Remediation of Polycyclic Aromatic Hydrocarbon-Contaminated Soils by Nonionic Surfactants: Column Experiments

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Abstract

Using flushing solutions with different nonionic surfactants, this study investigated the remediation of polycyclic aromatic hydrocarbon (PAH)-contaminated soils with different organic carbon contents. Naphthalene and anthracene are the two delegates of PAHs used in the study. Contaminated soil packed in a stainless-steel column was continuously flushed with a surfactant solution at room temperature at a constant flow rate. Results are of practical interest in developing effective surfactant remediation technology applied in ex situ or in situ PAH-contaminated soils. Nonionic surfactants can be used effectively to remediate hydrophobic organic compound-contaminated soils. For soil with 500 ppm PAH, enhanced solubility reached as high as 30 times that of water solubility. Compared with the efficiency in using sodium nitrate solution, desorption efficiencies of Tween 80 (T80) and Triton X-100 (TX-100) solutions in the naphthalene-contaminated soil were 2.4- and 2.0-fold higher, respectively. For different soils contaminated with anthracene, which is more hydrophobic than naphthalene, enhanced desorption efficiencies were 11 and 24 times greater than that of sodium nitrate solution when using T80 in Kun-Shan and Yun-Nun soils, respectively, and 14 and 27 times greater when using TX-100. It should be noted that the surfactant may cause colloid mobilization and then clog soil pores; therefore, the possibility of clogging should be taken into account during site remediation. Result demonstrates that the concentration of 0.1% of T80 and TX-100 is suitable for soil remediation in the field. It was also found that the sorption of surfactants to the soil affects the time and efficiency of remediation.

Key words: polycyclic aromatic hydrocarbons; Tween 80; Triton X-100; column experiment; soil remediation; surfactants

Introduction

Contamination of soils and groundwater by toxic or hazardous pollutants is a widespread environmental problem and the removal of hydrophobic organic compounds (HOCs) from soils has become a major concern. Polycyclic aromatic hydrocarbons (PAHs) are highly toxic and carcinogenic substances often produced by incomplete combustion of carbon compounds (Wheatly and Sadhra, 2004). Their solubility in water is typically less than 10^4 M and they are strongly sorbed in soils. Their desorption from soils strongly limits the efficiency of remediation techniques. Often thermal desorption and chemical oxidation are used for in-situ treatments of soil with low contamination. Thermal desorption requires to heat the contaminated soil to more than 150°C for PAHs larger than two rings (Smith et al., 2001). Chemical oxidation uses strong oxidizing agents such as KMnO_4 or H_2O_2 in acid solutions. It is expensive, is nonselective, and often produces toxic metabolites by incomplete oxidation (Anipsitakis and Dionisou, 2003).

In the late 1970s, the technology of soil flushing developed by the U.S. EPA was primarily used to treat the soil and groundwater contaminated with HOCs. The method of soil flushing was also adopted to remediate Cd-contaminated paddy field effectively (Makino et al., 2007). The flushing solutions such as surfactants were injected into subsurface to interact with the contaminants to change the partitioning or sorption of hydrophobic organics between stationary phase and aqueous phase.

Surfactants can increase the solubilities of HOCs by partitioning them into the hydrophobic cores of surfactant micelles above the critical micelle concentration and then enhancing the desorption and the flushing of HOCs from solid into aqueous phases, which would improve the bioavailability of HOCs for microbial remediation and phytoremediation. A few studies have been conducted for the practical application of surfactant-enhanced remediation in in-situ flushing or ex-situ washing for the field-contaminated soils, the results of which indicated the potential of using surfactants to clean up...
residual and sorbed HOCs from soils. Surfactant-enhanced remediation has been suggested as the promising technology for the remediation of contaminated soils and groundwater.

There are three types of adsorption for organics adsorbed onto solids (Fig. 1). First, dissolved organics complex with natural organic matter (NOM) and are then adsorbed onto solid surfaces. Second, the sorbed NOM on mineral surface decreases the hydrophilicity and enhances hydrophobic organics sorbed. The mechanism of NOM sorbed onto soil surface might be ligand exchange, which can change the property of mineral surfaces, resulting in a higher affinity between mineral surface and organics, and thereafter, more contaminants are adsorbed (Chi and Amy, 2004a, 2004b). Third, the organics sorbed onto the stationary particulates (colloids) that are derived from the organisms through the process of mineralization. Same as the system containing surfactant, the competition for HOCs existed between soil, aqueous phase, sorbed surfactant, and micellar surfactant phases (Fig. 2). Sorbed-phase surfactant may result in increased HOC partitioning onto soil until HOC solubilization by micellar phase surfactant successfully competes with increased HOC sorption on surfactant-modified soil (Laha et al., 2009). The cation exchange capacity was found to control the surfactant sorption onto the soils (Wang and Keller, 2008). Minerals of different nature showed different affinity for surfactants: for sodium dodecyl sulfate (SDS) and Triton X-100 (TX-100), the adsorption of aluminum oxide used in wastewater treatment is noneffective, whereas nature mineral shungite is efficient (Sineva et al., 2007). However, when both NOM and surfactant coexisted in the soil system, it was found that the remediation measures based on micellar solubilization are not significantly affected by the presence of NOM (Lippold et al., 2008).

It is important to understand the actual mechanisms of desorption as well as sorption. From the point of remediation, it is needed to increase the competability of surfactants with sorbed contaminants, which will then be detached from surfaces. Surfactants can both enhance the solubility (apparent solubility) of hydrophobic compounds and mobilize colloids, which have contaminants sorbed, and so remediation can be achieved. In addition, because of hydrophobicity of HOCs, surfactants are often used for soil bioremediation to increase bioavailability of HOCs by enhancing their solubilization (Volkering et al., 1998).

Unionic surfactant TX-100 can increase the apparent solubility of PAHs. In other words, increasing the concentration of

![FIG. 1. Three types of sorption occurred in the system containing minerals, polycyclic aromatic hydrocarbons (PAHs), and natural organic matter (NOM).](image1)

![FIG. 2. Sorption of PAHs, surfactants, and micelles occurred in the system.](image2)
TX-100 in the flushing solution increased the flushing efficiency. Compared with ionic surfactants for the removal of PAHs, PCE, and heavy metals in soils, TX-100 has a better effect on remediation (Diane et al., 2002; Zhu and Feng, 2003). It was found that the unionic surfactant Tween 80 (T80) can remove 4,4'-dichlorobiphenyl effectively by the formation of micelle in solution, and therefore, the solubility and mobility were enhanced (Chu and Kwan, 2003). Nonionic surfactants such as Brij 35 were used to wash Malathion-contaminated soil; the washing performance was dominated by the concentration of the surfactant used (Chu et al., 2005). In the study of an anionic surfactant, sodium C14-16 olefin sulfonate [Bio-terge AS-40], which was used to investigate the solubility changes of trichloroethylene (TCE) influenced by different concentrations of surfactant, a 2% solution of surfactant can increase TCE solubility 13 times, and TCE solubility increased with increasing surfactant concentrations (Ciajolo and Ragucci, 2001; Jeong and Corapcioglu, 2003).

In a study of removing crude oil from contaminated soils, it was found that different surfactants play different roles. SDS removed more of the aliphatic than aromatic hydrocarbons, whereas saponin removed the aromatic hydrocarbon preferentially to the aliphatic hydrocarbons (Urum et al., 2006). Diuron showed much higher solubility enhancement than atrazine with the micelles of either TX-100 or benzalkonium chloride (Wang and Keller, 2008).

To reduce cost, an aqueous solution of cyclodextrins used to wash phenanthrene- and pyrene-contaminated soils was successfully reused after being regenerated by colza oil (Petitgirard et al., 2009). A mixed surfactant solution of SDS with TX-100 showed greater flushing efficiencies for phenanthrene-contaminated soil than the individual surfactants (Zhou and Zhu, 2008). The combination of anion and nonionic surfactants used in this study decreases the critical micelle concentration, which increases the concentration of micelles formed, thereby increasing the flushing efficiency. In addition, it should be mentioned that a proper contact time and flow rate were needed to ensure efficient surfactant flushing in a diesel fuel-contaminated soil (Khalladi et al., 2008).

The overall objective of this study was to investigate the desorption efficiencies of TX-100 and T80 used in the soils contaminated with PAHs, such as anthracene and phenanthrene. Both batch and column experiments were conducted to find the optimal conditions for the technology of soil flushing applied in fields.

Materials and Methods

PAHs (anthracene, naphthalene), minerals (Kun-Shan [KS] and Yun-Nun [YN] soils), and surfactants (T80, TX-100) were the main materials used in this study. Fluorescence detector was used to measure the concentration of PAHs in solutions (Chu and Kwan, 2003; Awantha and Tamara, 2004; Chi and Amy, 2004b; Elena et al., 2004; Kima et al., 2004). Spectrophotometer was used to measure the concentration of dissolved organic carbon. The characteristics of soils, PAHs, surfactants, and the conditions of fluorescence spectroscopy used in this study are listed in Tables 1–3. Sodium nitrate was used both as a tracer to define pore volume (pv) and to adjust the ionic strength of solutions to 0.015 M.

Batch experiments

PAHs were added directly to the soils to prepare synthetic contaminated soils to investigate the desorption efficiency in the contaminated soils by the desorption solutions. Both batch and column experiments of PAHs desorption from the soils were conducted to understand the optimal conditions of equilibrium and kinetic, respectively. The steps are listed below:

1. PAH solution dissolved in ethyl ether was added into soils and then mixed thoroughly by shaker.
2. Desorption solution was added into 20 g of 500 mg/kg of PAH-contaminated soils in a flask (W/V = 1:10) and shaken for 24 h.
3. The supernatant was centrifuged at 4500 rpm for 5 min and measured by fluorescence spectroscopy.

Sodium nitrate, T80, and TX-100 are the three different flushing solutions investigated. All the concentrations were set at 0.1%.

Column experiments

A column with length 5 cm and diameter 1.9 cm was packed with soils in continuous flow column experiment. Stainless-steel frits (pore size 2 μm at the ends of the column) were used to spread the flow evenly across the diameter of the

<table>
<thead>
<tr>
<th>PAH</th>
<th>Formula</th>
<th>Molecular weight</th>
<th>Log Kow</th>
<th>Solubility (mg/L)</th>
<th>Excitation wavelength (nm)</th>
<th>Emission wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracene</td>
<td>C₁₄H₁₀</td>
<td>178.24</td>
<td>4.4</td>
<td>0.05</td>
<td>251</td>
<td>403</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>C₁₀H₈</td>
<td>128.16</td>
<td>3.4</td>
<td>31</td>
<td>264</td>
<td>335</td>
</tr>
</tbody>
</table>

PAH, polycyclic aromatic hydrocarbon; Kow, octanol-water partition coefficient.
column. A Darcy velocity of 5.1 mL/day (1 mL/min out of column) controlled by an high performance liquid chromatography (HPLC) pump was used to simulate the high flow rate of ground water. Different feed solutions were introduced during the sorption and desorption experiments. The operational conditions in column experiments were a pH of 6.0, ionic strength of 0.015 M, and room temperature. The pv was estimated from the breakthrough curve of sodium nitrate in the column (Chi and Amy, 2004a, 2004b). About 25 g of soil was packed in the column with the pv of 7.5 and 6.0 mL for KS and YN soils, respectively. Different flushing solutions were used to test the desorption efficiencies.

As the inner filter effect caused the free anthracene concentrations to be underpredicted (Gauthier et al., 1986) by up to a factor of 1.4, all the calculations were based on total PAH concentration data (after hexane extraction). The extraction method used by Liu and Amy (1993) and Johnson (2000) was adopted to measure total PAH. After collection of discrete PAH samples from the column, hexane was used to extract PAHs from samples. The ratio of hexane to sample was 1:1 by volume, and the mixture was shaken vigorously for 2 min with a vibrator, with subsequent removal of the hexane layer. The total PAH concentration was then measured in the hexane based on fluorescence intensity with a spectrofluorometer, according to Gauthier’s (1986) method. Linear relationships exist between fluorescence intensity and the PAH concentrations used in this study.

Results and Discussion

Batch experiment

Before conducting column experiments, the efficiency of flushing solution was first investigated in equilibrium experiments (Table 4). This study predicts that flushing solutions have higher affinities for highly hydrophobic anthracene than for naphthalene. Both T80 and TX-100 enhance the apparent solubility of anthracene and naphthalene, which were spiked in the soils at a concentration of 500 mg/kg. The solubility in sodium nitrate solution was set to 1 to be compared with the enhanced solubility of other flushing solvent solutions. The value of solubility times increases in Table 4. This means the ratio of enhanced solubility to the value of solubility increases in sodium nitrate solution in KS soil. The fraction of organic carbon (foc) of KS soil is three times higher than that in YN soil (Table 1), indicating increased difficulty in desorbing PAH from KS soil and a lower desorption efficiency.

From Table 4, it can be concluded that apparent solubilities of naphthalene and anthracene in both soils (500 ppm) increase in the presence of T80 and TX-100. It is clear that T80 and TX-100 have great abilities for enhancing anthracene solubility. The effect of anthracene removed by TX-100 is more efficient than by T80. There is also a better anthracene removing effect in YN soil than in KS soil.

The result also demonstrates that TX-100 can desorb more PAH from both soils than T80. This corresponds to the benzene structure and the low hydrophilic–lipophilic balance (HLB) value of TX-100, which may cause higher affinity for PAHs.

Naphthalene desorption from KS soil in column experiment

The desorption abilities of sodium nitrate and the surfactants T80 and TX-100 are compared in Fig. 3. The PAH solubility desorbed by sodium nitrate was set as C₀ to compare with other flushing solution efficiencies. This experiment finds that, because of the high concentration of naphthalene in KS soil (500 ppm), there is no apparent change of the naphthalene concentrations in 40 pv in sodium nitrate solution.

Table 3. Characteristics of Surfactants Used in Experiments

<table>
<thead>
<tr>
<th></th>
<th>TX-100</th>
<th>T80</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAS number</td>
<td>9002-93-1</td>
<td>9005-65-6</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C₁₄H₂₆O(C₂H₄O)ₙ (n = 9–10)</td>
<td>C₆₀H₁₂₄O₂₆</td>
</tr>
<tr>
<td>Molar mass (g/mol)</td>
<td>602–646</td>
<td>1310</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>1.07</td>
<td>1.0–1.09</td>
</tr>
<tr>
<td>Appearance</td>
<td>Viscous colorless liquid</td>
<td>Amber-colored viscous liquid</td>
</tr>
<tr>
<td>Flash point (°C)</td>
<td>251</td>
<td>113</td>
</tr>
<tr>
<td>Hydrophilic–lipophilic balance</td>
<td>13.4</td>
<td>15.0</td>
</tr>
<tr>
<td>Critical micelle concentration (mM)</td>
<td>0.2–0.9</td>
<td>0.012</td>
</tr>
<tr>
<td>Aggregation number</td>
<td>100–155</td>
<td>60</td>
</tr>
</tbody>
</table>

TX-100, Triton X-100; T80, Tween 80.

Table 4. Changes of Polycyclic Aromatic Hydrocarbon Solubility in Soils Spiked with Polycyclic Aromatic Hydrocarbons in the Presence of Flushing Solutions

<table>
<thead>
<tr>
<th>Soil</th>
<th>PAH (500 mg/kg)</th>
<th>Flushing solution</th>
<th>Times of solubility increases*</th>
</tr>
</thead>
<tbody>
<tr>
<td>KS soil</td>
<td>Naphthalene</td>
<td>NaNO₃</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T80</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TX-100</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>Anthracene</td>
<td>NaNO₃</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T80</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TX-100</td>
<td>14.7</td>
</tr>
<tr>
<td>YN soil</td>
<td>Naphthalene</td>
<td>NaNO₃</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T80</td>
<td>13.7</td>
</tr>
<tr>
<td></td>
<td>Anthracene</td>
<td>NaNO₃</td>
<td>21.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T80</td>
<td>21.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TX-100</td>
<td>21.7</td>
</tr>
</tbody>
</table>

*The solubility of PAH in NaNO₃ solution in KS soil was set as 1 unit.
YN, Yun-Nun.
After 40 pv, large fraction of naphthalene was still sorbed in KS soil. T80 was used to flush the naphthalene-contaminated KS soil, resulting in an apparent solubility increase after 2 pv. At 10 pv, solubility is 3.7 times higher than that of sodium nitrate. After 40 pv, apparent solubility in T80 desorption is lower than that of sodium nitrate. Desorption efficiency calculated from the total amount of naphthalene desorbed reveals that T80 is 2.7 times higher than sodium nitrate after 40 pv. In other words, the time needed for soil remediation can be shortened.

In the beginning of the study, the apparent solubility of TX-100 was lower than that of T80. However, after 10 pv, enhanced solubility was approximately 4 times higher than sodium nitrate. Although most of the sorbed naphthalene was desorbed after 30 pv, it showed a lower apparent solubility in TX-100 than sodium nitrate. Desorption efficiency is 2.1 times higher than sodium nitrate after 40 pv. Moreover, TX-100 shows a better desorption ability than T80 for the naphthalene-contaminated KS soil in the aspect of short remediation time. This most likely can be attributed to the lower HLB value of TX-100 than T80. It should be noted that the value of HLB is not the only factor determining desorption; the influence of soil organic carbon fraction should also be taken into account.

**Naphthalene desorption from YN soil in column experiment**

As shown in Fig. 4, 45% of naphthalene is desorbed after 50 pv by sodium nitrate solution in YN soil with low organic carbon content ($f_{oc}$). In the YN soil, 55% of naphthalene was still sorbed. When using T80 as the flushing solution, an enhanced solubility of 3.3 times higher than that of sodium nitrate solution was shown at 3 pv. The time to reach the highest $C/C_0$ is slower for TX-100 compared with T80. Desorption efficiencies are 1.8 and 2.2 times higher than that of sodium nitrate solution after 50 pv for T80 and TX-100, respectively. T80 shows a better remediation capability in naphthalene-contaminated YN soil in the aspect of remediation time. The rapid decrease of values after 18 pv by T80 can be attributed to the naphthalene deficit in the soil.

The reason for the difference between TX-100 and T80 in YN soil can be attributed to the higher affinity of TX-100 with YN soil. The sorption of TX-100 retards transportation in the soil with low organic fraction for the light hydrophobic compound of naphthalene. In other words, the breakthrough of TX-100 in YN soil determines the desorption efficiency. In contrast, T80 facilitates the transport of naphthalene more efficiently than TX-100.

**Desorption of anthracene-contaminated KS soil using surfactants**

Comparing the desorption of anthracene from KS soils by T80 and TX-100 with that of sodium nitrate solution (Fig. 5), the result shows a low desorption efficiency by sodium nitrate as expected. This is due to the negligible anthracene solubility in sodium nitrate. After 100 pv, <0.001% anthracene was desorbed from the soil because the sorption capacity of KS soil for anthracene is high. When 0.1% T80 was used to flush the anthracene-contaminated KS soil, the desorption was also limited by the high affinity of KS soil with anthracene. After 10 pv, enhanced solubility became apparent and reached 10. After 100 pv, enhanced solubility reached 11. In the same manner as T80, the apparent solubility of anthracene in TX-100 solution gradually increased after 15 pv, and with an apparent increase after 25 pv, its apparent solubility reached 30. After 100 pv, the desorption efficiency was 24 times higher than that of sodium nitrate solution.

After 50 pv, the packed soil column started to clog, so the experiment was stopped. From the desorption curves (Fig. 5), the use of T80 and TX-100 shows highly enhanced solubility. Batch experiments also demonstrate that the surfactants T80 and TX-100 enhance desorption of anthracene in KS soil (500 ppm) by 7.3 and 14.7 times, respectively.
Desorption of anthracene-contaminated YN soil (500 mg/kg) by the surfactants

Comparing the desorption of anthracene from YN soil by T80 and TX-100 with that of sodium nitrate solution (Fig. 6), the efficiencies using sodium nitrate to desorb anthracene from KS or YN soils were not efficient. Only 0.001% of anthracene was desorbed after 20 pv, and 99% of anthracene remained in soils. When 0.1% T80 was used to flush anthracene from YN soil, desorption efficiency was limited by the high affinity between T80 and YN soil in the beginning. After T80 breakthrough in YN soil column, the enhanced solubility increased gradually and reached 15 after 10 pv. The concentration of anthracene was 14 times higher than that of sodium nitrate solution after 100 pv.

When 0.1% TX-100 was used, the sorbed anthracene in YN soil did not desorb apparently. After 15 pv, the enhanced solubility started to increase, and there was a significant increase in desorption after 25 pv. Enhanced solubility reached 30 times that of C/Co after 100 pv; desorption efficiency was 27 times higher than that of sodium nitrate. When comparing with the batch experiment results, the enhanced solubilities were 13.7 and 21.7 times higher by T80 and TX-100, respectively. The pressure increased over the pump limit pressure at 100 pv, so the experiment was terminated.

In both soils, TX-100 shows a better desorption efficiency on anthracene-contaminated soils. It can be attributed to its lower HLB value than T80 or higher affinity between anthracene and TX-100. There was no significant difference in the desorption efficiency for phenanthrene-contaminated soils except for longer breakthrough time in YN soil with low organic carbon concentration. For PAH with high solubility, the desorption efficiency depends on the organic fraction of soils. The affinity between soils and surfactant should also be considered in the initial stage of remediation as adsorption may increase the hydrophobicity of the mineral surface and retard PAH transport. After TX-100 breakthrough, the transportation of hydrophobic contaminants can be enhanced.

As previously mentioned, nonionic surfactants (T80, TX-100) can increase apparent solubility from 2 to 30 times in soils with 500 mg/kg of PAHs in column experiments. Efficiency is for anthracene-contaminated soil rather than naphthalene-contaminated soil, which has higher water solubility.

Conclusions

The purpose of this study was to investigate the desorption efficiency of PAHs from KS (foc = 0.32%) and YN (foc = 0.1%) soils. The result shows that desorption efficiency rates depend on the fraction of organic carbon, contaminant characteristics, and desorption time. The higher the concentrations of organic matter, clay fraction, and the PAH hydrophobicity, the lower will be the desorption efficiency. Increasing desorption time can increase the amount of desorbed PAHs, but the desorption efficiency in the prolonged section might not be worth of it.

In column experiments, enhanced solubilities of PAHs in the effluent are increased by 2–30 times using 0.1% T80 and 0.1% TX-100 solutions, especially for anthracene-contaminated soil. The desorption efficiency of TX-100 is better than that of T80.

The breakthrough of T80 in soils is short, so the PAH in soil columns can be brought out quickly. The affinity of TX-100 with soils is high, so its breakthrough is slower than that of T80. Therefore, it takes longer for TX-100 to bring PAHs out of the soil columns.

If the surfactants used in column experiments result in clogging, it is probably due to colloid desorption from the particles. It is important to consider the applicability of surfactant concentrations in the field. The results show that 0.1% of T80 and TX-100 are suitable in column experiments. This finding shows that the results from column experiments are more applicable to the field than those done only by batch experiments.

Author Disclosure Statement

No competing financial interests exist.

References


