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Alkaline Enhanced-Separation of Waste Lubricant Oils from Railway Contaminated Soil

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A surfactant-enhanced washing process for the removal of waste lubricant oil from train station soil was investigated by performing batch and column experiments. Surfactants removed 24.8–29.1% of the lubricant oil from soil in batch system, while the removal was slightly lowered to 15.8–26.2% in the column experiment. Alkaline-enhanced surfactant washing increased the removal efficiency up to 52%, while the removal was 42% in alkaline soil washing. An alkaline solution enhanced the removal of lubricant oil from soil because of soap formation. Even though the alkali-enhanced surfactant washing/flushing process effectively removed the lubricant oil from the soil, the residual concentration still exceeded the Korean regulatory level. To meet that level, further research is needed to enhance the removal of the lubricant.

Keywords alkali-enhanced soil washing; lubricant oil; soap formation; surfactant-enhanced soil washing

INTRODUCTION

Recently, soil contamination has been an important environmental issue. In Korea, the sources of soil contamination include gas stations, military sites, and railway-related sites. Bioremediation and chemical oxidation methods have been applied to remediate the gas station and military sites contaminated with petroleum hydrocarbons. Thus far, however, research on railway-contaminated soil is limited (1,2). Railway-contaminated soil can be categorized on the basis of total petroleum hydrocarbon (TPH)-related contamination and heavy metal contamination. TPH-related contamination is caused by two different sources: diesel fuel and lubricant oil (1,2). In the case of diesel-related contamination, bioremediation is a common option for remediation because diesel fuel is biodegradable. However, lubricants are difficult to degrade by microorganisms, and chemical oxidation is not an effective treatment for lubricant-based contamination (2).

Soil washing/flushing processes have been widely used to remediate organic pollutants and heavy metal-contaminated sites. In soil washing, surfactants have been used as washing agents to treat hydrophobic organic compounds. The primary mechanisms for surfactant-enhanced soil washing are solubilization and mobilization. Solubilization increases the aqueous solubility of the organic phase by the dissolution of organic pollutants into the surfactant micelles, and solubilization might occur at a high concentration of surfactant. On the other hand, the mobilization mechanism reduces the interfacial tension at the interface of organic pollutant and flushing solution. Minimum interfacial tension for the surfactant solution is achieved at a low bulk surfactant concentration (3–6). The mobilization process prevails below the CMC. However, the CMC values changed according to the system. The soil washing or flushing system consists of surfactant, soil, aqueous phase, and pollutant phase. The surfactant can be adsorbed onto soil particles or partitioned into the pollutant phase. The CMC of the surfactant in this system increased considerably as compared to the aqueous system with aqueous phase and surfactant only. Generally, the term mobilization means the movement of nonaqueous phase liquid (NAPL). Lubricant oil in soil exists as a form adsorbed onto soil particles or onto soil organic matter. Consequently, the term desorption was used instead of mobilization in this study. Generally, surfactant dosage above the critical micelle concentration (CMC) is necessary for this soil washing to be effective. This mechanism has been widely researched in surfactant-enhanced soil washing (4–6). However, some chemical surfactants can be also categorized into hydrophobic

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organic pollutants, and the solubilization of pollutants into the aqueous phase might not be observed under any circumstances. That means the surfactant can be a secondary pollutant in the subsurface.

Hydrophilic-liphophilic balance (HLB) is the balance between the hydrophilic and hydrophobic portions of the surfactant molecule, which is an indicator of its solubilization behavior. Surfactants with similar value of HLB show similar characteristics of solubilization for contaminants (4–6). The higher value of HLB means the higher hydrophobicity of surfactant. Generally, surfactants with HLB value of 12–16 showed good washing ability in soil washing (4–6).

It is well known that an alkaline solution lowers the interfacial tension in enhanced oil recovery (7–13). In alkaline-enhanced oil recovery, oils contain organic acids, which react with the alkaline materials in the interface. As suggested, soaps formed under suitable conditions significantly decrease the interfacial tension, and a definite correlation exists between the interfacial tension lowering and the acid number of the oils (10). Lakatos-Szabo and Lakatos reported that the interfacial viscosity decreased dramatically in the presence of sodium hydroxide (4). Liu et al. showed that oil can be easily emulsified when alkali and very dilute surfactant are used together; they also explained that the interaction between the added surfactant and the in situ surfactant from the reaction of alkali and organic acids in oil significantly reduced the dynamic interfacial tension between oil and water (5).

In this study, a nonionic surfactant-enhanced soil washing process for railway soil contaminated with waste lubricant was investigated. Further, an alkaline-enhanced surfactant soil washing process for the removal of lubricant oil from soil was investigated.

MATERIALS AND METHODS

Materials

All surfactants used in the experiment were purchased from Aldrich Chemical Co. (Milwaukee, WI). Four nonionic surfactants, polyoxyethylene alcohols Brij30, Brij35, Brij36, and Brij56, were used in the experiment, and their properties are listed in Table 1. The surfactants were used to carry out soil washing (14). Other chemicals were purchased from Sigma-Aldrich Co. (St. Louis, MO) as ACS grade and used without further purification.

Soil

The lubricant-oil-contaminated soil used in this study was obtained from train stations in Korea. The collected soil was air dried and passed through a 2 mm sieve. Soil with a particle size of less than 2.0 mm was used for further experiments. The initial concentration of lubricant oil was 9040 mg/kg. The other physicochemical properties of the soil are summarized in Table 2.

Batch Soil Washing Experiments

First, batch tests were performed to screen the effective surfactant for the removal of lubricant oil. A mass of 20 g of soil contaminated with lubricant oil was added into a 250 ml Erlenmeyer flask and then filled with 100 ml of washing solution. The flasks were shaken at 150 rpm for 30 min. After washing the suspensions, they were centrifuged at 4000 rpm for 10 min. The soil was dried at 105°C for residual lubricant analysis. All the experiments were performed in a constant temperature room (20°C).

Column Experiment

Lubricant-oil-contaminated soil was packed into a column with an inner diameter of 2.5 cm and a height of 30 cm. The apparent soil height was 17 cm, and the bed volume of the soil was 83.5 cm^3. Glass wool was placed on both the sides of the columns to prevent soil loss by the washing solution. A ten-fold bed volume of flushing solution was continuously injected into the bottom of the soil column at 1.7 ml/min using a Masterflex L/S pump (Model No. 7524–45). The washing solution was exactly the same as that used in the batch test. After the column test, the soil was equally divided into three sections in order to analyze the residual lubricant oil. Then, the soil samples were analyzed after they were dried in an oven at 105°C for 5 h.

Analytical Method

For the analysis of lubricant oil, 10.0 g of soil was mixed with 3.0 g of anhydrous sodium sulfate in 100 ml conical

TABLE 1
Physico-chemical properties of non-ionic surfactants

Surfactant	Chemical name	Chemical structure	HLB[a]	CMC (mM)	MW
Brij30	POE[b](4) lauryl ether	$C_{12}H_{25}(CH_2CH_2O)_4OH$	9.7	0.055	362
Brij35	POE(23) lauryl ether	$C_{12}H_{25}(CH_2CH_2O)_{23}OH$	16.9	0.046	1198
Brij36	POE(10) lauryl ether	$C_{12}H_{25}(CH_2CH_2O)_{10}OH$	14.1	0.200	627
Brij56	POE(10) cetyl ether	$C_{16}H_{33}(CH_2CH_2O)_{10}OH$	12.9	0.023	683

[a] Hydrophillic-lipophilic balance.
[b] polyoxyethylene.

TABLE 2
Physico-chemical properties of soil

Properties	Contents
Initial pH	6.3
CEC (mequiv./100 g) (ASTM)	11.36
Organic contents (%) (ASTM)	5.1
Particle distribution (ASTM)	
Clay (%)	4.1
Silt (%)	23.9
Sand (%)	72.0
Initial concentration (KSTM)	
Lubricant oil (mg/kg) as a total petroleum hydrocarbon	9,040

flasks. Then 80 ml of dichloromethane was added to extract the lubricant oil, and the lubricant oil was separated by ultrasonic-enhanced solvent extraction. The extracts were concentrated with a rotary evaporator and purified by silica gel chromatography. A 2 μl solution of the extract was injected into a gas chromatograph fitted with a flame ionization detector (FID; Varian 3900, Varian, Inc., Palo Alto, CA) and an autosampler (CP-8400, Varian, Inc.). An HP-5 column (30 m length, 0.32 mm internal diameter, 0.25 μm film thickness) was used for the analysis of lubricant oil. The initial column temperature was maintained at 45°C for 2 min, increased from 45 to 310 at a rate of 10°C/min, and subsequently maintained at 310°C for 25 min. The temperatures of the injector and detector were 280°C and 320°C, respectively. Helium was used as a carrier gas at a flow rate of 1.0 cm^3/min.

RESULTS AND DISCUSSION

Screening of Surfactants

Various nonionic surfactants with different HLB values were investigated to screen the most suitable surfactant for surfactant-enhanced soil washing. Results of the batch tests showed that there was no significant difference in amount of lubricant removed by the different surfactants (Fig. 1). The deionized water without surfactant was not effective for the removal of any lubricant from soil because of the high viscosity and hydrophobicity of the oil. In a column study, the effect of HLB on differences in removal of lubricant oil were slightly clear compared to batch experiments; however, the removal efficiency was slightly lower than that of the batch experiments (Fig. 2). It was observed that an increase in hydrophile-lipophile balance (HLB) of the surfactant enhanced the removal of lubricant oil from the soil (Fig. 3). The relationship between the removal of lubricant and HLB was fitted with a linear model: removal = 10.96 + 1.015(HLB) for the batch experiment and removal = 2.59 + 1.333(HLB) for the column experiment. The correlation coefficients (R^2) were 0.97 and 0.64 for batch and column experiments, respectively. Probably, the enhancement of removal is attributed to the decrease in the adsorption of surfactant into the lubricant oil phase with an increase in the HLB values. The higher HLB values indicate that the surfactant is relatively hydrophilic, and a more hydrophilic surfactant has less hydrophobic interaction with the lubricant oil phase. A relatively small amount of surfactant was partitioned into the lubricant oil phase. A large portion of the surfactant played a role in removing the lubricant oil from the soil phase. As a result, the lubricant oil was removed more effectively from the soil phase by the relatively hydrophilic surfactant. Among the surfactants tested in this study, Brij35 showed the highest removal for lubricant oil.

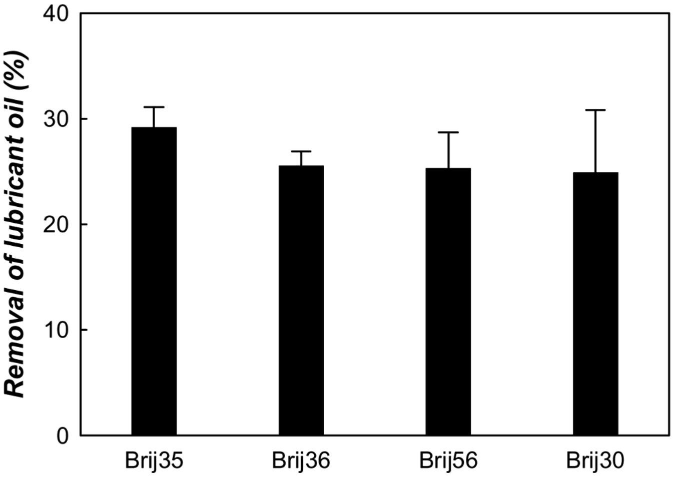

FIG. 1. Batch screening of non-ionic surfactant to removal lubricant oil 20.0 g of contaminated soil; 100 ml washing solution (0.5 wt% surfactant concentration); mixing at 150 rpm during 30 min.

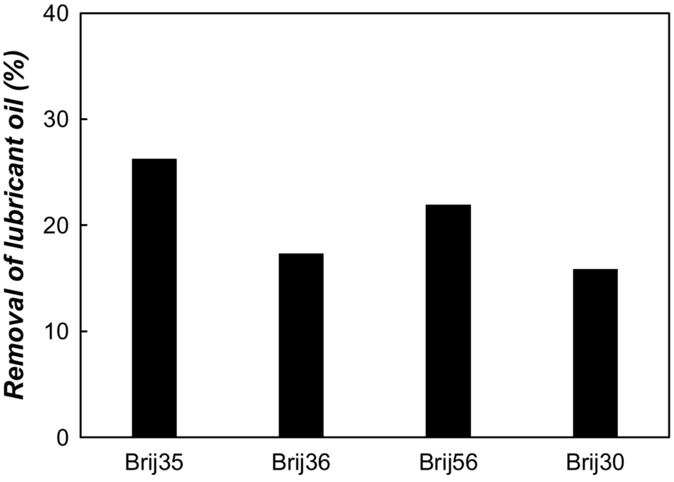

FIG. 2. Column screening of non-ionic surfactant to removal lubricant oil 10 bed volume of flushing solution containing 0.5 wt% surfactants.

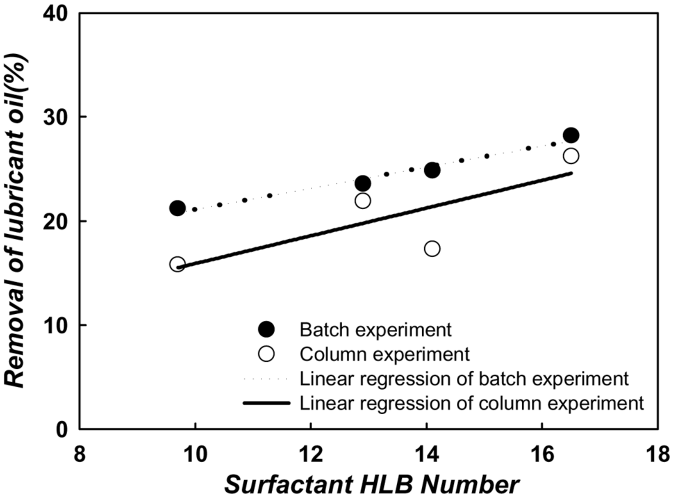

FIG. 3. Correlation between lubricant removal and hydrophilic-liphophilic balance (HLB).

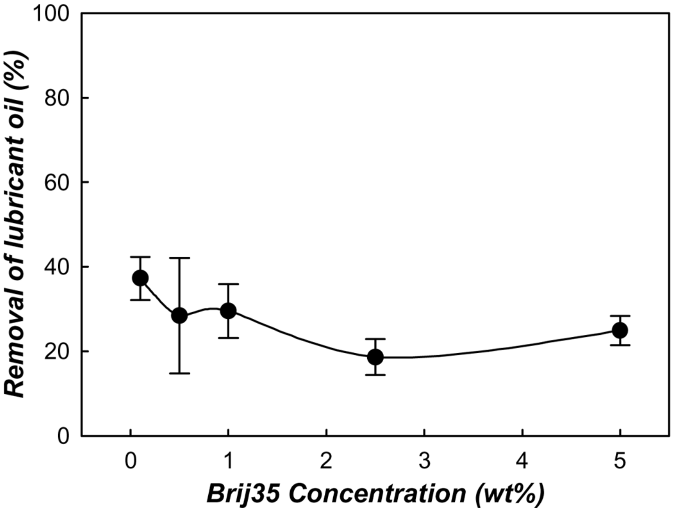

FIG. 5. Effect of Brij 35 concentration on the removal of lubricant oil in column test. 10 bed volume of flushing solution were washed the contaminated soil.

Optimization of Washing Process

To evaluate the optimum surfactant dose, the effect of surfactant concentration was investigated in a batch experiment. As the surfactant dose increased, the removal of lubricant oil gradually decreased, increased, and then reached a plateau, as shown in Fig. 4. The decrease in the amount of lubricant oil removed was attributed to the partitioning of the surfactant into the lubricant oil phase. The GC chromatogram showed a peak for surfactant with residual lubricant oil in the soil (data are not shown).

In the column experiment, the amount of lubricant oil removed decreased gradually with an increase in the concentration of the surfactant in the flushing solution (Fig. 5). Even though the partitioning of the surfactant into the lubricant oil or dissolution of the surfactant into the lubricant oil phase was relatively less than for other surfactants, the higher concentration of the surfactant increased the partitioning or dissolution of surfactant. Desorption occurred when the surfactant reduced the interfacial tension between lubricant oil and aqueous phase. At a low concentration of the surfactant, the desorption mechanism prevailed and the desorption of lubricant oil was enhanced by the surfactant. However, solubilization prevailed as the surfactant concentration increased. Because of the high hydrophobicity and viscosity of lubricant oil, the solubilization process was not active, while partitioning or dissolution of the surfactant into the lubricant oil phase occurred. In fact, the concentration of surfactant (0.1 wt%) was much higher than the CMC value of the surfactant; however, the adsorption of the surfactant onto soil organic matter and partitioning into the lubricant phase lowered the concentration of the surfactant in the aqueous phase (15). The surfactant that partitioned into the lubricant phase or adsorbed onto soil organic matter reduced the interfacial tension. As a result, a low concentration of the surfactant is more suitable to enhance the desorption process for the removal of lubricant oil from soil in the soil washing/flushing process.

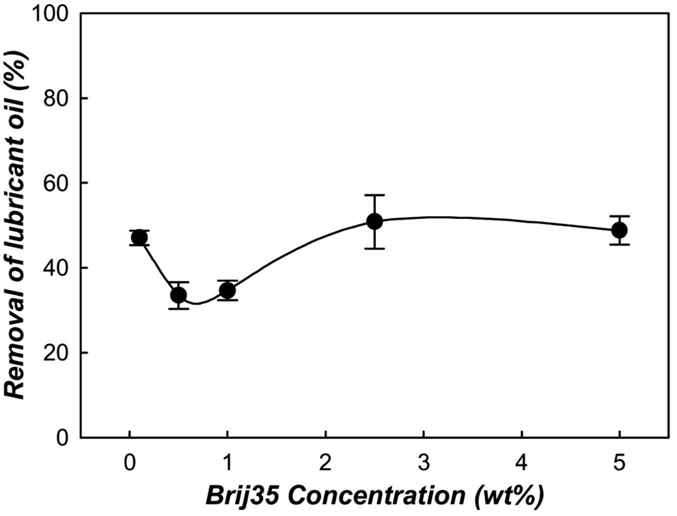

FIG. 4. Effect of Brij 35 concentration on the removal of lubricant oil in batch test. 20.0 g of contaminated soil; 100 ml washing solution; mixing at 150 rpm during 30 min.

Enhancement using Alkaline Solution

Even though the surfactant removed lubricant oil, the removal efficiency was still low and did not meet the Korean regulatory level (2000 mg/kg). Figure 6 shows the concentration effect of sodium hydroxide on the removal of lubricant oil by the soil washing process. An alkaline solution removed the lubricant oil by reducing the interfacial tension

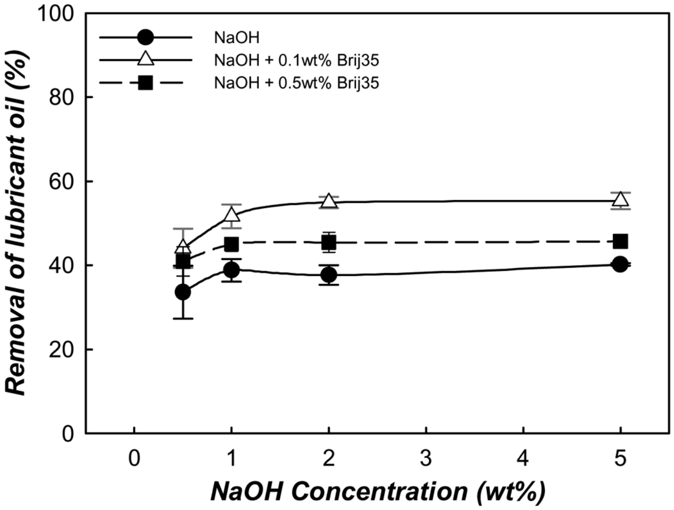

FIG. 6. Effect of alkali concentration on the removal of lubricant oil in batch test. 20.0 g of contaminated soil; 100 ml washing solution with/without Brij 35; mixing at 150 rpm during 30 min.

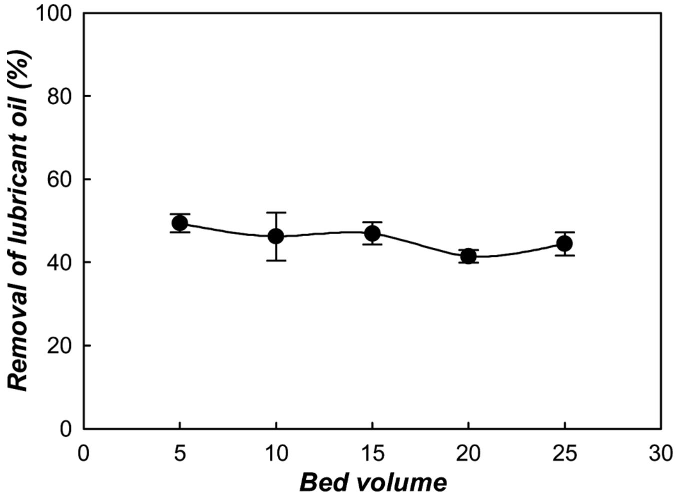

FIG. 7. Effect of bed volume on the removal of lubricant oil in column test. Flushing solution: 0.1 wt% Brij 35 in 1.0 wt% NaOH.

between the water phase and the lubricant oil phase. After a maximum removal was observed at 1.0 wt% of sodium hydroxide, the amount of lubricant oil removed gradually decreased with an increase in the concentration of the alkali. The removal efficiency of alkali only was similar to that of surfactant only, which means that alkali solution played a role similar to that of the surfactant in the system, probably forming a soap. Lubricant oil that is oxidized in soil contains a considerable amount of organic acid functional groups. The organic acid groups in the lubricant oil reacted with alkali, and finally formed a soap, a surfactant-like material. Instead of the surfactant, which can be a secondary pollutant in the subsurface, alkali solution can be an alternative. However, the removal efficiency was still too low to meet the regulatory level.

The synergy of alkali and surfactant in the removal of lubricant oil was expected because both the surfactant and the alkali reduced the interfacial tension. The addition of alkali enhanced the removal of lubricant oil in the surfactant-enhanced soil washing process (Fig. 6). A similar result was observed in the emulsification of heavy oil by alkali and surfactant (11). However, the higher concentration of the surfactant slightly decreased the removal of lubricant oil as compared to the lower concentration of the surfactant even though the removal efficiency was higher than with alkali only and surfactant only. At the higher concentration, the solubilization process was dominant, while desorption prevailed at a low concentration of the surfactant. Probably, a chemical reaction such as hydrolysis or soap formation occurred at the interface, which reduced the interfacial tension between the aqueous phase and the lubricant oil and finally enhanced the desorption of the lubricant oil from the soil.

The soil flushing process was simulated by a column experiment using alkali-enhanced surfactant (Fig. 7). The amount of lubricant removed decreased slightly as compared to that removed in the batch washing experiment. Even though more flushing solution enhanced the removal of pollutants, the effect of the bed volume of the flushing solution was negligible. Addition of alkali solution increased the amount of lubricant oil removed from 38% to 52%.

CONCLUSIONS

The removal of waste lubricant oil was proportional to the HLB value of nonionic surfactant. The dissolution of the surfactant, due to high hydrophobicity and viscosity of the oil, into the oil phase inhibited the removal of lubricant oil by surfactant at a high concentration of surfactant. Alkali solution enhanced the surfactant-enhanced soil washing and flushing process by a hydrolysis and soap formation reaction. Alkali-enhanced surfactant soil washing is a good alternative for the remediation of lubricant-contaminated soil.

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