Removal of Cationic Heavy Metal and HOC from Soil-Washed Water Using Activated Carbon

Chi Kyu Ahn, Young Mi Kim, Seung Han Woo, and Jong Moon Park

Abstract—Soil washing process with a surfactant solution is a potential technology for the rapid removal of hydrophobic organic compound (HOC) from soil. However, large amount of washed water would be produced during operation and this should be treated effectively by proper methods. The soil washed water for complex contaminated site with HOC and heavy metals might contain high amount of pollutants such as HOC and heavy metals as well as used surfactant. The heavy metals in the soil washed water have toxic effects on microbial activities thus these should be removed from the washed water before proceeding to a biological waste-water treatment system. Moreover, the used surfactant solutions are necessary to be recovered for reducing the soil washing operation cost. In order to simultaneously remove the heavy metals and HOC from soil-washed water, activated carbon (AC) was used in the present study. In an anionic-nonionic surfactant mixed solution, the Cd(II) and phenanthrene (PHE) were effectively removed by adsorption on activated carbon. The removal efficiency for Cd(II) was increased from 0.027 mmol-Cd/g-AC to 0.142 mmol-Cd/g-AC as the mole ratio of SDS increased in the presence of PHE. The adsorptive capacity of PHE was also increased according to the SDS mole ratio due to the decrement of molar solubilization ratios (MSR) for PHE in an anionic-nonionic surfactant mixture. The simultaneous adsorption of HOC and cationic heavy metals using activated carbon could be a useful method for surfactant recovery and the reduction of heavy metal toxicity in a surfactant-enhanced soil washing process.

Keywords—Activated carbon, Anionic-nonionic surfactant mixture, Cationic heavy metal, HOC, Soil washing

I. INTRODUCTION

ENHANCEMENT of the water solubility of HOCs (hydrophobic organic compounds) is the key step of

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remediation for HOC-contaminated site [1,2]. Many remediation methods such as soil flushing, soil washing or bioremediation were often used to surfactant solution for achieving this goal [3,4]. Surfactant is the one of the most common chemicals using in a soil washing process for enhancing the water solubility of HOC. The use of surfactant enhances the solubility of HOC significantly by partitioning HOCs into the hydrophobic cores of surfactant micelle. Therefore surfactant enhanced soil washing process becomes a potential technology for rapid removal of HOCs from contaminated soil [4]. The soil washing efficiency was significantly depending on types of surfactants, soil nature, soil organic carbon contents and so on. Especially the types of surfactant are one of the important factors for successful soil remediation, thus many researchers used to surfactant mixtures such as nonionic-anionic surfactant mixed solutions for enhancing the soil washing efficiency and reduction of unexpected side effects such as precipitation or surfactant losses by adsorption on soil [2, 5-7].

The surfactant mixture can extract not only organic compounds but also heavy metals from the complex contaminated soils with HOC and heavy metals. A few researchers reported that the addition of surfactant can enhance the desorption efficiency of heavy metals thus the soil-washed solution would be contained some amount of heavy metals and HOCs [8,9]. The heavy metals in washed water significantly affected to microbial enzyme activities [10]. Thus the proper studies to removal of heavy metals in washed water must be required. Moreover, the reason of operation cost from surfactant usage in a soil washing process was enforced to surfactant reuse [11]. Therefore, the simultaneous removal process for heavy metals and HOC was required treating the soil-washed water.

The objective of the present study is to investigate the feasibility of the simultaneous removal of heavy metal and HOC in a surfactant mixture using activated carbon.

II. MATERIALS AND METHODS

Cadmium (Cd) as a cationic heavy metal ($CdCl_2 \cdot 2.5H_2O$ (Acros)), sodium dodecyl sulfate (SDS; Sigma), Triton X-100 (TX100; Sigma) and phenanthrene (PHE: >98%; Sigma) were used to adsorption experiments. Methylene blue ($C_{16}H_{18}ClN_3S$) and chloroform ($CHCl_3$) for determination of SDS

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concentration was purchased Sigma and JT Baker, respectively. The chemical properties of the surfactants and phenanthrene were represented in TABLE I.

TABLE I
SELECTED PROPERTIES OF SURFACTANTS AND PHENANTHRENE

	Molecular formula	K_{ow}	Water solubility (mg/L)	CMC (mM)
PHE	$C_{14}H_{10}$	$10^{4.57}$	1.3	-
TX100	$C_8H_{17}C_6H_4OE*_{9.5}H$	-	-	0.17
SDS	$CH_3(CH_2)_{11}OSO_3Na$	-	-	5.4

*E: OCH_2CH_2

Activated carbon (granular type, Darco 20-40 mesh; GAC) was purchased from Sigma-Aldrich. The activated carbon was washed with deionized water several times, and then dried in an oven at 60℃ for several days. The functional group of GAC was determined by Boehm titration method [12].

The mole ratio of surfactants mixture (TX100:SDS) were prepared at 1:0, 2:1, 1:1, 1:2 and 0:1 for TX100 to SDS. The total concentration of mixed surfactant solution was adjusted to 10 mM.

The removal behaviors of PHE and Cd(II) were examined by measuring the final concentrations of PHE and Cd(II) in a batch system. Batch experiments were conducted in 250 mL Erlenmeyer flasks with a working volume of 100 mL at pH 6.0 (optimal pH). The optimal pH was determined by our previously study (data not shown) [13]. The pH of the suspension was maintained at the desired values, *i.e.* pH 6.0, by adding 1 N NaOH or H_2SO_4 solution during batch adsorption experiments at 100 rpm, 20℃ for 48h. To examine the adsorptive capacity of activated carbon, 0.1 g of GAC was added to 100 mL of mixed surfactant solution with 4.45×10^{-1} mmol/L and 2.8×10^{-1} mmol/L, for Cd(II) and PHE, respectively. However in the TX100:SDS=0:1 solution, the PHE concentration was adjusted to 5.6×10^{-2} mmol/L with the same amount of Cd(II) as 4.45×10^{-1} mmol/L because this surfactant mixture has a lower *MSR* (molar solubilization ratio) values as Fig. 1. Adsorption isotherms for Cd(II), TX100, PHE and SDS were examined with GAC using Langmuir or Linear models.

The surface charges of the activated carbon were measured using a zeta-potential analyzer (ELS-8000, Photal, Ostsuka Elec.). For this, the activated carbons were milled with a mortar, and then their surface charges were measured at various pHs in the range from 2.0 to 12.5.

The analytical methods for TX100 and PHE were determined using a HPLC (high performance liquid chromatography; Dionex) [14] and SDS was determined using modified methylene blue method [13]. The concentration of Cd(II) ions was determined using an atomic absorption spectrophotometer (SpectrAA-800, Varian) at a wavelength of 228.8 nm [13,14].

III. RESULTS AND DISCUSSION

A. The physico-chemical properties of GAC

TABLE II shows the physico-chemical properties of GAC including the specific surface area, total acidity content (TAC) and total basicity content (TBC). The surface area and pH_{pzc} (point of zero charge) of GAC were 643.5±8.4 m^2/g and pH 4.7, respectively.

TABLE II
THE PHYSICO-CHEMICAL PROPERTIES OF ACTIVATED CARBON
(SURFACE AREA, TAC, TBC AND pH_{ZPC})

AC	Surface area (m^2/g)	TAC (umol/g)	TBC (umol/g)	pH_{pzc}
GAC	643.5±8.4	244.2±17.7	289.1±11.0	4.7

B. Phenanthrene solubility

The plot of apparent PHE solubility as a function of the TX100:SDS mixture concentration with different composition is shown in Fig. 1.

The solubility of PHE was increased as concentration of surfactant mixture increased, in which the solubility increased linearly with the surfactant concentration above the CMC (critical micelle concentration). The linear increment of solubility for PHE was consistent with solubility data which were reported by other researchers [4]. Solubilization of PHE by micellar phase surfactant was characterized as the *MSR* that can be calculated as the slope of the apparent solubility curve above CMC (Fig. 1).
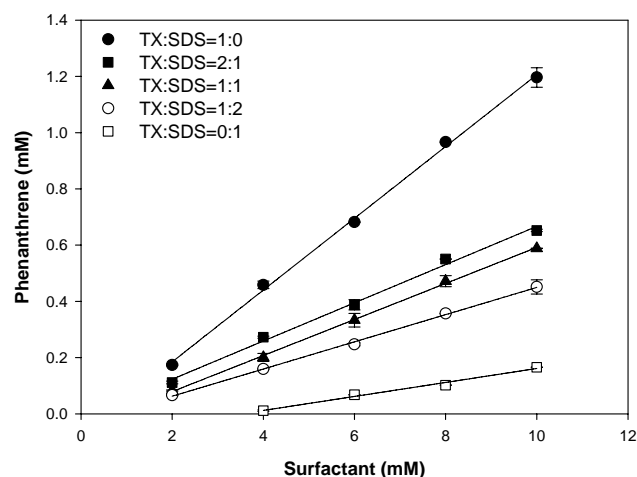

Fig. 1 The solubility of phenanthrene according to the concentration of nonionic-anionic surfactant mixture

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It was observed that the apparent solubilities of PHE in the surfactant mixtures were lower than those in single TX100 solutions. The addition of SDS in surfactant mixture is negatively affected to the PHE. It was likely because the solubility of PHE in SDS was greatly lower than that of TX100. Therefore, if the total mole concentration of surfactant mixture was fixed, the addition of SDS in TX100 solution has a negative effect on PHE solubility due to the decrement of actual TX100 concentration. For example, with a same total amount of mixed surfactant as 10 mmol/L, in which the mole ratios as TX100:SDS were 2:1, 1:1, 1:2 and 0:1, were 53.2, 48.1, 37.9 and 19.5% of the PHE solubility in the single TX100 solution, respectively.

C. Adsorption isotherms

The adsorption isotherms for Cd(II), TX100, SDS and PHE on GAC were shown in Fig. 2. The adsorption isotherms of Cd(II), TX100 and SDS on GAC were represented as Langmuir isotherm. However, for PHE, the adsorption isotherm is represented as Linear isotherm [13,14]. For the adsorption of polycyclic aromatic hydrocarbons, a linear relationship has often been observed on natural organic compounds, soils, or activated carbons in the range of PHE concentration having one or two orders magnitude [15].

The isotherm parameters are summarized in TABLE III. The adsorption isotherm of TX100 and SDS showed a plateau above 0.2 mmol/L. This appearance as a plateau for surfactants has been also observed in other reports using soils and activated carbons [16,17].
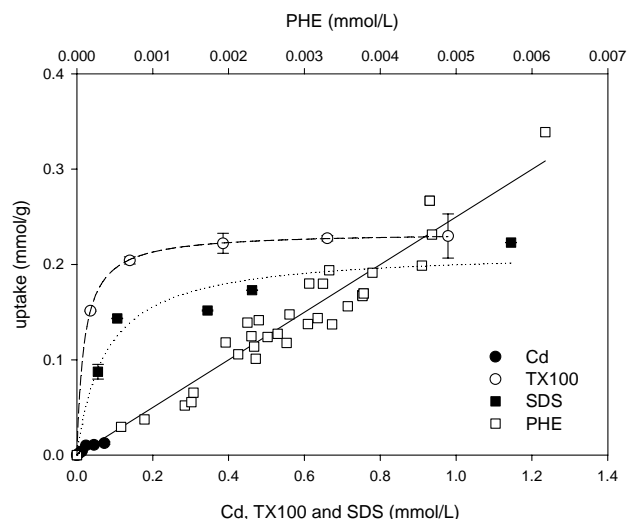

Fig. 2 Adsorption isotherm for Cd(II), TX100, SDS and PHE on GAC. The fitting curve is applied to Langmuir isotherm for Cd, TX100 and SDS, respectively. The adsorption isotherm of PHE is a Linear isotherm

TABLE III
THE LANGMUIR ISOTHERM AND LINEAR ISOTHERM PARAMETERS

Langmuir isotherm*	Q_o	K_L	R^2
Cd(II)	0.019	29.58	0.942
TX100	11.92	50.67	1.000
SDS	2.81	13.08	0.949
Linear isotherm**	K		R^2
PHE	49.958		0.921

* Langmuir isotherm: $q_e = \dfrac{Q_0 K_L C_e}{1 + K_L C_e}$

** Linear isotherm: $q_e = K C_e$

D. Adsorption of Cd and PHE on surfactant mixed system

The sorbed amounts of Cd(II) onto activated carbon in surfactant mixture presence or absence of PHE were represented in Fig 3. Fig 3-a) shows the sorption of TX100 and SDS in the absence of Cd(II) and PHE. In the absence of SDS (as TX100:SDS=1:0), the amount of adsorbed TX100 was highest except that in case of TX100:SDS=2:1. However, in the presence of SDS in surfactant mixture, sorbed amount of TX100 was strongly affected by addition of SDS, compared with TX100:SDS=1:0. In the composition of TX100:SDS=1:2, the sorbed amount of TX100 was significantly decreased by 52% compared with that of TX100 single solution(TX100:SDS=1:0), from 0.433 mmol/g to 0.227 mmol/g. On the other hand, the sorbed amount of SDS was increased as a function of SDS concentration, from 0.227 mmol/g to 0.948 mmol/g. This result indicated that the addition of SDS in TX100 solution significantly restricted the adsorption of TX100 onto GAC by the competition mechanism with SDS in the surfactant mixture. The competitive adsorption on activated carbon can occur when the molecular size of adsorbate is similar to each other or same adsorbable sites are involved into adsorption mechanisms [18,19]. In our case, the two surfactants (TX100 and SDS) would be attached to same adsorbable sites on activated carbon surface because the hydrophobic moieties of surfactant can be sorbed onto the hydrophobic surface of activated carbon [17]. Thus the competitive adsorption between TX100 and SDS would be occurred on the same site of activated carbon.
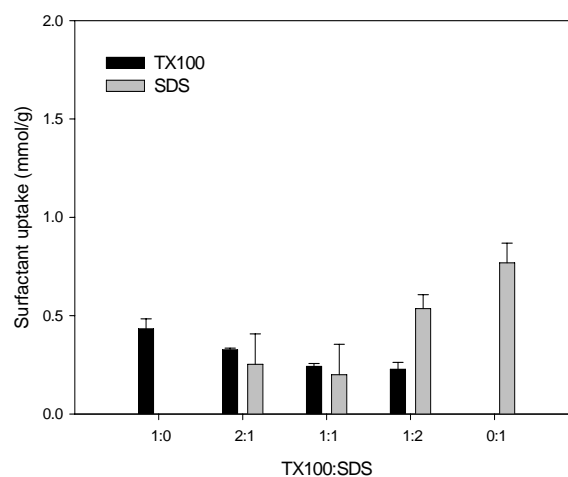
The decrement of sorbed amount of surfactant in nonionic-anionic surfactant mixture was also observed by Zhou and Zhu [6]. They reported that the addition of anionic surfactant in the nonionic surfactant affected to the adsorption of nonionic surfactant on soils thus the sorbed amount of nonionic surfactant was significantly decreased. They suggested that the formation of mixed micelles would affect the

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formation or structure of CMC thus this mechanism would affect to adsorption of surfactant onto activated carbon.
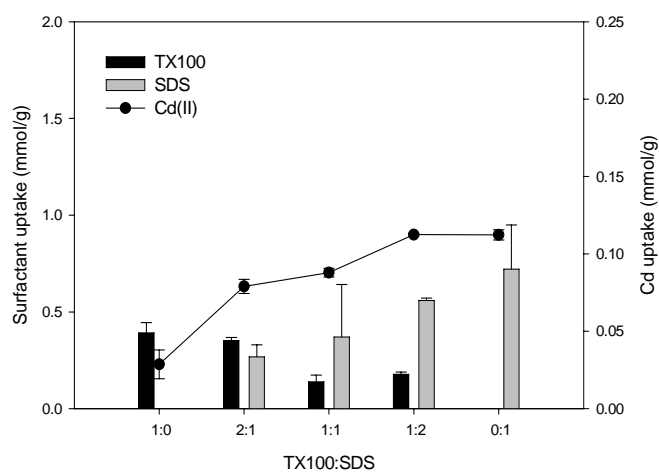
In the presence of Cd(II), the distributions of TX100, SDS and Cd(II) were shown in Fig. 3-b). The patterns of sorbed amount of TX100 and SDS were similar to that of absence of Cd(II) as Fig 3-a). However, the sorbed amount of Cd(II) on GAC was significantly increased as the SDS concentration increased. This suggested that added SDS could be played an important role in the Cd(II) adsorption. One suggested mechanism of Cd(II) adsorption is the sorbed SDS onto activated carbon would be acted as active sites as capable of binding the Cd(II) [13]. These active sites may exist on the activated carbon surface as the negatively charged head parts of the SDS. Therefore the positively charged Cd(II) ions can be adsorbed onto activated carbon by the electro-static attractions between negatively charged hydrophilic groups of SDS onto the activated carbon and cationic Cd(II) [20,21]. Another suggested mechanism for Cd(II) adsorption is hydrophobic interaction between the SDS-Cd(II) complex and activated carbon because the Cd(II) ions would be bound with negatively charged SDS as the SDS-Cd(II) complex in the nonionic-anionic surfactant mixture.

Fig. 3-c) shows the PHE adsorption in the surfactant mixtures without any Cd(II). The initial PHE concentration was adjusted according to PHE solubility of each surfactant system, which is 2.81×10^{-1} mmol-PHE/L for 1:0, 2:1, 1:1 and 1:2 and 0.56×10^{-1} mmol-PHE/L for 0:1 surfactant solution (*i.e.* single SDS solution). The increment of PHE adsorptive capacities on mixed surfactant system as SDS mole ratio increasing, might be caused that the solubilization capacities of PHE in surfactant solution (as *MSR*) were decreased from 0.1276 (1:0) to 0.0483 (1:2).
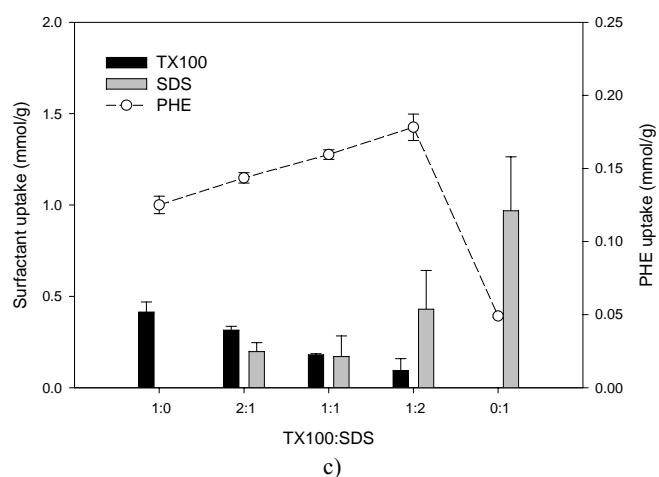
Fig 3-d) shows the sorbed amount of TX100, SDS and Cd(II) in the presence of PHE. The adsorption patterns of TX100 on GAC were similar to the previous case. For PHE, the adsorptive capacity was also similar whether presence or absence of Cd(II) as Fig 3-b) and 3-d). However the adsorptive capacity of Cd(II) in the presence of PHE was slightly higher than that in the absence of PHE. It suggested that the adsorption of PHE onto activated carbon would be changed the surface hydrophobicity of activated carbon to more hydrophobic. Thus if only the electro-attraction between Cd(II) and sorbed SDS on activated carbon is major adsorption mechanism, the expected sorbed amount of Cd(II) in the presence of PHE would be same as that in absence of PHE because the adsorption mechanism of Cd(II) was differed from that of PHE. However, the sorbed amount of Cd(II) on activated carbon was increased in the presence of PHE solution. This indicated that Cd(II) adsorption on activated carbon would be hydrophobic interaction and the sorbed PHE can positively affect on Cd(II) adsorption because the surface hydrophobicity of activated carbon might be more hydrophobic by adsorption of hydrophobic compound as PAH.

a)

b)

c)

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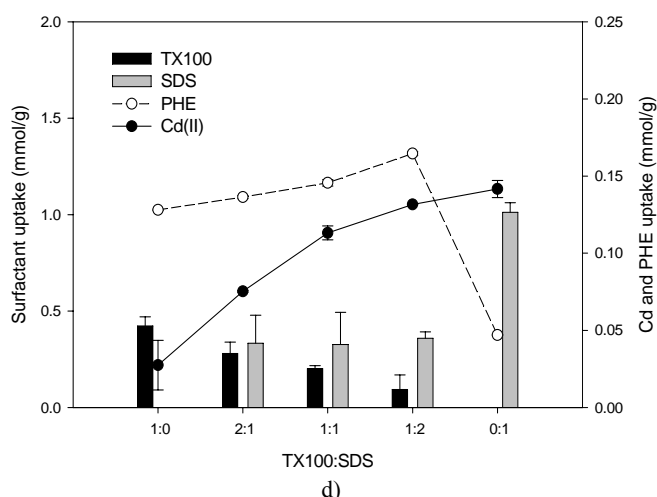Vol:3, No:1, 2009

Fig. 3 TX100, SDS, Cd(II) and PHE distributions on GAC in anionic-nonionic surfactant mixtures. a) this system contains TX100 and SDS, b) this system contains TX100, SDS and Cd(II), c) this system contains TX100, SDS, PHE, d) this system contained TX100, SDS, Cd(II) and PHE

IV. CONCLUSIONS

Soil washing process is a proven technology for remediation of HOC-contaminated sites. However, the soil washed water should be cautiously treated because the toxic heavy metals would be contained in the soil-washed water. Heavy metals in waste water would inhibit the survival of micro-organisms and consequently the treatment performance would be significantly decreased [10]. In this point of a view, simultaneous removal of HOC and heavy metals would be necessary for the successful treatment of the washed water and surfactant recovery.

The PHE and Cd(II) adsorption test, in the present study, was carried out with a nonionic-anionic surfactant mixed solution. The addition of SDS in the TX100 solution enhanced the sorption of Cd(II) and the effect is larger as SDS concentration increased. It is because sorbed SDS on GAC can act as a newly active site for Cd(II) adsorption or the SDS-Cd(II) complex are more abundant as the addition of SDS increasing.

The results of this study provide that activated carbon adsorption may be a good method for surfactant recovery and heavy metal removal in a soil washing process using nonionic-anionic surfactant mixed solution. The removal performance of the PHE and Cd(II) might depend on the types of activated carbon, adsorptive capacities of activated carbon itself for heavy metal, and activated carbon dose. Therefore, optimization of the activated carbon adsorption process would be required to achieve environmental regulation and to reduce soil washing operating cost.

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