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Batch washing of saturated hydrocarbons and polycyclic aromatic hydrocarbons from crude oil contaminated soils using bio-surfactant

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Abstract: Desorption of total saturated fractions (i.e. SAT, defined for this study as the summation of the concentrations of the saturated hydrocarbon from n-C_{10} to n-C_{26}) and polycyclic aromatic fractions (i.e. PAH, defined as the summation of the concentrations of all polycyclic aromatic fractions including the 16 EPA priority PAH) in two types of soils subjected to the changes of pH and salinity and different bio-surfactant concentrations were investigated. In general, compared with the experiments without bio-surfactant addition, adding rhamnolipid to crude oil−water systems at concentrations above its critical micelle concentration (CMC) values benefits SAT and PAH desorption. The results indicate that the change of pH could have distinct effects on rhamnolipid performance concerning its own micelle structure and soil properties. For loam soil, the adsorption of non-aqueous phase liquid (NAPL) and rhamnolipid would be the principle limiting factors during the NAPL removal procedure. For sand soil, less amount of rhamnolipid is adsorbed onto soil. Thus, with the increase of salinity, the solubilization and desorption of rhamnolipid solution are more significant. In summary, the pH and salt sensitivity of the bio-surfactant will vary according to the specific structure of the surfactant characteristics and soil properties.

Key words: bio-surfactant; salinity; desorption; total saturated fractions (SAT); polycyclic aromatic fractions (PAH)

1 Introduction

Soil contamination by crude oils due to pipeline breaks or other accidental spills is a major concern facing the oil and gas industries [1−2]. The crude oil contains compounds that have strong adsorption onto soils and are resistant to degradation, such as the saturated hydrocarbons (SAT) and polycyclic aromatic hydrocarbons (PAH) which are very difficult to remediate [3]. As compared with many other remediation approaches, soil washing has been used as a relatively inexpensive and convenient technology for removing a wide range of soil contaminants including petroleum hydrocarbons (PHCs) [4]. Its remediation mechanisms include the dissolution and mobilization of organic compounds adsorbed onto soil particles. However, when it is used for the removal of SAT and PAH compounds, the soil washing efficiency can be greatly hampered by their hydrophobic characteristics and strong soil adsorption [5−6]. It is thus of great importance to find appropriate methods to enhance the soil washing efficiency of these persistent compounds.

The application of surfactant has received much attention during the past years to improve the soil washing efficiency of organic compounds from contaminated soils, mainly based on the mechanisms of soil roll-up and pollutant solubilization [7−9]. For example, KHALLADI et al [10] applied an anionic chemical surfactant called sodium dodecyl sulfate (SDS) to enhance the continuous washing process of diesel fuel contaminated soil, and a diesel removal rate of 97% was achieved after a soil washing by 8 mmol/L of SDS solution. Their results also indicated that the SDS was efficient in eliminating the saturated hydrocarbons (n-alkanes) from soil, with n-alkanes removal rate of 3.5% and 73% at 4 mmol/L and 8 mmol/L of SDS solution, respectively [10]. PENG et al [6] investigated the washing treatment of PAH contaminated soil with two chemical surfactants, and they observed an average total PAH removal rate of 83% and 79% for TW80 (tween-80) and TX100 (Triton X-100), respectively. Generally, the application of chemical surfactants is associated with a number of problems because of their toxicity and low biodegradability [11−12].

In recent years, the application of bio-surfactants for contaminated soil remediation has received significant interests [13]. As compared with the chemical surfactants, bio-surfactants produced by microorganisms have more advantages, such as great biodegradability and

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biocompatibility, less toxicity, lower CMC value, and stable activity [11]. Consequently, bio-surfactant can be more effective in enhancing the soil washing efficiency of organic compounds contaminated soil, and numerous studies in this area were reported [14−16]. For example, LAI et al [11] investigated the effect of two bio-surfactants (e.g., rhamnolipid and surfactin) on the removal of PHCs from oil contaminated soil using the batch washing process, and observed a total petroleum hydrocarbons (TPH) removal rate of 23% and 14% for rhamnolipid and surfactin, respectively, when the soil had a low initial TPH concentration (3000 mg/kg). However, when the soil had a high initial TPH concentration (9 g/kg), the TPH removal efficiency was increased to 63% and 62% for these two bio- surfactants [11]. More recently, YAN et al [17] conducted a series of washing tests with rhamnolipid to investigate the influence of five factors (bio-surfactant concentration, liquid/solid ratio, washing time, stirring speed, and temperature) on oil removal from oil-based drill cuttings, and the results indicated a TPH removal efficiency of 85.2%.

It can be expected that the application of bio-surfactant can be an appropriate method to enhance the efficiency of soil washing for removing the SAT and PAH compounds from crude oil contaminated soil [3, 18]. Generally, the enhancement effect depends on many environmental factors, such as the bio-surfactant concentration, the pH value, and the salinity of the washing solution [8, 19−20]. Although many studies were conducted to explore the effect of different factors on the removal of organic compounds from oil contaminated soils, contradictory results even under similar situations have always been reported, and no general trend of bio-surfactant enhancement under different environmental conditions has been observed. For example, URUM and PEKDEMIR [21] observed that some bio-surfactants could not enhance the solubilization of crude oil in soil at concentrations greater than their CMC values. ABOUSEOUD et al [20] showed that salinity had a positive impact on the solubilization of naphthalene under sub-CMC concentrations of bio-surfactant, but had a negative impact when the bio-surfactant concentration was above its CMC value. Moreover, in terms of the removal of SAT and PAH compounds, few studies were reported on the effect of bio-surfactant assisted soil washing on individual SAT and PAH fractions. More research inputs in this field are thus desired. The objective of this work was then to examine the effect of bio-surfactant on the batch washing process for the removal of SAT and PAH compounds from crude oil contaminated soil. Rhamnolipid was selected as the study bio-surfactant. The rhamnolipid concentration, the pH value, and the salinity of the washing solution as well as the soil type, were investigated to examine their impacts on the washing efficiency. Particularly, the removal of individual SAT and PAH fraction was analyzed in addition to the examination of the total concentrations of SAT and PAH in soil.

2 Experimental

2.1 Preparation of bio-surfactant and crude oil contaminated soil

The rhamnolipid used in this study was supplied by Daqing Victex Chemical Industry Ltd. (China). The critical micelle concentration (CMC) of this bio-surfactant was measured as 0.001% in mass fraction by noting the concentration at which the surface tension first became minimum. Two types of unpolluted soil samples collected from the North China Electric Power University campus were oven dried, and sieved with a mesh-20 (850 μm) sieve to remove coarse particles. The textural classes of the two soil types were identified as loam and sand. Table 1 lists the soil properties. To prepare polluted soil samples in the laboratory, 6 g of crude oil obtained from Daqing Oil Field in China was dissolved in 300 mL of *n*-hexane solvent using electrical mixer for about 20 min, and was then added into 150 g of unpolluted soil for homogeneous mixing. The crude oil spiking was conducted for each type of soil. After oil spiking, the contaminated soils were placed in the fume hood for two weeks to evaporate the *n*-hexane solvent, and were then stored in the fridge (4 °C) using brown air-tight glass containers.

2.2 Batch washing experimental design

The batch soil washing experiments were conducted to examine the effect of four factors on the removal of SAT and PAH compounds from crude oil contaminated soil. These include soil type, the rhamnolipid concentration, the pH value, and the salinity of the washing solution. In order to examine the effect of rhamnolipid concentration on the soil washing efficiency, five concentration levels of rhamnolipid in the washing

Table 1 Properties of soil samples

Item	Soil size fraction/%			Textural class	pH	CEC (meq/100 g soil)	Organic matter/%
	Clay (≤ 0.002 mm)	Silt (0.002−0.05 mm)	Sand (0.05−0.2 mm)				
Soil 1	20.2	33.3	46.5	Loam	8.22	11.79	3.5
Soil 2	0.2	3.8	96.0	Sand	8.41	27.30	0.10

solution were used, including 0.01%, 0.02%, 0.04%, 0.08%, and 0.10% in mass fraction. For each soil type, 1.5 g of contaminated soil and 50 mL of washing solution with a given rhamnolipid concentration were introduced into a 100 mL conical flask with stopper. About 0.05−0.1 mL of 0.02% NaN_3 was added into the flask in order to inhibit the microbial activity. The washing solution had a pH value of 7 and a salinity of 0. The content in the flask was then shaken laterally at 200 r/min for 24 h at room temperature of 25−27 °C to complete the soil washing. At the end of each washing, the contents of flask were allowed to settle overnight and were sent for solid/liquid separation using a vacuum filtration apparatus that included a 1.6 μm-microfibre filter paper. The soil samples after filtration were air dried for 12 h, and 1 g of the soil samples was then used to determine the remaining crude oil concentration. All of the experiment procedures were carried out in triplicate. The soil washing using deionized water was used as the control.

In order to examine the effect of solution pH on the soil washing efficiency, six pH levels of the washing solution were used, including 2.0, 4.0, 6.0, 8.0, 10.0 and 12.0. The solution pH was adjusted with 10% HCl and NaOH. The washing solution had a salinity of 0 and a rahmnolipid concentration of 0.08% in mass fraction. In order to examine the effect of solution salinity on the soil washing efficiency, five levels of salinity were used by adjusting the NaCl concentration of the washing solution to 2%, 4%, 6%, 8% and 10% (w/v). The washing solution had a pH value of 7.0 and a rhamnolipid concentration of 0.08% in mass fraction. The experimental procedures for examining the effects of solution pH and salinity were similar to those for examining the effect of rhamnolipid concentration as described above.

2.3 Analysis of saturated hydrocarbons and polycyclic aromatic hydrocarbons

The concentration of the saturated hydrocarbons and polycyclic aromatic hydrocarbons in the soil sample was analyzed using GC-MS. Before sending for GC-MS analysis, the solid−liquid extraction of sample needs to be conducted [22].

1 g of soil sample was extracted with 10 mL of 1:1 hexane/acetone in volume ratio for 40 min using the ultrasonic cleaning instrument at a power of 150 W following the procedures recommended in U.S. EPA method 3550C, and the extraction was conducted three times. During the extraction process, the water bath of the ultrasonic cleaning instrument was kept at room temperature using ice cubes. After ultrasonic extraction, the extractions were centrifuged at a speed of 4000 r/min for 5 min. The aqueous phase containing the solvent and the extracted crude oil compounds after centrifugation was then collected into a 50 mL conical flask with stopper. Anhydrous sodium sulfate (dried at 400 °C for 4 h) was used to dehydrate the aqueous extract solution, and a rotating evaporator was used to concentrate the extract solution into 2 mL at (45±2) °C. The concentrated extract was then sent for a silica gel column cleanup process to remove moisture, particulate, and unwanted polar organic compounds [22]. The cleanup column consisted of a 30-cm-long and 16-mm-diameter glass column plugged with glass wool. Approximately 10 g of 80−120 mesh (125−180 μm) silica gel dissolved in dichloromethane (supplied by Qingdao Haiyang Chemical Co. Ltd., China, and activated at 110 °C for 16 h) was placed at the column bottom. The 2 mL of extract sample was carefully poured into the top of the column and then rinsed with 25 mL of hexane, and the collected eluent was used for analyzing the saturated hydrocarbons. The column was then further eluted with 50 mL 4:6 hexane/methylene dichloride in volume ratio and the collected eluent was used for analyzing the polycyclic aromatic hydrocarbons (PAH) [22]. The collected eluent sample after silica gel column cleanup was again reduced to less than 2 mL using rotary evaporator at a temperature of (37±2) °C. The sample was then brought to 1.5 mL with hexane and transferred into the GC vial for further GC-MS analysis.

The Agilent 7890a gas chromatography connected to the 5975C mass spectrometry detector (Agilent, USA) was employed to analyze the sample extracts (Table 2). The HP−5MS (30 m length, 0.25 mm diameter, 0.25 μm thickness) capillary column was used. Helium was employed as carrier gas. The analytes in the samples were identified by matching the retention time of each compound with the retention times in the standard solution (i.e., the FTRPH Calibration/ Window Defining Standard and PAH Solution Mix, AccuStandard) and the mass spectral library (NIST05, Agilent).

The removal efficiency of SAT or PAH can be

Table 2 Analysis procedures of saturated hydrocarbons and polycyclic aromatic hydrocarbons

Sample	Temperature program	Other parameter
SAT	1) Holding temperature of 70 °C for 1 min; 2) ramping to 100 °C at rate of 5 °C/min, 3) ramping to final temperature of 310 °C at rate of 10 °C /min, and 4) holding this temperature for 25 min	1) Split/splitless injector, 310 °C, 2) split mode, 10:1, 3) EI source, 70 eV, and 4) full-scan EI data, 50 to 600 amu
PAH	1) Holding temperature of 40 ºC for 4 min, 2) ramping to 270 °C at rate of 10 °C /min, and 3) holding this temperature for 20 min	1) EI source, 70 eV, and 2) single-ion monitoring (SIM)

calculated as follows:

$$\eta = \left(1 - \frac{C_{\text{rem}}}{C_{\text{ini}}}\right) \times 100\% \tag{1}$$

where η is the removal efficiency of SAT or PAH through soil washing; C_{ini} is the initial concentration of SAT or PAH in soil (mg/kg); C_{rem} is the remaining concentration of SAT or PAH in soil after soil washing (mg/kg).

3 Results and discussion

3.1 Initial concentration of crude oil components in soils

Figure 1 presents the initial concentrations of the individual fractions of saturated hydrocarbons (SAT) (*n*-alkanes) and polycyclic aromatic hydrocarbons (PAH) in two types of soils (loam and sand) after crude oil spiking. The alkanes (*n*-C10 to *n*-C26) with even number of carbons are used as examples to represent the individual fractions of SAT. The 16 priority PAHs identified by US EPA were used as examples to represent the individual fractions of PAH, and these include naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FlU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fuoranthene (BbF), benzo[k]fuoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenzo[a,h]anthracene (DahA), and benzo[g,h,i] perylene (BghiP) [23−24]. It can be found from Fig. 1(a) that the crude oil is rich in alkanes (saturated hydrocarbons) with middle number of carbons (i.e., *n*-C14 to *n*-C22), and such alkanes illustrate higher adsorption onto the soils. The *n*-C16 alkane has the highest soil concentration, followed by *n*-C14, *n*-C18, *n*-C20, *n*-C22, *n*-C24, and *n*-C12 alkanes (with concentration above 212 mg/kg). The *n*-C10 and *n*-C26 alkanes have the lowest soil concentration (below 54 mg/kg). In general, the alkanes from *n*-C12 to *n*-C26 account for about 90% of the total concentration of SAT, and the alkanes with less carbon number than 12 account for about 10% of the total concentration of SAT. It can be found from Fig. 1(b) that the crude oil used in the experiment is low in PAH. The total concentration of PAH compounds in soil is much lower than that of SAT compounds, with phenanthrene having the highest concentration of 16.21 mg/kg in sand and 14.24 mg/kg in loam. In terms of the individual PAH fractions, the soil concentrations of phenanthrene, pyrene, benzo(k) fluoranthene, dibenzo(a,h)anthracene, and benzo(b) fluoranthene are between 8 and 16 mg/kg. The concentrations of naphthalene, acenaphthylene, and acenaphthene are below 3 mg/kg, and the concentrations of other PAH compounds are between 3 and 7 mg/kg. No significant differences of SAT and PAH concentrations are observed between the two soil types.

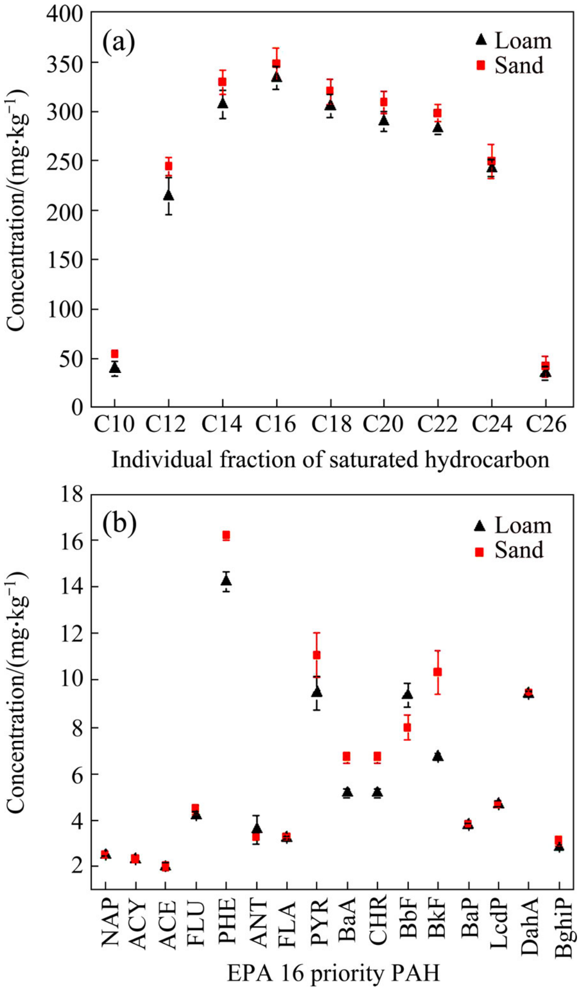

Fig. 1 Initial concentrations of crude oil components in loam and sand soils: (a) Individual fraction of saturated hydrocarbons (*n*-C10 to *n*-C26); (b) EPA 16 priority PAHs

3.2 Impact of rhamnolipid concentration on soil washing efficiency

Figure 2 presents the relationship between the rhamnolipid concentration in washing solution and the removal efficiency of the total saturated hydrocarbons and the total polycyclic aromatic hydrocarbons from two types of contaminated soils. It can be found that when the rhamnolipid concentration is above 0.04% in mass fraction, the bio-surfactant has a positive impact on the removal of SAT and PAH compounds from both types of crude oil contaminated soils. In general, the removal efficiency of both SAT and PAH is higher for sand than for loam soil. For example, when the rhamnolipid concentration is 0.10% in mass fraction, the total SAT removal is 92.2% from sand and 80.0% from loam, and the total PAH removal is 78.2% from sand and 51.2% from loam. This can be explained that the sand soil has larger particle sizes and less organic carbon contents than the loam soil, and thus has weaker adsorption capacity for organic compounds. The SAT and PAH compounds adsorbed onto the sand soil can therefore be desorbed more easily through the washing process than the loam soil. In addition, the rhamnolipid can also be adsorbed onto the soils, thus reducing its effective concentration in the washing solution [25]. As compared with the loam soil, the sand has a lower adsorption of rhamnolipid, and thus less amount of SAT and PAH compounds are incorporated into the soil-sorbed rhamnolipid, and a higher effective concentration of rhamnolipid in the washing solution is also resulted in. These effects would lead to higher removal efficiency of SAT and PAH from crude oil contaminated sand than from contaminated loam soil.

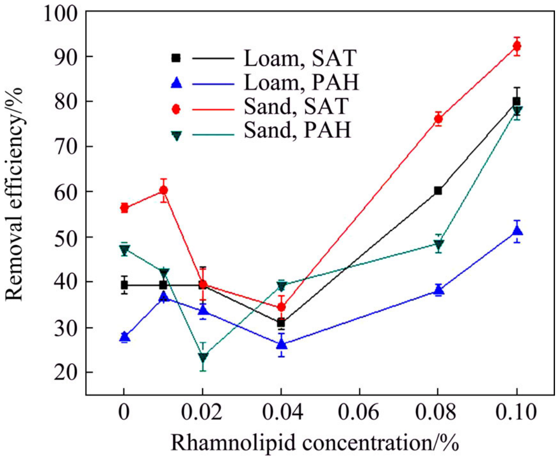

Fig. 2 Impact of rhamnolipid concentration in washing solution on removal efficiency of total saturated hydrocarbons (SAT) and total polycyclic aromatic hydrocarbons (PAH) from crude oil contaminated soils (error bar indicates standard deviation; experimental condition: salinity, 0; pH=7.0)

However, it can be found from Fig. 2 that when the rhamnolipid concentration is below 0.04% in mass fraction, the removal efficiency of the total SAT and PAH compounds from both soils through bio-surfactant assisted soil washing is close to or even lower than that through soil washing only using deionized water. This regressive phenomenon could be attributed to the adsorption of rhamnolipid onto soils [25]. Prior to the formation of bio-surfactant micelles in the soil solution, much of the rhamnolipid might be adsorbed onto the soils. The soil-sorbed rhamnolipid is very effective for the partitioning of SAT and PAH compounds, which could enhance the sorption of these organic compounds onto soils and thus led to lower removal efficiency of SAT and PAH than soil washing using deionized water. With the further increase of rhamnolipid concentration in the solution, the soil sorption of rhamnolipid reaches its maximum capacity, and the bio-surfactant micelles are formed in the soil solution to become an important partition phase. The SAT and PAH compounds then begin to partition from soil particles to the rhamnolipid micelles, leading to enhancing removal efficiency from soils. Therefore, the sorption of rhamnolipid onto soils may have a significant impact on the performance of bio-surfactant assisted soil washing to remove SAT and PAH compounds.

The impact of rhamnolipid concentration on the removal efficiency of individual SAT and PAH compounds from crude oil contaminated soils was further examined, and Fig. 3 presents the results. The *n*-C10, *n*-C12, *n*-C14, *n*-C22, *n*-C24, and *n*-C26 alkanes are used as examples of individual SAT compounds. The naphthalene (NAP), acenaphthylene (ACY), phenanthrene (PHE), fluoranthene (FLA), anthracene (ANT), and benzo[b]fuoranthene (BbF) are used as examples of individual PAH compounds. As shown in Fig. 3(a), the desorption efficiencies of representative *n*-alkanes in soil 1 (loam) are higher than 60% when rhamnolipid concentration was up to 0.1%. Generally, with the increase of carbon number, the final removal efficiency of *n*-C10, *n*-C12, *n*-C14, *n*-C16, *n*-C18 and *n*-C20 decrease (i.e. 87.9%, 89.3%, 81.2%, 77.1%, 75.7%, 75.5% and 64.5%, respectively) except *n*-C24 and *n*-C26. The reason for this phenomenon may be that through determining we found that loam soil showed higher adsorption capacity to this kind of rhamnolipid. Therefore, many rhamnolipid molecules are able to complete the adsorptive sites with *n*-C24, *n*-C26 and other higher componds, resulting in a decrease in the amount of *n*-C24, *n*-C26 adsorbed.

Figure 3(b) shows that except *n*-C24 and *n*-C26, the removal efficiencies of *n*-C10, *n*-C12, *n*-C14, *n*-C16, *n*-C18, *n*-C20 and *n*-C22 in sand are more than 86% (i.e. 95.6%, 96.9%, 90.9%, 86.6%, 89.7%, 87.9% and 94.7%, respectively). While the removal efficiencies of *n*-C24 and *n*-C26 only reach 36.2% and 31.9%, respectively. The desorbed amount of each saturated hydrocarbon is much more than that of soil 1. That is probably because soil 2 (i.e. sand) includes 96% sandy particles (Table 1) which have small surface areas and large pore-size so that all saturated hydrocarbons fractions are desorbed by rhamnolipid effectively. And this result also indicates that the rhamnolipid is better qualified for enhancing desorption of saturated hydrocarbon fractions.

Figure 3(c) shows that the difference of ∑PAH fractions in removal efficiency is very large. For loam, except BbF and BkF, the removal efficiencies of other 14 PAHs are lower than 10% and the addition of rhamnolipid has little effect on desorbed PAH due to their strong hydrophobic property. It may be that too low concentration (e.g. 2.5 mg/kg for NAP and 2.1 mg/kg for ACY in Fig. 1(b)) will result in a very low removal efficiency because the value is close to the residual

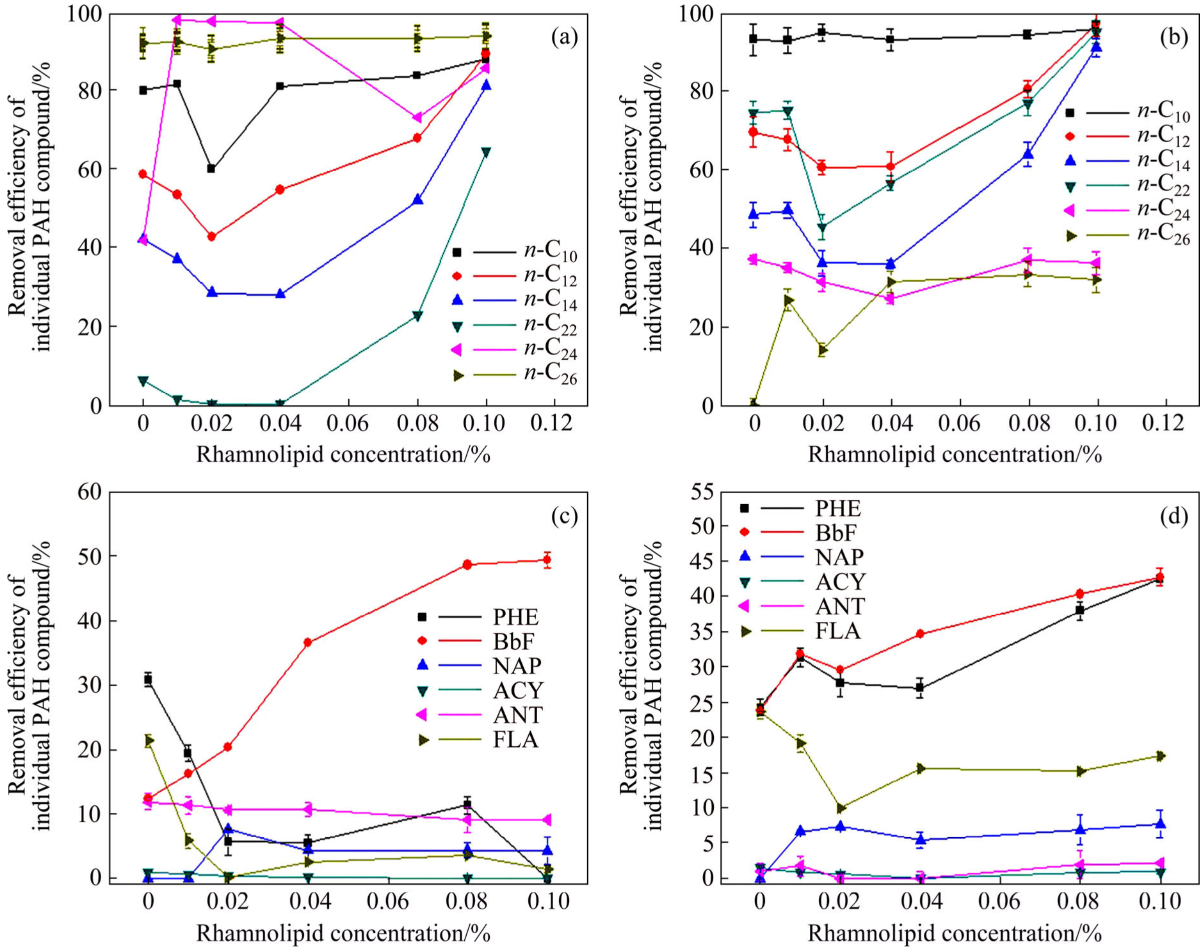

Fig. 3 Impact of rhamnolipid concentration in washing solution on removal efficiency of individual SAT and PAH compounds from crude oil contaminated soils: (a) SAT removal from loam; (b) SAT removal from sand; (c) PAH removal from loam; (d) PAH removal from sand (error bar indicates standard deviation)

concentration which cannot further decrease under mild conditions. Therefore, low initial concentrations of NAP and ACY perhaps also contribute to their low removal efficiency to some extent. Furthermore, the higher removal efficiency of PAH compounds for BbF and BkF, only reach to 49.3% and 28.7%, respectively.

For sand, the removal efficiency of BkF is detected at a highest value of 56.3%. And removal efficiencies of lighter molecular mass PHE and BbF also achieve 42.4% and 42.7%. For higher molecular mass PAH, such as IcdP, DahA and BghiP, the addition of rhamnolipid has no obvious effect on the removal efficiency. Therefore, the higher concentration of rhamnolipid solution should be suggested to remediate the PAHs polluted site.

In particular, Figs. 3(a) and (c) reveal that the loam soil which has large surface area and small pore-size is favorable to the increase of the adsorption of petroleum hydrocarbon fractions. Therefore, when deionized water or low concentration rhamnolipid solution is implemented in the desorption procedure, the effects are more significant on SAT and PAH fractions desorption.

3.3 Impact of solution pH on soil washing efficiency

Solution pH in natural waters significantly affects the mobility of ions on the surface and subsurface system [26−27]. VIPULANANDAN and REN [28] and SHIN et al [29] demonstrated that the effect of a bio-surfactant on the surface tension and dispersion of phenanthrene was a function of pH. On one hand, a decrease in pH of the surfactant solution can decrease the interfacial tension between the aqueous and the non-aqueous phase liquids (NAPL). Reduced interfacial tension results in mobilization of residual NAPL from soil. On the other hand, the increase of pH leads to the release of soil organic matter into aqueous, decreasing the NAPL adsorption [30−31]. In this work, an increased removal of the total saturated hydrocarbons (SAT) from the loam soil is observed with an increasing pH value (i.e., from 2 to 6) in the acidic range (Fig. 4(a)), but a decreased removal of SAT is found when the solution pH value is increasing (i.e., from 8 to 12) in the alkaline range. The maximum removal of the total saturated hydrocarbons from crude oil contaminated loam soil occurred at a solution pH value of 6.0, with a removal efficiency of

76.1%. This illustrates that the solution pH value close to the neutral range might be helpful for the soil washing efficiency of SAT from the loam soil. However, a different trend is observed for the impact of washing solution pH value on the removal of SAT from the sand soil. A minimum removal efficiency of SAT (i.e. 43.9%) from sand is observed at a solution pH value of 6.0 (Fig. 4(a)). The SAT removal efficiency of over 90% from the sand soil (e.g., 93.6%, 94.1%, and 96.1%) was found at solution pH value of 4.0, 8.0, and 12.0, respectively. In general, the increasing alkalinity of the solution pH might be conducive for the removal of SAT from sand soil.

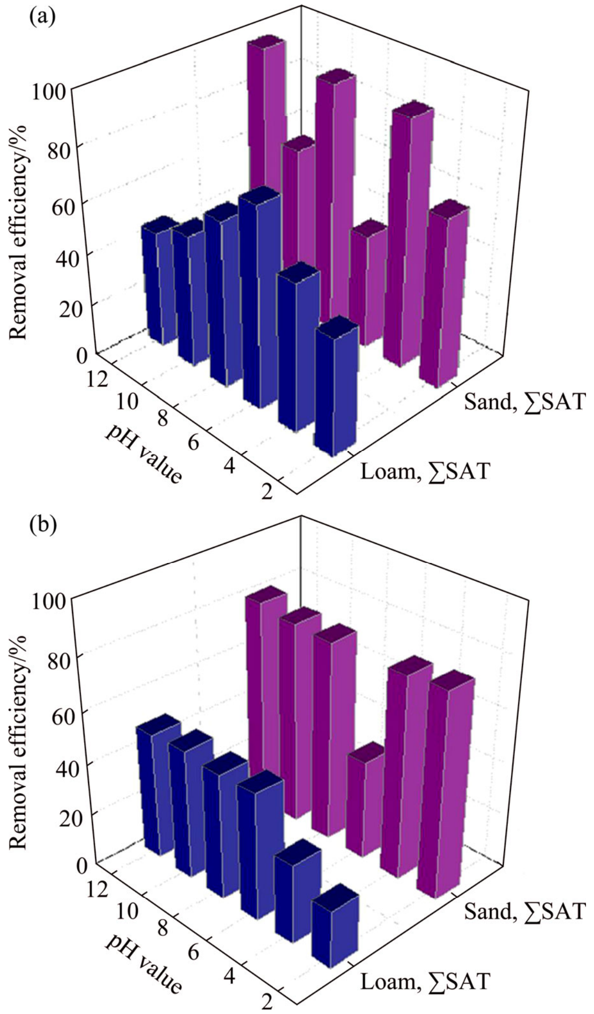

Fig. 4 Impact of washing solution pH value on removal efficiency of total saturated hydrocarbons (SAT) (a) and total polycyclic aromatic hydrocarbons (PAH) (b) from crude oil contaminated soils (experimental condition: rhamnolipid concentration, 0.08%; salinity, 0)

Different impacts of washing solution pH on the removal of the total polycyclic aromatic hydrocarbons (PAH) are also observed for the loam and sand soils (Fig. 4(b)). For the loam soil, it was found that the removal efficiency of PAH increases from 21.8% to 48.6% with an increasing pH value from 2 to 6 in the acidic range. In the alkaline range, the PAH removal efficiency increases greatly, and a nearly stable removal of PAH is observed. For the sand soil, a PAH removal efficiency of only 38.3% is observed at a solution pH value of 6.0, but a nearly stable removal efficiency of over 77.0% is found for all other examined pH values (e.g., pH of 2, 4, 8, 10, and 12). The increasing alkalinity of washing solution shows slightly higher PAH removal. In general, the solution pH value in the alkaline range is helpful for the soil washing efficiency of PAH from both the loam and the sand soils.

3.4 Impact of solution salinity on soil washing efficiency

The salinity can significantly affect the solubility of petroleum hydrocarbon fractions. The existence of ionic strength could weaken the electronegativity of soil surface, reducing the repulsion between soil and organic anions. The addition of Na^+ enhances the adsorption of NAPL onto soil [32−33]. Figure 5 presents the relationship between the washing solution salinity and the removal rate of crude oil compounds from two types of soil. It can be found that the increasing salinity has a positive impact on the removal of crude oil compounds from the sand soil, but a negative impact from the loam soil.

In terms of sand soil, the removal of SAT was 43.9% when the solution salinity is zero. The removal efficiency increases to 74.4% when the salinity increases to 2%. Further increase of salinity led to nearly stable SAT removal efficiency. The SAT removal efficiency maintains 95.9% for other salinity levels of 4% to 10% (Fig. 5(a)). The removal efficiency of PAH is 38.3% when the salinity is zero, but increase to 78.0% when the salinity is 2%. Further increase of salinity also led to nearly stable PAH removal efficiency. The PAH removal efficiency ranges from 78.2% to 80.7% for other salinity levels of 4% to 10% (Fig. 5(b)). In terms of the loam soil, when the solution salinity is zero, the removal efficiency of the total saturated hydrocarbons (SAT) is 62.2%. When the salinity increases to 2% and 6%, the removal efficiency decreases to 41.5% and 37.8%, respectively (Fig. 5(a)). The removal of the total polycyclic aromatic hydrocarbons (PAH) is 48.6% when salinity is zero, but this removal efficiency significantly decreases to 4.1% when the solution salinity is 2% (Fig. 5(b)). And the removal efficiency of PAH from loam soil ranges from 18.7% to 21.2% for other salinity levels of 4% to 10%. The different impacts of solution salinity on the removal of crude oil compounds might be caused by different soil properties. The loam soil contains more fine particles and organic carbon contents as compared with the sand soil. With the increasing salinity, the organic carbon contents solubility drops and hydrophobic increases. Thus, the SAT and PAH compounds desorbed by rhamnolipid can be easily re-adsorbed by organic carbon contents in loam soil. On the other hand, the electrochemical double layer between soil particles and emulsified oil particles surface thickness decreases with the rise of salinity in solution, which results in increasing of attractive force between crude oil compounds and soil particles. Therefore, removal efficiency of SAT or PAH reduces with the increasing of salinity [9, 34].

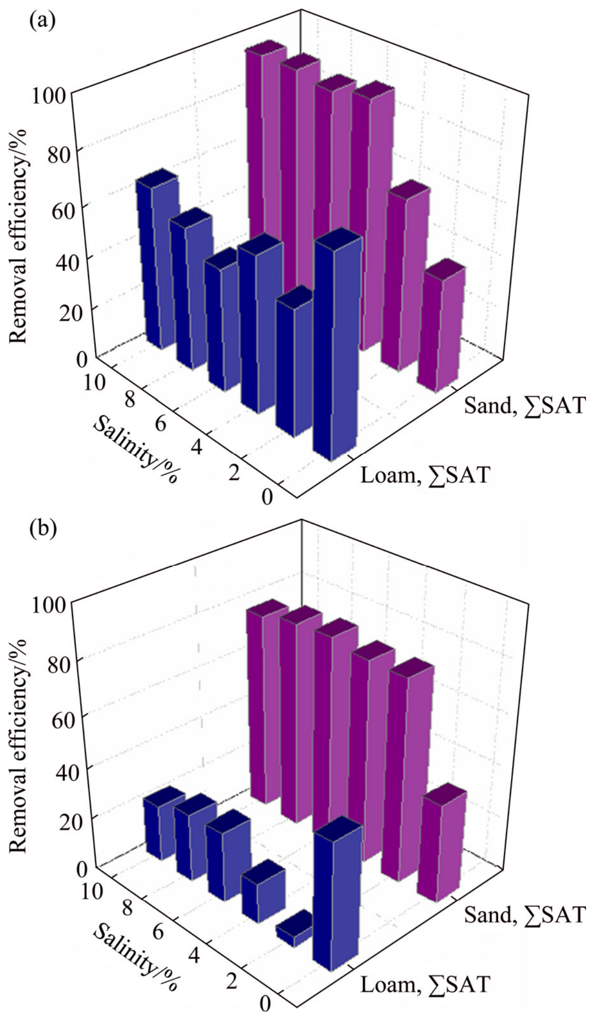

Fig. 5 Impact of washing solution salinity on removal efficiency of total saturated hydrocarbons (SAT) (a) and total polycyclic aromatic hydrocarbons (PAH) (b) from crude oil contaminated soils (experimental condition: rhamnolipid concentration, 0.08%; pH=7.0)

4 Conclusions

1) The crude oil contaminated soil is rich in alkanes with middle number of carbons, while the total concentration of PAH compounds in soil is much lower than that of SAT compounds. The bio-surfactant rhamnolipid has a positive impact on the removal of SAT and PAH compounds from both sand and loam soils. Rhamnolipid shows more remarkable effectiveness on SAT and PAH removal from crude oil contaminated soil with higher sandy content.

2) With the increasing rhamnolipid concentration, more and more SAT and PAH fractions begin to desorb from soil particles by rhamnolipid micelles and then dissolve in water. As well as, the sorption of bio-surfactant onto soils shows a significant effect on the performance of bio-surfactant in enhancing SAT and PAH fractions desorption.

3) The solution pH value close to the neutral range might be helpful for the soil washing efficiency of SAT from loam soil. And the increasing alkalinity of the solution pH might be conducive for the removal of SAT from sand soil. And the solution pH value in the alkaline range is helpful for the soil washing efficiency of PAH from both the loam and the sand soils.

4) The increasing salinity has a negative impact on the removal of crude oil compounds from the loam soil, but a positive impact from the sand soil. And the different impacts of solution salinity on the removal of crude oil compounds might be caused by different soil properties. For sand, which contained more sandy content, less amount of rhamnolipid is adsorbed onto soil, thus with the increase of salinity, the solubilization and desorption of rhamnolipid solution are more significant.

5) Generally, the sorption of bio-surfactant onto soils shows a significant effect on the performance of bio-surfactant in enhancing SAT and PAH desorption. And the removal trend of crude oil compounds of loam and sand soils are different under various environment conditions, probably because of the different chemical and physical properties of soil.

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