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Perchloroetylene and Dibutyltin Dichloride Removal from Packed Column by Surfactant Solution

Seelawut Damrongsiri[1,2], Chantra Tongcumpou[1,2], David A. Sabatini[3]

[1] Center of Excellence on Hazardous Substance Management
Chulalongkorn University, Bangkok, Thailand
[2] Environmental Research Institute, Chulalongkorn University
[3] School of Civil Engineering and Environmental Science,
The University of Oklahoma, Oklahoma, USA
Correspond author: E-mail: tchantra@chula.ac.th

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Abstract

Surfactant enhanced remediation is viewed as a potential method for removing organometallic compounds from contaminated aquifers. Dibutyltin dichloride (DBT), as a representative organometallic compound, was applied in sand packed columns to observe its solubilization behavior compared to that of perchloroetylene (PCE), a normal organic solvent. Ottawa sand was used as the porous media. A mixture of DBT and PCE was applied as the contaminant. The tracer study exhibited the plug flow condition with a retention time of 79.9 min. The surfactant solution was a mixture of 3.6 wt.% SDHS and 0.4 wt.% C16DPDS with various concentrations of $CaCl_2$. The column experiments were carried out by single and gradient surfactant systems. The effluent exhibited a general solubilization pattern for PCE, governed by a rate limiting mechanism. However, the concentration of DBT in the effluent observed in every experiment was just a slice of its solubilization capacity. The adsorption of DBT on the sand was suspected to be the cause of the problem. The solubilization of DBT by a surfactant was ineffective at removing DBT from the contaminated media. It may be concluded that DBT exhibits the properties of both an organic and inorganic compound; it could be solubilized by a surfactant and absorbed strongly on sand. Nevertheless, the results indicate that trapped DBT could be removed by mobilization in the form of a PCE-DBT mixture and that adsorption could be prevented by a very low pH condition.

Keywords: Surfactant; solubilization; organometallic compound; dibutyltin dichloride

Introduction

Organometallic compounds (i.e., compounds containing bonds between a carbon and a metal) have been employed in numerous applications. For example, they have been used as catalysts, stabilizers in plastic industries, wood preservatives, and agricultural biocides. Accidental contamination due to spillage or leakage during production, transport, blending, storage and disposal has caused soil and groundwater contamination problems [1, 2, 3, 4, 5].

This research originated from a request from a chemical factory that was looking for an approach to remediate a contaminated aquifer. The aquifer was contaminated by a mixture of an organic solvent and organometallic compound that had leaked into it from production and transportation activities. Some remediation approaches were taken under consideration. However, methods for destroying the contaminants like bioremediation and chemical oxidation would not be able to sufficiently eliminate the risks associated with organometallic compounds since the resulting heavy metals (e.g., lead) would remain at the contaminated site as their metabolites. Thus, the removal of organometallic compounds from the subsurface is the target of this study. The pump and treat method has been traditionally used to treat aquifers; it is aided by the flow of water and requires a massive volume of water. More recently, surfactant solutions have been applied to modify the pump and treat method to increase its treatment efficiency by releasing and solubilizing the formally-insoluble contaminant into the pumped aqueous solution. This modified technique is generally known as surfactant enhanced aquifer remediation (SEAR). It shows promise as a technique for removing organometallic compounds and their metabolites from contaminated soil and aquifers [6, 7].

When a surfactant is added into a system of oil and water, surfactant monomers accumulate at the oil/water interface, lowering the interfacial tension (IFT) between the oil/water interface. Greatly reducing the IFT induce the mobilization that allows the trapped oil to be released from the soil pores and move as its own phase [8,9]. Mobilization is vastly more effective than solubilization in removing oil [10,11,12], but it can also cause the vertical migration of dense non-aqueous phase liquid (DNAPL), which produces new and more complicated contamination problems.

Another important treatment mechanism generated by a surfactant is solubilization. It is derived from the partitioning of the contaminant into the oil like core of the micelle formed in the aqueous surfactant solution. Apparent aqueous solubility of an insoluble contaminant is enhanced by those surfactant micelles [13,14]. A surfactant micelle is formed when the concentration of a surfactant is higher than the critical micelle concentration (CMC). Even though the solubilization mechanism can contribute to a lower removal efficiency in comparison to mobilization, it is not the cause of vertical migration. Both mechanisms could occur at the same time. However, the most significant induced mechanism is the IFT.

In 1979, Hun [15] established the Chun-Hun relationship, which is the relation between the quadratic equation of solubilization and 1/IFT. The equation exhibits how the increase of solubilization would decrease the IFT until it reached the optimum point. Thus, when a surfactant system is designed to increase the solubilization capacity of a system, its mobilization potential is inevitable increased.

Among the various parameters influenced by the mobilization described by Pennell [8], the IFT was the one that could be dramatically modified based on the surfactant formulation. A lower IFT responded to a lower residual saturation of the trapped oil. To prevent mobilization, Sabatini et al. [9] applied the relation founded by Pennell by introducing the gradient concept, in which the IFT of a surfactant system is sequentially adjusted to minimize vertical migration and still maintain its remediation efficiency. By applying this method, the most mobile fraction of trapped oil would be removed by solubilization step by step. The treatment starts by using a surfactant solution that produces a high IFT to minimize the mobilization of the trapped oil and shift the surfactant solution to produce lower IFT and higher solubilization when the residual saturation decreases to release the oil that is trapped, while maintaining proper IFT to the minimize mobilization. The IFT of an anionic surfactant system could be altered simply by adjusting the salinity of the solution. When the salinity of an aqueous anionic surfactant system is increased, the IFT of the system decreases until the system reaches its optimum point.

Although the surfactant behavior, treatment mechanisms, and limitations of surfactants for the remediation of various organic solvents have been studied extensively, research on organometallic compounds is limited. Fundamental knowledge on organometalic compound remediation by a surfactant should be thus explored. Dibutyltin dichloride (DBT) was applied in the study as the surrogate organometalic compound. It was selected for its proper chemical structure, for safety reasons, and the readiness of the laboratory as mentioned in the previous studies [16, 17]. Our previous research focused on the solubilization behavior of DBT as a single compound and in a mixture with an organic solvent (perchloroethylene, PCE) [17]. The solubilization capacity in various surfactant systems were observed systematically. DBT was found to be able to solubilize in the same manner with a polar organic compound that solubilize in the outer part of the micelle surfactant solution. It could penetrate into the core of the micelle only by dissolving it in an organic solvent that solubilizes in the core. In this study, the same PCE-DBT mixture was applied in the sand packed column to simulate the contaminated aquifer and the selected surfactant solution was used as the treatment solution. The objective of this research was to investigate the solubilization behavior of DBT as an organometallic compound and PCE as organic solvent that was trapped in the sand pores. Three single surfactant systems were evaluated. A gradient surfactant system was applied in order to minimize the mobilization and observe the solubilization. The results are discussed and compared to those of our previous solubilization study.

Materials and Methods

1) Materials

The analytical grade DBT used in this study was purchased from the Sigma-Aldrich Corporation, while the PCE was purchased from Ajax Finechem. The PCE and DBT mixture was applied at a molar ratio of 0.962:0.038, the same ratio that was used in our previous research [17]. The anionic surfactant C16 diphenyloxide disulfonates (C16DPDS), under the trade name Dowfax 8390, was supplied by Dow Chemical Company. Sodium dihexyl sulfosuccinate (SDHS) known as AMA was purchased from Fluka Co.

Analytical grade calcium chloride ($CaCl_2$, 100%) was purchased from LabScan. Analytical grade calcium nitrate ($Ca(NO_3)_2$, 100%) used to prepare the column was from Ajax Finechem. All chemicals in this research were used as received without further purification. The 15 mΩ deionized (DI) water used in the experiment was produced by ELGA, PURELAB Option. The surfactant solution used in the experiment was a mixture of 3.6 wt.% SDHS and 0.4 wt.% C16DPDS with various concentrations of $CaCl_2$, which were the same as those applied in our previous study [17]. 20-30 mesh Ottawa sand (Fisher Scientific) was applied as the aquifer media in the experiment. It was washed using DI water and dried before being packed into the column.

2) Methods

2.1) Column packing procedure and preparation

The column packing and residual oil preparation procedures were adapted from Childs et al. and Acosta et al. [18, 19]. A 2.54 cm-diameter glass column was utilized. The pump was a piston pump (Model QG6, Fluid Metering Inc.). The joints and valves of the system were made from stainless steel. The column preparation could be divided in to four steps: (1) preparation of the bottom piping system, (2) packing of Ottawa sand and pore volume quantification, (3) preparation of the top pumping system, and (4) establishing the residual saturation of the PCE-DBT mixture.

Preparation of the piping system (A)

The pumping system (A) during the sand packing procedure allowed water to flow in an up-flow direction to dispel the air bubbles in the apparatus. The column was prepared by connecting the pumping system (*A*) to the bottom end of the column and then DI water was pumped to displace air in the bottom pipeline. After that, the water was drained out until the surface of the water was at the bottom end of the column.

Ottawa sand packing and pore volume quantification

The 20-30 mesh Ottawa sand was packed into each column using the wet packing technique to prevent air bubbles from being retained in the column. About 50 mL of water and 200 g of Ottawa sand were prepared for each container and weighed in their container. Then, the water was poured into each column until it was 4 cm above the sand surface. The surface level of the added water was maintained at about 4 cm above the sand surface, while the height of the sand filled each time was about 2 cm. The sand was stirred and packed every time after being filled to dispel the air bubbles. The water and sand were filled gradually until the sand height reached 16 cm (Figure 1A). Then water was drained out through the vent valve of the piping system (*A*) until the surface of the water in column reach the surface of the sand. The drained water was collected in a water container. After that, the remaining water in the container was weighed again (with its container) to calculate the pore volume of the packed column. The pore volume ($\forall_p$) was the difference in weight of the water in the container before (W_{w1}) and after being packed with sand (W_{w2}) divided by the density of the water (D_W), as show in Eq. 1. The sand was also weighed to discover the mass of the sand in the column.

$$\forall_p = \frac{(W_{W1} - W_{W2})}{D_W} \qquad (1)$$

Preparation of the pumping system (B)

The pumping system (B) was designed to accommodate the synthetic groundwater and remedial solution. The sand was saturated with water from the previous packing procedure, and the pumping system (*B*) had a flow adapter fitted on top of the column. The vent valve of the pumping system (*B*) had to be opened during assembly to allow the release of air and water. DI water was then flowed from the bottom end in an up-flow direction to dispel the air out at the top of the column (Figure 1B). The flow was stopped once all air bubbles were dispelled from every part of the column and pumping system. The vent valve of the pumping system (*B*) was closed and the pump (*A*) was then detached from the bottom pipeline.

Establishment of the residual saturation of the PCE-DBT mixture

The packed column was conditioned by the synthetic groundwater; the 10 pore volumes (PV) of 0.01 M $Ca(NO_3)_2$ flowed at a pore velocity of 2 cm min^{-1} via the pumping system (*B*). After that, the bottom of the column was connected to a reservoir containing the PCE-DBT mixture through a bottom pipe, as shown in Figure 1C. Residual saturation of the PCE-DBT mixture (as the contaminant) was established by replacing the water in the column with the PCE-DBT mixture using the head different technique. The vent valve of the pumping system (*B*) was opened to allow the flow from the PCE-DBT mixture reservoir. The oil was allowed to fill the packed column slowly (control by the vent valve of the pumping system (*B*)) until it reached the top of the packed sand layer. Then, 10 pore volumes of synthetic groundwater flowed at the pore velocity of 2 cm min^{-1} to displace the free phase oil. The remaining trapped oil was defined as residual oil. Residual saturation (Rs) was defined as the percent volume of retained oil within the pore volume of the saturated area (Rs = volume of residual oil / $\forall_p \times 100$). The amount of entrapped oil was quantified, in the same manner of the pore volume, from a mass balance of the oil before and after the contamination procedure. The volume of the retained oil (V_{oil}) can be calculated from the weight of the oil with the container before (W_{oil1}) and after (W_{oil2}) the saturation procedure and the oil density (D_{oil}) (see Eq. 2).

$$V_{oil} = \frac{(W_{oil1} - W_{oil2})}{D_{oil}} \qquad (2)$$

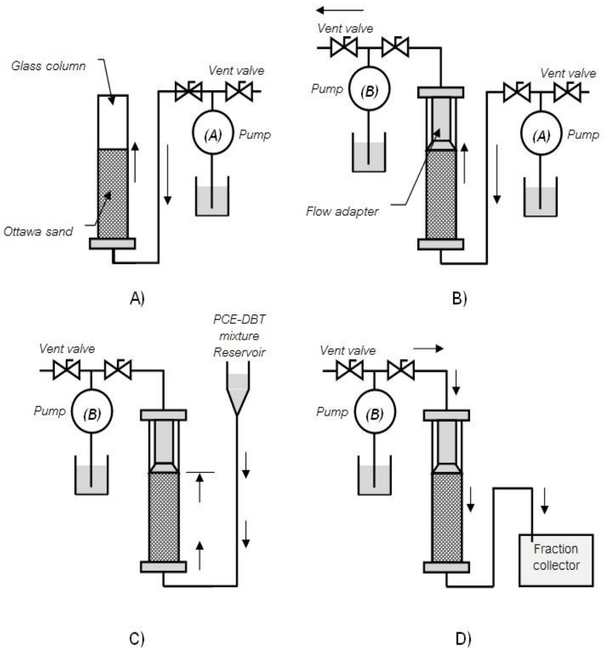

Figure 1 Experimental setup for the column experiments

2.2) The experimental procedure

After the residual contaminant was established, the bottom pipe was detached from the reservoir of the PCE-DBT mixture and connected to the fraction collector (Redi Frac, Pharmacia Biotech) (Figure 1D). All experiments were carried out at 25 °C. Each experiment began with the flow of the surfactant solution through the contaminated packed column at a pore velocity of 0.2 cm min^{-1} (adopted from Childs et al., 2004 [14]). The effluent was collected by a fraction collector at 20 min per sample. Surfactant flushing was carried out until PCE was absent from the effluent. Three surfactant solutions were used to flush each single surfactant system separately: (1) 3.6 wt.% SDHS and 0.4 wt.% C16DPDS without $CaCl_2$; (2) 3.6 wt.% SDHS and 0.4 wt.% C16DPDS with 0.2 wt.% $CaCl_2$; and (3) 3.6 wt.% SDHS and 0.4 wt.% C16DPDS with 0.4% $CaCl_2$. In the gradient surfactant system, four surfactant solutions were applied in one experiment. Flushing in the gradient surfactant system experiment began using 4 PV of 3.6 wt.% SDHS and 0.4 wt.% C16DPDS without $CaCl_2$; follow by 4.5 PV 3.6 wt.% SDHS and 0.4 wt.% C16DPDS with 0.2 wt.% $CaCl_2$; follow by 4 PV 3.6 wt.% SDHS and 0.4 wt.% C16DPDS with 0.4% $CaCl_2$; and finally 3.6 wt.% SDHS and 0.4 wt.% C16DPDS with 0.6 wt.% $CaCl_2$ until PCE was absent from the effluent. These surfactant solutions were used in our previous study [17] on the solubilization behavior of DBT. They were also applied in this study to evaluate the solubilization behavior of DBT as a trapped contaminant in a sand packed column and to compare the results of both studies.

2.3) Extraction

After the surfactant was flushed out, sand in the column was collected in a 250 mL glass bottle with a cap to determine the remaining DBT in the column. There were three extraction steps: (1) 100 mL of the surfactant solution (3.6 wt.% SDHS and 0.4 wt.% C16DPDS 0.5 wt.% $CaCl_2$) was added to a bottle, which was shaken for one day and then the sand was separated from the surfactant solution. After that, the sand was washed with DI water. The surfactant solution and washing water were collected and adjusted to a volume of 250 mL to measure the PCE and DBT. (2) 100 mL of 12.5 wt.% HCl solution was added to a bottle and then it was shaken for one day after which time the acid solution was separated from the surfactant solution. The sand was washed with DI water. The acid solution and washing water were collected in the same manner as with the first step and adjusted to a volume of 250 mL to measure for DBT. (3) Finally, the sand was dried and then 5 g of sand was weighted to perform the same DBT digestion procedure with the aqueous sample to extract any remaining DBT adsorbed from the sand samples.

2.4) Effluent result analysis and measurement

There were five types of samples: those of the (1) mobilized fraction, (2) solubilized fraction, (3) fraction extracted by a surfactant solution, (4) fraction extracted by acid, and (5) fraction extracted from sand. The solubilized PCE and DBT refer to the PCE and DBT present in the effluent aqueous solution. The mobilized fraction was the free oil phase present in the effluent. The mobilized oil was separated from the aqueous solution and quantified by weigh. The mass from fractions (1) and (2) was considered as PCE and DBT removal, while fractions (3), (4), and (5) accounted for the amount of PCE and DBT that still remained after treatment. The total mass was the accumulation of those five fractions.

The solubilized PCE was measured by gas chromatography (Clarus 500, PerkinElmer) with an FID detector connected to a head-space auto sampler (Turbomatrix 40, Perkin Elmer). Nitrogen was used as the carrier gas. The sample volume of 100 µL was equilibrated by the headspace auto sampler at a temperature of 80 ºC for 30 min before being injected to the GC system. The column flow was maintained at a pressure of 6 psi. The oven temperature was set at 140 ºC isotopic system.

DBT was measured as the total tin in the solution. The samples were digested by a microwave digester (Ethos pro, Milestone) before being measured for tin with an ICP-OES system (Vista-MPX, Varian). The digestion procedure was adapted from the digestion method described by Hargreaves [20]: 500 µL of the sample was mixed with 9 mL of 65 wt.% hydrochloric acid and 3 mL of 35 wt.% nitric acid. The temperature program started by increasing the temperature to 175 ºC within 13 min and holding it at 175 ºC for another 10 minutes. It should be noted that general digestion using only nitric acid may result in the precipitation of tin.

2.5) Tracer study

The tracer test and calculation were adapted from a method described by Tchobanoglous et al. [21]. This tracer study was done to determine the actual flow characteristics of a packed column. The tracer was bromide. Theoretically, a tracer is introduced into the influent end of the reactor with pulse injection. However, that theoretical idea could not be applied to our experiment as our flow was very low and the effluent needed to be collected within a period time. In addition, the appearance flow characteristics through the influent pipe, pump, joint, packed column until to the effluent end were should be included in our pumping system. Thus, in our tracer study, 10 mg L^{-1} of bromide solution flowed continuously from the reservoir through the pumping system (B) with the effluent collected by the fraction collector every 10 min. The bromide concentration was plotted in relation to the pore volume to make a response curve. The curve is in the form of a cumulative curve, so it was calculated using the method used by Tchobanoglous et al. [21], which turned it into a normal distribution curve to compute the column's characteristics.

Results and Discussion

1) Packed column properties

The same column packing procedure was performed each time in order to make every column analogous. The pore volume was about 30±0.85 mL, and porosity was 0.37±0.01. The flow was calculated based on the desired pore velocity of 0.2 cm min^{-1} and porosity of that packed column, which resulted in values between 0.35 to 0.39 mL min^{-1}. Nonetheless, the actual flow used in the experiment was 0.38 mL min^{-1}, which resulted in a small fluctuation in the pore velocity (0.20±0.01 cm min^{-1}) that corresponded to the retention time of 79±2 min.

2) Tracer study

The tracer study evaluated 2 curves: (1) the flow from the reservoir to the top end of the column, and (2) the flow from the reservoir to the bottom end of the column. 10 mg L^{-1} of bromide solution was allowed to flow continuously as our tracer. The response curve, a type of cumulative curve, was calculated according to the method described by Tchobanoglous et al. [21], which turn it into a normal curve, as showed in Figure 2. The resident time was estimated as the mean resident time based on the discrete time step measurement ($t_{\Delta C}$), which was calculated using Eq. 3: where $t_{\Delta C}$ is the mean resident time (min), t_i is the time at measurement i, C_i is the bromide concentration at measurement i, and Δt_i is the time increment at about C_i.

$$t_{\Delta C} = \frac{\sum t_i C_i \Delta t_i}{\sum C_i \Delta t_i} \qquad (3)$$

The resident time from the tracer response curve from the reservoir to the top end of the column was 68.1 min, and from the reservoir to the bottom end of the column, it was 148.0 min. Thus, the retention time of the solution within the column was 79.9 min. Another calculated resident time was derived from the average pore volume of the column and actual flow, which was 79.1 min. Both resident time values were very close indicating that the quantification of the pore volume and flow measurement was reliable. The ideal plug flow has a Morrill dispersion index (MDI) of 1. The U.S. EPA (1986) categorizes a plug flow column as one that has an MDI of less than or equal to 2.0 [21]. The MDI was the values of *P90/P10*, where *P10* and *P90* are the 10 and 90 percentile values from the log-probability plot, respectively. The percentile values are obtained from the log-probability plot of time in log scale versus the cumulative percentage of the total tracer. The tracer study results were used to calculate the MDI, which turned out to be 1.25, meaning that the column used in this study could be considered a plug flow column.

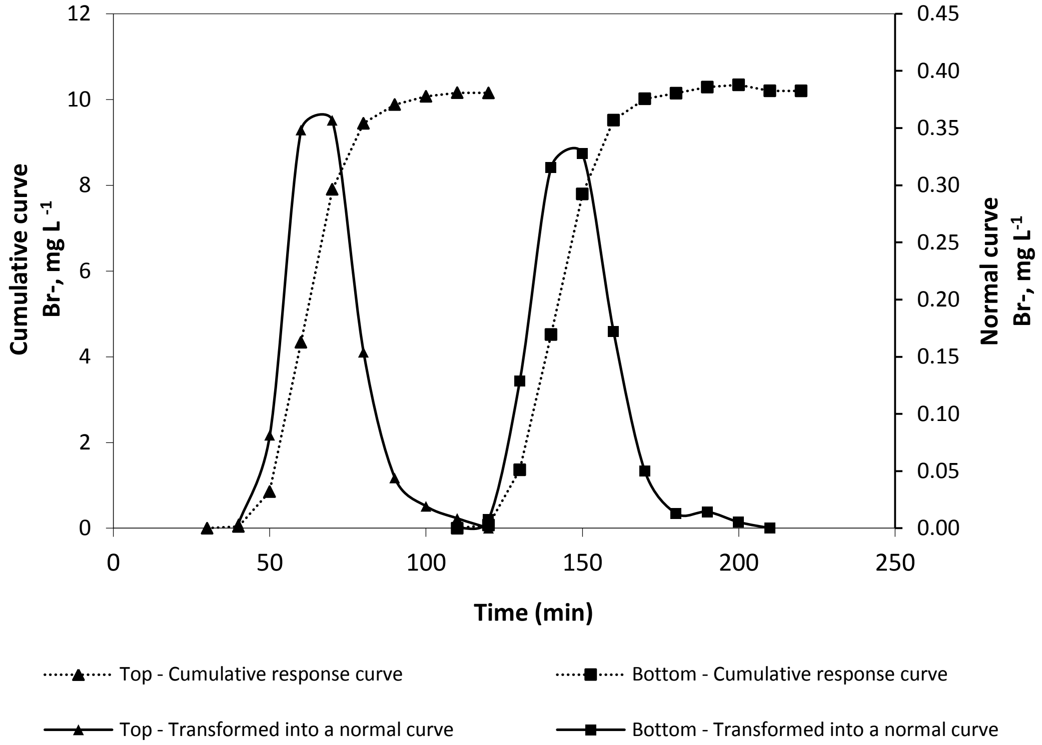

Figure 2 The results of the two tracer experiments

3) Effluent results of column experiments

The solubilized PCE and DBT and mobilized PCE-DBT mixture in the column effluent were plotted versus the volume of the flushed surfactant solution in the PV unit. The PV unit was applied as a normalized unit to define the volume of the solution that flowed through the column (PV = volume of solution / $\forall_p$). It was used to exclude the effect of the different pore volume sizes of each column. The results from single surfactant systems are shown in Figure 3 and those of the gradient surfactant system are shown in Figure 4. It should be noted again that the system with the higher salinity had a higher solubilization capacity and produced lower IFT.

In the single surfactant system experiments, mobilization of the trapped PCE-DBT mixture was only found in the surfactant system with 0.4 wt.% $CaCl_2$ (Figure 3 C), which had the lowest induced IFT in this study. The fraction of the mobilized oil mixture was observed before an increase in solubilization. This is the general trend as observed by other studies [9,11,18]. The remaining trapped oil tends to be solubilized afterwards. Even though 75% of the trapped PCE-DBT mixture was mobilized, the remaining 25% of trapped PCE-DBT was enough to observe their solubilization behavior.

The aqueous concentration of PCE in the effluent of the column was the result of solubilization by surfactant micelles as the surfactant solution flowed through the trapped contaminant. The PCE concentration in the effluent increased steeply at the beginning until it reached a plateau due to the large amount of oil mixture that was trapped in the sand pores, and after that, for a period of time when the amount of trapped oil mixture was reduced, the PCE concentration declined gradually until it reach the trace concentration. In the experiments with the single surfactant systems, the concentrations at the plateaus or maximum concentration levels were derived from flushing the surfactant was the mean concentrations of the samples located after the steep rise of PCE in the sample before its decline (Figure 3). Nevertheless, to help contrast the solubilization derived from the column experiments and their capacities, the highest scaling of the y-axis in Figure 3 (i.e., 20,000 mg L^{-1} in Fig. 3A) was set to the solubilization capacity derived from the solubilization experiment in our previous study [17]. Table 1 exhibits the solubilization capacity from our previous research (derived from a batch study), the maximum concentration from the column experiment by single surfactant systems, and the percentage of the solubilization capacity. The maximum concentrations in these column experiments were found between 20% to 45% of their capacity. Solubilization could not reach their capacity possibly because of the shorter contact time and limited contact area, as it is a rate limiting mechanism [10, 22]. However, a higher solubilization capacity percentage was observed in the system with higher salinity even though the retention times in all the columns were considered equal. Thus the different solubilization capacity percentages should respond to the shorter equilibrium time of system located close to optimum condition (higher salinity) [11]. Therefore, disregarding mobilization, the remediation of a surfactant system closing to the optimum condition benefited not only from a higher solubilization capacity but also a faster solubilization rate. The volume of the surfactant solution required to completely remove PCE from the column was different depending on its solubilization. Nonetheless, the removal of PCE could be definitely achieved by flushing a single surfactant system

In the gradient experiment, the surfactant solution with the lowest salinity was used first and followed by the surfactant solution with the second lowest salinity and so forth. One pore volume of DI water was allowed to flow through the column before it was followed by a surfactant solution. The surfactant solutions applied in this gradient study contained 3.6 wt.% SDHS and 0.4 wt.% C16DPDS with different $CaCl_2$ concentrations, as described in Section 2.2. The effluent results are shown in Figure 4. Little mobilization was observed when the surfactant solution shifted the salinity to 0.2 wt.% and 0.4 wt.% $CaCl_2$, which was about 450 and 600 mg of oil (6.4% and 8.6% of total trapped oil), respectively. About 85% of trapped oil was left after mobilization and then removed by solubilization through the aqueous effluent. The concentration of PCE in the effluent increased sequentially together with the salinity of the surfactant solution before falling down when the majority of trapped oil was removed. The mean PCE concentration in each gradient step was similar to the maximum concentration derived from the experiments with single surfactant systems, which could be described by the same reason.

The concentration of DBT in the effluent of every experiment was found much lower than its solubilization capacity. DBT was present in trace concentrations. No solubilization pattern was observed. The maximum concentration of DBT in the single surfactant system experiment was assumed to be the mean concentration of DBT from the same samples found the maximum PCE concentration. That maximum concentration of DBT and its solubilization capacity percentage are shown in Table 1. A very low solubilization capacity percentage indicates that the solubilization of DBT to surfactant micelles was somehow obstructed.

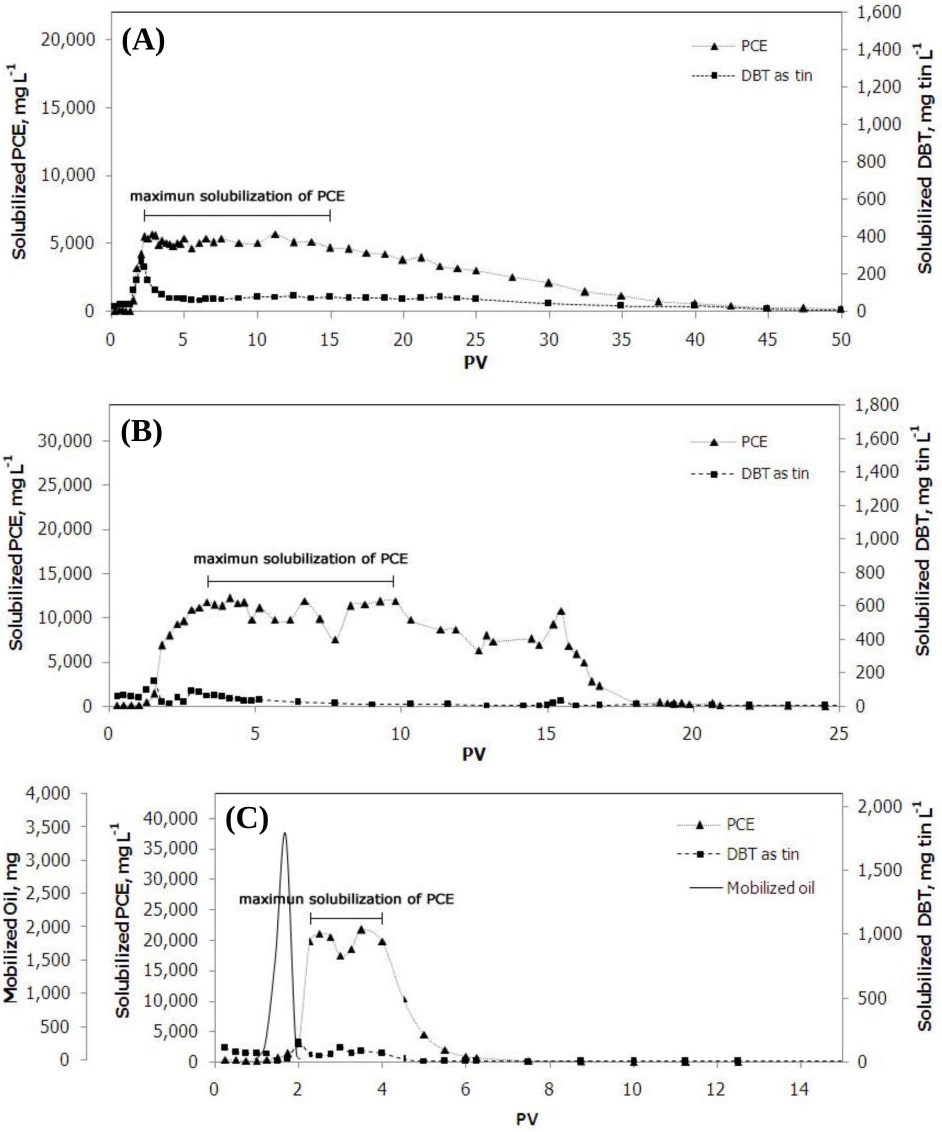

Figure 3 Effluent results of the column experiments by single surfactant systems, (A) 3.6 wt.% SDHS and 0.4 wt.% C16DPDS without $CaCl_2$, (B) 3.6 wt.% SDHS and 0.4 wt.% C16DPDS with 0.2 wt.% $CaCl_2$, and (C) 3.6 wt.% SDHS and 0.4 wt.% C16DPDS with 0.4 wt.% $CaCl_2$

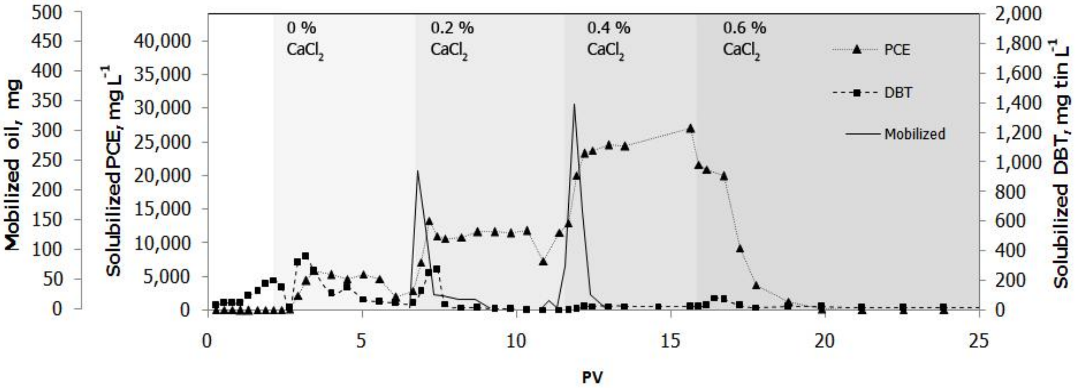

Figure 4 Effluent results of the column experiment using the gradient surfactant system

Table 1 Solubilization capacity and solubilization from the column experiment with different surfactant solutions.

Surfactant solution	Solubilization capacity		Maximum concentration from column experiments			
	mg L^{-1}		mg L^{-1}		solubilization capacity (%)	
	PCE	DBT	PCE	DBT	PCE	DBT
3.6 wt.% SDHS 0.4 wt.% C16DPDS without CaCl$_2$	22,000	1,600	5,100	80	23	5
3.6 wt.% SDHS 0.4 wt.% C16DPDS with 0.2 wt.% CaCl$_2$	34,000	1,800	11,000	25	32	1
3.6 wt.% SDHS 0.4 wt.% C16DPDS with 0.4 wt.% CaCl$_2$	44,000	2,100	20,000	70	45	3

4) Solubilization behavior of DBT and PCE in the column experiment

PCE was applied to produce a general pattern of a solubilized organic solvent in the effluent. The solubilization behavior of PCE, as a normal organic solvent, was as described in the previous section. The concentration pattern of PCE in the effluent corresponded to the concentration of the surfactant in the stream, resulting in a steep increase in the PCE concentration at the beginning of the resulting curve. In addition, it was influenced by the amount of trapped oil, which resulted in the gradual decline of the PCE concentration when the amount of the trapped oil mixture was reduced. The maximum concentration of PCE in the effluent did not reach its solubilization capacity because it was limited by the contact time and contact area.

The percentages of DBT solubilization obtained from the column experiments of both the single and gradient surfactant systems were extremely low. Thereby, a pattern of solubilized DBT in the effluent was hard to detect. The mean maximum concentration of DBT in the effluent from all experiments was less than 5% of its solubilization capacity. This result is extremely different from the solubilization result of PCE, indicating that more than contact time and contact area limitations had taken place. Aside from contact time and contact area, the presence of sand was a factor that was not present in our prior batch experiments, the problem should be caused by adsorption of DBT on sand surface.

The adsorption of DBT in clay-rich sediment was observed by Hoch et al. [23]. The adsorption of DBT was caused by electrostatic interactions between DBT and the sand surface. Our results illustrate that solubilization via surfactant micelles could not overcome this electrostatic interaction.

5) Extraction results

When the surfactant flow was stopped, the extraction was carried out to evaluate the remaining DBT in the packed column. PCE was not detected in the extracted fluid since the experiment was stopped after PCE was absent from the effluent. In contrast, a significant concentration of DBT was found in the extracted solution. The DBT concentrations in extracted solutions varied depending on the amount of remaining DBT there was in the sand sample from each experiment. In the first extraction step, the contaminated sand was collected and extracted with 3.6 wt.% SDHS and 0.4 wt.% C16DPDS with 0.5 wt.% $CaCl_2$, which was the same surfactant used in the column experiment but with higher salinity in the surfactant solution. The extracted DBT concentration in this solution was still low. The maximum value (from those 4 sand samples from each column experiment) was 52 mg L^{-1} as tin, while its solubilization capacity of DBT (without PCE) was 250 mg L^{-1} as tin. The solubilization of DBT by a surfactant solution could not reach its solubilization capacity (equilibrium value) even when it was shaken.

The second step was performed using a solution of hydrochloric acid. The concentration of DBT in the acid solution was as high as 380 mg L^{-1} as tin. All the remaining DBT on the sand samples was extracted during this extraction step. The forms of these tin compounds in our acid solution were unknown. An absent or negligible amount of DBT was extracted in the third step.

6) Removal of DBT from porous sand media

All column experiments were carried out until PCE was no longer detected in the effluent; however, a significant fraction of DBT still remained in the packed sand columns. Different amounts of DBT remained for different reasons.

When a surfactant solution without $CaCl_2$ was used, the experiment was ended at 50 PV and 80% of the DBT was removed; meanwhile, when a surfactant solution with 0.2 wt.% $CaCl_2$ was used, the experiment was ended at 20 PV and 20% of the DBT was removed. The DBT concentrations in the effluent of both experiments were similar, so the higher removal of DBT was simply derived from the larger volume of flushed solution. When a surfactant solution with 0.4 wt.% $CaCl_2$ was used, mobilization occurred, and 75% of the trapped PCE-DBT mixture was released from the column. When the experiment was done at only 14 PV, 80% of the DBT was removed; however, almost all of it was removed via mobilization.

Similar limited removal of DBT was also observed in the experiment that used the gradient surfactant system: when the mobilization was minimized, the removal of DBT was obstructed. These results reveal that DBT removal by solubilization using a surfactant was ineffective. The result from the first extraction step emphasizes that the solubilization of DBT was obstructed by the presence of sand. The adsorption of DBT onto sand was suspected to be the cause and solubilization via surfactant micelles could not overcome the adsorption onto sand by electrostatic interaction. In addition, these results indicate that the solubilization of each organic compound in an organic mixture from the source zone to the surfactant micelles was independent, depending on its individual properties.

However, the use of a surfactant solution with 0.4 wt.% $CaCl_2$ indicated that DBT could be removed by mobilization in the form of a non-aqueous liquid of DBT like a PCE-DBT mixture. The mobilization mechanism let the trapped oil moved as its free oil phase, which may be able to prevent the adsorption of DBT on sand. Besides, all remaining DBT on sand was extracted during the second extraction step when the acid solution was applied. A high DBT concentration was observed in this acid solution. According to Hoch et al. [23], low pH conditions could prevent the adsorption of DBT by altering the surface charge of the sand and altering the form of DBT.

Conclusion

The column experiments were carried out by three single surfactant systems and a gradient surfactant system. PCE as a normal organic solvent exhibited a general solubilization result pattern in column effluent that could be explained by its rate limiting mechanism. However, the concentration of DBT in column effluent was very low; the maximum concentration of DBT in the effluent was not more than 5% of its solubilization capacity. The results indicate that the contact time and contact area were not the only mechanisms that obstructed DBT solubilization. Solubilization by surfactant micelles could not remove DBT efficiently. The adsorption of DBT onto the sand surface was suspected to be the cause of this problem of limited solubilization. This study illustrates that solubilization via surfactant micelles may not be able to overcome the electrostatic interacttions. The adsorption of DBT should be of concern to eliminate this problem. Additionally, it indicates that the solubilization of each compound from an organic mixture from the source zone to the surfactant micelles tends to be independent depending on a compound's individual properties. This research indicates that DBT demonstrates the properties of both an organic and inorganic compound, as it could be solubilized by a solvent (PCE) and surfactant micelles and also able to be absorbed strongly on sand, which makes it different from a normal organic compound. These unique properties of DBT, however, may also be found in other organometallic compounds.

Even though the solubilization of DBT was limited, the results point out that mobilization was a mechanism that was able to remove DBT by moving it together with its solvent; however, the vertical migration of the oil also needs to be concerned. Moreover, the results from the extraction process indicate that altering the pH may possibly improve the remediation efficiency.

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