

Soil washing using various nonionic surfactants and their recovery by selective adsorption with activated carbon

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Abstract

The performance of activated carbon in soil washing and subsequent selective adsorption for surfactant recovery from the washed solution was investigated. Sandy loam soil contaminated with phenanthrene at 200 mg kg⁻¹ was washed with four different nonionic surfactants: Tween 40, Tween 80, Brij 30 and Brij 35. The efficiency of soil washing was highest when using Brij 30 with the highest solubilizing ability for phenanthrene and low adsorption onto soil. In the selective adsorption step, surfactant recovery was quite effective for all surfactants ranging from 85.0 to 89.0% at 1 g L⁻¹ of activated carbon (Darco 20–40 mesh). Phenanthrene removal from the solution washed with Brij 30 was only 33.9%, even though it was 54.1–56.4% with other surfactants. The selectivity was larger than 7.02 except for Brij 30 (3.60). The overall performance considering both the washing and surfactant recovery step was effective when using Tween 80 and Brij 35. The results suggest that higher solubilizing ability of surfactants is a requirement for soil washing but causes negative effects on phenanthrene removal in the selective adsorption. Therefore, if a surfactant recovery process by selective adsorption is included in soil remediation by washing, the overall performance including the two steps should be considered for properly choosing the surfactant.

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1. Introduction

Remediation of soil contaminated with polycyclic aromatic hydrocarbons (PAHs) is a major environmental concern due to their toxic, mutagenic and carcinogenic properties [1–3]. The major sources of PAHs contamination are old gas manufacturing plants and leaking underground storage tanks [4]. Due to their hydrophobicity, PAHs have low water solubility and are strongly sorbed to soils and sediments [1,5]. Therefore, biodegradation of PAHs is very slow, resulting in their environmental persistence for long periods of time.

A potential technology for rapid removal of PAHs sorbed to soils is soil washing with a surfactant solution [6,7]. A surfactant

molecule has a hydrophilic head and one or more hydrophobic tails (i.e. amphiphilic compound). The unique amphiphilic structure of surfactants acts to reduce the free energy of the system by replacing the bulk molecules of higher energy at an interface [5,7]. At low concentrations in aqueous solution, single molecules (i.e. monomers) are present. However, beyond a certain concentration, referred to as the critical micelle concentration (CMC), the surfactant molecules will aggregate, form micelles and reduce the thermodynamic energy in the system. The use of surfactants enhances the solubility of PAHs significantly by partitioning it into the hydrophobic cores of surfactant micelles [8,9]. Surfactants are also able to promote the mass transfer of PAHs from a solid into an aqueous phase by micelles that decrease the interfacial tension between PAH and water.

While the use of surfactants significantly enhances the performance of soil washing, operating costs increase as surfactant dosages increase [10]. Current approaches to reduce surfactant dosage are based on selective physical separation or chemical degradation of contaminants from surfactant solutions. The

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Table 1
The selected properties of surfactants used in this study

Surfactant	Molecular formula	Hydrophobic group	MW ^a (g mol ⁻¹)	CMC ^b (mg L ⁻¹)	HLB ^c	WSR ^d (mg g ⁻¹)
TW40	C ₁₆ S ^e E ₂₀ ^f	Palmitic acid	1282	29	15.6	31.0
TW80	C ₁₈ SE ₂₀	Oleic acid	1308	13	15.0	29.2
B30	C ₁₂ E ₄	Dodecanol	362	7–14	9.7	69.5
B35	C ₁₂ E ₂₃	Dodecanol	1198	70–110	16.9	23.3

^a Molecular weight [32].

^b Critical micelle concentration [32].

^c Hydrophilic lipophilic balance number [32].

^d Weight solubilization ratio for PHE obtained in this study.

^e Sorbitan ring (C₆H₉O₅).

^f Ethylene oxide group (CH₂CH₂O).

technologies for recovering and reusing surfactants include ultrafiltration [11,12], pervaporation [13], precipitation [14], foam fractionation [15,16], solvent extraction [17] and photochemical treatment [18]. However, some of these methods are limited due to high-energy requirements, incomplete separation or the formation of potentially hazardous intermediates. Therefore, it is necessary to develop a surfactant recovery technology that is more simple, economic and effective.

In our previous study we suggested the use of activated carbon for surfactant recovery in soil washing solution by selective adsorption of contaminants [19]. The results demonstrated that selective adsorption was potentially effective to reuse surfactant in a soil washing process since the partitioning coefficients of PAHs are much higher than nonionic surfactants. In a model system using phenanthrene (PHE) as a contaminant and Triton X-100 as a nonionic surfactant, selectivity of PHE from surfactant in the adsorption process was obtained in the range of 6–75. In field washing processes, biodegradable nonionic surfactants are commonly used since they are environmentally agreeable and cost effective. Furthermore, they possess lower CMC values, and have a lower tendency to flocculate clay particles in the soil compared to ionic surfactants [7,8]. For effective soil washing, the surfactant should have higher solubilizing ability for contaminants and less sorption to soil. However, if the recovery of the surfactants is taken into consideration, a selective sorption capacity compared to contaminants on activated carbon will also significantly affect overall performance of the washing and recovery process. In this study, the effects of four types of biodegradable nonionic surfactants were used for washing soil contaminated with PHE, and subsequently recovered through selective adsorption by activated carbon. The performance of the whole process including the two steps was compared to find more effective surfactants.

2. Materials and methods

2.1. Materials

All chemicals used in the experiments were purchased from Aldrich (USA). PHE (C₁₄H₁₀, purity >98%) is a three-ring PAH with a molecular weight of 178 g mol⁻¹. Four biodegradable nonionic surfactants, polyoxyethylene sorbitan fatty acid esters (Tween 40 (TW40) and Tween 80 (TW80)) and polyoxyethylene

alcohols (Brij 30 (B30) and Brij 35 (B35)) were used in the experiments and their properties are presented in Table 1.

Charcoal-based activated carbon (Darco 20–40 mesh, Aldrich) was treated by steam activation and acid-washing processes for activation. The activated carbon has particle sizes between 0.42 and 0.85 mm. Prior to use in experiments, the activated carbon was washed with de-ionized water several times, dried at 80 °C for 24 h and stored in desiccators. The specific surface area and pore volume of activated carbon was determined on the basis of nitrogen adsorption isotherm at 77.3 K by using a surface area analyzer (ASAP 2010, Micromeritics, USA). The specific surface area was calculated according to the Brunauer–Emmett–Teller (BET) method. Specific surface area was 629 m² g⁻¹, total pore volume 0.748 mL g⁻¹, micropore volume 0.264 mL g⁻¹, mesopore volume 0.190 mL g⁻¹ and macropore volume 0.294 mL g⁻¹.

Approximately 100 kg of soil was collected from a depth of 10–40 cm beneath the ground surface at the playground of Pohang University of Science of Technology. It was air-dried for 3 days and screened to pass a US Standard No. 20 mesh (0.5 mm) sieve. The soil texture was determined by the hydrometer method [20]. The texture of the soil was sandy loam, containing 74.6% sand, 22% silt and 3.4% clay. Therefore, most of the soil particles could be removed by sedimentation for 2 h. The soil had a neutral pH (7.85) with low organic matter content (1.15 ± 0.01%). Organic matter content was calculated from the weight difference after burning at 550 °C in the furnace for 3 h. The pH of soil was determined at 20 wt% of soil in deionized-water. To prepare PHE-contaminated soil, 400 mg of phenanthrene was dissolved in 400 mL of methylene chloride and mixed with 2 kg of soil in a stainless steel container. The completely solvent-wet soil was then evaporated at room temperature with gentle shaking on a rotary shaker combined with intermittent manual mixing in a hood. The PHE-contaminated soil in the closed box was stored in the hood and used for soil washing experiments within a week.

2.2. PHE solubilization

Batch tests for solubilization of PHE in each surfactant solution ranging in concentrations (0–5 g L⁻¹) were performed. An individual 20 mL glass vial sample consisted of a 10 mL solution containing excess PHE in a given concentration of surfactant

solution. The vial was sealed with an open-port screw cap, which was fitted with a Teflon-lined septum to prevent loss of PHE from the solution. Duplicate vials for a given concentrations were shaken at 200 rpm for 76 h at 20 °C. The liquid was sampled and PHE was analyzed after filtration (0.2 µm PTFE filter; Whatman, USA). Weight solubilization ratio (WSR), mass of solubilized PHE divided by mass of surfactant dose, was obtained from the slope of the apparent solubility curve that correlates with surfactant concentrations in excess of the CMC.

2.3. Adsorption isotherm

Adsorption isotherm experiments onto soil or activated carbon were performed for each chemical of PHE and four surfactants. The adsorption experiments for surfactants was performed with two concentration ranges: various surfactant concentrations (0.5–5 g L⁻¹) at a fixed concentration of activated carbon (0.2 g L⁻¹) or soil (20 g L⁻¹) and various concentrations of activated carbon (0–2 g L⁻¹) or soil (0–20 g L⁻¹) at a fixed concentration of surfactant (0.5 g L⁻¹). The soil or activated carbon was added to 250 mL Erlenmeyer flasks and then filled with 100 mL surfactant solution. The flasks were shaken at 100 rpm on a rotary shaker at 20 °C for 48 h to reach equilibrium. For PHE, various amounts of soil (0–50 g L⁻¹) or activated carbon (0–0.1 g L⁻¹) were added to 200 mL of PHE-saturated water in 500 mL Erlenmeyer flasks. For the preparation of PHE-saturated water, de-ionized water containing PHE crystals was autoclaved at 121 °C for 20 min and excess crystals were removed by filtration. After adsorption, solid particles were removed by filtration with a 0.45 µm hydrophilic PTFE syringe filter (Whatman) and the filtrates were used for the analyses of PHE and surfactants. PHE loss by volatilization or degradation was negligible within 5%, which was confirmed by control tests without the addition of activated carbon. Analyses were run on the liquid phase and concentrations of sorbed compound were computed as the difference from the initial concentrations.

2.4. Soil washing

Fifty grams of soils contaminated with PHE at a concentration of 200 mg kg⁻¹ was added to a 1 L Erlenmeyer flask which was then filled with 500 mL of surfactant solution at 2 g L⁻¹. Soil washing was performed with duplicates for the same condition at 160 rpm on a rotary shaker for 48 h to reach equilibrium. The soil within the washed water was settled for 2 h. The supernatant was used for a subsequent selective adsorption step by adding activated carbon.

2.5. Selective adsorption

The selective adsorption experiments were performed with solutions containing both surfactant and PHE after soil washing. Activated carbon at a concentration of 1.0 g L⁻¹ was added into 250 mL Erlenmeyer flasks and then filled with 100 mL of soil washed solution. Selective adsorption tests

were performed with soil-washed solutions and model solutions to investigate the effects of soil particles. The model solutions did not contain any soil particles but were prepared with de-ionized water at concentrations of PHE and surfactant identical to the actual soil-washed solution. The adsorption process and analyses were the same as in the isotherm experiments.

2.6. Analytical methods

PHE was analyzed by high-performance liquid chromatography (HPLC, Dionex, USA) using a UV detector at 250 nm. The analytical column was a reverse-phase SUPELCOSIL LC-PAH column (150 mm × 4.6 mm). The mobile phase (85% acetonitrile and 15% de-ionized water) was eluted at a flow rate of 1.5 mL min⁻¹. Approximately 1.5 mL of liquid sample was withdrawn with a disposable glass Pasteur pipette and filtered by a pre-conditioned 0.2 µm PTFE filter (Whatman). All liquid samples were immediately measured within 1 h after sampling in order to minimize adsorption onto the wall of the sample vial. Surfactant concentration was determined by a total organic carbon (TOC) analyzer (Shimadzu TOC-V, Japan) after filtration by a GF/C filter (Whatman) to remove soil particles. This analytical method by TOC was confirmed by comparing a known concentration of surfactant solution with or without supernatant obtained from soil washing and sedimentation for 2 h.

2.7. Data calculation

The fraction of surfactant dissolved in solution ($f_{1,\text{surf}}$, %) after adsorption by activated carbon and the fraction of PHE sorbed to activated carbon ($f_{\text{AC},j}$, %) can be obtained from experimental adsorption data as following equation:

$$f_{1,\text{surf}} = \frac{C_{1,\text{surf}}}{C_{1,\text{surf,ini}}} \times 100 \quad (1)$$

$$f_{\text{AC},j} = \frac{C_{\text{AC},j} f_{\text{AC}/1}}{C_{1,j,\text{ini}}} \times 100 \quad (2)$$

where $C_{1,\text{surf}}$ is the concentration of surfactant in the liquid after adsorption (g L⁻¹), $C_{1,\text{surf,ini}}$ is the initial concentration of surfactant in the liquid before adsorption (g L⁻¹), $C_{\text{AC},j}$ is the concentration of PHE sorbed to activated carbon (mg g⁻¹), $f_{\text{AC}/1}$ is the fraction of activated carbon in liquid (g L⁻¹) and $C_{1,j,\text{ini}}$ is the initial concentration of PHE in the liquid before adsorption (mg L⁻¹).

The efficiency of the selective adsorption process can be determined by selectivity (S), expressed as:

$$S = \frac{C_{\text{AC},j}}{C_{1,j}} \times \frac{C_{1,\text{surf}}}{C_{\text{AC},\text{surf}}} \quad (3)$$

where $C_{1,j}$ is the concentration of PHE in the liquid after adsorption (mg L⁻¹) and $C_{\text{AC},\text{surf}}$ is the concentration of surfactant sorbed to activated carbon (g g⁻¹).

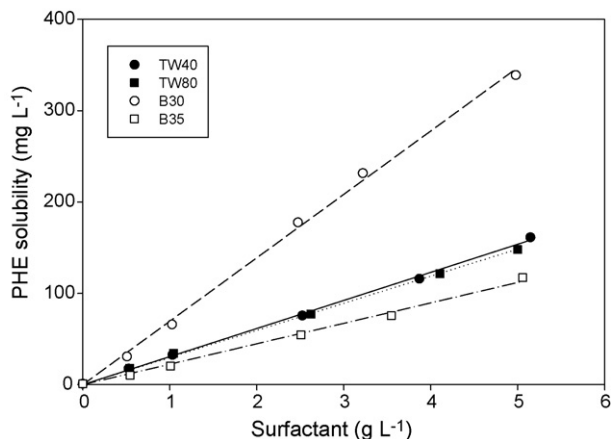


Fig. 1. Solubilization of PHE by nonionic surfactants. The slope of the solubilization curve is equal to the weight solubilization ratio.

3. Results and discussion

3.1. PHE solubilization

The plot of apparent PHE solubility versus concentration of each surfactant is shown in Fig. 1. Solubilization of PHE by micellar surfactant is characterized by the weight solubilization ratio (WSR) [9,21]. The value of WSR was highest (69.5 mg g^{-1}) for B30, which was two to three times greater than WSR values of the other three surfactants in the range of $23.3\text{--}31.0 \text{ mg g}^{-1}$. The solubility of PHE in surfactant solution was dependent on hydrophilic lipophilic balance (HLB) value of surfactant. In most cases, solubilizing ability of surfactant increases with decreasing HLB (i.e. more lipophilic). Thus, it was reasonable that B30 having the shortest hydrophilic ethylene oxide group and the lowest HLB value (9.7) showed the highest WSR value. The results of solubility experiments indicate that B30 will have the highest soil washing efficiency.

3.2. Adsorption isotherms of surfactants

The adsorption results for four surfactants onto soil are shown in Fig. 2. The adsorption of surfactant onto soil was categorized by two patterns. The first is the case for B30 and B35, which showed the formation of a plateau starting at a low equilibrium concentration (approximately 0.2 g L^{-1}) (Fig. 2). The second pattern showed an undistinguished plateau but a gradual increase of surfactant sorbed, which was in the case with TW40 and TW80. The appearance of a plateau for micelle-forming nonionic surfactants was also observed in other reports using silica [22] and soils [21,23].

The experimental data have been fitted to the Langmuir model [24] and to the Freundlich model [21,23]:

$$\text{Langmuir: } C_{s,\text{surf}} = \frac{Q_o b C_{1,\text{surf}}}{1 + b C_{1,\text{surf}}} \quad (4)$$

$$\text{Freundlich: } C_{s,\text{surf}} = K_F C_{1,\text{surf}}^{1/n} \quad (5)$$

where $C_{s,\text{surf}}$ is the equilibrium concentration of surfactant sorbed onto soil (g g^{-1}), Q_o is the monolayer adsorption capac-

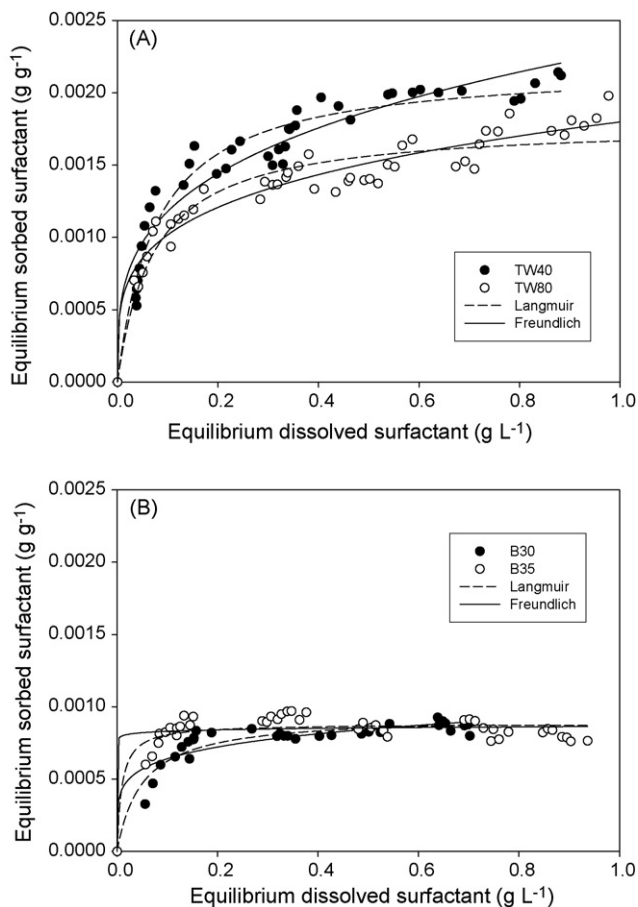


Fig. 2. Equilibrium adsorption isotherms of each nonionic surfactant by soil. (A) TW40 and TW80 and (B) B30 and B35.

ity (g g^{-1}), b is the parameter related to the adsorbate–adsorbent interaction energy, $C_{1,\text{surf}}$ is the equilibrium concentration of surfactant in the liquid (g L^{-1}), K_F is a measure of sorption capacity and $1/n$ is an indicator of the curvature of the isotherm. The parameters (Q_o , b , K_F and n) for four surfactants are summarized in Table 2.

The fitting with experimental data was generally in good agreement with both isotherm models except for B35. The K_F

Table 2

The isotherm constants for surfactant adsorption onto soil and activated carbon

	Surfactant	Soil			Activated carbon		
		K_F	$1/n$	r^2	K_F	$1/n$	r^2
Freundlich	TW40	0.0029	0.287	0.917	0.259	0.186	0.956
	TW80	0.0018	0.247	0.932	0.236	0.147	0.943
	B30	0.0010	0.172	0.842	0.332	0.119	0.865
	B35	0.0009	0.017	0.743	0.296	0.104	0.931
	Surfactant	Soil			Activated carbon		
		Q_o	b	r^2	Q_o	b	r^2
Langmuir	TW40	0.0022	13.0	0.943	0.284	12.6	0.706
	TW80	0.0018	13.9	0.888	0.242	30.0	0.795
	B30	0.0009	19.9	0.906	0.334	294.1	0.563
	B35	0.0009	106.6	0.781	0.292	121.6	0.761

value of the Freundlich model and the Q_0 value of the Langmuir model indicate that the adsorption capacity of surfactant on the soil was higher in the sequence of TW40 > TW80 > B35 or B30. Although Tween series showed a gradual increasing pattern, the sorbed amount was nearly constant at higher surfactant concentrations (above 0.6 g L^{-1} for TW40 and 0.8 g L^{-1} for TW80). The maximum amounts of surfactants sorbed on soil were in the range of $0.75\text{--}2.2 \text{ mg g}^{-1}$. The values were used for the design of soil washing experiments.

The adsorption isotherms for activated carbon are shown in Fig. 3. For all surfactants, the equilibrium concentration of surfactant sorbed was increased gradually above approximately 0.5 g L^{-1} equilibrium surfactant concentration. The Freundlich model showed good agreement with experimental data for all surfactants. However, the fitting by the Langmuir model showed large discrepancy at higher surfactant concentrations. The Langmuir model assumes that there is no interaction among adsorbed molecules and there is a constant average adsorption free energy. The results indicate that some lateral interactions between surfactant molecules occurred at high concentrations of surfactant. It has been known that the possible configurations of the flexible hydrophilic chain of adsorbed surfactants in solution and at the solid–liquid interface are numerous ranging from a flat to a ran-

dom coil [24]. Thus, a possible mechanism of high discrepancy from the Langmuir model for activated carbon compared to soil would be a more significant alteration of surface characteristics in activated carbon through pore blocking by hydrophilic chains.

The maximum amounts of surfactants sorbed on activated carbon were in the range of $0.25\text{--}0.46 \text{ g g}^{-1}$, which were greater than two orders of magnitude of those for soil. The adsorption capacity of surfactant on the activated carbon was higher in the sequence of B30 > B35 > TW40 > TW80. The sequence of adsorption capacity of surfactants on activated carbon was different from that on soil. This difference seems to be caused by much higher hydrophobicity of activated carbon and its high porosity. High adsorption capacity of B30 on activated carbon is possibly attributed to its high hydrophobicity (or low HLB) and small size. In particular, B30 is able to enter smaller pores than the size of other surfactants. In hydrophobic surface like activated carbon, hydrophobic group directs to surface. Thus, TW40 and TW80 having a larger hydrophobic group seemed to be sorbed in a less amount compared to B30 and B35. As a result, B30 and B35 was more effective for soil washing due to lower sorption capacity, but was less effective in surfactant recovery using activated carbon due to a higher sorption capacity.

3.3. Adsorption isotherms of phenanthrene

The adsorption isotherms for PHE onto the soil and activated carbon are shown in Fig. 4. The K_F values of the Freundlich isotherm model were 0.034 ($r^2 = 0.823$) and 51.9 ($r^2 = 0.955$) for soil and activated carbon, respectively. The $1/n$ values were close to 1 (1.00 and 1.09 for soil and activated carbon), indicating that the experimental data also fit the linear isotherm model expressed as:

$$C_{AC,j} = K_L C_{l,j} \quad (6)$$

where K_L is the linear partition coefficient of PHE between soil or activated carbon and liquid (L g^{-1}).

The adsorption constants for both the Freundlich isotherm and the linear isotherm are summarized in Table 3. The partition coefficient (K_L) in the linear isotherm model was approximately 1400 times higher for activated carbon (50.0) than for soil (0.035). For the adsorption of polycyclic aromatic hydrocar-

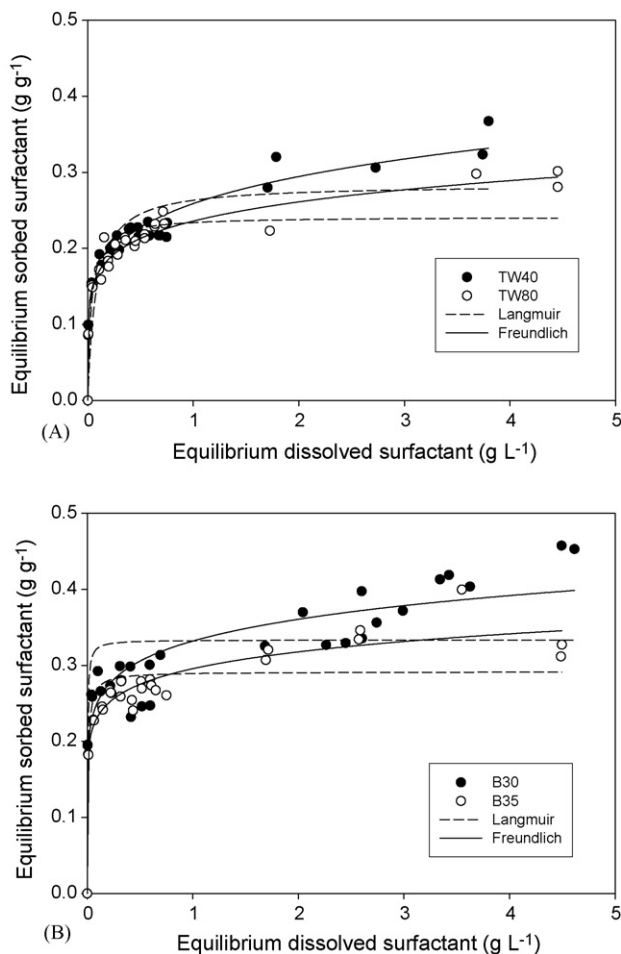


Fig. 3. Equilibrium adsorption isotherms of each nonionic surfactant by activated carbon. (A) TW40 and TW80 and (B) B30 and B35.

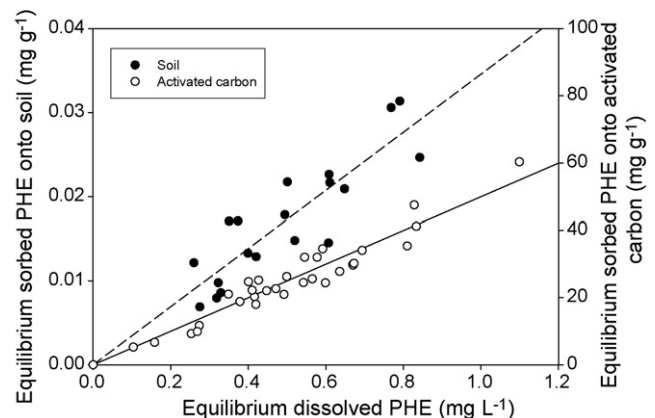


Fig. 4. Equilibrium adsorption isotherms of PHE by soil or activated carbon.

Table 3
The isotherm constants for PHE adsorption onto soil and activated carbon

	Freundlich isotherm			Linear isotherm	
	K_F	$1/n$	r^2	K_L	r^2
Soil	0.034	1.00	0.823	0.035	0.823
Activated carbon	51.9	1.09	0.955	50.0	0.921

bons, a linear correlation is often observed on natural organic compounds or soils [2,25,26]. In the case of activated carbon, equilibrium partitioning of a hydrophobic organic compound was described by a linear isotherm when the span of concentrations is not too large [27]. At the same liquid concentration, the amount of PHE sorbed on activated carbon can be deduced to be much higher than that of all surfactants (Figs. 2 and 3), indicating that selective adsorption of PHE to the surfactants on activated carbon is possible.

3.4. Soil washing

The four surfactants were used for soil washing in soil contaminated with PHE at a concentration of 200 mg kg^{-1} . Since the maximum adsorption capacity of surfactants onto soil was obtained below 0.0022 g g^{-1} in the adsorption isotherm tests, the minimum requirement of surfactant was 0.11 g for 50 g soil and 0.5 L solution per batch flask. The concentration of surfactant in the washing solution was determined to be 2 g L^{-1} , which was expected to be sufficient to dissolve PHE in the soils by considering the weight solubilization ratio (Table 1).

Soil washing would be more effective when surfactants with a low adsorption capacity to soil were used. Most surfactants, approximately above 90%, remained in liquid after washing (Table 4). Among them the surfactant remaining in liquid the least amount was TW40 (87.5%) due to its high adsorption capacity, as expected. Another important factor for efficient soil washing is the WSR value of the surfactant, since surfactants with higher WSR values more efficiently solubilize PHE with the addition of equal amounts of surfactant. The highest WSR value was obtained with B30 (69.5 mg g^{-1}) and the values of others were in the range of $23.3\text{--}31.0 \text{ mg g}^{-1}$.

Overall washing efficiency is determined mainly by the combined effects of adsorption capacity and WSR. For example, although WSR of TW40 was higher than B35, the averaged washing efficiency in TW40 ($55.5 \pm 8.1\%$) was not higher

Table 5
Selectivity values for actual soil-washed solutions and model water solution during activated carbon adsorption

Surfactant	Solution	$f_{i,\text{surf}}^a$ (%)	$f_{\text{AC},j}^b$ (%)	Selectivity
TW40	S	89.0 ± 0.6	56.4 ± 0.8	10.5 ± 1.01
	W	85.9 ± 0.2	79.5 ± 3.2	23.9 ± 4.32
TW80	S	86.9 ± 0.1	54.1 ± 3.5	7.86 ± 1.15
	W	88.2 ± 0.9	68.6 ± 10.0	17.3 ± 6.54
B30	S	87.5 ± 1.0	33.9 ± 1.5	3.60 ± 0.09
	W	87.9 ± 0.5	32.7 ± 3.4	3.57 ± 0.72
B35	S	85.0 ± 0.6	54.9 ± 4.4	7.02 ± 1.58
	W	86.2 ± 0.3	75.1 ± 4.4	19.4 ± 4.93

S, Actual soil-washed solution; W, model water solution containing the same PHE and surfactant concentrations as S solution.

^a The fraction of surfactant dissolved in the solution.

^b The fraction of PHE sorbed to activated carbon.

than that in B35 ($71.6 \pm 16.3\%$). It was caused by the lower liquid concentration of TW40 ($1.74 \pm 0.16 \text{ g L}^{-1}$) than B35 ($2.02 \pm 0.04 \text{ g L}^{-1}$) after adsorption of the surfactants onto soil. The overall washing results indicated that the most efficient surfactant for soil washing was B30.

3.5. Selective adsorption by activated carbon

The soil within washed solution was settled for 2 h and the supernatant was used for the selective adsorption step. In the settling procedure, $99.4 \pm 0.1\%$ of soil particles were removed. The concentration of surfactants sorbed onto the activated carbon ranged from 0.20 g g^{-1} (TW40) to 0.30 g g^{-1} (B35), which was close to the maximum sorption level. The remaining fraction of surfactant after adsorption onto activated carbon was quite high, ranging from 85.0 to 89.0%, and not very different among nonionic surfactants (Table 5). This is because the volume of the solution was relatively high (1 L to g activated carbon) compared to the mass of the activated carbon. Only a small amount of surfactant was required to adsorb onto the activated carbon even at maximum levels. Thus, the difference in adsorption isotherms among surfactants did not significantly affect the surfactant recovery in the selective adsorption step. In the case of PHE, the amount of PHE sorbed onto activated carbon ranged from 5.52 to 9.11 mg g^{-1} . The fraction of PHE sorbed to activated carbon was in the range of 54.1–56.4% for TW40, TW80 and B35. However, in the case of B30, the fraction

Table 4
Overall performance for PHE removal and surfactant recovery using various surfactants

Surfactant	Washing step		Selective adsorption step ^a		Overall surfactant recovery (%)
	PHE removal (%)	Surfactant loss ^b (%)	PHE removal (%)	Surfactant loss ^b (%)	
TW40	55.5 ± 8.1	12.5 ± 7.4	29.3 ± 0.4	10.2 ± 0.6	82.3 ± 0.6
TW80	72.4 ± 10.5	5.8 ± 4.1	40.5 ± 2.6	12.9 ± 0.1	85.5 ± 0.1
B30	84.1 ± 5.1	5.0 ± 0.1	27.6 ± 1.3	11.7 ± 1.0	82.3 ± 1.0
B35	71.6 ± 16.3	N.A.	45.6 ± 3.7	15.0 ± 0.6	85.0 ± 0.6

The values are based on the initial masses of PHE and surfactant.

^a The value excludes the amount in the washed solution and represents the amount removed by activated carbon only.

^b Surfactant loss occurred by adsorption onto soil or activated carbon.

was quite low (33.9%). The low efficiency in PHE sorption by activated carbon in the B30 solution was likely due to its high WSR value, which caused a greater shift of PHE partitioning into solution. There is a possibility that sorbed surfactant enhances the sorption of PHE by surfactant–PHE interaction. However, such an effect did not appear significantly since the amount of sorbed surfactant was very small compared to that in liquid and also the difference of sorbed amount of each surfactant was not very high.

The selectivity value was highest (10.5) for TW40, ranging from 3.60 to 7.86 for the other surfactants (Table 5). Surfactant recovery is considered successful only if the adsorption process removes relatively more contaminants than surfactants. For effective surfactant recovery, a higher sorbed fraction of PHE and liquid fraction of surfactant is preferred. A selectivity value larger than 1 indicates that more contaminants relative to surfactant are adsorbed to the activated carbon, and that surfactant recovery is theoretically possible. In field washing process, although wastewater treatment is reduced by surfactant reuse, additional facilities are required for the operation of the recovery process. Although the goal of selectivity to attain a successful recovery process depends on cost evaluation based on additional investment on the process, much higher selectivity than 1 at least would be acceptable in practical application.

The liquid fraction of surfactant in actual soil-washed solutions was quite similar to a model water solution containing the same PHE and surfactant concentration as the soil-washed solution. However, there was a slight decrease (0–23%) in the sorbed fraction of PHE in the soil-washed solution compared to the model water solution. Such a decrease in the sorbed amount of PHE in the soil-washed solution is likely due to natural organic matter present in the solution. Although the amount of particles and dissolved organic matter from soil were very small (approximately 0.6 g L^{-1}), they had some effects on PHE solubility and sorption capacity of activated carbon. Soil organic matter in a dissolved form may cause an increase in PHE solubility by changing micellar structure or by direct interaction with PHE [28,29]. Another reason may be a decrease in the adsorption surface of activated carbon through the adsorption or pore blocking by organic matters. It has been reported that natural organic matter negatively affects the sorption capacity of sorbent [30,31]. These results suggest that soils containing high amounts of clay particles and organic matter may significantly reduce the efficiency of a selective adsorption process, and removal of soil particles will be very important to overall performance.

3.6. Overall performance

The overall performance for PHE removal and surfactant recovery based on the initial mass of those chemicals is summarized in Table 4. Lower PHE removal in the selective adsorption step than that of the washing step is because the remaining PHE in the solution after selective adsorption will not be removed in strict meaning when the solution is reused for soil washing. Therefore, the PHE removal in the selective adsorption step is

assumed to be identical to overall PHE removal in the entire process.

The effectiveness of surfactant varied for different separation steps. In the washing step, the best surfactant was B30 showing 84.1% PHE removal due to its superior solubilizing ability as estimated by the WSR. The worst surfactant was TW40 showing 55.5% PHE removal due to large surfactant loss (12.5%) by sorption onto soil. In the selective adsorption step, PHE removal was relatively higher for TW80 and B35 than for TW40 and B30. The effectiveness of TW40 was reduced by surfactant loss in the previous washing step, even though the selectivity was highest in the selective adsorption step (Table 5). B30 also was not effective in the selective adsorption step and in overall performance, even though its washing efficiency was highest. Thus, higher washing efficiencies will not always indicate the best choice in surfactant with respect to the selective sorption process and reuse of the surfactant.

4. Conclusion

The performance of soil washing and selective adsorption by activated carbon was investigated using four different nonionic surfactants. Soil washing efficiency was high when using a surfactant with high solubilizing ability for PHE and low adsorption to soil. In this context, B30 showed the highest efficiency with 84.1% PHE removal from soil at a surfactant concentration of 2 g L^{-1} . However, such a high solubilizing ability caused negative effects on PHE removal by activated carbon in the selective adsorption step. PHE removal from the solution washed with B30 was only 33.9%, even though it was 54.1–56.4% with other surfactants. As a result, the overall performance considering both the washing and surfactant recovery step was effective when using TW80 and B35. In the selective adsorption step, surfactant recovery was quite effective for all surfactants used and ranged from 85.0 to 89.0% at 1 g L^{-1} of activated carbon. Thus, higher washing efficiency will not always indicate the best choice of surfactant with respect to the selective sorption process and reuse of the surfactant. Effective removal of PHE by selective adsorption can be achieved by increasing activated carbon amounts without a significant reduction in surfactant recovery.

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