



Mathematical evaluation of activated carbon adsorption for surfactant recovery in a soil washing process

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ABSTRACT

The performances of various soil washing processes, including surfactant recovery by selective adsorption, were evaluated using a mathematical model for partitioning a target compound and surfactant in water/sorbent system. Phenanthrene was selected as a representative hazardous organic compound and Triton X-100 as a surfactant. Two activated carbons that differed in size (Darco 20–40 mesh and >100 mesh sizes) were used in adsorption experiments. The adsorption isotherms of the chemicals were used in model simulations for various washing scenarios. The optimal process conditions were suggested to minimize the dosage of activated carbon and surfactant and the number of washings. We estimated that the requirement of surfactant could be reduced to 33% of surfactant requirements (from 265 to 86.6 g) with a reuse step using 9.1 g activated carbon (>100 mesh) to achieve 90% removal of phenanthrene (initially 100 mg kg⁻¹ soil) with a water/soil ratio of 10.

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1. Introduction

Remediation of soil contaminated with polycyclic aromatic hydrocarbons (PAHs) is a major environmental concern due to their toxic and carcinogenic properties [1–3]. Due to their hydrophobicity, PAHs have low water solubility and are strongly sorbed to soils and sediments, resulting in its persistence in environments for long periods. A potential technology for rapid removal of PAHs sorbed to soils is soil washing with surfactant solution [4,5]. Beyond a certain concentration, referred to as the critical micelle concentration (CMC), the surfactant molecules form micelles and enhance the solubility of PAHs significantly by partitioning them into the hydrophobic cores of surfactant micelles [6–8].

However, the surfactant-enhanced remediation is often not economically acceptable, since operation costs can be increased by up to 50% due to chemical costs of surfactant [9]. Therefore, surfactant solution after washing should be separated from contaminants and reused. Current approaches to recovering and reusing surfactant include ultra-filtration [10,11], precipitation [12], foam fractionation [13], solvent extraction [14], photochemical treatment [15,16], and selective adsorption by activated carbon [17].

Amongst the numerous techniques of surfactant recovery, selective adsorption is an alternative process since the operation is simple and requires low energy. The major requirement for the successful recovery of surfactant from soil washed solution is high selectivity of contaminants from surfactant in the adsorption process. Activated carbon is an excellent selective adsorbent because PAHs are highly hydrophobic compared to most nonionic surfactants used in soil washing processes. Our previous study demonstrated that selective adsorption by activated carbon was greatly effective to reuse surfactant in a soil washing process since the partitioning coefficients of PAHs are much higher than nonionic surfactants [17]. In a model system using phenanthrene (PHE) as a contaminant and Triton X-100 (TX100) as a non-ionic surfactant, these compounds were widely used to laboratory researches due to less toxic the selectivity of PHE was obtained in the range of 6–75. Generally, the concentration of surfactant is much higher than the concentration of contaminant in a washed solution. This fact also provides advantages for surfactant reuse by selective adsorption since only small amount of contaminant needs to be removed from the bulk surfactant solution.

The effectiveness of the surfactant recovery process varies with the operating conditions and the concentrations of the different components, including contaminant, surfactant, and activated carbon, in the adsorption system. Therefore, it is necessary to understand the key factors and estimate the feasibility of the process mathematically before conducting labor-intensive experimental tests for all conditions. In this study, the process feasibility

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was evaluated using a mathematical model for partitioning the target compound and surfactant in the water/soil and water/activated carbon systems. Adsorption isotherms data for both PHE and TX100 were used for model calculations for two activated carbons with different particle size. The optimal process conditions were suggested to minimize the dosage of activated carbon and surfactant and the number of washings. The performance of the process including surfactant reuse was compared to the performance of the conventional process without the reuse step.

2. Model simulation

2.1. Surfactant reuse process

A schematic of the conceptual process for surfactant reuse by activated carbon adsorption in soil washing is presented in Fig. 1. In the actual process, the separation process (e.g., sedimentation or filtration) of solid particles from solutions in flows 5 and 8 should be included. However, it was assumed that the separation was complete and the solutions did not contain any particles for simplicity during model simulation. Therefore, the modeling results will reflect only the behavior of dissolved chemicals in the solutions.

The unit process of adsorption was assumed to be a completely mixed batch system. The surfactant recovery was considered successful only if the adsorption process removed more contaminants than surfactants. The efficiency of the adsorption process was determined by selectivity, expressed as:

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

where $C_{AC,j}$ (mg kg^{-1}) and $C_{l,j}$ (mg L^{-1}) are the concentrations of PAH, designated as compound j , in activated carbon and liquid, and $C_{AC,surf}$ (g kg^{-1}) and $C_{l,surf}$ (g L^{-1}) are the concentrations of surfactant in activated carbon and liquid, respectively. A selectivity value larger than 1 indicates that more contaminants relative to surfactant are adsorbed to activated carbon and that surfactant recovery is theoretically possible.

2.2. PAH or surfactant partitioning in the water/sorbent system

Partitioning of chemicals occurs in two systems: the PAH/surfactant/water/soil system for soil washing and the PAH/surfactant/water/activated carbon system for selective adsorption. The partitioning equations can be applied identically to both systems except for sorption capacity of each sorbent, soil and activated carbon. In the initial step, a simplified PAH/water/sorbent or surfactant/water/sorbent system was assumed in order to derive partitioning equations for each chemical in the absence of the other chemical.

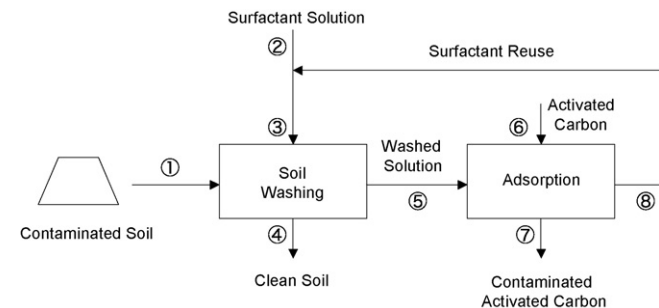


Fig. 1. Schematic of the soil washing process using surfactant recovery unit by selective adsorption.

First, in the PAH/water/sorbent system, the total concentration of PAH is the sum of PAH partitioning to liquid and sorbent:

$$C_{t,j} = C_{aq,j} + f_{s/l} C_{sorb,j} \quad (2)$$

where $C_{t,j}$ is the total concentration of PAH in the system (mg L^{-1}), $C_{aq,j}$ is the concentration of PAH in liquid phase (mg L^{-1}), $f_{s/l}$ is the concentration of sorbent in liquid (kg L^{-1}), and $C_{sorb,j}$ is the concentration of PAH sorbed to sorbent (mg kg^{-1}).

Equilibrium partitioning of a hydrophobic organic compound in most soil-slurry systems can be described by a linear isotherm when the span of concentrations is not too large [18,19]. A linear isotherm can also be applied to activated carbon as a sorbent [17]. The partitioning equation of PAH is expressed as:

$$C_{sorb,j} = K_d C_{aq,j} \quad (3)$$

where K_d is the partition coefficient of PAH between sorbent and liquid (L kg^{-1}). K_d for soil can be estimated using the following relationships, provided the octanol/water partition coefficient of compound j (K_{ow}) and the fraction of organic carbon in soil ($f_{oc,soil}$, $\text{kg organic carbon (kg soil)}^{-1}$) are known [18]:

$$K_d = 0.63 f_{oc,soil} K_{ow} \quad (4)$$

Second, in the surfactant/water/sorbent system, the surfactant exists in three forms: monomer, micelle, and sorbed to sorbent:

$$C_{t,surf} = C_{l,mon} + C_{l,mic} + f_{s/l} C_{sorb,surf} \quad (5)$$

where $C_{t,surf}$ is the total concentration of surfactant in the system (g L^{-1}), $C_{l,mon}$ is the concentration of surfactant as monomer in liquid phase (g L^{-1}), $C_{l,mic}$ is the concentration of micelle in liquid phase (g L^{-1}), and $C_{sorb,surf}$ is the concentration of surfactant sorbed to sorbent (g kg^{-1}).

It has been reported that sorption of micelle-forming nonionic surfactants to soil shows a maximum value, independent of the soil to water ratio [20]. A micelle begins to form in the liquid phase when more than the maximum value of surfactants is added to the system. Therefore, the critical micelle concentration (CMC) in the water/sorbent system is increased as much as the sorbed amount [20,21]. Likewise, when activated carbon was used as the sorbent, similar phenomena were observed [17]. The CMC value in the water/sorbent system can be expressed as:

$$\text{CMC}(s) = f_{s/l} Q_{\max} + \text{CMC} \quad (6)$$

where $\text{CMC}(s)$ is the critical micelle concentration when sorbent exists (g L^{-1}), and C_{\max} (g kg^{-1}) is the concentration of surfactant sorbed to sorbent at $\text{CMC}(s)$. Monomer and micelle concentrations in the water/sorbent system were then calculated according to the total dose of surfactant.

$$C_{l,mic} = C_{t,surf} - \text{CMC}(s) \quad \text{and} \quad C_{l,mon} = \text{CMC} \quad (\text{if } C_{t,surf} \geq \text{CMC}(s)) \quad (7a)$$

$$C_{l,mic} = 0 \quad (\text{if } C_{t,surf} < \text{CMC}(s)) \quad (7b)$$

2.3. PAH partitioning in the surfactant/water/sorbent system

The organic carbon fraction in sorbent ($f_{oc,sorb}^*$, g g^{-1}), after sorption of surfactants, is changed as follows:

$$f_{oc,sorb}^* = f_{oc,sorb} + f_{c,surf} C_{sorb,surf} \times 10^{-3} \quad (8)$$

where $f_{oc,sorb}$ is the fraction of organic carbon in the original sorbent (g g^{-1}), $f_{c,surf}$ is the weight fraction of carbon in the surfactant molecule (g g^{-1}), and $f_{sorb,surf}$ is the concentration of surfactant sorbed to sorbent (g kg^{-1}).

The partition coefficient of PAH between sorbent and aqueous phase at CMC(s) ($K_{d,cmc}$, $L\ kg^{-1}$) is expressed as [22]:

$$K_{d,cmc} = K_d \left(\frac{S_w}{S_{cmc}} \right) \left(\frac{f_{oc,sorb}^*}{f_{oc,sorb}} \right) \quad (9)$$

where S_w is the total apparent solubility of PAH in pure liquid ($mg\ L^{-1}$), and S_{cmc} is the total apparent solubility of PAH at CMC ($mg\ L^{-1}$).

The molar solubilization ratio (MSR, $mol\ mol^{-1}$) can be obtained from the micellar phase/aqueous phase partitioning coefficient of PAH (K_m). The value of K_m is constant in the presence or absence of separate-phase PAH, whereas the value of MSR in the absence of separate-phase PAH varies with surfactant dose as a result of changes in the aqueous-phase PAH concentration. The value of MSR can be expressed as [22]:

$$K_m = \left(\frac{1}{\bar{C}_{aq,j} V_w} \right) \frac{MSR}{1 + MSR} \quad \text{or} \quad MSR = \frac{K_m V_w \bar{C}_{aq,j}}{1 - K_m V_w \bar{C}_{aq,j}} \quad (10)$$

where V_w is the molar volume of water in a system ($L\ mol^{-1}$). The upper bar on the concentration symbol represents the molar concentration.

The single known variable, $C_{aq,j}$, can be obtained from the following mass balance of PAH. Assuming a theoretical system in the absence of surfactant (designate as superscript 'I'), the total PAH is the same as that in the system containing surfactant (designated as superscript 'II').

$$\bar{C}_{aq,j}^I + f_{s/l} \bar{C}_{sorb,j}^I = \bar{C}_{aq,j}^{II} + \bar{C}_{mic,j}^{II} + f_{s/l} \bar{C}_{sorb,j}^{II} \quad (11)$$

$$\bar{C}_{sorb,j}^I = K_d \bar{C}_{aq,j}^I \quad (12)$$

$$\bar{C}_{mic,j}^{II} = MSR \bar{C}_{aq,j}^{II} \quad (13)$$

$$\bar{C}_{sorb,j}^{II} = K_{d,cmc} \bar{C}_{aq,j}^{II} \quad (14)$$

where $\bar{C}_{mic,j}$ is the concentration of PAH in micelle ($mol\ L^{-1}$).

Incorporation of (12)–(14) into (11) and rearranging yields a quadratic equation, which upon the solution [22] yields

$$\bar{C}_{aq,j}^{II} = \frac{-b + (b^2 - 4ac)^{0.5}}{2a} \quad (15)$$

$$a = -K_m V_w (1 + K_{d,cmc} f_{s/l}) \quad (16a)$$

$$b = \bar{C}_{aq,j}^I K_m V_w (1 + K_d f_{s/l}) + (1 + K_{d,cmc} f_{s/l}) + K_m V_w \bar{C}_{aq,j}^{II} \quad (16b)$$

$$c = -\bar{C}_{aq,j}^I (1 + K_d f_{s/l}) \quad (16c)$$

Then, the concentrations of compound j in sorbed, micellar, and aqueous phases, respectively, are determined. The set of analytical equations was solved using Microsoft Excel. Some variables, including the water to soil ratio, initial contamination, and soil conditions, were fixed in the model simulations (Table 1). The partition coefficients of PHE and TX100 were obtained experimentally for the two activated carbons. The model simulations were carried out with critical variables, such as surfactant and activated carbon dose.

3. Materials and methods

3.1. Materials

All chemicals used in the experiment were purchased from Aldrich (USA). PHE ($C_{14}H_{10}$, purity >98%) is a three-ring polycyclic aromatic hydrocarbon with a molecular weight of $178\ g\ mol^{-1}$. TX100 ($C_8H_{17}C_6H_4O(CH_2CH_2O)_{9.5}H$) is a nonionic octylphenol ethoxylate surfactant with a molecular weight of $625\ g\ mol^{-1}$. TX100 was used to as a model surfactant in this study since it is known to be one of the most widely used surfactant

Table 1
Summary of parameter values in model calculations

Parameter	Value
Soil mass (kg)	1
$C_{soil,j,ini}$ ($mg\ kg^{-1}$)	100
$f_{s/l,soil}$ ($kg\ L^{-1}$)	0.1
$f_{s/l,AC}$ ($kg\ L^{-1}$)	0–0.01
$C_{t,surf}$ ($g\ L^{-1}$)	0–10
CMC ($g\ L^{-1}$)	0.106 ^a
S_w ($mol\ L^{-1}$)	1.0 ^a
S_{cmc} ($mol\ L^{-1}$)	1.3 ^a
$f_{c,surf}$	0.634
$\log K_m$	5.70 ^a
$f_{oc,soil}$	0.015
K_{ow}	$10^{4.57a}$
K_d ($L\ kg^{-1}$)	351.1
K_d ($L\ kg^{-1}$) ^b	5.3×10^4
K_d ($L\ kg^{-1}$) ^c	7.9×10^5
Q_{max} ($g\ kg^{-1}$) ^d	12.0
Q_{max} ($g\ kg^{-1}$) ^b	301
Q_{max} ($g\ kg^{-1}$) ^c	404

^a From ref. [6].

^b D20.

^c D100.

^d From ref. [20].

for soil washing in laboratory researches and field applications [5,22,23].

Two types of charcoal-based activated carbons, Darco 20–40 mesh (D20, granular activated carbon) and >100 mesh sizes (D100, powdered activated carbon), was used for the adsorption experiments. Prior to use in experiments, the activated carbons were 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 $629\ m^2\ g^{-1}$ for D20 and $984\ m^2\ g^{-1}$ for D100. Total pore volume was $0.748\ mL\ g^{-1}$ for D20 and $0.768\ mL\ g^{-1}$ for D100, respectively.

3.2. Adsorption experiments

The adsorption isotherms for TX100 and PHE at 20 °C were newly determined with the activated carbon D100 since the experiments for D20 had been already performed in our previous paper [17]. The procedure for adsorption experiment is the same as previously reported one [17,23], and should be described briefly here. The adsorption experiments for surfactant were performed with two concentration ranges: various surfactant concentrations (0.5–5.0 $g\ L^{-1}$) at a fixed concentration of activated carbon (0.2 $g\ L^{-1}$) and various concentration of activated carbon (0–2.0 $g\ L^{-1}$) at a fixed concentration of surfactant (0.5 $g\ L^{-1}$). The flasks were shaken at 100 rpm for 48 h to reach equilibrium. For PHE, various amounts of activated carbon were added to 200 mL of PHE-saturated water in 500-mL Erlenmeyer flasks. Approximately 1.5 mL of liquid sample was withdrawn with a disposable glass Pasteur pipette and filtered by pre-conditioned 0.2 μm PTFE filter (Whatman, USA). PHE and TX100 were analyzed by high-performance liquid chromatography (HPLC; Dionex, USA) using an ultraviolet detector at 250 and 230 nm for PHE and TX100, respectively. The analytical methods were also described in details in the previous paper [17,23]. Analyses were run during the liquid phase; sorbed compound concentrations were computed as the difference from the initial concentration.

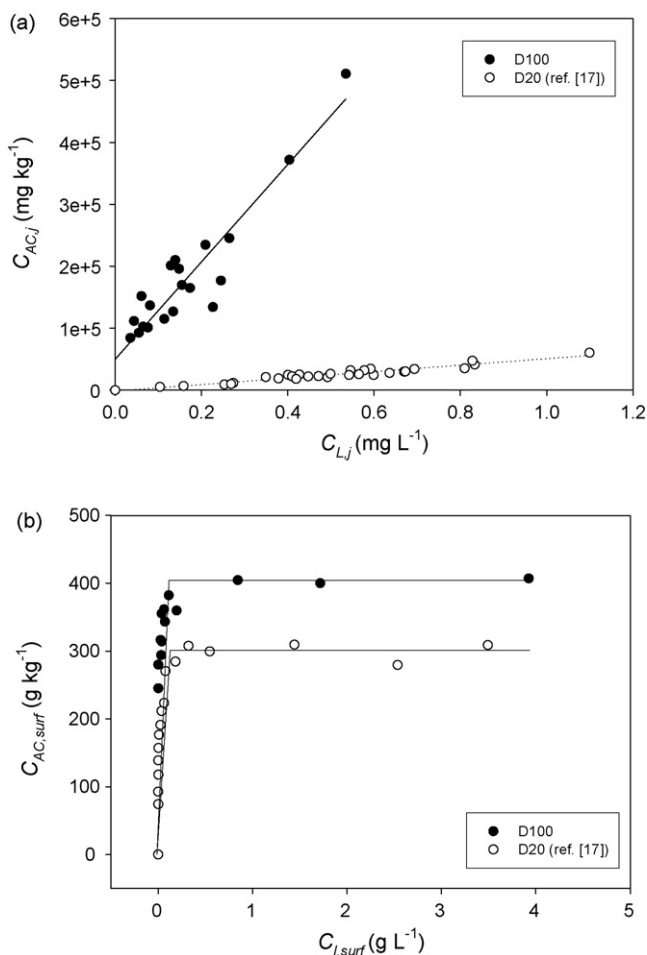


Fig. 2. Equilibrium adsorption isotherms of PHE (a) and TX100 (b) by activated carbons with different particle sizes.

4. Results and discussion

4.1. Adsorption isotherms

The adsorption isotherms for PHE and TX100 on the activated carbons are shown in Fig. 2. The adsorption isotherms of PHE for the powdered activated carbon D100 were linear in good agreement like granular activated carbon D20. The linear constant for D100 was $7.9 \times 10^5 \text{ L kg}^{-1}$ ($r^2 = 0.871$) and much higher than that of D20 ($5.3 \times 10^4 \text{ L kg}^{-1}$, $r^2 = 0.926$). For the adsorption of polycyclic aromatic hydrocarbons, a linear relationship has often been observed on natural organic compounds, soils [18,19,24], or activated carbons in the range of PHE concentrations having one or two orders of magnitude [25–27].

The adsorption isotherms of TX100 showed a plateau above approximately 0.2 g L^{-1} . The appearance of a plateau for nonionic surfactants has been also observed in other reports using silica [28] soils [20,21] and activated carbons [29,30]. These adsorption data could be expressed accurately with multi-step Langmuir isotherms [30,31]. However, at concentrations of surfactant above the CMC value in this study, two linear periods can also be applied to the experimental data with quite a good correlation using Q_{\max} [20,21]. This approach can simplify the model simulation without significant error on the mathematical prediction. In fact, soil washing should be performed at much higher concentrations of surfactant than the CMC value. Therefore, the Q_{\max} value is actually the single most important adsorption parameter. The Q_{\max} values were 301

and 404 g kg^{-1} for D20 and D100, respectively. The partition coefficient of PHE was much higher than TX100, indicating that selective adsorption of PHE on activated carbon is possible. Furthermore, D100 activated carbon would be more favorable than D20 since the adsorption of PHE increases substantially more (from 5.3×10^4 to $7.9 \times 10^5 \text{ L kg}^{-1}$) than the increase (from 301 to 404 g kg^{-1}) of the adsorption of TX100.

4.2. Effects of activated carbon dose

The effect of the activated carbon dose on the process performance was examined by model simulations (Fig. 3). As expected, the fraction of PHE sorbed to activated carbon after selective adsorption process ($f_{AC,j}$) increased with the activated carbon dose. The increase in adsorbed PHE was observed only with the addition of a small amount of activated carbon (e.g., 90.3% adsorption at 0.5 g L^{-1}). The fraction of surfactant in liquid after selective adsorption process ($f_{j,surf}$) decreased linearly in proportion to the amount of activated carbon added. This is because TX100 is adsorbed to activated carbon at maximum capacity (Q_{\max}) for these relatively small activated carbon quantities. The molar solubilization ratio decreased dramatically with increasing activated carbon dosage, meaning that molar PHE included in unit molar micelle decreased. The value was decreased from 0.0046 to 0.00055 when activated carbon concentrations were increased from 0.01 to 0.5 g L^{-1} . This decrease in MSR indicates that activated carbon adsorbs much more micellar-phase PHE than aqueous-phase PHE, even though aqueous-phase PHE is also decreased by adsorption on activated carbon under the same K_m value. The micelles are evacuated by the addition of activated carbon and can be reused to solubilize more PHE after separation from activated carbons. The simulation results

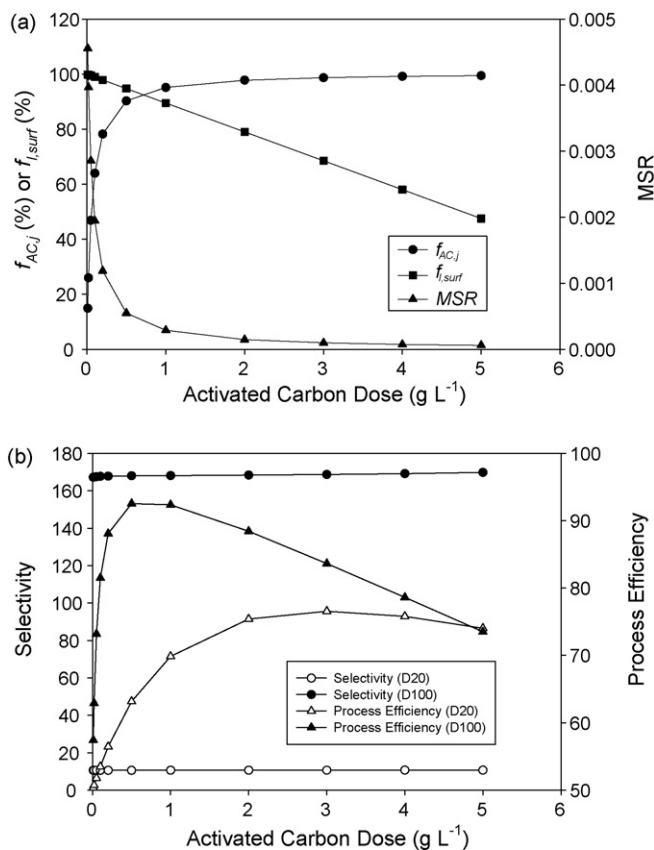


Fig. 3. Effect of activated carbon dose (D100) on various parameters with 5 g L^{-1} TX100. (a) Fractions of PHE adsorbed on activated carbon and TX100 in liquid, and molar solubilization ratio (MSR) of PHE and (b) selectivity and process efficiency.

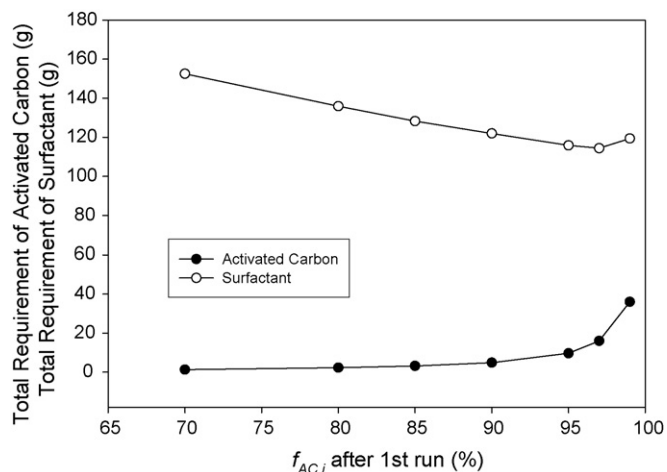


Fig. 4. Effect of adsorption level of the first run on total requirement of surfactant and activated carbon (D100) needed to achieve 90% removal of initial PHE after the second washing run.

suggest that only a small amount of activated carbons is needed to remove PHE effectively from surfactant solution. For example, the addition of activated carbons at 0.5 g L^{-1} removed 90.3% of the initial PHE from the liquid, but 94.8% of surfactants still remained in the liquid and could be reused after separation of activated carbons from the solution.

The change of selectivity was negligible with increasing activated carbon dosage because the partition coefficients were identical for all the conditions (Fig. 3b). The selectivity values for PHE to TX100 were larger than 1 for both kinds of activated carbons, indicating that recovery of surfactants is possible by selective adsorption of PHE using these activated carbons. A higher selectivity (approximately 170) was obtained for the activated carbons with smaller size (D100) than for D20 (producing a sensitivity value of approximately 11).

The f_{ACj} value on activated carbon dosage showed an inverse relationship to that of $f_{i,surf}$ value as seen in Fig. 3a, although both values were required to be high for the effective performance (Fig. 3b). Therefore, the concept of process efficiency $[(f_{ACj} + f_{i,surf})/2]$ was used to find the most effective dosage of activated carbons. The two chemicals are completely separated when the process efficiency value is 100. It was assumed that the importance of separation for each chemical was identical at the onset, although PHE separation is more important than that of surfactant in view of environmental control. In the case of D100, the highest value of process efficiency (92.5) was obtained at an activated carbon concentration of 0.5 g L^{-1} . Process efficiency decreased when the concentration of activated carbons was increased beyond than this dose, since $f_{i,surf}$ was continuously decreased although f_{ACj} was not. The highest process efficiency (76.6) for D20 was lower than those of D100, even when a greater amount of activated carbons (3 g L^{-1}) was used.

In terms of overall cost efficiency, a small number of surfactant reuse processes is preferred. Therefore, two runs of soil washing (with only one adsorption process) were assumed. The first run used fresh surfactant solution and the second used reused surfactant solution with the addition of fresh surfactant to make up the difference from the first run. The adsorption level (e.g., f_{ACj}) of the first run affects the overall efficiency of the process. The final goal of washing was assumed to be 90% removal of initial PHE in the soil using the initial surfactant concentration of 5 g L^{-1} . The total requirement of activated carbon and surfactant in the simulation using D100 is presented in Fig. 4. As the adsorption level of the

first run increased, the total requirement of activated carbon was increased and that of surfactant was decreased. This means that more activated carbons are required if a greater amount of PHE is to be removed in the adsorption step of the first run. However, in this case, the total requirement of surfactant was decreased; although less surfactant was recovered in the first run, more was required in the second run. When the adsorption level of the first run increased above 95%, the activated carbon requirement began to increase dramatically and even the surfactant requirement increased slightly. Therefore, in the first run, the addition of large amounts of activated carbon for complete removal of PHE is not an efficient strategy. Approximately 90% removal in the first run would be a good goal.

4.3. Effects of the number of washing operations

The effect of the initial surfactant concentration on the number of recovery processes necessary to achieve 90% removal of initial PHE in soil was examined (Fig. 5). It was assumed that fresh activated carbon was added to remove 90% of PHE in the washed solution (i.e., f_{ACj} is 90%) in each recovery process. Likewise, surfactant was also added in each run and was adjusted to equal the initial concentration to make up for surfactants adsorbed to activated carbon in each recovery process. As the surfactant concentration was increased from 2 to 5 g L^{-1} , the number of washing processes required decreased from 11 to 3. It is definitely preferable that the number of surfactant recovery processes is minimized in terms of overall cost efficiency. Therefore, two runs of soil washing is the best choice, which requires only one recovery process.

The total requirement of surfactant and activated carbon is shown in Fig. 6 (using the same model simulations as in Fig. 5). As the surfactant concentration increases, the total requirement of surfactant increases although the number of washing processes decreases. Given the same number of washing runs, the washing efficiency was higher (i.e., less surfactants and more activated carbons were required) when a lower surfactant concentration was used. However, it should be noted that a very low surfactant concentration requires more washing processes. The lowest concentration of surfactant using two runs was 8.3 g L^{-1} , which would be the optimal condition.

4.4. Overall performance of surfactant recovery process

The overall performance of the soil washing process was evaluated by comparing the process without surfactant recovery (case

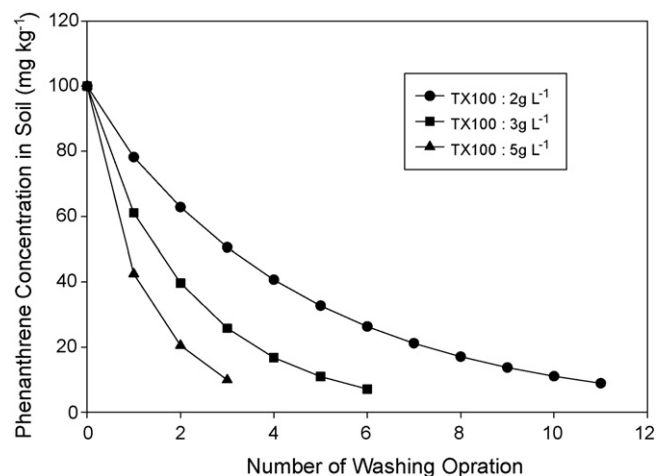


Fig. 5. Required number of washings using different concentrations of TX100 to achieve 90% removal of initial PHE. The activated carbon (D100) was added in each run to adsorb 90% of liquid PHE.

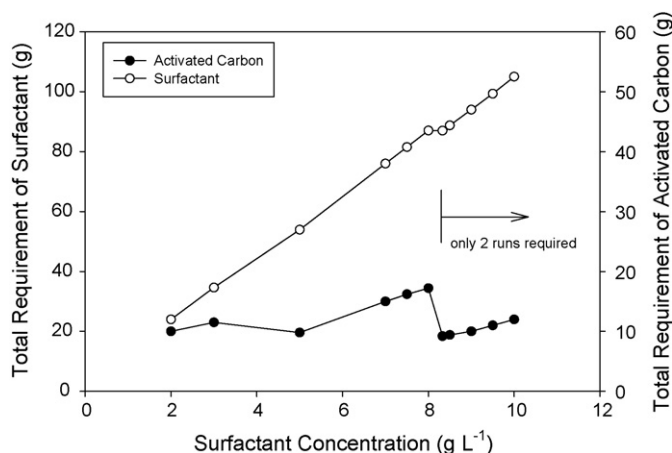


Fig. 6. Effect of surfactant concentration on the required amount of surfactant and activated carbon (D100) necessary to achieve 90% removal of initial PHE. The number of washings was not constrained in the simulation. The surfactant dose was changed only at the last run, and new activated carbon was added in each run to adsorb 90% of liquid PHE.

A) and with surfactant recovery using D20 (case B) or of D100 (case C). The distribution of PHE and surfactant in the relative positions of process flow in Fig. 1 was summarized in Table 2. For the reuse processes (cases B and C), the dosage of activated carbon necessary to remove 90% of PHE in washed solution was determined. The final removal of PHE from soil was assumed to be 90% in determining the consequent amount of surfactant required. For the reuse processes, some surfactant should be added in the second run to adjust this goal.

The total requirement of surfactant was 265, 116, and 86.6 g for cases A, B, and C, respectively. Thus, the surfactant reuse process could significantly reduce the total requirement of surfactant. The required quantity of activated carbon was not large (109 and 9.1 g for cases B and C, respectively). If effective activated carbon is used (i.e. D100 as in case C), a much smaller amount of activated carbon is required and consequently the amount of surfactant recovered is greatly increased from 54.0 to 94.9%.

It should be noted that solid waste of activated carbon contaminated with PHE and surfactant was produced at high concentrations for the reuse processes. The used activated carbon could be regenerated by proper methods such as the extraction by using organic

solvents. However, since the amount of the used activated carbon can be significantly decreased by using high adsorptive activated carbon such as case C, the used activated carbon may be dumped if only it is acceptable economically and environmentally. The concentrations of PHE and surfactant in wastewater were much lower for cases B and C than for case A since more surfactant was used for case A. Thus, although the reuse process may require increased facility, it can greatly reduce material costs for surfactants by up to 70%, as was the case here. Most of surfactant required in case C was used for the first run, and the surfactant requirement could be farther reduced depending on the contamination level and the treatment goal.

Other materials including natural organic matter, other contaminants, salts and debris may affect the adsorption capacity of activated carbon and recovery efficiency. For example, in our previous study, actual soil-washed solutions including natural organic matters decreased PHE sorption onto activated carbon (0–23%), while surfactant recovery was quite similar to that in the absence of natural organic matter (Ahn et al. [23]). Thus, soil organic matter in a dissolved form may cause an increase in contaminant solubility by changing micellar structure or by direct interaction with the contaminant, and a decrease in the adsorption surface of activated carbon through the adsorption or pore blocking by organic matter. Although surfactant recovery is not highly affected by the existence of natural organic matter, the reduction of PHE sorption may cause an environmental issue and more significant treatment may be required. These results suggest that soils containing high amounts of clay particles and organic matter may reduce the efficiency of the surfactant recovery process, and removal of soil particles before the recovery process will be very important to overall performance.

5. Conclusions

Our results provide theoretical evidence that selective adsorption of contaminants by activated carbon and recovery of surfactant in washed solution is possible with a high selectivity. The simulation results suggest that only a small amount of activated carbon is necessary to effectively remove contaminants from surfactant solutions. The surfactant requirement could be reduced to approximately 30% using an optimized recovery step with the addition of 9.1 g of activated carbon per liter. The adsorption technology is simple, fast, and inexpensive, and thus may be a reasonable alternative to recovery surfactants in soil washing process. The application of this technology to actual soil contaminated with various kinds of hazardous organic compounds and treatment methods wasted activated carbon will be the subject of future investigations.

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Table 2
Mass flows of contaminant and surfactant under different soil washing scenarios

Process flow		Case A ^a		Case B ^b		Case C ^c	
		First run	Second run	First run	Second run	First run	Second run
$C_{t,surf}$ (g L ⁻¹)	2	26.5	8.3	3.3	8.3	0.36	
$C_{t,AC}$ (g L ⁻¹)	6	–	10.9	–	0.91	–	
$M_{t,surf}$ (g)	2	265	83	33	83	3.6	
$M_{t,AC}$ (g)	6	–	109 ^{sw}	–	9.1 ^{sw}	–	
$C_{soil,j}$ (mg kg ⁻¹)	4	10.0	28.3	10.0	28.3	10.0	
$C_{soil,surf}$ (g kg ⁻¹)	4	11.9	11.9	11.9	11.9	11.9	
$C_{i,j}$ (mg L ⁻¹)	5 or 8	9.00 ^{5ww}	0.71 ⁸	2.54 ^{5ww}	0.72 ⁸	2.54 ^{5ww}	
$C_{i,surf}$ (g L ⁻¹)	5 or 8	25.3 ^{5ww}	3.84 ⁸	7.11 ^{5ww}	6.75 ⁸	7.11 ^{5ww}	
$C_{AC,j}$ (mg kg ⁻¹)	7	–	592 ^{sw}	–	7090 ^{sw}	–	
$C_{AC,surf}$ (g kg ⁻¹)	7	–	301 ^{sw}	–	404 ^{sw}	–	
$f_{AC,j}$ (%)	7	–	90.0	–	90.0	–	
$f_{i,surf}$ (%)	8	–	54.0	–	94.9	–	

Using 1 kg soil and 10 L washing solution; ww: wastewater and sw: solid waste.

^a Washing without reuse.

^b Washing with reuse (D20).

^c Washing with reuse (D100).

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