Technical Note

Removal of PAHs with surfactant-enhanced soil washing: Influencing factors and removal effectiveness

Sheng Peng, Wei Wu, Jiajun Chen *

School of Environment, The Key Laboratory of Water and Sediment Sciences (Ministry of Education), Beijing Normal University, Beijing 100875, China

ARTICLE INFO

ABSTRACT

PAH removal with surfactant enhanced washing was investigated through a series of laboratory tests to examine the effect of stirring speed, washing time, surfactant concentration, liquid/solid ratio, temperature, and on-and-off mode. The first four factors show significant influence on the PAH removal while the latter two do not. Total removal ratio and a new proposed parameter, solubilization percentage, are used to evaluate the effectiveness quantitatively.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

PAHs are potential carcinogenic and mutagenic compounds having raised appreciable environmental concerns around the world. As a result, researches and projects addressing PAH remediation have been increasing in recent decades. PAHs are highly hydrophobic and readily adsorbed onto soil particles; therefore resistant to be removed. Many techniques have been developed or applied to tackle its removal from soil. Among them, surfactant-enhanced soil washing has been suggested a promising technique since it has relative high removal ratio while is cost-effective (e.g., Paria, 2008; Laha et al., 2009).

Surfactants enhance the solubility of hydrophobic organic compounds by partitioning them into the hydrophobic cores of surfactant micelles (Abriola et al., 1993; Brown et al., 1994; Goudar et al., 1999). This process can be affected by several factors (e.g., Chang et al., 2000; Zhao et al., 2005; Haapea and Tuhkanen, 2006; Elgh-Dalgren et al., 2009). However, most of the researches had different focuses on part of the influencing factors and there is relatively little systematic study. In addition, there has been no research on on-and-off washing mode, a possible influencing factor to our knowledge.

In this paper, removal of five target PAHs in a local site cleanup project: benzo[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-

cd]pyrene (InP) with two selected nonionic surfactants was investigated systematically on different influencing factors, including stirring strength, washing time, surfactant concentration, liquid soil ratio (L/S), and temperature. Different on-and-off stirring modes are also tested for their effectiveness. A new parameter, solubilization percentage, based on the solubilization capacity of the surfactant is defined to evaluate the effectiveness.

2. Materials and methods

2.1. Soil samples

Soil samples were taken from an abandoned coal-chemical plant in the east of Beijing. Contamination with PAHs was detected from the surface to a depth of 3 m in sites around coke planting and recycling sites. Soil samples were air dried for 7 d. They were tapped to break aggregated soils and then homogenized before sieving to remove >2 mm gravels. Selected physical and chemical properties of the soil samples are listed in Table 1.

2.2. Surfactants

TW80 (tween-80) and TX100 (triton X-100) (both from Guangdong Chemical Engineering, Guangzhou, China) were selected for this study. The critical micellar concentration (CMC) of these two surfactants was determined as 156 and 59 mg L^{-1} using the method of Du Nouy tensiometer (Harkmgs, 1959), respectively. These CMCs are somehow different from those in literatures, where

* Corresponding author. Tel.: +86 10 58807597.
  E-mail address: jeffchen@bnu.edu.cn (J. Chen).

Table 1
Selected physichemical properties of soil samples.

Initial water content (%)	3.0
pH	8.0
TOC (%)	0.5
CEC (Cmol kg^{-1})	9.7
Particle size distribution (%)	
<50 μm	17
50–75 μm	37
75–125 μm	23
125–250 μm	13
250–500 μm	8
500–2000 μm	1
PAHs (mg kg^{-1})[*]	
BaA	3.2 ± 1.5
BbF	3.6 ± 0.8
BkF	1.2 ± 0.3
BaP	1.7 ± 0.5
InP	2.9 ± 2.5

[*] PAHs were measured before each of the six tests as described in Section 2.4.

ranges of 13–45 and 106–130 mg L^{-1} were reported for TW80 and TX100, respectively (e.g., Edwards et al., 1991; Yeom et al., 1996). The difference may be attributed to the different qualities of the surfactants. Nevertheless, since we used the surfactants through out all the experiments, the comparisons of removal and analysis of the influencing factor's effects should be still valid. In soil system, there is adsorption of surfactant on the soil particles, which will result in an apparent higher CMC. In this case, the effective CMC (CMC$_{eff}$) was determined as 1013 and 602 mg L^{-1} for TW80 and TX100, respectively.

2.3. Surfactant solubilization test

Pure PAHs were added into surfactant solutions with different concentrations to measure their maximal solubility (S_{max}). To mimic the conditions in soil washing for the sake of comparison, the same conditions of the best scenario determined in soil washing tests were applied. The results from this test define the surfactants' solubilization capacity.

2.4. Laboratory soil washing experiments

Six sets of experiments were conducted to examine the effect of six influencing factors on PAH removal with TW80 and TX100. The six factors were tested in the order of: (1) stirring speed, (2) washing time, (3) surfactant concentration, (4) L/S, (5) temperature, and (6) on-and-off mode. When each of the factors was tested at different values or modes, the other five kept constant. The value generating the best removal was adapted in the following test. The pH of soil-surfactant solution mixture was measured to vary between 7.1 and 7.2 with both TW80 and TX100 in the tested concentrations. Therefore, pH's effect was not investigated herein. Air-dried soil and surfactant solution were added into a 500 mL flask in certain ratio and stirred with a two-paddle-agitator. An ice-bath and an electrical water-bath were used for the tests of different temperatures, while other tests were all at room temperature (20 ± 2 °C). In different on-and-off modes, the agitator was turned on and off with different time intervals. Extraction of PAHs was performed on soil samples using an Accelerated Solvent Extractor (ASE 300, Dionex Corp.). Sixteen PAHs in the USEPA priority list (including the five target PAHs) were measured using a ThermoQuest Trace 2000 GC–MS (San Jose, CA, USA) for both PAH concentrations in the contaminated soils and the washing solutions. More detailed description of the PAH measurement in soils is in Li et al. (2010).

2.5. Removal effectiveness evaluation

The PAH removal ratio (R) can be determined as the quotient of PAHs in solution (S) divided by initial PAHs in soil (S_i):

$$R = \frac{S}{S_i} \tag{1}$$

where S is in unit of mg L^{-1}, S_i is originally mg kg^{-1} and transferred to mg L^{-1} based on L/S (L kg^{-1}) to generate a dimensionless R. Total removal of the five target PAHs is presented to evaluate the performance of the surfactants in this paper.

Molar solubilization ratio (MSR) defined by Edwards et al. (1991) is often used to quantify the effectiveness of a surfactant in solubilizing a given solute. MSR for soil washing system can be calculated as:

$$MSR = \frac{S - S_{CMC}}{C - CMC} \tag{2}$$

where S (mg L^{-1}) is the apparent solubility of organic compounds at surfactant concentration C (mg L^{-1}) and S_{CMC} (mg L^{-1}) is the apparent solubility of organic compounds at the CMC. To account for surfactant adsorption, S_{CMCeff} and CMC$_{eff}$ should be used in Eq. (2). Replacing S in Eq. (2) with $R * S_i$, it can be seen that MSR is linear with R when (C − CMC$_{eff}$) and S_i are constant, which is the case for tests 1, 2, 5, and 6 since where C and CMC$_{eff}$ was kept unchanged and in each test S_i is the same. In test 4, measurement of solubility (S_{CMC}) of PAHs at different CMC$_{eff}$ with different L/S is not included in this study. Therefore, MSR is only used to determine the best concentration in test 3.

In order to compare the overall solubility of PAHs in soil washing system and the solubility capacity of the surfactant solution, a new coefficient is defined herein as solubilization percentage (SP):

$$SP = \frac{S}{S_{max}[C - (CMC_{eff} - CMC)]} = \frac{RS_i}{S_{max}[C - (CMC_{eff} - CMC)]} \tag{3}$$

(CMC$_{eff}$ − CMC) represents the concentration of sorbed surfactant; C − (CMC$_{eff}$ − CMC) hence denotes the effective concentration of surfactant in soil-surfactant-water system. Subsequently, the denominator in Eq. (3) represents the effective solubilization capacity of the surfactant in the soil-surfactant-water system. It is worth to note that SP is linear with R when other parameters are constant; therefore, SP was only used to determine the best scenario in tests 3 and 4.
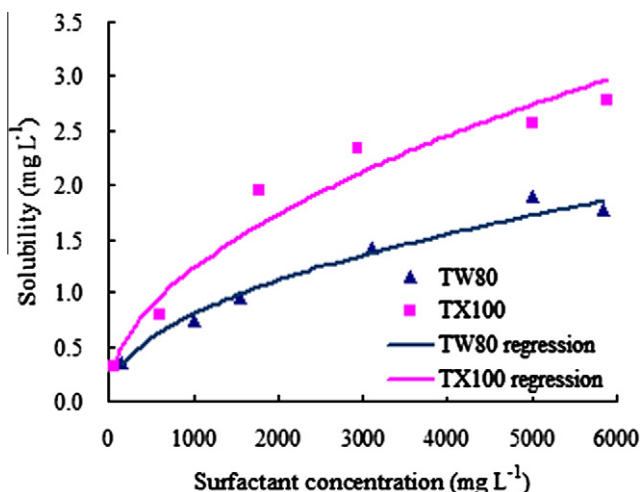

Fig. 1. Total solubility of five target PAHs in surfactant–water system at different concentrations for TW80 and TX100.

3. Results and discussions

3.1. Surfactant solubilization

Surfactant solubilization tests were conducted at concentrations from 1CMC (TW80: 156 mg L^{-1}, TX100: 59 mg L^{-1}) to 6000 mg L^{-1} for both surfactants. Fig. 1 shows the results. Solubility of total PAHs increases with increasing surfactant concentrations in a nonlinear pattern. TX100 shows greater solubilization capacity than TW80 at the same concentration.

3.2. Surfactant soil washing

The removal of individual PAH shows similar trend (data not shown); therefore the total removal ratio of the five target PAHs is discussed thereafter. Fig. 2a–f present the removal ratios of tests 1–6. Observation of these figures reveals that the first four factors, i.e., stirring speed, washing time, surfactant concentration, and L/S have significant influence on the removal; while temperature and on-and-off mode does not show obvious influence.
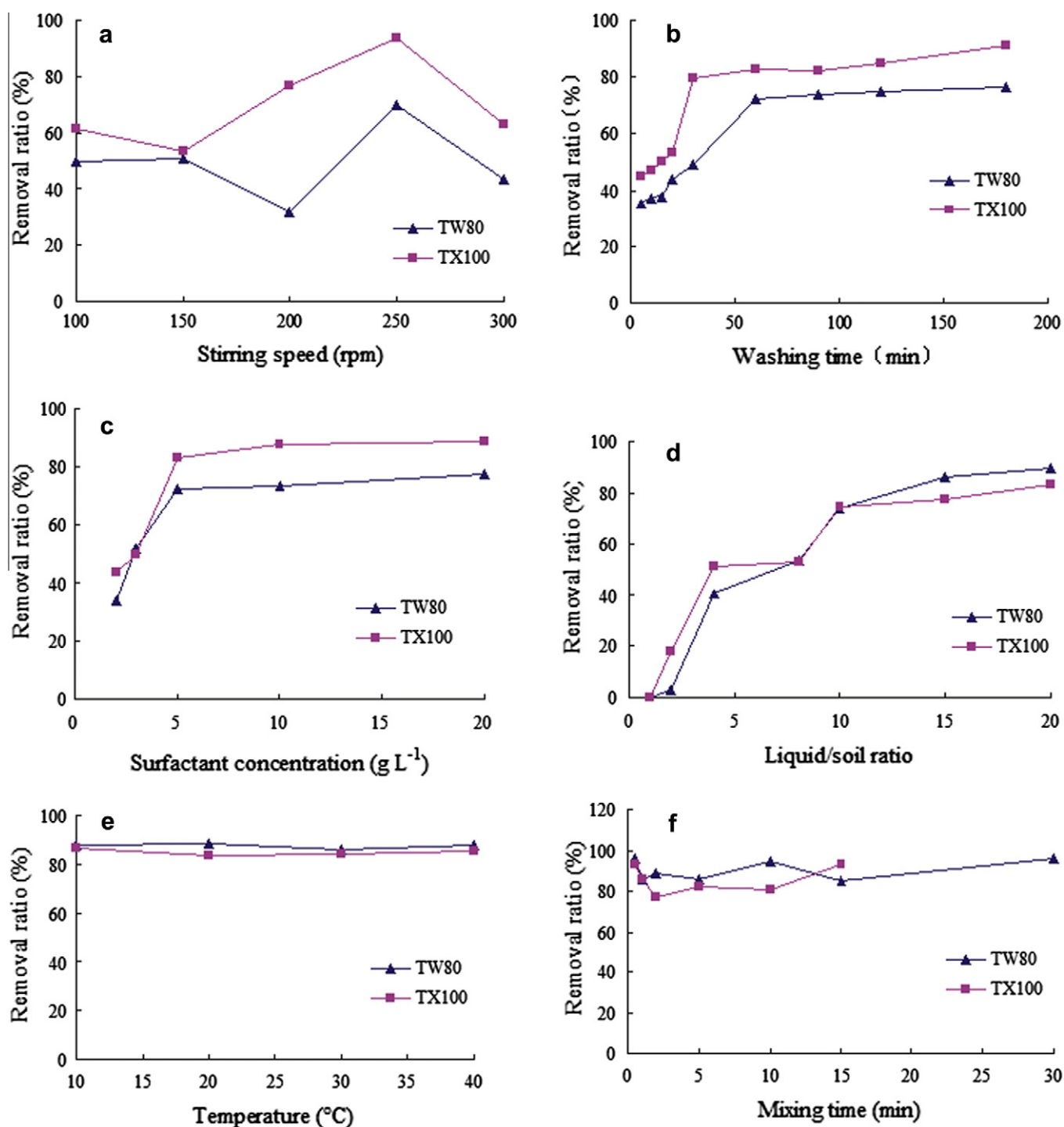

Fig. 2. Removal ratios of total PAHs with TW80 and TX100 at different tests: a. test 1: different stirring speeds; b. test 2: removal kinetics; c. test 3: different surfactant concentrations; d. test 4: different liquid/solid ratios; e. test 5: temperature effect; f. test 6: different mixing times in on-and-off mode tests.

3.2.1. Stirring speed

Test 1 was conducted under conditions of: $C = 5$ g L^{-1}, L/S = 10:1, washing time = 30 min. In test 1, the removal ratio has a tendency to increase with increasing stirring speed until it rises to 250 rpm, after which the removal ratio is dropping at 300 rpm (Fig. 2a). This indicates that the collision between soil particles becomes stronger with increasing stirring speed which helps the stripping of the adsorbed or crusted contaminants. However, further increase of the stirring strength will cause the slurry to move in bulk formation with less relative movement so that the collision is reduced, which in turn leads to lower removal.

3.2.2. Washing time

Test 2 was carried on with stirring speed of 250 rpm as the optimal value determined in test 1. The other conditions were the same as in test 1. Fig. 2b shows that the removal ratio has a relatively quick increase with time at the initial phase within 30 and 60 min for TX100 and TW80, respectively, and then is approaching a stable level. The kinetic characteristics of the removal curves indicates the washing-off process is time-dependent. This can be caused by rate-limited dissolution, and/or desorption of PAHs. Break/separation of incrustation or soil-trapped may also contribute to this time-dependent process. Further study on the surfactant and PAH sorption will be conducted to evaluate the removal kinetics more quantitatively.

3.2.3. Surfactant concentration

From test 3, washing time of 30 and 60 min was applied to TX100 and TW80 tests respectively. It can be observed that removal ratios of both TX100 and TW80 increase sharply with increasing concentration up to 5 g L^{-1} (Fig. 2c). After that point, further increase of concentration does not result in appreciable enhancement in removal.

MSR and SP were compared to determine the optimal concentration. The results are presented in Fig. 3a and b, respectively. For MSR calculation, concentration of 2 g L^{-1} and the corresponding solubility were used in replacement of CMC$_{eff}$ and S_{CMCeff} since S_{CMCeff} is not available (this replacement should be valid since comparison of MSR is more of interest than the absolute value of MSR). Observation of Fig. 3a and b reveals that both MSR and SP are tending upwards until concentration reaches to 5 g L^{-1} for TX100. After that, both MSR and SP are dropping. This indicates that although removal ratio is keeping increasing with concentration, there is an inflection point for effectiveness. Therefore, 5 g L^{-1} can be taken as the optimal concentration for TX100 in this case. The situation of TW80 is similar with SP, which has the highest value at 5 g L^{-1}; while the largest MSR occurs at 2 g L^{-1} and keeps decreasing afterwards. At 2 g L^{-1}, the removal ratio with TW80 is only 38%, which is obviously not the best scenario in this case. This suggests that SP can be a better index in determining the best scenario along with R.

3.2.4. Liquid/soil ratio

L/S is an important parameter in soil washing: higher L/S indicates greater capacity of solubilization. It can be seen from Fig. 2d that close to zero removal ratio was achieved at L/S of 1:1, while close to 90% removal ratio was achieved at L/S of 20:1. Basically, R increases with increasing L/S in a nonlinear pattern. Above L/S of 10:1, the increase of R slows down. SP for L/S from 8:1 to 20:1 is calculated based on measured CMC$_{eff}$ for each L/S. The highest SP occurs at L/S of 10:1 for TX100. For TW80, SP has similar higher value at 8:1 and 10:1. Further increase of L/S leads to decrease of SP. In addition, in real-world project, higher L/S indicates more water use, which will pose a higher requirement for the equipment and energy and will generate more wastewater for post-treatment. Therefore, L/S ratio of 10:1 can be taken as the optimal in this case.
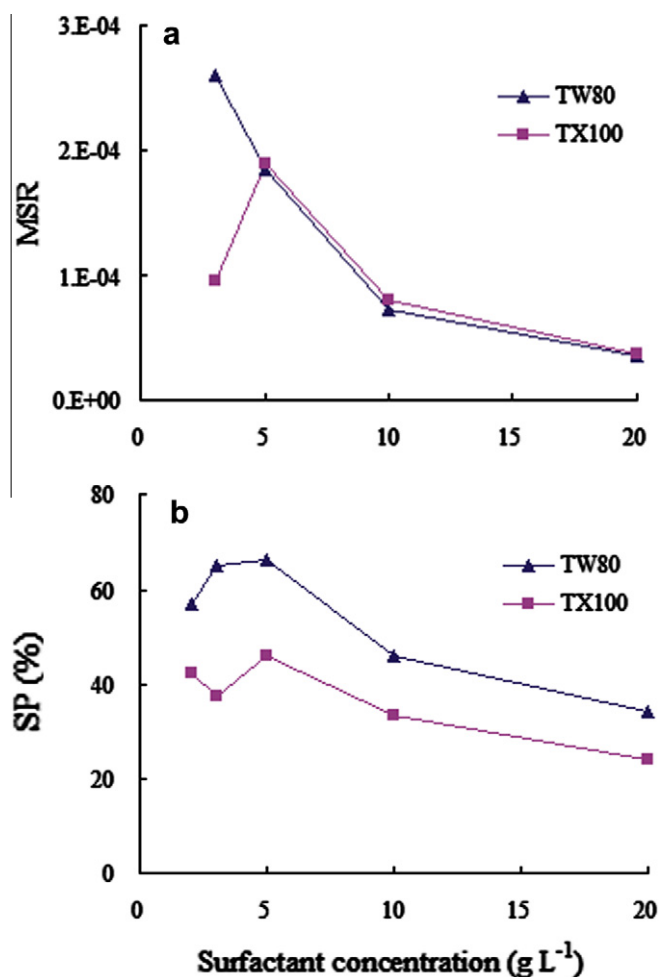

Fig. 3. Removal effectiveness of total PAHs with TW80 and TX100 at test 3. (a) Molar solubilization ratios; (b) solubilization percentages.

3.2.5. Temperature

Observation of Fig. 2e can reveal that the removal performance basically is not affected by temperature within the tested range, although there is minor variation. Among the processes controlling the removal, desorption and dissolution are both temperature-dependent processes, while break/separation of incrustation or soil-trapped PAHs is determined mostly by mechanical conditions. Therefore, the results from this test indicate that the effect of incrustation and/or soil-trapped PAHs may play more important role than desorption and dissolution.

3.2.6. On-and-off mode

In order to raise the collision between soil grains thus to increase the break/separation of incrustation, several on-and-off modes were applied to investigate their influence on the removal. According to a preliminary test, it took 15 s for the soil particles to settle down after stirring stopped. Mixing times of 0.5, 1, 2, 5, 10 and 30 min (on mode) followed in each case by 15 s (off mode) of settling were tested. The overall washing duration was 30 and 60 min for TX100 and TW80, respectively. However, as shown in Fig. 2f, although there is some variation of removal ratio with different on-and-off ratios, no obvious relationship between them can be seen. This indicates slight influence of on-and-off mode on the break/separation of incrustation and/or soil-trapped PAHs.
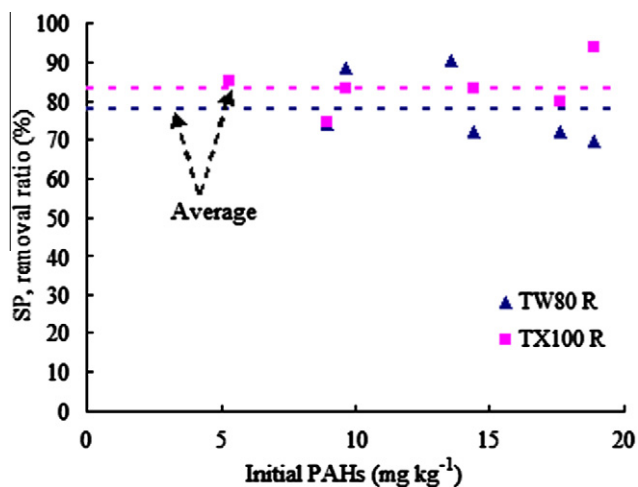
Fig. 4. The relationship between removal ratio of total PAHs with initial PAH concentration.

3.3. Comparison of effectiveness for best scenarios in all tests

The conditions of the best scenarios for the six tests are coincidently the same except for the washing time for TW80 in test 1, which is 30 min (while in other tests it is 60 min). The removal ratios under these conditions are consistently stable, with an average value of 83% and 78% for TX100 and TW80, respectively (Fig. 4). This indicates the reproducibility of the removal tests. It is noticeable that the initial PAH contents in soil samples vary from 5 to 19 mg kg^{-1}, while R is not affected significantly by it (Fig. 4). This indicates a constant partitioning between the soil and surfactant solution regardless of initial PAH concentration within the tested range.

SP is calculated for the best scenario of each test. It displays a linear relationship with initial PAH content (Fig. 4), as expected from Eq. (3) when R and effective solubilization capacity are constant. The effective solubilization capacity of TW80 and TX100 at the best scenarios is equivalent to 16 and 26 mg kg^{-1}, respectively, which are larger than the initial PAH contents except for that in tests 1 and 2 with TW80. Less than 100% removal ratio indicates that sorption of PAHs and/or residual incrustation or soil-trapped PAHs exist. Further study on PAH sorption should be conducted to investigate quantitatively its influence.

4. Conclusions

A series of washing tests were conducted with TW80 and TX100 to investigate the effect of six influencing factors on the removal of PAHs from a contaminated soil. The best scenario is determined based on R for stirring speed and washing duration for each set of tests. The new defined parameter SP is used in combination with R to determine the optimal value for surfactant concentration and L/S. Temperature and on-and-off mode do not show significant influence on the PAH removal. The conditions in each best scenario are basically the same for all tests, that is, stirring speed = 250 rpm, surfactant concentration = 5 g L^{-1}, L/S = 10:1 for both TW80 and TX100 and washing time = 60 and 30 min for TW80 and TX100,

respectively (the exception is in test 1 with TW80, washing time = 30 min). The basically stable removal ratio under these conditions (with averages of 79% and 83% for TW80 and TX100, respectively) indicates the repeatability of the experiments. The average removal ratios also indicate good efficiency has been accomplished for the transfer of PAHs from solid phase to liquid phase. In real project, solid and liquid phase needs be separated before the cleaned soil can be reused or backfilled, while the contaminated water needs to be treated. Since the cost of wastewater treatment is far less than that of contaminated soil, ten-fold increase in volume (at L/S = 10:1) is economically feasible.

The removal ratio does not change with initial PAH concentrations, which indicates a constant partitioning of PAHs between residual phase and dissolved phase. Residual PAHs may exist in the form of incrustation on the soil surface, soil-trapped phase, or sorbed phase. The results from temperature test (test 5) indicate the minor influence of sorption/desorption of PAHs while more important influence of mechanical factors on the removal. Further study on the sorption of surfactants and sorption of PAHs need to be conducted to confirm quantitatively the influence of PAH sorption.

Acknowledgement

References

Abriola, L.M., Dekker, T.J., Pennell, K.D., 1993. Surfactant-enhanced solubilization of residual dodecane in soil columns. 2. Mathematical modeling. Environ. Sci. Technol. 27, 2341–2351.

Brown, C.L., Pope, G.A., Abriola, L.M., Sepehrnoori, K., 1994. Simulation of surfactant-enhanced aquifer remediation. Water Resour. Res. 30, 2959–2977.

Chang, M.C., Huang, C.R., Shu, H.Y., 2000. Effects of surfactants on extraction of phenanthrene in spiked sand. Chemosphere 41, 1295–1300.

Edwards, D.A., Luthy, R.G., Liu, Z., 1991. Solubilization of polycyclic aromatic hydrocarbons in micellar nonionic surfactant solutions. Environ. Sci. Technol. 25, 127–133.

Elgh-Dalgren, K., Arwidsson, Z., Camdzija, A., Sjöberg, R., Ribé, V., Waara, S., Allard, B., von Kronhelm, T., van Hees, P.A.W., 2009. Laboratory and pilot scale soil washing of PAH and arsenic from a wood preservation site: changes in concentration and toxicity. J. Hazard. Mater. 172, 1033–1040.

Goudar, C., Strevett, K., Grego, J., 1999. Competitive substrate biodegradation during surfactant-enhanced remediation. J. Environ. Eng. 125, 1142–1148.

Haapea, P., Tuhkanen, T., 2006. Integrated treatment of PAH contaminated soil by soil washing, ozonation and biological treatment. J. Hazard. Mater. 136, 244–250.

Harkmgs, W.D., 1959. Physical methods of organic chemistry. In: Weissberger, A. (Eds), vol.1, Part 1, Interscience Inc., New York (Revised by A. E. Alexander).

Laha, S., Tansel, B., Ussawarujikulchai, A., 2009. Surfactant-soil interactions during surfactant-amended remediation of contaminated soils by hydrophobic organic compounds: a review. J. Environ. Manage. 90, 95–100.

Li, H., Chen, J., Wu, W., 2010. Distribution of polycyclic aromatic hydrocarbons in different size fractions of soil from a coke oven plant and its relationship to organic carbon content. J. Hazard. Mater. 176, 729–734.

Paria, S., 2008. Surfactant-enhanced remediation of organic contaminated soil and water. Adv. Colloid. Interface Sci. 138, 24–58.

Yeom, I.T., Ghosh, M.M., Cox, C.D., 1996. Kinetic aspects of surfactant solubilization of soil-bound polycyclic aromatic hydrocarbons. Environ. Sci. Technol. 30, 1589–1595.

Zhao, B., Zhu, L., Gao, Y., 2005. A novel solubilization of phenanthrene using Winsor I microemulsion-based sodium castor oil sulfate. J. Hazard. Mater. B119, 205–211.