

Solubilization Effect of Surfactants on Morphological Transformation of Cadmium and Pyrene in Co-Contaminated Soils

Qian Wang · Xiaoyan Liu · Chuanhua Wang ·
Xinying Zhang · Hongbing Li · Tingru Chen ·
Yunyun Hou · Xueping Chen · Xia Liang

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Abstract Four kinds of surfactants were used to increase accessibility of pyrene and cadmium (Cd) in simulated pyrene, Cd, and pyrene-Cd soils in this study. Tea saponin (TS) at 40 mg L⁻¹ groups (exchangeable fraction of Cd and bioaccessible fraction of pyrene were 8.96 and 36.93 mg kg⁻¹) showed more preferable potential application in improving solubilization capability than other surfactants. The morphology of Cd was transformed from Fe-Mn oxides (8.86 to 7.61 and 8.67 to 7.99 mg kg⁻¹ in Cd and pyrene-Cd soil) and associated to carbonates fractions (4.46 to 4.36 and 4.28 to 4.36 mg kg⁻¹ in Cd and pyrene-Cd soil) to exchangeable fraction with adding TS. These two morphological changes were important processes in the solubilization

of Cd. The morphology of pyrene was transformed from associated fraction (72.15 to 61.95 and 71.02 to 63.48 mg kg⁻¹ in pyrene and pyrene-Cd soil) to bioaccessible fraction (26.66 to 33.71 and 26.91 to 36.93 mg kg⁻¹ in pyrene and pyrene-Cd soil) with adding TS. This morphological transformation was important in the improving of solubilization capacity of pyrene. In contrast, the solubilization of pyrene was promoted in the presence of Cd in pyrene-Cd soil (the bioaccessible fractions were 33.71 and 36.93 mg kg⁻¹ in pyrene and pyrene-Cd soil), but the solubilization of Cd was hindered in the presence of pyrene (the exchangeable fractions of Cd were 8.86 and 8.67 mg kg⁻¹ in Cd and pyrene-Cd soil). These findings will be beneficial for application of surfactants in soil remediation.

Highlights • Tea saponin (TS) improved the solubilization of pyrene(PY) and Cd.
• Surfactants obviously enhanced the accessibility of PY and Cd in polluted soils.
• Surfactants changed pollutants from difficultly utilized to accessible fractions.
• Solubilization of PY was promoted in the existence of Cd in PY-Cd soil.
• Solubilization of Cd was hindered in the presence of PY in PY-Cd soil.

Keywords Solubilization · Pyrene · Cadmium · Combined contaminated soil · Biodegradable surfactants · Accessibility

1 Introduction

Soil pollution has become a dangerous and serious problem, both in inorganic polluted soils such as heavy metals and in organic polluted soils such as polycyclic aromatic hydrocarbons (PAHs) (Xia et al. 2009). Huangpu River wetland acts as significant sinks for the PAHs from Huangpu River water by the adsorption and sedimentation. PAH contamination of soil is often connected with the existence of high concentrations of potentially toxic metals

Q. Wang · X. Liu (✉) · C. Wang · X. Zhang · H. Li ·
T. Chen · Y. Hou · X. Chen · X. Liang
Laboratory of Environmental Remediation, College of
environment and chemical engineering, Shanghai University,
Shanghai 200444, China
e-mail: lxy999@shu.edu.cn

C. Wang
College of life and environment science, Wenzhou University,
Wenzhou, Zhejiang 325035, China

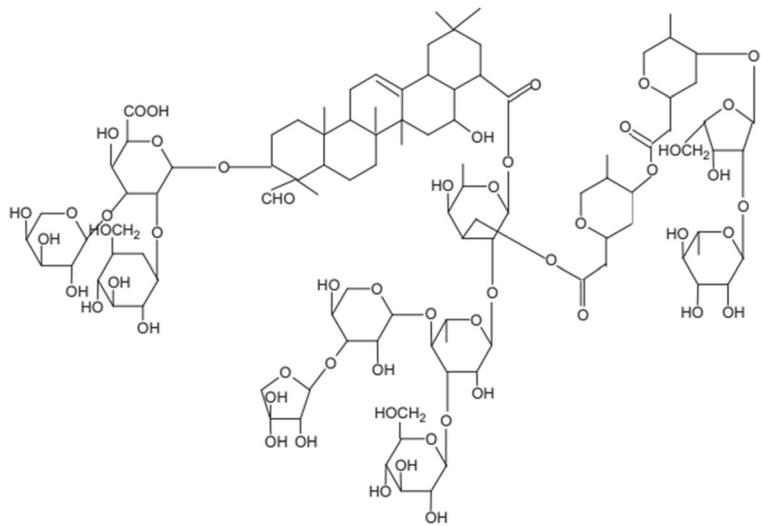
which have impact on PAH biodegradation (Obuekwe and Semple 2013). Simultaneously, PAHs cannot be degraded easily and finally accumulate in soils in the river basins and wetlands (Liu et al. 2013). It has been researched that many methods are applied to practice on the remediation of heavy metals and PAHs. Most researchers have put emphasis on the effect of organic matter degradation as well as the effect of heavy metal enrichment in single and combined contaminated soils. But the mechanism of degradation or enrichment is not thorough and detailed analysis. The morphological transformations of both heavy metals and PAHs with adding surfactants were few studied. So, surfactant-enhanced remediation by improving the process of solubilization has been suggested as a promising technology for the remediation of organic and heavy metals contaminated soils.

Wang et al. (2010) dislodged phenanthrene and lead from artificially polluted soils with glycine- β -cyclodextrin. Many other researchers have utilized the solubilization properties of surfactants to improve desorption of organic pollutants and heavy metals in the contaminated soils. As the concentration of surfactant is increased beyond its critical micelle concentration (CMC), micelles with a hydrophobic core can be formed by monomers accumulated. With a growth in the number of micelles in the solution, both the surface and interfacial tensions decrease significantly, improving desorption effect of PAHs from soil surfaces (Haigh 1996; Mulligan et al. 2001; Zhao et al. 2005). The surfactants will be more beneficial for plants and microbes to absorb or accumulate the pollutants, such as tea saponin (TS), rhamnolipid (RL), alkyl polyglucoside (APG), sodium dodecylbenzenesulfonate (SDS), and so on. Phytoremediation and microbial remediation are emerging technologies for treating heavy metals or a final polishing process for the high-level organic contamination, and are also suitable for remediation of heavy metal and organic combined contaminated soils. The concentration of contaminants in soils can be reduced by enriched, absorbed, or degraded effect of plants and microorganisms. The degradation of PAHs and enrichment of heavy metals depend on metabolic effect of rhizospheric microorganisms. The bioaccessibility of the pollutants is a limiting factor to the degradation effect (Megharaj et al. 2011). It is of great importance to improve the accessibility of the contaminants or promote the solubilization of the pollutants from difficultly utilized to accessible fractions by plants and

microorganisms. PAHs in soils can be divided into bioaccessible fraction, associated fraction (chemically adsorbed by soil particles and unbioaccessible until desorption), and bound fraction with reducing underlying for biodegradation based on their morphological features (Gao et al. 2009). And heavy metals can also be separated into exchangeable fraction, associated to carbonates fraction, associated to Fe–Mn oxides (or reducible) fraction, associated to organic matter (or oxidizable) fraction, and residual fraction (Alborés et al. 2000). If there were more accessible fraction of pollutants, with the addition of surfactants, it was easier and faster for the plants and microorganisms to accelerate the accumulation process and biodegradation of adsorbed pyrene and Cd. Studying availabilities of PAHs and heavy metals is crucial to the remediation in contaminated sites. The addition of environmentally acceptable agents, such as surfactants, microorganisms, and plant, and the application of treatment methods demanding minimal handling to decrease the conveyance of the pollutants within and from the soil should be premeditated (Ortega-Calvo et al. 2013).

Tea saponin (TS) is a type of tea seed-derived natural surfactant. It is a plant-derived biosurfactant (Urum and Pekdemir 2004; Zhou et al. 2011) and can be degraded automatically without toxic effect to soils. Its hydrophilic groups contain hydroxyl groups and ester groups. TS exerts excellent surface activity in comparison to synthetic ones. The structure of TS is shown in Fig. 1 (Zhou et al. 2011). It is a triterpene glycoside substance with carboxyl groups of sugar moiety in hydrophilic fraction from Soap tree bark. It is a non-ionic surfactant, and its elemental analysis shows 51 % oxygen, 44 % carbon, and 6 % hydrogen (Urum and Pekdemir 2004). Saponin is more effective in improving PAHs solubilization than synthetic non-ionic surfactants, and it has underlying application in removing organic pollutants from polluted soils. TS is a kind of non-ionic biosurfactant, but its molecule contains an ionizable group of glucuronic acid, some charged species would exist in TS solutions. So, ionic strength can affect the CMC value of TS solution and then the solubilization for pyrene and Cd pollutants (Zhou et al. 2011).

Rhamnolipid (RL) is produced by microbial fermentation. Application of rhamnolipid in metal removal needs the theory of rhamnolipid–metal complexation reaction (Ochoa-Loza et al. 2001). The removal of phenanthrene with the addition of rhamnolipid and SCOAs gradually improved as the SCOAs increased up

Fig. 1 Chemical structure of saponin

to a concentration of 300 mmol L⁻¹ (An et al. 2011). Alkyl polyglucosides (APG) are generated from renewable resources such as fatty alcohols and glucose obtained from recyclable starch (Fukuda et al. 2001; Momin and Yeole 2011). They are regarded as safe and environment-friendly substances which are nontoxic, biodegradable (Iglauer et al. 2009; Zhang et al. 2012; Liu et al. 2013). Sodium dodecyl benzene sulfonate (SDS) is the most widely applied for both industrial and domestic applications as it is biodegradable (Almeida et al. 2009). Compared with the synthetic surfactants, high specificity, low toxicity, and high biodegradability were their advantages (Roy et al. 1997).

Some kinds of surfactants are non-biodegradable; however, biodegradation is an important issue that we need to consider. TS, RL, APG, and SDS are all biodegradable surfactants and non-contaminated to the soil. The contamination of pyrene and Cd in the wetland soils of Yangtze River estuary is an urgent issue to be solved.

The aim of this study was to detect the influence of surfactants on the solubilization properties of pyrene and Cd in single and combined soils. Mutual interactions between surfactants and the influences of two kinds of pollutants (pyrene and Cd) were also revealed in this study. Four kinds of surfactants (TS, RL, APG, SDS) were chosen to study the solubilization of pyrene and cadmium by increasing accessibility of pollutants with adding surfactants in soil. The morphological transformation of pyrene and Cd were researched in this study.

2 Materials and Methods

2.1 Chemicals

Pyrene (98 % purity) was purchased from Aladdin Reagent. TS (tea saponin) was obtained from Hangzhou Choisun Tea Sci-Tech Co., Ltd. Quality Department. Rhamnolipid was purchased from Huaian HongMa biological technology Co., Ltd. APG (alkyl polyglucoside) used in this experiment was C12/14-APG (APG1214) obtained from China Research Institute of Daily Chemical Industry (Shanxi, China). Sodium dodecylbenzene sulfonate (SDS) and all other chemicals were analytical grade or better and bought from Sinopharm.

2.2 Soils

The experimental soil in this study was collected from 0 to 20 cm top layer of the soil without exposing to pyrene and Cd before at Shanghai University, China. The soil was air-dried, ground, and passed through a 2-mm sieve to dislodge coarse fragments and dead leaves. The physicochemical characteristics of the soil were as follows: pH 8.2, organic matter 19.53 g kg⁻¹, total nitrogen 0.51 g kg⁻¹, clay 7.3 %, silt 60.6 %, and sand 31.8 %. For the contaminated process, 1000 mg of pyrene was dissolved in 100 mL of dichloromethane and mixed with 1 kg of clean soil to uniformity. After the solvent evaporated for 2 days, the soil was mixed with 9 kg of clean soil to make the final pyrene concentration to be

100 mg kg⁻¹. The soil was mechanically mixed to ensure homogeneity and aged for 3 months in the dark before experiment. The cadmium nitrate (Cd(NO₃)₂, analytical grade) aqueous solution was applied to the clean soil to make the final Cd concentration to be 22 mg kg⁻¹. The polluted method of Cd was the same as pyrene. The cadmium nitrate (Cd(NO₃)₂, analytical grade) aqueous solution was applied to the pyrene-contaminated soil to obtain the pyrene-Cd polluted soil, and the final concentrations of pyrene and Cd were 100 and 22 mg kg⁻¹, respectively.

2.3 Experimental Setup

In the preliminary experiment, 13 groups of microcosms were set up only in combined pyrene-Cd soil to study the solubilization of contamination (Table 1). One group was a control without surfactant, the other groups were experimental treatments of different concentrations (20, 40, 80 mg L⁻¹) of TS, RL, APG, SDS added separately to the pyrene-Cd soil. The ratio of water and soil was 5:1. The 13 groups were incubated for 48 h with 200 rpm at 25 °C in the dark in the shaker. After that, soil samples were freeze-dried immediately and stored at -80 °C till analysis. Every setup was prepared in triplicates in this study.

Table 1 Settings of thirteen groups of microcosms

Group names	Designs
C	Control without surfactants
A1	APG at 20 mg L ⁻¹
A2	APG at 40 mg L ⁻¹
A3	APG at 80 mg L ⁻¹
R1	RL at 20 mg L ⁻¹
R2	RL at 40 mg L ⁻¹
R3	RL at 80 mg L ⁻¹
S1	SDS at 20 mg L ⁻¹
S2	SDS at 40 mg L ⁻¹
S3	SDS at 80 mg L ⁻¹
T1	TS at 20 mg L ⁻¹
T2	TS at 40 mg L ⁻¹
T3	TS at 80 mg L ⁻¹

2.4 Analytical Methods

Different morphological pyrene in soil was detected by a three-step sequential extraction method according to previous studies. The bioaccessible fraction was extracted by vortex mixing 5 mL of butanol with 1 g of freeze-dried soils for 30 s. The mixture was centrifuged at 4000 rpm for 15 min. Then the supernatant was removed cautiously, and concentrated to detect pyrene concentration (Gomez-Eyles et al. 2010). After that, the associated fraction was ultrasonically extracted from the residual solid phase with 10 mL dichloromethane for 30 min, and this process was repeated three times. The resulting liquids were combined, evaporated, and redissolved in 1 mL of *n*-hexane to be analyzed. At last, bound pyrene was extracted from the remaining soil with adding 10 mL of 2 M NaOH solution. With 5 mL of 6 M hydrochloric acid, the supernatant was acidified to pH <2 and extracted with 10 mL of dichloromethane. It was also redissolved in 1 mL of *n*-hexane to be analyzed (Ma et al. 2012). The concentration of pyrene was quantified by GC-MS (Agilent 6890 N/5975B) equipped with a DB-5 column (30 m × 0.25 mm × 0.25 μm). The temperature was held at 100 °C for 2 min, after that increased 10 °C min⁻¹ to 300 °C, where it was kept for 5 min (Ma et al. 2012; Wei et al. 2014).

Different morphology of Cd in soil was detected by Tessier gradual separation technology (Alborés et al. 2000). Exchangeable Cd was extracted from 0.25 g of freeze-dried soil with adding 8 mL of 1 mol L⁻¹ MgCl₂ (pH=7) solution and shaken for 1 h at 25 °C. Associated to carbonates Cd was extracted from the residual solid phase with adding 8 mL of 1 mol L⁻¹ NaOAc (pH=5) solution and shaken for 5 h at 25 °C. Associated to Fe-Mn oxides (or reducible) Cd was extracted from the residual solid phase with adding 20 mL of 0.04 mol L⁻¹ NH₂OH HCl in 25 % *m/v* HOAc solution and shaken for 6 h at 96 °C. Associated to organic matter (or oxidizable) Cd was extracted from the residual solid phase with adding 3 mL of 0.02 mol L⁻¹ HNO₃ solution and 5 mL of 30 % *m/v* H₂O₂ solution and shaken for 2 h at 85 °C, then added 3 mL of 30 % *m/v* H₂O₂ solution and shaken for 3 h at 85 °C, then added 5 mL of 3.2 mol L⁻¹ NH₄OAc solution for 30 min at 25 °C. The residual Cd was extracted from residual solid phase with adding HNO₃-HClO₄-HF for heating digestion. The extraction was conducted in 50 mL of polyethylene tubes, which were also used for centrifugation to minimize the

possible loss in the centrifuge-washing processes. After each extraction step, the supernatant liquid was separated from the solid phase by centrifugation at 4000 rpm for 5 min. It was then transferred into polyethylene vessels with 5 % dilute nitric acid to 10 mL and stored at 4 °C before analysis to reduce variation. The concentration of Cd in aqueous solution was measured by inductively coupled plasma (ICP). Measurements were made in triplicate in each experiment to reduce errors.

2.5 Statistical Analysis

Each data was the mean value (\pm SD) of three replicates in this study. SPSS 17.0 was used for ANOVA. Significant differences in the main effect were further analyzed by pairwise comparisons, with the Duncan's multiple range tests and $p < 0.05$ taken to indicate statistical significance.

3 Results and Discussion

3.1 Accessibility of Pyrene and Cd in Combined Contaminated Soil with Adding Surfactants

Four kinds of surfactants were selected to be added into the pyrene-Cd contaminated soil, and the solubilization effect of surfactants on pyrene and Cd was determined by comparing the changes of accessibility of pyrene and Cd.

Different fractions of Cd with adding different concentrations of surfactants in pyrene-Cd soil were shown in Fig. 2.

Exchangeable and associated to Fe-Mn oxides fractions took a larger proportion than any other fractions of Cd in all groups (Fig. 2). The accessibility of Cd in the experimental subgroups contributed much more than that of the control group. Similarly, it was indicated that surfactants are often found in estuarine areas, due to urban and industrial effluent discharges, which may determine metal distribution in those environments (Almeida et al. 2009). Compared with control group, the SDS at 40 mg L⁻¹ (8.56 mg kg⁻¹) and RL at 40 mg L⁻¹ (8.53 mg kg⁻¹), especially TS at 40 mg L⁻¹ (8.96 mg kg⁻¹) groups all had a significant improvement of exchangeable fraction. Ramamurthy et al. (2007) had also observed that SDS could improve the desorption of Cu from soil. The effect enhanced with the increase of

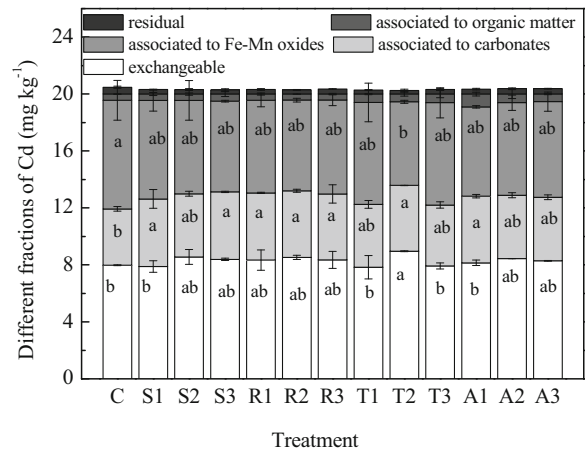


Fig. 2 Different fractions of Cd with adding four kinds of surfactants in pyrene-Cd soil. (C) Control without surfactants, (A) APG, (R) RL, (S) SDS, (T) TS. (1) 20 mg L⁻¹, (2) 40 mg L⁻¹, (3) 80 mg L⁻¹. Error bars denote the standard deviations. Different minuscule letters in the columns indicate statistically significant differences in the fractions of Cd subgroups among treatments (Duncan test, $P < 0.05$, $n = 3$)

the SDS concentration, reaching a peak near SDS CMC point (while concentration was above the CMC, the removal of Cu from the soil decreased due to the precipitation of the surfactant). Associated to carbonates fraction (4.28 mg kg⁻¹) of Cd was lower in TS group at 80 mg L⁻¹, but as to the SDS group at 20 mg L⁻¹ (4.74 mg kg⁻¹), it showed slight higher than other groups with surfactants. The concentration of associated to carbonates fraction of Cd with different surfactants did not show significant differences. But they were obviously higher than the control group (3.96 mg kg⁻¹). For associated to Fe-Mn oxides of Cd, the TS group at 40 mg L⁻¹ was the least (5.88 mg kg⁻¹) of all groups with adding surfactants. Compared with the control group, significant differences were shown in the experimental groups for Fe-Mn oxides of Cd (5.88–7.64 mg kg⁻¹) with different surfactants. The concentrations of associated to organic matter and residual of Cd were very low and had no significant differences. It has been concluded that some surfactants, like biosurfactants, can complex the free metal fraction, increasing metal concentration in solution (Singh and Cameotra 2004), which can increase the metal availability to the plant and enhance metal absorption. According to the results, it can be obtained that the morphology of Cd was largely transformed from Fe-Mn oxides and associated to carbonates fractions to exchangeable fraction with the

addition of TS at 40 mg L⁻¹. Morphological changes of Fe-Mn oxides and associated to carbonates fractions to exchangeable fraction were the critical key processes in the solubilization of Cd.

Different fractions of pyrene with adding different concentrations of surfactants in pyrene-Cd contaminated soil were shown in Fig. 3.

It was observed that the concentration of bioaccessible fraction of pyrene in the groups with adding different kinds of surfactants were all higher than that in the control group without adding surfactants (Fig. 3). It was illustrated that the concentration of bioaccessible fraction of pyrene was improved by surfactants. It was also discovered that the removal of pyrene in the rice rhizosphere resulted mainly from the significant degradation of bioaccessible fraction (Macleod and Semple 2003; Ma et al. 2012). The concentration of bioaccessible fraction of pyrene (34.50 mg kg⁻¹) with adding TS was a little higher than other surfactant groups in the same concentration level of 20 mg L⁻¹. It can be found that the concentration of bioaccessible fraction of pyrene (36.93 mg kg⁻¹) was higher in TS group at 40 mg L⁻¹ than any other groups. The associated fraction of pyrene had significant differences among different surfactants. It can be easily concluded that TS at 40 mg L⁻¹ showed a great advantage of solubilization capability in improving bioaccessible fraction of pyrene and promoting the morphological transformation of pyrene from associated

fraction to bioaccessible fraction. A small proportion was accounted by bound fraction in the three fractions of pyrene. It had only relatively small transformation in the morphological transformation of pyrene. It was indicated that the morphological transformation of pyrene from associated fraction to bioaccessible fraction was an important process in improving the solubilization of pyrene.

Some researchers have studied that TS appeared to be effective in improving the uptake of PCBs and Cd into corn and sugarcane within a certain range of concentrations. The greatest promotion of PCBs by corn appeared at 0.01 % of TS in solution, which was 0.2 times the CMC of TS (Xia et al. 2009). From the conclusion of my primary experiments, TS at 40 mg L⁻¹ was chosen in the next experiment in the single and combined contaminated soils.

3.2 Accessibility of Pyrene and Cd in Single and Combined Contaminated Soils with Adding TS

Different fractions of pyrene and Cd with adding TS at 40 mg L⁻¹ in single and combined contaminated soils were shown in Figs. 4 and 5, respectively.

In Fig. 4, compared with CC, C, and CM, M groups in single Cd and pyrene-Cd contaminated soils, the concentration of exchangeable fraction in experimental group (C, M) were both higher than that in the control

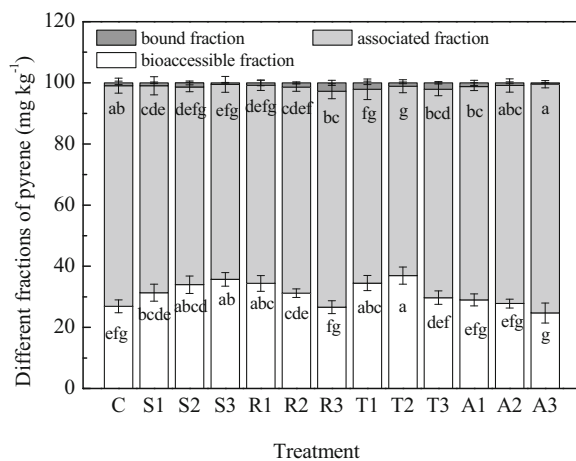


Fig. 3 Different fractions of pyrene with adding four kinds of surfactants in pyrene-Cd soil. (C) Control without surfactants, (A): APG, (R) RL, (S) SDS, (T) TS. (1) 20 mg L⁻¹, (2) 40 mg L⁻¹, (3) 80 mg L⁻¹. Error bars denote the standard deviations. Different minuscule letters in the columns indicate statistically significant differences in the fractions of pyrene subgroups among treatments (Duncan test, $P < 0.05$, $n = 3$)

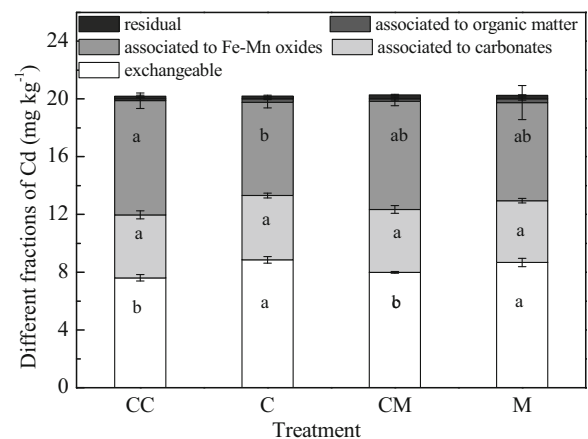


Fig. 4 Different fractions of Cd with adding TS in Cd and pyrene-Cd contaminated soils. (CC) Control without surfactants with Cd, (C) TS at 40 mg L⁻¹ with Cd, (CM) control without surfactants with pyrene-Cd, (M) TS at 40 mg L⁻¹ with pyrene-Cd. Error bars denote the standard deviations. Different minuscule letters in the columns indicate statistically significant differences in the fractions of Cd subgroups among treatments (Duncan test, $P < 0.05$, $n = 3$)

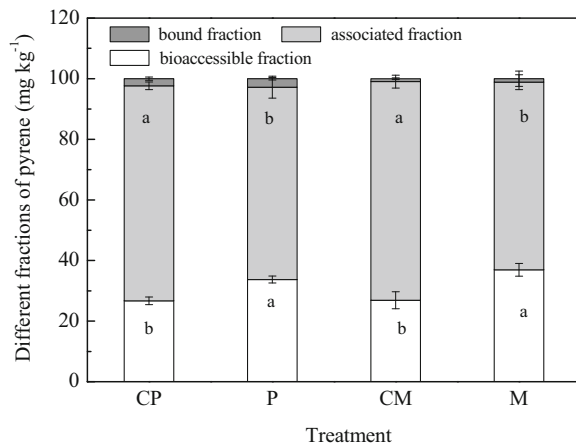


Fig. 5 Different fractions of pyrene with adding TS in pyrene and pyrene-Cd contaminated soils. (CP) Control without surfactants with pyrene, (P) TS at 40 mg L⁻¹ with pyrene, (CM) control without surfactants with pyrene-Cd, (M) TS at 40 mg L⁻¹ with pyrene-Cd. Error bars denote the standard deviations. Different minuscule letters in the columns indicate statistically significant differences in the fractions of pyrene subgroups among treatments (Duncan test, $P < 0.05$, $n = 3$)

groups (CC, CM). The amount of associated to carbonates fraction had no significance among the four groups. However, compared with CC, C, and CM, M groups, the concentration of Fe-Mn oxides in control groups (CC, CM) were lower than that in the experimental group (C, M). According to the results, it can be concluded that TS showed an obvious solubilization of Cd. The concentrations of morphological transformation of Fe-Mn oxides to exchangeable fraction were 8.86 to 7.61 mg kg⁻¹ in Cd soil and 8.67 to 7.99 mg kg⁻¹ in pyrene-Cd soil, respectively. A very low proportion was accounted by associated to organic and residual fractions in the five fractions of Cd. The improving solubilization effect of Cd was largely due to the morphological transformation from Fe-Mn oxides and associated to carbonates fractions to exchangeable fraction. The results indicated that the enrichment effect of heavy metals can be enhanced by surfactants in the later phytoremediation.

In Fig. 5, it was shown that a larger proportion was accounted by associated fraction in the three fractions of pyrene in the four groups. Compared with CP, P, and CM, M groups in single pyrene and pyrene-Cd contaminated soils separately, the concentrations of bioaccessible fraction in experimental groups (P, M) were both higher than that in control groups (CP, CM). However, the concentrations of associated fraction in experimental

groups (P, M) were lower than that in control groups (CP, CM). This phenomenon can be explained by an obvious solubilization effect of TS on the morphological transformation of pyrene from associated fraction (72.15 to 61.95 mg kg⁻¹ in pyrene-contaminated soils and 71.02 to 63.48 mg kg⁻¹ in pyrene-Cd contaminated soil) to bioaccessible fraction with a concentration of 26.66 to 33.71 mg kg⁻¹ in pyrene-contaminated soil and 26.91 to 36.93 mg kg⁻¹ in pyrene-Cd contaminated soils. Then it can be concluded that the increase of bioaccessible fraction of pyrene was promoted with the addition of TS at 40 mg L⁻¹.

In Figs. 4 and 5, it was also obtained that TS took an active part in improving the solubilization of Cd and the morphology of Cd transformed from Fe-Mn oxides and associated to carbonates fractions to exchangeable fraction with the addition of TS in Cd and pyrene-Cd soils. As well as pyrene, the solubilization of pyrene was enhanced and the morphology of pyrene transformed from associated fraction to bioaccessible fraction with the addition of TS. Thus, TS was more effective in enhancing pyrene and Cd solubilization and had potential application in improving the removal of pyrene and Cd from organic and heavy metals contaminated soils.

3.3 Interaction and Influence Mechanisms Between Pyrene and Cd

The contrast rangeability of accessible fractions of pyrene and Cd with adding TS at 40 mg L⁻¹ in single and combined contaminated soils were shown in Figs. 4 and 5, respectively. From the significant different figures, it was observed that the concentration of exchangeable fraction of Cd in C group was higher than that in M group in Fig. 4. However, the concentration of bioaccessible fraction of pyrene in P group was lower than that in M group in Fig. 5. It can be easily concluded that the solubilization of pyrene was much higher in combined soil than in pyrene soil, but the solubilization of Cd was much lower in combined soil than in Cd soil. This phenomenon can be explained that the solubilization of Cd could not be increased in the presence of pyrene. It has the similar conclusion in other's study. They reported that the ability of Cu phytoextraction would be inhibited under co-contamination of high level of pyrene in highly Cu-polluted soil. In the treatment of 400 mg kg⁻¹ Cu and 500 mg kg⁻¹ pyrene, the accumulation of Cu was less than half of that in 400 mg kg⁻¹ Cu treatment (Lin et al. 2008).

A conclusion can be obtained that the solubilization of pyrene was promoted in the presence of Cd in combined contaminated soils (bioaccessible fraction were 33.71 mg kg^{-1} in pyrene-contaminated soil and 36.93 mg kg^{-1} in pyrene-Cd contaminated soil), but the solubilization of Cd was hindered in the presence of pyrene (the exchangeable fraction of Cd were 8.86 mg kg^{-1} in Cd soil and 8.67 mg kg^{-1} in pyrene-Cd contaminated soil) in the study. Similarly, it was found that PAHs sorption was improved in soil in the existence of heavy metals (Luo et al. 2010). The results in the experiment will be more beneficial for the degradation of pyrene in the pyrene-Cd co-contaminated soils.

4 Conclusions

Biosurfactants exert great advantages in the remediation of contaminated soils as the environmental friendly nature. The morphological transformation of pyrene and Cd with adding surfactants in combined soil was a great improvement to the utilization of plants. The addition of TS at 40 mg L^{-1} showed a great advantage of solubilization capability than other surfactants in enhancing accessible fraction of pyrene and Cd.

The morphology of Cd transformed from Fe-Mn oxides and associated to carbonates fractions to exchangeable fraction with the addition of TS at 40 mg L^{-1} in Cd and pyrene-Cd contaminated soils. Morphological changes of Fe-Mn oxides and associated to carbonates fractions were important processes in the solubilization of Cd. As well as pyrene, the solubilization of pyrene was largely promoted and the morphology of pyrene transformed from associated fraction to bioaccessible fraction with the addition of TS at 40 mg L^{-1} in pyrene and pyrene-Cd contaminated soil. The morphological transformation from associated fraction to bioaccessible fraction of pyrene was of importance in the improvement of solubilization capacity of pyrene.

The solubilization of pyrene was improved much higher in combined soil than in pyrene soil. But the solubilization of Cd was improved much lower in combined contaminated soil than in Cd soil. In contrast, the solubilization of pyrene was promoted in the presence of Cd in combined soil, but the solubilization of Cd was hindered in the presence of pyrene in combined soil in the study. It will be beneficial for the degradation of

pyrene in pyrene-Cd soil. The results provide valuable information to better understand the influence of remediation with surfactants in both single and combined contaminated soils. As TS is a plant-derived non-ionic biosurfactant, and it can be degraded automatically, it has no toxic effect to soil. Application of TS will have broad prospects in soil remediation field.

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Ethical Statement

Conflict of Interest The authors declare that they have no conflict of interest.

References

- Alborés, A. F., Cid, B. P., Gómez, E. F., & López, E. F. (2000). Comparison between sequential extraction procedures and single extractions for metal partitioning in sewage sludge samples. *The Analyst*, *125*(7), 1353–1357.
- Almeida, C. M., Dias, A. C., Mucha, A. P., Bordalo, A. A., & Vasconcelos, M. T. (2009). Influence of surfactants on the Cu phytoremediation potential of a salt marsh plant. *Chemosphere*, *75*(2), 135–140.
- An, C. J., Huang, G. H., Wei, J., & Yu, H. (2011). Effect of short-chain organic acids on the enhanced desorption of phenanthrene by rhamnolipid biosurfactant in soil-water environment. *Water Research*, *45*(17), 5501–5510.
- Fukuda, K., Olsson, U., & Ueno, M. (2001). Microemulsion formed by alkyl polyglucoside and an alkyl glycerol ether with weakly charged films. *Colloids and Surfaces B: Biointerfaces*, *20*, 129–135.
- Gao, Y., Zeng, Y., Shen, Q., Ling, W., & Han, J. (2009). Fractionation of polycyclic aromatic hydrocarbon residues in soils. *Journal of Hazardous Materials*, *172*(2-3), 897–903.
- Gomez-Eyles, J. L., Collins, C. D., & Hodson, M. E. (2010). Relative proportions of polycyclic aromatic hydrocarbons differ between accumulation bioassays and chemical methods to predict bioavailability. *Environmental Pollution*, *158*(1), 278–284.
- Haigh, S. D. (1996). A review of the interaction of surfactants with organic contaminants in soil. *The Science of the Total Environment*, *185*, 161–170.
- Iglauer, S., Wu, Y., Shuler, P., Tang, Y., & Goddard, W. A. (2009). Alkyl polyglycoside surfactant–alcohol cosolvent formulations for improved oil recovery. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *339*(1-3), 48–59.
- Lin, Q., Shen, K., Zhao, H., & Li, W. (2008). Growth response of *Zea mays* L. in pyrene-copper co-contaminated soil and the

- fate of pollutants. *Journal of Hazardous Materials*, 150(3), 515–521.
- Liu, F., Wang, C., Liu, X., Liang, X., & Wang, Q. (2013). Effects of alkyl polyglucoside (APG) on phytoremediation of PAH-contaminated soil by an aquatic plant in the Yangtze Estuarine Wetland. *Water, Air, & Soil Pollution*, 224(7), 1633–1643.
- Luo, L., Zhang, S., & Christie, P. (2010). New insights into the influence of heavy metals on phenanthrene sorption in soils. *Environmental Science & Technology*, 44(20), 7846–7851.
- Ma, B., Wang, J., Xu, M., He, Y., Wang, H., Wu, L., & Xu, J. (2012). Evaluation of dissipation gradients of polycyclic aromatic hydrocarbons in rice rhizosphere utilizing a sequential extraction procedure. *Environmental Pollution*, 162, 413–421.
- Macleod, C. J. A., & Semple, K. T. (2003). Sequential extraction of low concentrations of pyrene and formation of non-extractable residues in sterile and non-sterile soils. *Soil Biology and Biochemistry*, 35(11), 1443–1450.
- Megharaj, M., Ramakrishnan, B., Venkateswarlu, K., Sethunathan, N., & Naidu, R. (2011). Bioremediation approaches for organic pollutants: a critical perspective. *Environment International*, 37(8), 1362–1375.
- Momin, S. A., & Yeole, P. (2011). Comparative study of effect of surfactant-polymer interactions on properties of alkyl polyglucosides and alpha olefin sulphonate. *Journal of Surfactants and Detergents*, 15(3), 291–298.
- Mulligan, C. N., Yong, R. N., & Gibbs, B. F. (2001). Surfactant-enhanced remediation of contaminated soil: a review. *Engineering Geology*, 60, 371–380.
- Obuekwe, I. S., & Semple, K. T. (2013). Impact of zinc-copper mixtures on the development of phenanthrene catabolism in soil. *International Biodeterioration & Biodegradation*, 85, 228–236.
- Ochoa-Loza, F. J., Artiola, J. F., & Maier, R. M. (2001). Stability constants for the complexation of various metals with a rhamnolipid biosurfactant. *Journal of Environmental Quality*, 30, 479–485.
- Ortega-Calvo, J. J., Tejada-Agredano, M. C., Jimenez-Sanchez, C., Congiu, E., Sungthong, R., Niqui-Arroyo, J. L., & Cantos, M. (2013). Is it possible to increase bioavailability but not environmental risk of PAHs in bioremediation? *Journal of Hazardous Materials*, 261, 733–745.
- Ramamurthy, A. S., Vo, D., Li, X. J., & Qu, J. (2007). Surfactant-enhanced removal of Cu (II) and Zn (II) from a contaminated sandy soil. *Water, Air, & Soil Pollution*, 190(1–4), 197–207.
- Roy, D., Kommalapati, R. R., Mandava, S. S., Valsaraj, K. T., & Constant, W. D. (1997). Soil washing potential of a natural surfactant. *Environmental Science & Technology*, 31(3), 670–675.
- Singh, P., & Cameotra, S. S. (2004). Enhancement of metal bioremediation by use of microbial surfactants. *Biochemical and Biophysical Research Communications*, 319(2), 291–297.
- Urum, K., & Pekdemir, T. (2004). Evaluation of biosurfactants for crude oil contaminated soil washing. *Chemosphere*, 57(9), 1139–1150.
- Wang, G., Zhou, Y., Wang, X., Chai, X., Huang, L., & Deng, N. (2010). Simultaneous removal of phenanthrene and lead from artificially contaminated soils with glycine-beta-cyclodextrin. *Journal of Hazardous Materials*, 184(1–3), 690–695.
- Wei, J., Liu, X., Wang, Q., Wang, C., Chen, X., & Li, H. (2014). Effect of rhizodeposition on pyrene bioaccessibility and microbial structure in pyrene and pyrene-lead polluted soil. *Chemosphere*, 97, 92–97.
- Xia, H., Chi, X., Yan, Z., & Cheng, W. (2009). Enhancing plant uptake of polychlorinated biphenyls and cadmium using tea saponin. *Bioresource Technology*, 100(20), 4649–4653.
- Zhang, X. Y., Liu, X. Y., Liu, S. S., Liu, F. H., Chen, L. S., Xu, G., Zhong, C. L., Su, P. C., & Cao, Z. N. (2012). Response characteristics of scirpus triquetrand its rhizosphere to pyrene contaminated soils at different growth stages. *International Journal of Phytoremediation*, 14(7), 691–702.
- Zhao, B., Zhu, L., & Gao, Y. (2005). A novel solubilization of phenanthrene using Winsor I microemulsion-based sodium castor oil sulfate. *Journal of Hazardous Materials*, 119(1–3), 205–211.
- Zhou, W., Yang, J., Lou, L., & Zhu, L. (2011). Solubilization properties of polycyclic aromatic hydrocarbons by saponin, a plant-derived biosurfactant. *Environmental Pollution*, 159(5), 1198–1204.