

Influence of mixed-surfactant on reductive dechlorination of trichloroethylene by zero-valent iron

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Abstract—Mixed nonionic and cationic surfactants were used to enhance the reductive dechlorination rate of trichloroethylene (TCE) with zero valent iron (ZVI). Among tested combinations of four cationic and three nonionic surfactants, a mixed surfactant system of hexadecyl-trimethyl ammonium (CTAB) and Brij30 at a mixing ratio of 1 : 1 with 0.5 critical micelle concentration (CMC) exhibited the highest reaction rate constant, 0.0269 h^{-1} ; the dechlorination rate constant of TCE with ZVI in the absence of surfactant was 0.0206 h^{-1} . The effect of this mixed surfactant on the reductive dechlorination of TCE was investigated using ZVI in a column to simulate field conditions. Unlike batch tests, column tests of the mixed surfactant system exhibited higher and lower TCE removal as compared to a nonionic and a cationic surfactant system, respectively. Consequently, if surfactants are applied for surfactant-enhanced aquifer remediation (SEAR), the performance of a permeable reactive barrier (PRB) system using ZVI to remove the residual TCE in groundwater might be affected by surfactant types; thus, the application should be carefully considered.

Key words: Dechlorination, Mixed Surfactant, Reductive Rate Constant, Trichloroethylene, Zero-valent Iron

INTRODUCTION

A permeable reactive barrier (PRB) is a slurry wall filled with a reactive material to remediate contaminated groundwater [1,2]. Dissolved contaminants are transported to the PRB by groundwater flow and are removed as they pass through the barrier. Generally, PRBs have been used to treat contaminants, including chemical fertilizers, light non-aqueous phase liquids (LNAPLs), dense non-aqueous phase liquids (DNAPLs), heavy metals and radioactive wastes [1-5]. A PRB is a passive system that depends on ground water flux and velocity to remediate contaminated groundwater. If a proper reactive medium is selected for remediation, a PRB system could be applied to remove various contaminants from groundwater. A reactive medium should be chosen based on field characteristics and contaminants [6]. The major reactions in a PRB are precipitation, biodegradation, sorption and oxidation-reduction [1,2]. Precipitation is a solidification process for the removal of heavy metals from groundwater. Sorption is one of the chemical and physical mass transfer methods from an aqueous stream to a solid surface. Oxidation-reduction is applied to the removal of inorganic contaminants or halogen organic compounds in groundwater.

A surfactant is an amphiphilic compound that has molecules with hydrophilic and hydrophobic properties, and it can be used to increase the solubility of DNAPLs in groundwater. Surfactant-enhanced aquifer remediation (SEAR) is a flushing and recovery technology

used to increase the aqueous solubility of DNAPL components and reduce interfacial tension to increase the rate of DNAPL extraction [7]. After the application of SEAR, small amounts of the surfactant and dissolved DNAPL still exist in the groundwater. However, most researches on dissolved contaminants have focused on contaminant removal by PRB in the absence of surfactant [8-11]. Thus far, there have been few reports on the performance of a PRB system with a surfactant and trichloroethylene (TCE) mixture. It is necessary to evaluate a PRB system for treating TCE in the presence of a surfactant. After the SEAR application, the residual surfactant in the groundwater influences the adsorption of TCE onto ZVI and increases or decreases TCE reductive dechlorination using ZVI in the PRB reaction. Fig. 1 shows a conceptual diagram for a PRB system in the presence of a surfactant after SEAR applications.

Recently, various studies on the effect of surfactants on the treatment of chlorinated organic compounds using ZVI have been reported [12-14]. According to Cho and Park [13], increasing the TCE adsorption to ZVI with a surfactant promoted TCE dechlorination using ZVI. In the case of a cationic surfactant, the temporary electrostatic interaction between the electronegative chlorine group in the TCE and the cationic head group of the surfactant enhanced the adsorption and reduction of TCE on ZVI [12]. It was also reported that a non-toxic, nonionic surfactant decreased the TCE removal rate [15]. More recently, a study was carried out on the use of mixed surfactants to remove chlorinated organic compounds [14]. A cationic surfactant is not usually used in the SEAR process because the charge of soil surface is generally negative and the surfactant is easily adsorbed in the soil particles. However, a recent study has

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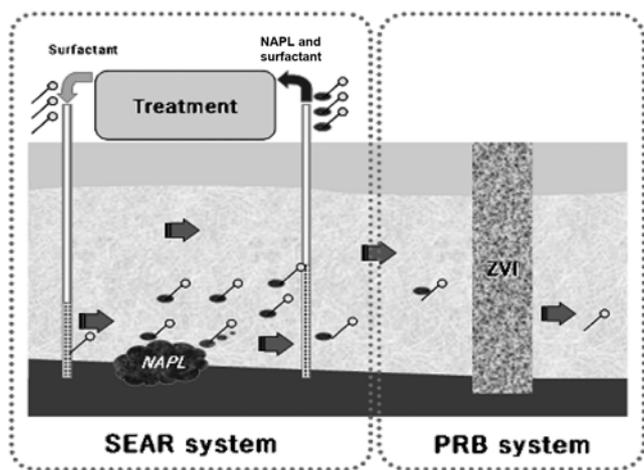


Fig. 1. Conceptual diagram of ideal SEAR-PRB composition system.

shown that cationic surfactants can be used to increase the organic carbon content of aquifer materials, creating enhanced sorbent zones for organic contaminants migrating in groundwater [16]. Recently, Zhao et al. [14] reported that mixed surfactants would be preferred over single surfactants for solubilization remediation of NAPL because the nonionic surfactant partitioning to NAPL was minimized in a mixed surfactant system. This means that the mixed surfactant could be released to groundwater with organic solvents after SEAR. Additionally, a cationic surfactant is more toxic than an anionic or a nonionic surfactant [17]. A mixed surfactant could reduce the CMC of the cationic surfactant [18], implying that the amount of surfactant used could be reduced.

We investigated a mixed surfactant system that combined cationic and nonionic surfactants to reduce the toxicity of the cationic surfactant and increase the reduction rate. In an attempt to develop an optimum mixed surfactant system, this study investigated the effect of a cationic-nonionic mixed surfactant on the reductive dechlorination of TCE by ZVI in relation to the surfactant types and mixing ratio. A column test was also performed to evaluate the feasibility of using the system in the field.

MATERIALS AND METHODS

1. Materials

A TCE stock solution was prepared by diluting 10% (V/V) TCE (99.5%, Sigma-Aldrich, USA) in methanol (J. T. Backer, USA). ZVI was obtained from Junsei (Japan) with a particle size of less than 100 mesh (<0.15 mm) and was used without further purification or treatment. The BET surface area of the ZVI was 0.5 m² g⁻¹. The cationic surfactants used in this study were 1-dodecylpyridinium chloride (DPC, Sigma-Aldrich), dodecyltrimethyl ammonium chloride (DTAC, Fluka), cetylpyridinium chloride (CPC, Sigma-Aldrich), and cetyltrimethyl ammonium bromide (CTAB, Sigma-Aldrich). The nonionic surfactants used in this study were polyoxyethylene (4) dodecyl ether (Brij30, B30), polyoxyethylene (10) lauryl ether (Brij36, B36), and polyoxyethylene (10) cetyl ether (Brij56, B56) from Sigma-Aldrich. The estimated EC₅₀ values of DPC and CPC for *Acinetobacter junii*, which is a phosphate accumulating

bacterium, growth inhibition were $7.3 \pm 2.6 \times 10^{-5}$ mol L⁻¹ and $4.9 \pm 1.3 \times 10^{-7}$ mol L⁻¹, respectively, when that of sodium dodecyl sulfate, an anionic surfactant, was $5.00 \pm 2.95 \times 10^{-6}$ mol L⁻¹ [19,20].

The TCE concentration was analyzed using high-performance liquid chromatography (HPLC, Agilent 1100, USA) equipped with a UV detector at 210 nm, along with a symmetry C₁₈ reverse phase column (Waters, USA). The mobile phase was 60% acetonitrile and 40% pure water and the flow rate was 1 mL min⁻¹. The detection limit of TCE concentration measured by HPLC/UV was 0.03 mg L⁻¹.

2. Batch System

22-ml open-top screw vials with Teflon septa were used for the experiments. Mixed surfactant solutions of 0.5 CMC were prepared at two cationic/nonionic surfactant molar ratios (2 : 8 and 5 : 5) in deionized water; the solutions were adjusted to a pH of 3.0 using HCl. 0.5 CMC of surfactant was used because cationic surfactants enhanced the dechlorination rate of TCE at a concentration below CMC compared to pure ZVI [21], whereas concentrations above CMC inhibited the dechlorination of chlorinated solvents [22]. It was assumed that the CMC of the mixed surfactant was comparable to that of the nonionic surfactant because this similarity has been reported when the molar ratio of the nonionic surfactant was greater than 0.5 in the mixed surfactant [23]. This assumption was applied to different combinations of cationic and nonionic surfactants. 2 g of ZVI and 20 mL of mixed surfactant solutions were added to the vials, which were capped with the Teflon septa. All the vials were then spiked with the TCE stock solution (1,000 mg L⁻¹ in methanol) using a microsyringe, resulting in an initial TCE concentration of 36.4 mg L⁻¹. The vials were agitated for 96 h at 20-30 rpm on an over-end shaker (AG FINEPCR, Korea). Samples were taken from each vial at specific sampling times (0 h, 1 h, 5 h, 10 h, 24 h, 48 h, 72 h, and 96 h). The samples were centrifuged for 10 min at 3,000 rpm, and the supernatant was transferred to a 2-ml vial without a headspace. The TCE concentration in the aqueous phase was analyzed by HPLC. All of the experiments were performed at 20 °C in the laboratory and carried out in triplicate.

The dechlorination of TCE by ZVI was assumed to be a pseudo-first-order kinetic reaction. The reaction rate can be calculated by the following equation [24-26]:

$$\ln(C/C_0) = -kt \quad (1)$$

where C is the concentration (mg L⁻¹) of the TCE in the solution phase at any time t ; C_0 , the initial concentration (mg L⁻¹); t , the reaction time (h); and k , the observed rate constant (h⁻¹). The degradation rate constant for the amount of available surface area can be described by

$$k_{sA} = k/(A_s \cdot \rho_m) \quad (2)$$

where k_{sA} is the specific rate constant (h⁻¹ m⁻² L); A_s , the specific surface area of ZVI (m² g⁻¹); and ρ_m , the mass concentration of ZVI (g L⁻¹).

3. Column System

Five glass columns (Pyrex) were prepared, each with a length of 250 mm and a diameter of 15 mm. One column packed with glass beads was used as a control test using deionized water as a flushing solution. Columns 1, 2, 3 and 4 were packed with ZVI and the flushing solutions were deionized water, CTAB (0.5 CMC), Brij 36 (0.5

CMC) and a mixture of CTAB and Brij36 (0.5 CMC with surfactant molar ratio of 2 : 8), respectively. The inlet and outlet ports were filled with glass fibres and the columns were packed with 85 g of ZVI. Silicon stoppers were used to cap the tops of the columns. Because TCE is volatile at normal temperatures, a Tedlar bag without head space was used to minimize the loss of TCE by volatilization.

The TCE concentration was adjusted to 4.0-5.5 mg L⁻¹ in a Tedlar bag. Deionized water was circulated in each column for 24 h to saturate the inside of the column, after which the surfactant solutions containing the TCE were made to flow into the bottom of the columns. The influent and effluent TCE concentrations were measured from samples taken at the inlet and outlet ports, respectively. The flow rate was maintained at approximately 0.38-0.43 mL min⁻¹ for 150 h in an early stage and then increased to 0.733-0.876 mL min⁻¹. The dechlorination of TCE by ZVI was assumed to be a pseudo-first-order kinetic reaction. All of the analytical methods and calculations for the reaction rate constant followed the procedures described for the batch system. In case of the mixed surfactant system, CATB and Brij56 system was tested to evaluate its effectiveness.

RESULTS AND DISCUSSIONS

1. Batch System

Fig. 2 and Fig. 3 show the removal efficiency and the reductive

rate of TCE. Table 1 shows a summary of the reduction rate constants for the TCE in the experiments using the various mixed surfactant systems. The TCE reduction rate constant was estimated for a mixed surfactant concentration of 0.5 CMC. In the presence of a mixed surfactant of DPC and Brij30, Brij36 and Brij56, the cationic surfactant ratio affected the TCE reduction rate constant. The reduction rate constant at a cationic to nonionic surfactant ratio of 2 : 8 was slightly lower than that at a 5 : 5 ratio. At a 5 : 5 ratio, the reduction rate was higher than that in the absence of a surfactant. The mixed surfactant of DPC and Brij36 with a higher hydrophilic-lipophilic balance (HLB) decreased the TCE dechlorination rate, whereas other mixed surfactant systems did not affect the dechlorination. It appears that a high concentration of surfactant inhibited the adsorption between TCE and ZVI in the interface between the aqueous phase and the solid surface [15].

In the presence of low concentrations of 0.5 CMC mixed surfactants of CPC and Brij30, Brij36 and Brij56, the TCE dechlorination rate increased. The TCE reduction rate constant was also shown to increase more substantially at a low cationic surfactant ratio. Therefore, a mixed surfactant of CPC and Brij enhanced the TCE dechlorination and a higher reduction rate constant was shown for a low-concentration solution of the mixed surfactant.

In the presence of low concentrations of 0.5 CMC mixed surfactants of DTAC and Brij30, Brij36 and Brij56, the TCE reduc-

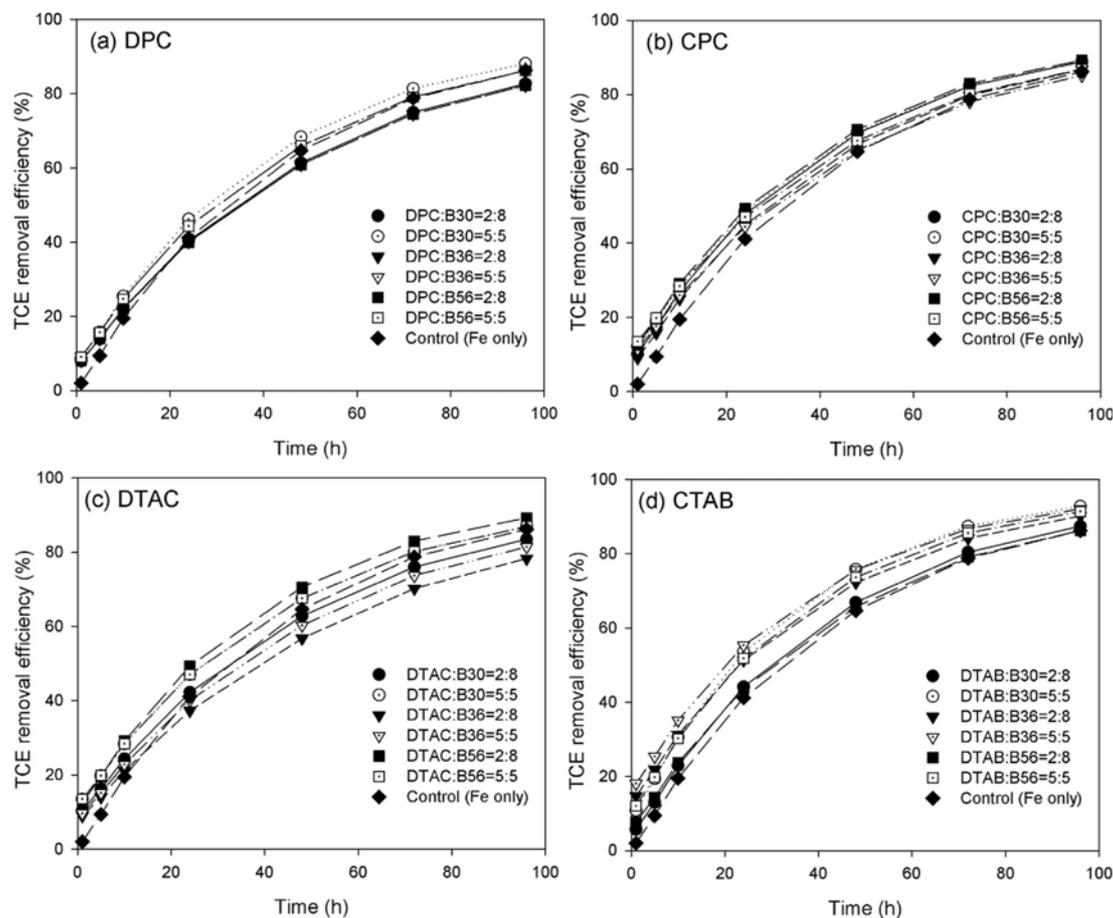


Fig. 2. TCE removal efficiency with ZVI in the presence of mixed surfactant using (a) DPC, (b) CPC, (c) DTAC, and (d) CTAB and B30, B36, and B56 in batch system.

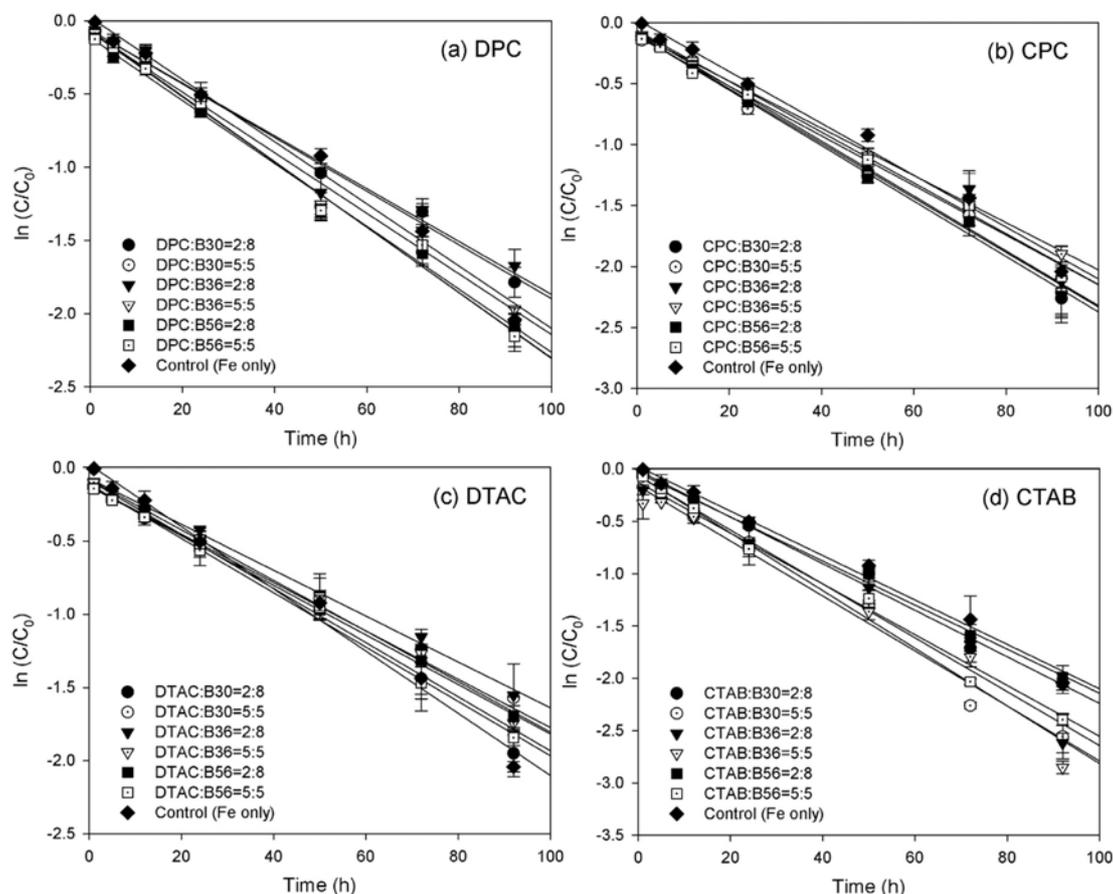


Fig. 3. TCE degradation kinetics with ZVI in the presence of mixed surfactant using (a) DPC, (b) CPC, (c) DTAC, and (d) CTAB and B30, B36, and B56 in batch system.

Table 1. Summary of rate constants in the dechlorination of TCE by ZVI in presence of low concentration surfactants

| Conditions | k^a | $k_{sA}^b (\times 1000)$ | Conditions | k^a | $k_{sA}^b (\times 1000)$ | | |
|------------|--------|--------------------------|------------|------------|--------------------------|--------|--------|
| Control | 0.0206 | 0.0048 | Control | 0.0206 | 0.0052 | | |
| DPC : B30 | 2 : 8 | 0.0183 | 0.0043 | DTAC : B30 | 2 : 8 | 0.0176 | 0.0041 |
| | 5 : 5 | 0.0224 | 0.0053 | | 5 : 5 | 0.0158 | 0.0037 |
| DPC : B36 | 2 : 8 | 0.0180 | 0.0042 | DTAC : B36 | 2 : 8 | 0.0149 | 0.0035 |
| | 5 : 5 | 0.0207 | 0.0049 | | 5 : 5 | 0.0165 | 0.0039 |
| DPC : B56 | 2 : 8 | 0.0215 | 0.0051 | DTAC : B56 | 2 : 8 | 0.0161 | 0.0038 |
| | 5 : 5 | 0.0223 | 0.0052 | | 5 : 5 | 0.0176 | 0.0041 |
| CPC : B30 | 2 : 8 | 0.0229 | 0.0054 | CTAB : B30 | 2 : 8 | 0.0216 | 0.0051 |
| | 5 : 5 | 0.0227 | 0.0053 | | 5 : 5 | 0.0269 | 0.0063 |
| CPC : B36 | 2 : 8 | 0.0212 | 0.0050 | CTAB : B36 | 2 : 8 | 0.0237 | 0.0056 |
| | 5 : 5 | 0.0196 | 0.0046 | | 5 : 5 | 0.0256 | 0.0060 |
| CPC : B56 | 2 : 8 | 0.0231 | 0.0054 | CTAB : B56 | 2 : 8 | 0.0205 | 0.0048 |
| | 5 : 5 | 0.0207 | 0.0049 | | 5 : 5 | 0.0249 | 0.0059 |

^aRate constant (Unit: h^{-1})

^bSurface area normalized rate constants (Unit: $\text{h}^{-1} \text{m}^{-2} \text{L}$)

tion rate constant decreased. Except for the DTAC-Brij30 mixed surfactant, the TCE reduction rate constant increased with an increase in the cationic surfactant ratio; however, the change in the rate constant was not significant. Therefore, the effect of the DTAC-Brij mixed surfactant on the reductive dechlorination of TCE using

ZVI was not significant, but was similar to the effect of Brij alone.

In the presence of low concentrations of 0.5 CMC mixed surfactants of CTAB and Brij30, Brij36 and Brij56, the TCE reduction rate constant increased. The TCE reduction rate constant was very high for the 0.5 CMC mixed surfactants of CTAB. The effect

of the mixed surfactants of CTAB and Brij strongly depended on the CTAB molar ratio. Though a system with CTAB/Brij30 ratio of 5 : 5 exhibited the highest reduction rate, the use of CTAB/Brij30 ratio of 2 : 8 was preferred due to the toxicity of the cationic surfactant.

Each mixed surfactant system exhibited slightly different TCE reduction rate constants as a function of the cationic/nonionic surfactant ratio and surfactant types. The reaction rate constant (k_{red}) of TCE was calculated to be $4.8 \times 10^{-6} \text{ h}^{-1} \text{ m}^{-2} \text{ L}$ in the control experiment without surfactant. The reaction rate constants of TCE were $4.2\text{--}5.3 \times 10^{-6}$, $4.6\text{--}5.4 \times 10^{-6}$, $3.5\text{--}4.1 \times 10^{-6}$ or $4.8\text{--}6.3 \times 10^{-6} \text{ h}^{-1} \text{ m}^{-2} \text{ L}$ in the presence of mixed surfactants of DPC, CPC, DTAC, or CTAB and nonionic surfactants, respectively. Surfactants increase the reaction rate constants according to the order CTAB, CPC, DPC and DTAC. The highest reaction rate constant was achieved in the presence of CTAB and Brij mixed surfactants. CTAB and Brij might form an ideal structure at the interface between the aqueous phase and the ZVI solid surface [27,28]. This structure was also found in the surfactant and activated carbon system [29]. The surfactant is sorbed at the surface of ZVI and the surface becomes hydrophobic. Aqueous TCE is partitioned onto the ZVI surface and the dechlorination of TCE occurs readily. If the concentration of surfactant is above CMC, aqueous TCE is competitively partitioned onto both the ZVI surface, which is modified by the surfactant, and the surfactant micelle. This implies that the dechlorination of TCE by ZVI is affected by surfactant types and concentration as well as surfactant adsorption onto the ZVI surface. In addition, Cho and Park [13] reported that adsorption of cationic and anionic surfactants onto the ZVI surface was higher than that of nonionic surfactants. The reaction rate constants in 5 : 5 mixed surfactants were higher than those in 2 : 8 mixed surfactants. This result indicates that since the adsorbed amount of nonionic surfactant onto the ZVI surface was low, the partitioned TCE onto the ZVI surface was also low.

2. Column System

To evaluate the TCE loss while passing through the column, the TCE concentration was measured at the inlet and outlet of a column filled with glass beads. After 500 pore volumes (PVs), the inlet and

outlet concentrations were similar. This result suggests that there was no loss in the column. Even though the flow rate of each column was fixed, the flow rate was changed by the pump status. The flow rate of each column was measured every day. The flow rate was maintained at approximately $0.38\text{--}0.43 \text{ mL min}^{-1}$ for 150 h during the early stage and subsequently increased to $0.733\text{--}0.876 \text{ mL min}^{-1}$.

Fig. 4 shows the results of an investigation on the effect of the deionized water flow on the TCE reduction by ZVI. At 3000 PV, the flow rate increased and caused the residence time of the TCE in the column to decrease. As a result, the outlet concentration increased sharply. The effluent concentration was maintained below 0.8 mg L^{-1} when the influent concentration was 4.0 mg L^{-1} . After 3500 PV, when the flow rate was increased to 0.73 mL min^{-1} in the ZVI column, the concentrations of the influent and effluent were maintained at 5.3 mg L^{-1} and 2.95 mg L^{-1} , respectively.

To investigate the effect of the nonionic surfactant on TCE reduction by ZVI, the TCE solution with Brij36 was passed through the ZVI column at a flow rate of 0.43 mL min^{-1} and an analysis was performed on the influent and effluent sampled at different times. The TCE concentration in the influent was 4.0 mg L^{-1} and remained at this level during the early stage, whereas the effluent was maintained at 2.0 mg L^{-1} . After 4000 PV, when the flow rate was increased to 0.87 mL min^{-1} in the ZVI column, the concentrations of the influent and effluent were maintained at 5.5 mg L^{-1} and 4.2 mg L^{-1} , respectively. The TCE reduction rate for the nonionic surfactant decreased as compared to the control experiment. To investigate the effect of the cationic surfactant on TCE reduction by ZVI, the TCE solution with CTAB was passed through the ZVI column at a flow rate of 0.38 mL min^{-1} , and an analysis was performed on the influent and effluent sampled at different times. The effluent exceeded 3500 PV after 150 h. The influent TCE concentration was 4.2 mg L^{-1} and remained at this level during the early stage, whereas the effluent was maintained at $0.2\text{--}0.4 \text{ mg L}^{-1}$. The concentrations of the influent and effluent were maintained at 5.1 mg L^{-1} and 2.5 mg L^{-1} , respectively, when the flow rate in the ZVI column was increased to 0.83 mL min^{-1} . The TCE reduction rate for the cationic surfactant increased as compared to the control experiment.

To investigate the effect of the mixed surfactant on TCE reduction by ZVI, the TCE solution with the 2 : 8 CTAB/Brij36 ratio was passed through the ZVI column at a 0.41 mL min^{-1} flow rate, and an analysis was performed on the influent and effluent sampled at different times. The effluent exceeded 4,000 PV after 150 h. The TCE concentration of the influent was 4.0 mg L^{-1} and was maintained during the early stage, whereas the effluent was maintained at 1.4 mg L^{-1} . The concentrations of the influent and effluent were maintained at 5.5 mg L^{-1} and 3.5 mg L^{-1} , respectively, when the flow rate in the ZVI column was increased to 0.84 mL min^{-1} .

The TCE reduction rate of the mixed surfactant was found to be lower than the rate of the control experiment. This differs from the batch test result. The TCE reduction rates in the column tests had the following order: cationic surfactant > control > mixed surfactant > nonionic surfactant. In the batch system, the cationic surfactant, nonionic surfactant, TCE and ZVI were well-mixed, but not so in the column system. In addition, the continuous supply of mixed surfactant solution to ZVI might enhance desorption of TCE from the ZVI surface. Sorbed surfactant on ZVI can have various effects on TCE reduction. Because surfactants promote solubilization, sorp-

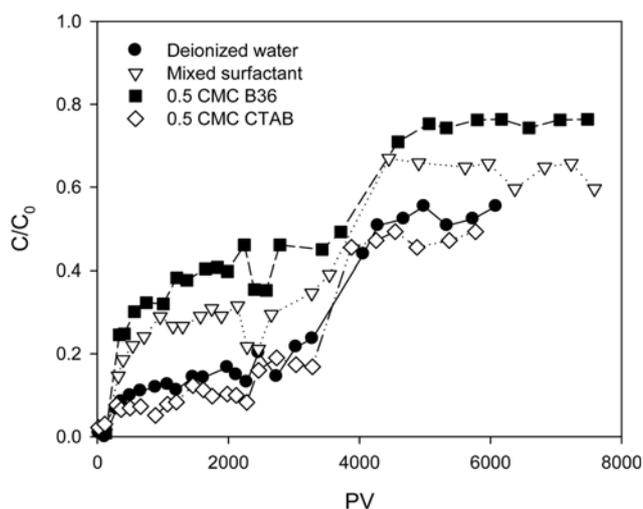


Fig. 4. Reduction efficiency of TCE in column system. Mixed surfactant was CTAB/Brij36 of 2 : 8 mixed surfactant solution.

tion and reaction, they may enhance and inhibit TCE degradation [27]. In this study, the cationic surfactants enhanced TCE degradation, whereas the nonionic surfactants did not. The adsorption of the nonionic surfactants on ZVI might be low and the remaining surfactant concentration in the aqueous phase was high. This leads to the reduction of TCE partitioning onto the ZVI surface. In addition, as compared to the cationic surfactant, the larger nonionic surfactant can block the reactive sites. Zhu et al. [30] reported that the large natural organic matter (NOM) molecule might block the reactive sites of Pd/Fe nanoparticles for the dechlorination of trichlorobenzene. Therefore, the dechlorination of chlorinated hydrocarbons was significantly inhibited in the NOM solutions.

CONCLUSIONS

The effect of 0.5 CMC mixed surfactant on TCE reductive dechlorination by ZVI was evaluated as a reactive medium of PRB. Mixed surfactants were prepared from cationic and nonionic surfactants because cationic surfactants have been found to enhance the TCE reduction by ZVI and nonionic surfactants are non-toxic. The mixed surfactant of CTAB and Brij30 was found to most significantly enhance the reductive dechlorination of TCE by ZVI.

The effect of mixed surfactants on the reductive dechlorination of TCE was investigated using ZVI in a column to simulate field conditions. In this case, the cationic surfactant was more efficient than the control. This coincided with the results of the batch experiments. Even though the mixed surfactant exhibited a higher reduction rate than the control in the batch experiment, the column experiment showed that the TCE reduction rate of the mixed surfactant was lower than those for the cationic surfactant and the control. Consequently, if surfactants are applied for SEAR to remove the residual TCE in groundwater, the performance of a PRB system using ZVI might be affected by surfactant types; thus, the application should be carefully considered.

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NOMENCLATURES

A_s : the specific surface area [$\text{m}^2 \text{g}^{-1}$]
 B30 : Brij30, polyoxyethylene (4) dodecyl ether
 B36 : Brij36, polyoxyethylene (10) lauryl ether
 B56 : Brij56, polyoxyethylene (10) cetyl ether
 C : the concentration of TCE [mg L^{-1}]
 C_0 : the initial concentration of TCE [mg L^{-1}]
 CMC : critical micelle concentration
 DNAPL : dense non-aqueous phase liquids
 CPC : cetylpyridinium chloride
 CTAB : cetyltrimethyl ammonium bromide
 DPC : 1-dodecylpyridinium chloride
 DTAC : dodecyltrimethyl ammonium chloride
 HPLC : high-performance liquid chromatography
 k : the observed rate constant [h^{-1}]

k_{SA} : the specific rate constant [$\text{h}^{-1} \text{m}^{-2} \text{L}$]
 LNAPL : light non-aqueous phase liquids
 NOM : natural organic matter
 PRB : permeable reactive barrier
 PV : pore volume
 SEAR : surfactant enhanced aquifer remediation
 t : time [h]
 TCE : trichloroethylene
 UV : ultraviolet
 ZVI : zero valent iron
 ρ_m : the mass concentration [g L^{-1}]

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