

The effect of ionic strength and hardness of water on the non-ionic surfactant-enhanced remediation of perchloroethylene contamination

Eun-Sik Kim^a, Dal-Heui Lee^a, Byoung-Woo Yum^b, Ho-Wan Chang^{a,*}

^a School of Earth and Environmental Sciences (BK21), College of Natural Sciences, Seoul National University, Sillim 9-dong, Gwanak-gu, Seoul 151-747, Republic of Korea

^b Groundwater Resource Group, Korea Institute of Geoscience and Mineral Resources, 30 Gajeong-dong, Yuseong-gu, Daejeon 305-350, Republic of Korea

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Abstract

The objective of this study is to evaluate the perchloroethylene (PCE) removal by an aqueous surfactant solutions based on influential factors (ionic strength, hardness) of various groundwaters and surface waters contaminated with PCE. The experimental methods used in this study were separatory funnel experiments and batch experiments. Separatory funnel experiments were performed to determine which surfactants are good solubilizers for PCE. Batch experiments were performed to evaluate the effect of ions in sampled water for PCE removal. The results of separatory funnel experiments indicated that the surfactant polyoxyethylene (20) sorbitan monostearate (Tween 60) showed to be a predominant solubilizer for the removal of PCE (87.3%). Separatory funnel experiments also showed that the hydrophilic–lipophilic balance (HLB) number and the chemical structure of the surfactants were good indicators of surfactant effectiveness for removal of PCE from water. The results of batch experiments showed that non-ionic surfactants are affected by the ionic strength of sampled water. The % of PCE removal of the Tween 60 surfactant solution was measured to be 88.3% by batch experiments. This result was affected by the characteristics of the surfactant (HLB, chemical structures) and the ionic strength of water. Therefore, the ionic strength of contaminated water, HLB and chemical structures of surfactants must be considered in surfactant-enhanced remediation.

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1. Introduction

Soil and water (groundwater, surface water) contamination by PCE has caused significant concern in industrial areas. PCE has been used in industrial and commercial applications such as metal degreasing, the cleaning of electronic components, and dry cleaning. PCE contaminates aquifers through its infiltration into the under the groundwater table because of its higher density. PCE can persist as a long-term source of contamination in soils and water due to its low aqueous

solubility and slow rates of dissolution [1,2]. From the viewpoint of motion, gravity and capillary forces are the main physical parameters of PCE migration in subsurface environments [3]. Many papers published on the study of remediation dealt with issues of PCE by vapor extraction methods or bioremediation [4,5]. A pump-and-treat method was frequently evaluated by many researchers [6,7] and it used for a conventional remedial method of contaminated water. Especially, the pump-and-treat method is a treatment technology to remediate groundwater contaminated by organic materials. Treatment methods (air stripping, steam stripping, activation by carbon filtration, etc.) are differently applied according to target compounds or field configurations [8–11]. Moreover, denser-than-water nonaqueous-phase liquids (DNAPLs) are difficult to remediate from aquifers because these compounds

* Corresponding author. Tel.: +82 2 880 6734/6742; fax: +82 2 872 7643/880 6742.

E-mail addresses: changhow@snu.ac.kr, euntico@hanmail.net (H.-W. Chang).

tend to remain in a separate phase [12]. The pump-and-treat method is limited by parameters such as water flow rates, the organic material's composition, mass transfer rates, and the surface area available for mass transfer of constituents [13–15].

Surfactant-enhanced remediation techniques for removing PCE from soil and groundwater are now receiving a lot of attention [16]. Moreover, surfactants can help the extraction of organic contaminants from an aquifer by reducing the interfacial tension between DNAPLs and groundwater, and by increasing the solubility of the contaminants. A surfactant molecule contains a hydrophilic head and a hydrophobic tail. The hydrophilic head is a polar moiety, which has an affinity for water and the other polar substances, while the hydrophobic tail is nonpolar moiety [17]. The tail, usually a long hydrocarbon acts to reduce solubility in water while the hydrophilic head has opposite effect [18]. Surfactants enhance the remediation of PCE-contaminated sites by increasing the PCE's aqueous phase concentration via micelle/emulsion formation. Surfactants are able to improve the mass transfer of hydrophobic pollutants from solids [19]. The unique amphiphilic structures and properties of surfactants are able to be applied in many areas. Therefore, surfactants are widely used for solubilization/mobilization purposes in agricultural and industrial areas.

In recent years, surfactant-enhanced remedial methods have been employed to remove PCE from contaminated groundwater [20]. Results from several laboratory studies on the use of surfactants for washing hydrophobic contaminants from soils have shown that this enhanced washing method has a good potential [13,21]. Results collated from many papers showed the % of PCE removal [5] between 33 and 85% and total petroleum hydrocarbon (TPH) recoveries between 60 and 90% [22]. Published papers on surfactant research reformulated deionized water in their experiments [3,10,13,15,18] and field tests [23]. Natural water (groundwater, surface water) has various anions and cations that affect the forming of surfactant micelles. Also, the ionic strength of natural water affects its activity. Therefore, more laboratory work is needed to understand the factors affecting PCE removal using surfactant. The objective of this study was to evaluate the % of PCE

removal of different aqueous non-ionic surfactant solutions based on ionic strength and hardness of various groundwaters and surface waters contaminated with PCE.

2. Materials and methods

2.1. Materials

Four different surfactants – POE (polyoxyethylene) (20) sorbitan monolaurate (Tween 20), POE (20) sorbitan monopalmitate (Tween 40), POE (20) sorbitan monostearate (Tween 60) and POE (20) sorbitan monooleate (Tween 80) – were used in this study. Tween series surfactants (Tween 20, Tween 40, Tween 60, Tween 80) are non-ionic surfactants, which have been noted for their unfavorable tendency of sorption to aquifer solids, and low critical micelle concentration (CMC). Non-ionic surfactants do not have any ionic group of dissociated in the solution of contaminant materials. Tween 20 had 12 carbons in a hydrophobic moiety named “laurate” and Tween 40 had 16 carbons in a hydrophobic moiety named “palmitate”. Tween 60 and Tween 80 each have 18 carbons, but are different in their organic saturation. Their nomenclatures were “stearate” and “oleate”, respectively. These surfactants were selected because they have a similar HLB number but different hydrophobic moieties. In addition, their carbon structures are different. For example, Tween 60 has a saturated organic carbon bonding and Tween 80 has an unsaturated organic carbon bonding. Tween series surfactants were purchased from Yakuri Chemicals, Japan. The characteristics of Tween series surfactants are shown in Table 1, and their chemical structures are shown in Fig. 1. Tween 60 was in a gel state and the other surfactants were in liquid states at room temperature. The PCE used in this study was an analytical-grade reagent. The molecular weight of PCE ($\text{Cl}_2\text{C}=\text{CCl}_2$) is 165.83 g/mol and its density and aqueous solubility are 1.6227 g/ml and 150 mg/l, respectively. PCE (>99% purity) was purchased from Merck Chemical, USA.

The separatory funnel experiments used deionized water that was distilled with a Milli-Q distillation system (Milli-

Table 1
The characteristics of Tween series surfactants

Commercial name	Tween 20 ^a	Tween 40 ^a	Tween 60 ^a	Tween 80 ^a
Chemical name	Polyoxyethylene (20) sorbitan monolaurate	Polyoxyethylene (20) sorbitan monopalmitate	Polyoxyethylene (20) sorbitan monostearate	Polyoxyethylene (20) sorbitan monooleate
Molecular weight (g/mol)	1227.5	1283.6	1311.7	1309.7
Density (g/ml)	1.11	1.10	1.07	1.06
CMC ^b (mM)	0.05	0.04	0.02	0.04
HLB ^c	16.7	15.6	14.9	15
Type	Nonionic	Nonionic	Nonionic	Nonionic
Phase	Liquid	Liquid	Gel	Liquid

^a Data from MSDS (Material Safety Data Sheets).

^b CMC: critical micelle concentration.

^c HLB: hydrophile–lipophile balance.

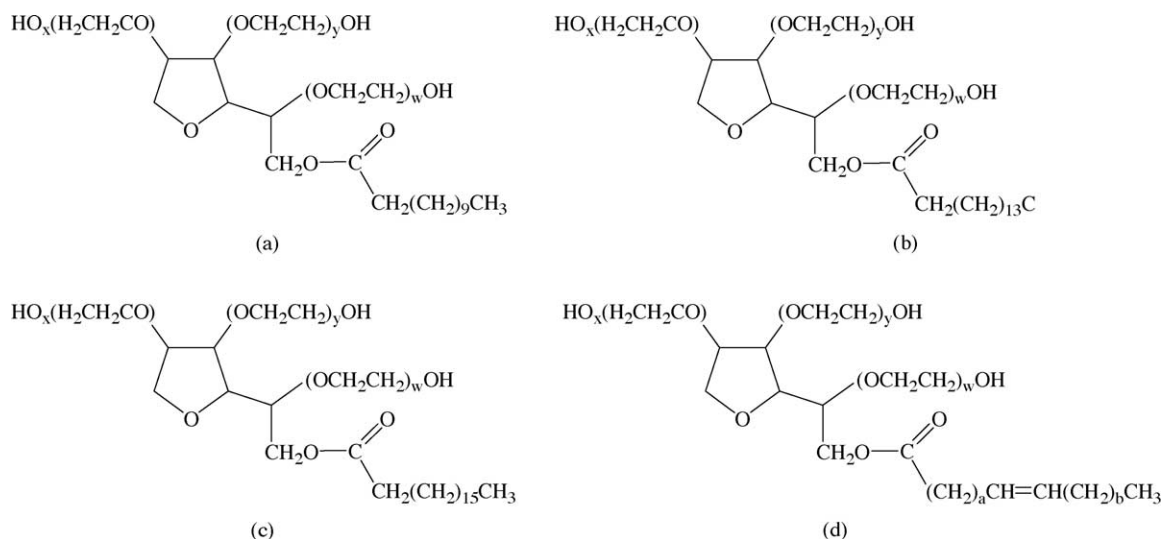


Fig. 1. Chemical structures of test surfactants: (a) polyoxyethylene (20) sorbitan monolaurate, (b) polyoxyethylene (20) sorbitan monoplamitate, (c) polyoxyethylene (20) sorbitan monostearate and (d) polyoxyethylene (20) sorbitan monooleate.

pore). The groundwater and surface water used for batch experiments originated from Yeongwol, Gangwon, Korea. Samples 1 and 4 were shallow groundwater from a granite bedrock and they had a high nitrate concentration because they were contaminated by an anthropogenic source (Table 2). The difference between sample 1 and sample 4 was in their ionic strength value. Sample 4 had the highest ionic strength value in sampled water due to local geology. Samples 2 and 3 were deep groundwater from a shale-sandstone bedrock and a limestone bedrock, respectively. Samples 5, 6 and 7 were surface water from a tributary of the south Han-river. Ordovician limestones and Permian carboniferous coal-bearing sedimentary rocks are widely distributed in the study area. Moreover, the limestones are locally skarnized by intrusion of the Mesozoic granites. Sampled groundwater and surface water properties are presented in Table 2.

2.2. Ionic strength and hardness

To interpret the results, the ionic strength of groundwater and surface water samples was calculated. The results of ionic strength and hardness are shown in Table 2. Ionic strength and hardness were calculated by the equation [24] and their C_i unit were mmol/l and mg/l, respectively.

2.3. Experimental procedures

The experimental methods used in this study were separatory funnel experiments and batch experiments. Separatory funnel experiments provided a rapid, qualitative and fairly reliable methods for determining which surfactants were good solubilizers [25]. Sample solutions were prepared in a constant temperature laboratory for separatory

funnel experiments. The concentrations of the used surfactants were 10% (v/v) for selected surfactants (50 ml) (Tween 20, Tween 40, Tween 60 and Tween 80). We took the high concentration of surfactants because of fast distributions of mixed solution in a separatory funnel during the test. PCE (15 ml) was chosen as a model contaminant. Deionized water volume was 150 ml. Three liquids (deionized water, contaminants and surfactant solutions) were added to a 500-ml beaker at once and stirred for 1 h. Then, the mixed solutions were put into separatory funnels and placed on stands for 90 h at constant room temperature. During the 90 h, the mixed solutions separated into different layers, namely an aqueous layer and an organic layer. After 90 h, acquired samples from the aqueous and organic layers were diluted with *n*-hexane for analysis by gas chromatography.

Batch experiments in this study considered the characteristics of groundwater and surface water, such as ionic strength and hardness. Both a rotary shaker table (GFL-TUV product service, Germany) and a centrifugal separator (Biofuge pico-Heraeus instruments, Germany) were used in these experiments. Batch experiments with 28 samples were conducted in glass vials (Wheaton) sealed with Teflon films. Twenty-eight samples are shown in Table 3. The 20-ml sample vials contained 4.6 ml of surfactant solution (Tween series surfactant), 1.4 ml of contaminants (PCE) and 14 ml of sampled groundwater or surface water. The vials were stirred on a rotary shaker table (100 rpm) at room temperature (23 ± 2 °C) for 144 h. The organic concentration of the aqueous layer was measured four times at 18, 36, 72 and 144 h. At the selected times, the vials were removed from the shaker table and centrifuged at 10,000 rpm for 7 min. The centrifuged samples were transferred into a gas tight syringe for analysis by gas chromatog-

Table 2
The characteristics of sampled groundwater and surface water

Number	Water	T ($^{\circ}\text{C}$)	pH	DO^{a}	EC^{b}	Eh^{c} (mV)	F (mg/l)	Cl (mg/l)	NO_3 (mg/l)	SO_4 (mg/l)	Alk ^d (meq)	Ba (mg/l)	Ca (mg/l)	Fe (mg/l)	K (mg/l)	Mg (mg/l)	Na (mg/l)	Si (mg/l)	Sr (mg/l)	Ionic strength (mM)	Hardness (mg/l)
Sample 1	Groundwater 1	16.7	6.52	4.55	203.4	455.1	0.07	24.27	49.93	8.70	0.47	0.011	23.2	0.015	1.39	4.09	7.64	6.27	0.152	4.63	74.77
Sample 2	Groundwater 2	18.1	6.88	2.75	343.2	574.1	0.15	35.19	46.38	4.77	1.78	0.028	42.8	0.004	1.06	7.06	4.69	5.19	0.172	6.18	135.94
Sample 3	Groundwater 3	15.0	7.27	2.87	276.5	475.1	0.19	9.13	5.44	6.55	2.41	0.275	43.9	0.015	4.76	9.06	3.58	3.76	0.268	5.68	146.93
Sample 4	Groundwater 4	14.1	6.75	4.38	670.6	373.1	0.13	49.70	52.16	14.26	1.88	0.007	43.3	0.004	3.75	7.22	85.4	7.83	0.423	8.56	137.85
Sample 5	Surface water 1	18.5	8.16	7.92	350.0	243.0	0.17	16.27	22.58	49.31	1.27	0.017	50.8	0.015	2.75	11.3	2.68	2.62	0.285	6.39	115.13
Sample 6	Surface water 2	20.6	8.62	8.96	225.0	230.0	0.09	9.31	11.70	11.81	1.58	0.015	35.8	0.004	1.64	6.25	2.72	1.21	0.200	3.99	57.78
Sample 7	Surface water 3	21.1	8.77	7.43	134.0	164.0	0.09	10.14	10.66	4.15	0.89	0.015	19.0	0.009	2.06	2.51	3.91	2.09	0.076	2.62	209.15

^a DO: dissolved oxygen.

^b EC: electrical conductivity ($\mu\text{S}/\text{cm}$).

^c Eh: oxidation–reduction potential.

^d Alk: alkalinity.

raphy. Each batch experiment yielded a data set of the % of PCE removal of non-ionic surfactants versus experimental time.

2.4. Analytical methods

Prior to the analysis of samples by gas chromatography, a calibration curve was prepared. The quantitative determination of PCE concentrations was based on internal standard reference compounds, so that sample peak areas could be compared with those of their respective internal standards [26]. A Tekmar 3000 Purge and Trap concentration instrument (Tekmar, USA) coupled on-line with the GC system and equipped with a Supelco's BTEX trap, was used to extract the samples. A HP 6890 series gas chromatograph (Agilent technologies, USA) equipped with flame ionization detector (FID) was used for GC-FID analysis. Helium was used as the carrier gas, and chromatographic separation was performed in a HP-VOC capillary column. Signal acquisition was performed using the HP Chemstation program (Agilent technologies, USA). *n*-Hexane was used as a solvent to calibrate the quantitative analysis of the gas chromatography.

Table 3
The characteristics of test solutions in batch experiments

	Water (14 ml)	Contaminant (1.4 ml)	Surfactants (4.6 ml)
1	Groundwater 1	PCE ^a	Tween 20 ^b
2	Groundwater 1	PCE	Tween 40 ^c
3	Groundwater 1	PCE	Tween 60 ^d
4	Groundwater 1	PCE	Tween 80 ^e
5	Groundwater 2	PCE	Tween 20
6	Groundwater 2	PCE	Tween 40
7	Groundwater 2	PCE	Tween 60
8	Groundwater 2	PCE	Tween 80
9	Groundwater 3	PCE	Tween 20
10	Groundwater 3	PCE	Tween 40
11	Groundwater 3	PCE	Tween 60
12	Groundwater 3	PCE	Tween 80
13	Groundwater 4	PCE	Tween 20
14	Groundwater 4	PCE	Tween 40
15	Groundwater 4	PCE	Tween 60
16	Groundwater 4	PCE	Tween 80
17	Surface water 1	PCE	Tween 20
18	Surface water 1	PCE	Tween 40
19	Surface water 1	PCE	Tween 60
20	Surface water 1	PCE	Tween 80
21	Surface water 2	PCE	Tween 20
22	Surface water 2	PCE	Tween 40
23	Surface water 2	PCE	Tween 60
24	Surface water 2	PCE	Tween 80
25	Surface water 3	PCE	Tween 20
26	Surface water 3	PCE	Tween 40
27	Surface water 3	PCE	Tween 60
28	Surface water 3	PCE	Tween 80

^a PCE: tetrachloroethylene.

^b Tween 20: polyoxyethylene (20) sorbitan monolaurate.

^c Tween 40: polyoxyethylene (20) sorbitan monopalmitate.

^d Tween 60: polyoxyethylene (20) sorbitan monostearate.

^e Tween 80: polyoxyethylene (20) sorbitan monooleate.

n-Hexane was purchased from Mallinckrodt, USA. The GC column was cleaned after every 20 samples.

3. Results and discussion

3.1. Separatory funnel experiments

A total of 90 h runs were completed during the separatory funnel experiments. The variations in the volume of the layers during 90 h are shown in Table 4 and Fig. 2. Table 4 shows that PCE volume of each layer in separatory funnel and the % of PCE removal after 90 h. This removal was calculated from PCE's absolute quantity volume and percentage showed that the ratio of initial volume of PCE and residual volume of PCE. Fig. 2 is the photograph of the initial and final steps using Tween 60 and Tween 40 surfactants in separatory funnel experiments. In these experiments, PCE degradation products such as trichloroethylene (TCE), dichloroethylene (DCE), vinyl chloride (VC), and evaluated chloride ions were not observed during the experimental periods. As a result, the organic layer showed a much larger variable range than the aqueous layer when the mixture had reached equilibrium

Table 4
The results of separatory funnel experiments after 90 h

Sample	Layer	PCE volume (ml)	PCE removal (%)
Tween 20 + PCE	Organic layer	11.8	78.7
	Aqueous layer	2.7	
Tween 40 + PCE	Organic layer	12.2	81.3
	Aqueous layer	2.4	
Tween 60 + PCE	Organic layer	13.1	87.3
	Aqueous layer	1.6	
Tween 80 + PCE	Organic layer	12.0	79.8
	Aqueous layer	2.4	

state. The organic layer was supposed to need a number of surfactant monomers in building up the micelle. The decreased volume of PCE solutions were 13.8% of organic layer and 2.4% of aqueous layer as average. These total volumes contained the volume of macro- and micro-micelles. Each of them could be estimate the equilibrium states. Fig. 3 shows the % of PCE removal by surfactant solutions in separatory funnel experiments. The % of PCE removal means that $[(\text{PCE concentration in the surfactant solution})/(\text{initial PCE concentration in water})] \times 100$. Such results could be anticipated on the basis of the physical or chemical characteristics of the

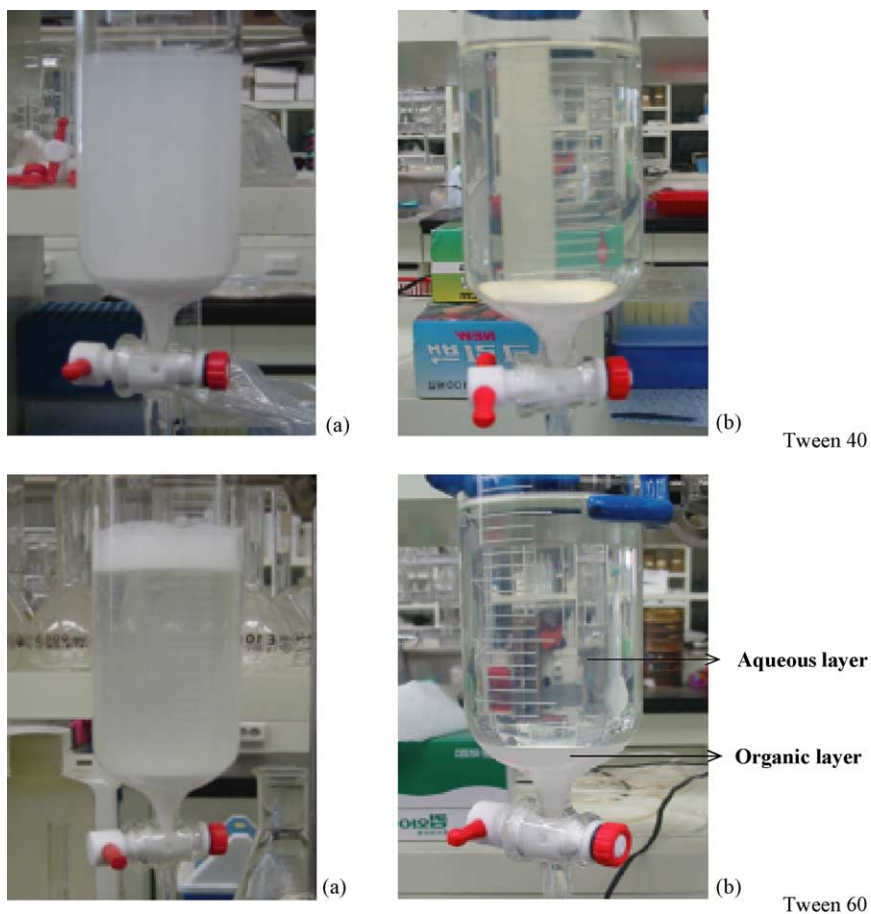


Fig. 2. The variation of layer (aqueous layer, organic layer) in separatory funnel experiments (Tween 40, Tween 60): (a) initial time (0h) and (b) finish time (after 90h).

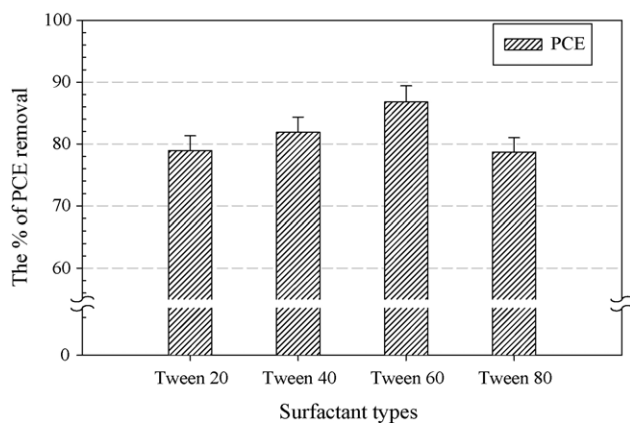


Fig. 3. The % of PCE removal by non-ionic surfactant in separatory funnel experiments.

surfactant types. In comparison of surfactants' removal ability, Tween 60 was the best result of PCE removal. For this result, there were many factors affecting the extent of the surfactant's solubilization. Factors may include the structure of the surfactant, CMC value, HLB number, temperature, pH and ionic strength [27]. Tween series surfactants in non-polar solvents possess low critical micelle concentration values. In considering Tween series surfactants' removal, Tween 60 had the highest the % of PCE removal than others. Tween 40 showed the second high the % of PCE removal and Tween 20 and Tween 80 have almost equal value of PCE removal. Using visual observation, there were no differences of solubility between Tween 60 and Tween 40, but gas chromatography analyses showed different results in each layer, due to the chemical structure of the hydrophobic moiety [27]. The HLB number of a surfactant could be calculated from their structural group [28]. The molecular structure and the HLB number of the surfactants were found to be essential in determining their solubilization power for the hydrophobic olubilizates [27,28]. The hydrophobic solubility meant the hydrophobicity. The hydrophobicity of surfactants could be roughly estimated from its HLB number [25,27,28]. In aqueous solutions, surfactants with lower, but not too low HLB numbers, will tend to form micelles that contain a more hydrophobic environment in their cores. The HLB number of surfactants showed from 14.9 to 16.7. Rosen [27] suggested that the HLB numbers were low for hydrophobic surfactants and high for hydrophilic surfactants. The effects of surfactant HLB number on the % of PCE removal in Tween 20, Tween 40 and Tween 60 solutions are shown in Fig. 4. Tween 80 was excluded from the plots because Tween 80 surfactant differed in the chemical bonding of its hydrophobic moiety. Results in Fig. 4 show a decrease in the % of PCE removal with an increase in HLB number of non-ionic surfactants. Tween 80 also had approximately HLB number 15, and 18 organic carbons. The difference between Tween 60 and Tween 80 was the degree of saturation in organic carbons. Tween 60 was composed of a saturated organic carbon chain and Tween 80 had an unsaturated organic carbon chain in hy-

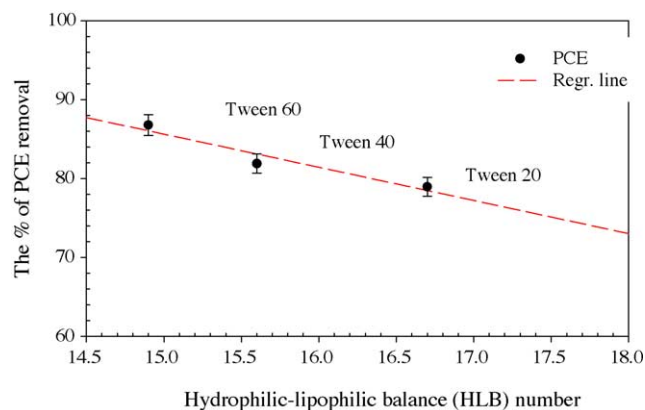


Fig. 4. Relation of HLB number and the % of PCE removal by Tween 20, Tween 40 and Tween 60 surfactants in separatory funnel experiments.

drophobic moiety. The % of PCE removal of these surfactants showed remarkable difference in experimental results. In these cases, the results were consistent with references to the % of PCE removal being correlated with the degree of saturation, and it could explain the result of the experiments. Surfactant molecules of hydrophobic moiety were thought to be correlated with surfactants' removal. In these separatory funnel experiments, it could be used to estimate the equilibrium states of Tween surfactant solutions and to evaluate the chemical structures affected to equilibrium states.

3.2. Batch experiments

Batch experiments were conducted to evaluate ionic effect (ionic strength and/or hardness) of groundwater and surface water in surfactant-enhanced remediation. Sampled groundwater and surface water showed the difference of ionic distribution. The chemical compositions of the water samples used are shown in Table 2. The groundwater and surface water samples showed major chemical ion (Cl^- , Na^+ , Ca^{2+} , NO_3^- , SO_4^{2-} , HCO_3^- , Mg^{2+}) distribution and these major ions comprised more than 90% of the sampled water composition. Results of these experiments were analyzed for the % of PCE removal in each surfactant solution. Generally, the results showed similar trends to the separatory funnel results. Tween 40 and Tween 60 had the equilibrium state at 36 h and Tween 20 and Tween 80 had the equilibrium state at 72 h. These trends were attributed to aqueous solubility within surfactant micelles. The removal of contaminants by the surfactant solution is shown in Table 5 and Fig. 5.

The trend of ionic strength magnitude in the sampled water corresponded to the trends of the % of PCE removal in Tween series surfactant solutions. These results are shown in Fig. 6. The micelle formation theory of non-ionic surfactant is that the hydrophilic moieties in non-ionic surfactant are dissolved into water, because hydrophilic moieties of non-ionic surfactant contained oxygen or the hydroxy group ($-\text{OH}$), which is easy to bond with hydrogen in water [28]. The ionic strength of aqueous phase had a strong effect on activity,

Table 5
The % of PCE removal of Tween series surfactant solutions in batch experiments

Water type	Surfactant	PCE removal (%)				
		0 h	18 h	36 h	72 h	144 h
Groundwater 1	Tween 20	0.0	66.7	75.1	75.0	75.4
	Tween 40	0.0	72.1	77.7	79.6	78.6
	Tween 60	0.0	76.4	79.8	79.7	80.1
	Tween 80	0.0	70.4	73.4	74.0	74.7
Groundwater 2	Tween 20	0.0	73.7	77.4	79.0	79.5
	Tween 40	0.0	76.5	80.7	81.0	81.4
	Tween 60	0.0	80.1	84.6	85.4	86.6
	Tween 80	0.0	71.1	76.5	78.5	78.7
Groundwater 3	Tween 20	0.0	70.6	73.1	76.9	77.5
	Tween 40	0.0	74.6	76.7	77.3	77.9
	Tween 60	0.0	78.4	81.9	82.7	83.1
	Tween 80	0.0	73.9	74.1	77.6	78.1
Groundwater 4	Tween 20	0.0	77.1	79.8	80.7	81.4
	Tween 40	0.0	78.9	80.1	82.4	83.5
	Tween 60	0.0	85.4	87.1	88.2	88.3
	Tween 80	0.0	76.1	78.2	80.7	81.4
Surface water 1	Tween 20	0.0	69.7	75.8	77.4	78.9
	Tween 40	0.0	74.1	76.8	79.8	81.5
	Tween 60	0.0	78.9	81.6	83.9	85.7
	Tween 80	0.0	70.9	74.8	77.4	79.4
Surface water 2	Tween 20	0.0	71.0	73.5	74.9	75.1
	Tween 40	0.0	74.2	75.1	76.8	77.4
	Tween 60	0.0	74.6	77.4	79.0	79
	Tween 80	0.0	69.4	70.5	72.4	73.7
Surface water 3	Tween 20	0.0	67.7	69.8	71.9	72.9
	Tween 40	0.0	70.6	72.9	74.1	74.7
	Tween 60	0.0	72.0	73.9	76.4	77.6
	Tween 80	0.0	70.4	72.7	73.8	74.4

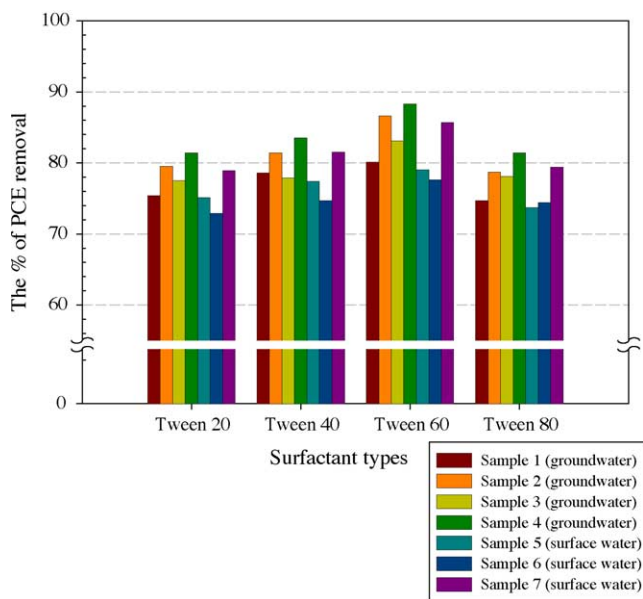


Fig. 5. The % of PCE removal by non-ionic surfactants solution in batch experiments after 144 h.

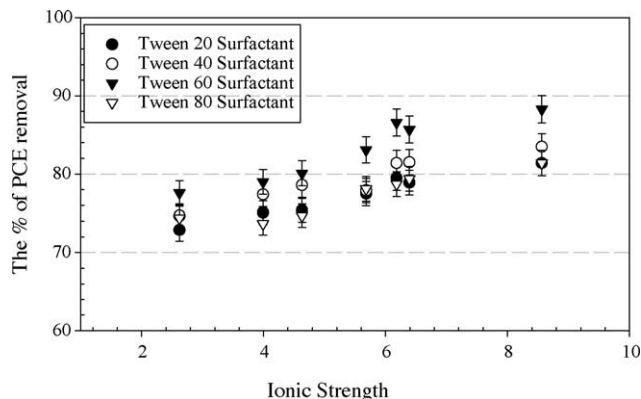


Fig. 6. Relation of the % of PCE removal by differences of ionic strength.

which decreased when ionic strength was increased. When the activity was decreased, the formation of hydrogen bonding between the water molecules and the hydrophilic moiety was weakened, so that solubilization by surfactant solution was increased. Solubilization by surfactant solution meant the forming micelles [27]. The trend of the % of PCE removal in Tween series surfactants showed a similar trend with ionic strength. However, when these results were compared with the hardness value of the sampled water, there was no correspondence with the trends of ionic strength. In the case of hardness differences, the % of PCE removal was affected by cation concentration and it affected to anionic surfactants' removal ability [29]. Also, Mezzanotte et al. [30] and Stasiuk and Schramm [31] suggested that a non-ionic surfactant was not affected by hardness and the CMC was determined by surfactant in different hardness. Because the hydrophilic ions of anionic surfactants were converted into anionic hydrated ions and a suitable quantity of inorganic cations in aqueous phase could improve the solubilization capacities of anionic surfactants. In addition, the % of PCE removal in anionic surfactants considered counter-ion effects. Almost all anionic surfactants have a Na^+ ion or cation in the hydrophilic moiety. This Na^+ ion affects the counter-ion that dissociated into the aqueous solution. Rosen [27] suggested the addition of electrolytes to an anionic surfactant solution decreases the CMC, increases the aggregation number and increases micelle size. Moreover, Bystryak et al. [32] reported an unusual increase in conductivity upon the binding of anionic to weak polyelectrolytes, which was attributed to an enhanced mobility of the Na^+ counter-ions. In accordance with these experiments results, non-ionic surfactants were more influenced by ionic strength in water than water hardness.

4. Conclusions

Separatory funnel experiments on PCE removal were performed at the constant temperature laboratory using non-ionic surfactants and distilled water. These experiments were designed to evaluate the solubilization capacity of non-ionic surfactants by different chemical structures. Moreover, these

experiments show that the partitioning ability of surfactants by similar HLB value. Experimental results show that the Tween 60 surfactant has the highest removal of PCE and its value is about 87.3% of the initial PCE concentration. Also, this non-ionic surfactant has clear partitioning patterns during the 90-h experimental times. That means that solubilization by surfactant solution for aqueous solution was higher than Tween series surfactants (Tween 20, Tween 40 and Tween 80) that were used in this experiment.

In batch experiments, various groundwater and surface waters were used to indicate the ionic effect for surfactant remediation. The results of batch experiments confirm the effects of ionic strength in sampled water and the % of PCE removal by non-ionic surfactants in the presence of residual PCE. The results showed that high ionic strength value was related to high PCE removal. In the similar results of separatory funnel experiments, Tween 60 has the best % of PCE removal in various sampled water. Its highest PCE removal was 88.3% when ionic strength of sampled water was 8.56 mM. In addition, Tween 40, Tween 20 and Tween 80 also showed high PCE removal when ionic strength values were high, but they had different % of PCE removal according to their aqueous solubility resulted from separatory funnel experiments. This is because, the ionic strength of water could effect on activity, which decreased when ionic strength was increased. When the activity was decreased, the formation of hydrogen bonding between the water molecules and the hydrophilic moiety of surfactants was weakened, so that surfactant aqueous solubility was increased. The results of these experiments demonstrate that surfactant choice for PCE remediation of water is important, and suggest the information that must be considered about ionic distributions in target water.

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References

- [1] B. Conant Jr., J.A. Cherry, R.W. Gillham, A PCE groundwater plume discharging to a river: influence of the streambed and near-river zone on contaminant distributions, *J. Contam. Hydrol.* 73 (2004) 249–279.
- [2] H. Rosenthal, L. Adrian, M. Steiof, Dechlorination of PCE in the presence of Fe⁰ enhanced by a mixed culture containing two dehalococoides strains, *Chemosphere* 55 (2004) 661–669.
- [3] V. Jain, A.H. Demond, Conductivity reduction due to emulsification during surfactant enhanced-aquifer remediation. I. Emulsion transport, *Environ. Sci. Technol.* 36 (2002) 5426–5433.
- [4] J.-C. Chai, N. Miura, Field vapor extraction test and long-term monitoring at a PCE contaminated site, *J. Hazard. Mater.* 110 (2004) 85–92.
- [5] C.M. Kao, S.C. Chen, J.Y. Wang, Y.L. Chen, S.Z. Lee, Remediation of PCE-contaminated aquifer by an in situ two-layer biobarrier: laboratory batch and column studies, *Water Res.* 37 (2003) 27–38.
- [6] D.M. Mackay, R.D. Wilson, M.J. Brown, W.P. Ball, G. Xia, D.P. Durfee, A controlled field evaluation of continuous vs. pulsed pump-and-treat remediation of a VOC-contaminated aquifer: site characterization, experimental setup, and overview of results, *J. Contam. Hydrol.* 41 (2000) 81–131.
- [7] E. Küster, F. Dorusch, C. Vogt, H. Weiss, R. Altenburger, On line biomonitors used as a tool for toxicity reduction evaluation of in situ groundwater remediation techniques, *Biosens. Bioelectron.* 19 (2004) 1711–1722.
- [8] D.M. Mackay, J.A. Cherry, Groundwater contamination: pump and treat remediation, *Environ. Sci. Technol.* 23 (1989) 630–635.
- [9] P.A. Forsyth, E.A. Sudicky, Discrete wellbore simulations of pump-and-treat strategies for remediation of LNAPL-contaminated aquifers, *J. Contam. Hydrol.* 31 (1998) 57–81.
- [10] M. Oostrom, C. Hofstee, R.C. Walker, J.H. Dane, Movement and remediation of trichloroethylene in a saturated, heterogeneous porous medium. 2. Pump-and-treat and surfactant flushing, *J. Contam. Hydrol.* 37 (1999) 179–197.
- [11] F. Nadim, G.E. Hoag, S. Liu, R.J. Carley, P.J. Zack, Detection and remediation of soil and aquifer systems contaminated with petroleum products: an overview, *Petrol. Sci. Eng.* 26 (2000) 169–178.
- [12] G.-J. Marta, G.-L. Cesar, N.-A. Jose-Luis, O.-C. Jose-Julio, Biosurfactant and biodegradation-enhanced partitioning of polycyclic aromatic hydrocarbons from nonaqueous-phase liquids, *Environ. Sci. Technol.* 37 (2003) 2988–2996.
- [13] J.C. Fountain, A. Klimek, M.G. Beikirch, T.M. Middleton, The use of surfactants for in situ extraction of organic pollutants from a contaminated aquifer, *J. Hazard. Mater.* 28 (1991) 295–311.
- [14] J.T. Gellar, J.R. Hunt, Mass transfer from nonaqueous phase liquids in water-saturated porous media, *Water Resour. Res.* 29 (1993) 833–845.
- [15] D.-H. Lee, R.D. Cody, D.-J. Kim, S. Choi, Effect of soil texture on surfactant-based remediation of hydrophobic organic-contaminated soil, *Environ. Int.* 27 (2002) 681–688.
- [16] D.-H. Lee, Experimental investigation of the removal of hydrophobic organic compounds from two Iowa soils using food grade surfactants and recovery of used surfactants, Ph.D. dissertation, Iowa State University, Ames, IA, 1999.
- [17] D.A. Edwards, R.G. Luthy, Z. Liu, Solubilization of polycyclic aromatic hydrocarbons in micellar nonionic surfactant solutions, *Environ. Sci. Technol.* 25 (1991) 127–133.
- [18] J.-L. Li, B.-H. Chen, Solubilization of model polycyclic aromatic hydrocarbons by nonionic surfactants, *Chem. Eng. Sci.* 57 (2002) 2825–2835.
- [19] A. Tiehm, Degradation of polycyclic aromatic hydrocarbons in the presence of synthetic surfactants, *Appl. Environ. Microb.* 1 (1994) 258–263.
- [20] J.D. Childs, E. Acosta, R. Knox, J.H. Harwell, D.A. Sabatini, Improving the extraction of tetrachloroethylene from soil columns using surfactant gradient systems, *J. Contam. Hydrol.* 71 (2004) 24–45.
- [21] Abdul, S. Abdul, C.C. Ang, In situ surfactant washing of polychlorinated biphenyls and oils from a contaminated field site: Phase II pilot study, *Groundwater* 32 (1994) 727–734.
- [22] D.-H. Lee, R.D. Cody, D.-J. Kim, Surfactant recycling by solvent extraction in surfactant-aided remediation, *Sep. Purif. Technol.* 27 (2002) 77–82.
- [23] J.C. Fountain, R.C. Starr, T. Middleton, M. Beikirch, C. Taylor, D. Hodge, A controlled field test of surfactant-enhanced aquifer remediation, *Groundwater* 34 (1996) 910–916.
- [24] V.L. Snoeyink, D. Jenkins, *Water Chemistry*, Wiley, New York, 1980.
- [25] D.-H. Lee, R.D. Cody, B.L. Holye, Laboratory evaluation of the use of surfactants for groundwater remediation and the potential for recycling them, *Ground Water Monit. R.* 21 (2001) 49–57.

- [26] P. Kuran, L. Sojak, Environmental analysis of volatile organic compounds in water and sediment by gas chromatography, *J. Chromatogr. A* 733 (1996) 119–141.
- [27] M.J. Rosen, *Surfactants and Interfacial Phenomena*, Wiley, New York, 1989.
- [28] W. Dingcong, A study of identifying the emulsion type of surfactant: volume balance value, *J. Colloid Interf. Sci.* 247 (2002) 389–396.
- [29] E.-S. Kim, Surfactant-enhanced remediation of organic contaminated groundwater, Master Thesis, Seoul National University, Seoul, Korea, 2004.
- [30] V. Mezzanotte, F. Castiglioni, R. Todeschini, M. Pavan, Study on anaerobic and aerobic degradation of different non-ionic surfactant, *Bioresource Technol.* 87 (2003) 87–91.
- [31] N.B. Stasiuk, L.L. Schramm, The temperature dependence of the critical micelle concentrations of foam-forming surfactants, *J. Colloid Interf. Sci.* 178 (1996) 324–333.
- [32] S.M. Bystryak, M.A. Winnik, J. Siddiqui, Unusual conductivity changes for sodium dodecyl sulfate solutions in the presence of polyethyleneimine and polyvinylamine, *Langmuir* 15 (1999) 3748–3751.