4Cl, 10.7; plus 3.35 mg of trace elements which include $FeSO_4 \cdot 7H_2O$, 1; $MnSO_4 \cdot 4H_2O$, 1; $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 0.25; $Na_2B_4O_7 \cdot 10H_2O$, 0.25; $CoCl_2 \cdot 6H_2O$, 0.25; $CuCl_2 \cdot 2H_2O$, 0.25; $ZnCl_2$, 0.25; NH_4VO_3, 0.1 [26].

2.2. Surfactant selection study

Three major objectives of this surfactant selection study included: (1) evaluation of the surfactant solubilization, (2) evaluation of the effects of applied surfactant on TCE biodegradation, and (3) selection of appropriate surfactant for TCE-contaminated aquifer flushing. Three non-ionic surfactants were used in the surfactant selection experiment including Simple Green^{TM} (SG), Triton X-100, and Tween 80. Surfactant SG was purchased from Sunshine Makers, Inc. (USA), and Triton X-100 and Tween 80 were purchased from J.T. Baker, Inc. (USA). The properties such as critical micelle concentration (CMC) and hydrophile–lipophile balance (HLB) were taken into consideration during the selection and were shown in Table 1. The HLB [calculated as HLB = %wt. EO (Ethylene Oxide)/5] were 13.4 for Tween 80, 13.6 for Triton X-100, and 15.0 for SG. The

Table 1
Chemical and physical properties of selected commercial surfactants

Compound	Molecular formula	MW ($g\,mol^{-1}$)	CMC (mM)	HLB	Cost (US$ L^{-1})
SG	$HOCH_2H_2O{-}(CH_2)_3CH_3$	88	9.43	15.0	7.8
Triton X-100	$C_8H_{17}C_6H_4O(CH_2CH_2O)_nH$	625	0.24	13.6	30.3
Tween 80	$C_{18}H_{37}S_6^*(OC_2H_4)_{20}OH$	1309	0.012	13.4	30.3

n: average value of *n* is 9.5. S_6^*: a sorbitan ring $-C_6H_9O_5-$.