Synergistic effects of inorganic salt and surfactant on phenanthrene removal from aqueous solution by sediment

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ABSTRACT

The economic and effective application of surfactant enhanced remediation (SER) technology in a sediment-freshwater/saline water system was investigated by batch method using the combined effects of inorganic salt (sodium chloride, NaCl) and anionic surfactant (sodium dodecylbenzene sulfonate (SDBS)) on phenanthrene (PHE) removal via sorption by sediment. In all cases, PHE sorption followed a linear equation and partition as the main mechanism for PHE removal from aqueous solution. Separate addition of SDBS (2 mmol L^{-1}) and NaCl (2–100 mmol L^{-1}) moderately enhanced PHE removal, while with their combined addition the enhancement was substantial, and the removal efficiency achieved a peak of 92.8%. The combined effect expressed a synergy, and the sorption enhancement increased by factors of 2.7, 3.2 and 3.4 when compared with the sum of the separate entities at elevated salinity. This was because the sorbed SDBS, with increasing amount and a high packing conformation at elevated salinity, outcompeted aqueous SDBS for PHE partition. Moreover, a combination of 2 mmol L^{-1} SDBS and 2 mmol L^{-1} NaCl was optimal for PHE removal. Therefore, SER technology appears more effective for PHE removal in saline water than in freshwater, and preliminary water quality monitoring is essential for economic and efficient SER application.

Key words | inorganic salt, phenanthrene, removal, sorption, surfactant, synergistic effect

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are classified as persistent toxic contaminants due to their persistent, mutagenic and carcinogenic properties (Desalme *et al.* 2013). Contamination of PAHs in urban runoffs and wastewater has been found widely (Barco-Bonilla *et al.* 2013), which can run into water bodies and subsequently sink into sediments via sorption processes (Chamorro *et al.* 2013). Surfactant enhanced remediation (SER) has been proposed as a promising technology for the remediation of PAHs contaminated water and sediment, as it is of growing concern in recent years (Sun *et al.* 2009; Masrat *et al.* 2013).

At low concentration, surfactants are present as dispersed molecules. However, the surfactant monomers tend to aggregate into micelles consisting of a hydrophobic core and a hydrophilic shell when concentrations are above the critical micelle concentration (CMC), thereby causing a significant increase in the water solubility of PAHs by partitioning them into micelles in solution (Masrat *et al.* 2013; Zhou *et al.* 2013). Thus, according to the concentration

applied, the SER technology is divided into two branches, i.e. mobilization and in-situ immobilization. The former refers to surfactant aided soil-washing to improve the PAHs' mobilization with a concentration above its CMC (Zhou *et al.* 2013); by contrast, the latter refers to enhancing PAHs sorption at the localized scale with a concentration below its CMC, in which the surfactant tends to be sorbed on sediment and then serves as a more effective phase for PAHs sorption than the native sediment organic matter (SOM) (Ahn *et al.* 2010; Jin *et al.* 2013). Accordingly, the SER of in-situ enhanced sorption would be favorable for removal of PAHs from water, as well as the ex-situ remediation of PAHs contaminated sediment.

Generally, ions such as Na$^+$, Ca^{2+}, NO$_3^-$ and Cl$^-$ are ubiquitous in the aquatic environment, and the corresponding salinity ranges from 1 to 500 mmol L^{-1} (Turner 2003). However, the application of SER technology in the saline environment has been seldom reported. It has been indicated that the addition of inorganic salt can reduce the solubility of

PAHs, thus promoting PAHs sorption on sediment (Oh *et al.* 2013). Similarly, surfactant sorption was also enhanced as salinity increased, ascribed to the reduction in electrostatic repulsions between surfactant monomers and sediment particles (Paria 2008). Hence, PAHs sorption would be further facilitated by sorption onto the increasing amount of sorbed surfactant. Consequently, it is supposed that the SER of in-situ enhanced sorption would be more effective in a saline than a freshwater environment. In other words, the combined utilization of inorganic salt and surfactant would be more efficient in PAHs removal and sediment ex-situ remediation.

Therefore, in the present study, an inorganic salt (sodium chloride, NaCl) and an anionic surfactant (sodium dodecylbenzene sulfonate (SDBS)) were employed, and batch tests were conducted to investigate their combined effects on phenanthrene (PHE, a model PAH compound) removal via sorption by sediment. Results of this study will help to clarify PAHs transport in the natural aquatic system and extend the application of SER technology to a saline environment.

MATERIALS AND METHODS

Materials

PHE was purchased from Merck, Germany, with a purity >97%. SDBS, NaCl and other reagents were purchased from Xi'an Chemical Corporation (Xi'an, China), and were all of analytical grade.

Sediment was collected from the top 0–15 cm of the Weihe riverbed, in Xi'an, China. Samples were air-dried, ground, sieved through a 130 mesh and stored in a closed container. The basic properties of the sediment are listed in Table 1. Sediment organic carbon content (f_{oc}) was determined by the wet dichromate oxidation method (Rivas *et al.* 2008). As described by Ahn *et al.* (2010), pH was determined at a sediment/liquid ratio of 1:10 (v/v) in deionized water after vigorously mixing for 10 min, and the specific surface area (SSA) and pore size were analyzed by the N_2-BET method. Cation exchangeable capacity (CEC) was measured at pH 7.0 using 1 mol L^{-1} ammonium acetate following Zhou & Haynes (2011).

PHE sorption experiments

Batch experiments were conducted to determine PHE equilibrium sorption isotherms, as described by Rivas *et al.* (2008). 0.2 g sediment was weighed into 50 ml glass vials followed by 20 ml background solution containing 0.02% $HgCl_2$ to inhibit bacterial growth. A given amount of PHE stock solution in high-performance liquid chromatography (HPLC)-grade methanol was added to set the initial concentration to range evenly from 0.1 to 0.6 mg L^{-1}. The vials were shaken (120 rpm) in the dark at room temperature for enough time to reach equilibrium conditions (48 h). Suspensions were centrifuged at 4,000 rpm for 20 min, and the supernatants were filtered through 0.45 μm membrane and analyzed for PHE concentrations. In the absence of sediment, the control vials indicated that PHE losses caused by volatilization and sorption to the vials were negligible. Thus the sorbed amounts could be calculated by mass balance. All experiments were performed in triplicate, and data in figures and tables are presented as an average of the triplicates with standard deviations less than 5%.

Deionized water (18.2 MΩ) was used in freshwater experiments. A fixed concentration of SDBS (2 mmol L^{-1}, below its CMC in freshwater) and/or various concentrations of NaCl (2, 10, 100 mmol L^{-1}) were applied as background solutions, with the aim of studying their combined effects on PHE removal by sediment.

Analysis

Aqueous PHE concentration was analyzed by an HPLC system equipped with a reverse phase C18 column (TIANHE Kromasil, 150 mm × 4.6 mm, 5 μm particle size) and fluorescence detector with an excitation wavelength of 250 nm and an emission wavelength of 364 nm. An isocratic 80/20 was used as the mobile phase at a flow rate of 1 ml min^{-1}. The CMC of SDBS was determined using the Du Nouy tensiometer method (Masrat *et al.* 2013), and the CMC obtained in freshwater is 6 mmol L^{-1} in the present test condition.

RESULTS AND DISCUSSION

PHE removal enhanced by SDBS and NaCl

Kinetic experiments of PHE removal via sorption on sediment were conducted at initial PHE concentration of 0.1 mg L^{-1},

Table 1 | Basic properties of the tested sediment

f_{oc} (%)[a]	pH	CEC[b] (cmol kg^{-1})	SSA[c] (m^2 g^{-1})	Pore size (nm)
4.77	8.1	10.54	7.27	92.8

[a]Organic carbon content determined by wet dichromate oxidation method.
[b]CEC measured using 1 mol L^{-1} ammonium acetate.
[c]SSA analyzed by N_2-BET method.
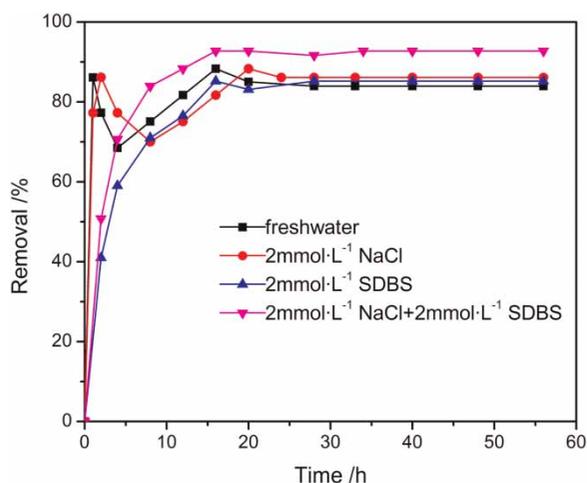
Figure 1 | PHE removal with the addition of SDBS, NaCl and their combination.

Figure 2 | PHE sorption isotherms with the addition of SDBS, NaCl and their combination.

with the addition of 2 mmol L^{-1} SDBS, 2 mmol L^{-1} NaCl and their combination, and the results are shown in Figure 1. The removal efficiencies were 85.2 and 86.1% with separate addition of SDBS and NaCl, respectively, which were slightly higher than 83.9% in freshwater, indicating that PHE removal was moderately enhanced by SDBS or NaCl. Moreover, the removal efficiency was significantly enhanced by the combination of SDBS and NaCl, and achieved a peak of 92.8%. This suggested that their combination had a positive impact on PHE removal and exhibited the synergistic potential for effective PHE removal via sorption on sediment. Consequently, a separate study of the effects and mechanisms of SDBS (2 mmol L^{-1}), NaCl (2–100 mmol L^{-1}), and their combination on PHE removal is needed, and is discussed below.

Effects of SDBS on PHE removal

PHE sorption on sediment was determined with and without SDBS (2 mmol L^{-1}). Linear (1) and Freundlich (2) equations are used to model sorption isotherms (Figure 2), and their parameters are summarized in Table 2, such that

$$Q_e = K_d C_e \tag{1}$$

$$Q_e = K_F C_e^n \tag{2}$$

where Q_e ($\mu g\ g^{-1}$) and C_e (mg L^{-1}) are the equilibrium solid and aqueous solute concentrations, respectively, K_d represents the partition coefficient (L kg^{-1}), K_F is the Freundlich capacity parameter [($\mu g\ g^{-1}$)(mg L^{-1})$^{-n}$], and n (dimensionless) is a measure of isotherm nonlinearity.

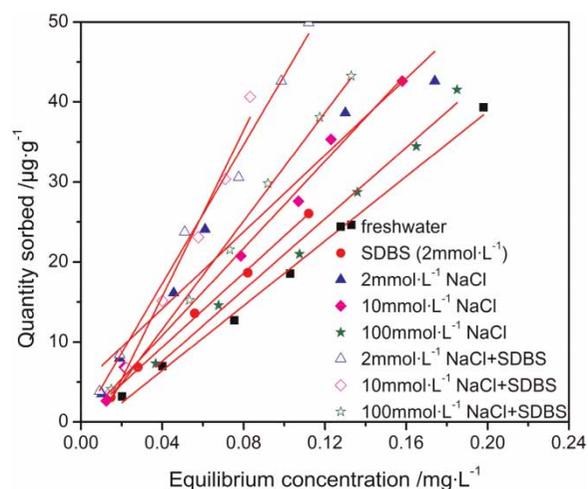As presented in Table 2, PHE sorption can be better described by the linear equation in the concentration range examined, in view of the fact that the corresponding correlation coefficients were higher than those of the Freundlich equations, and the n values were close to 1.0. This indicates that partitioning of PHE into SOM is the dominant mechanism for PHE removal from aqueous solution (Gao *et al.* 2007). Clearly, PHE removal was moderately enhanced by SDBS with the K_d value increased by 14.5%, which is consistent with many previous studies (Ahn *et al.* 2010; Jin *et al.* 2013). The result is that surfactant tends to be sorbed on the sediment surface at a concentration below its CMC, and the sorbed surfactant is more effective on a carbon-normalized basis for PHE partition than the native SOM, as well as the surfactant being present in solution as both monomers and micelles. An effectiveness factor is introduced to describe the effectiveness with which the sorbed surfactant can act as a sorbent for PAHs on a carbon-normalized basis, and the effectiveness factor is assumed to be 1.0 for the soil/sediment (Edwards *et al.* 1994). As reported in Ahn *et al.* (2010), the effectiveness factor of the sorbed surfactant was calculated to be 10.9–117.2, which was much higher than that of the bulk soil. Furthermore, the n value increased from 0.908 to 0.970, implying a more linear sorption when SDBS was sorbed on the sediment.

Effects of NaCl on PHE removal

PHE sorption isotherms on sediment were evaluated in NaCl concentrations of 2, 10 and 100 mmol L^{-1}, and the results are summarized in Table 2. As shown in Table 2, partition is still the main mechanism for PHE removal from

**Table 2** | PHE sorption coefficients and Freundlich parameters

Hydrochemical condition	Linear isotherms		Freundlich isotherms		
	$K_d \pm$ SE	R^2	log$K_F \pm$ SE	$n \pm$ SE	R^2
Freshwater	202.2 ± 6.2	0.996	2.36 ± 0.02	0.908 ± 0.017	0.999
SDBS[a] (2 mmol L^{-1})	231.5 ± 6.1	0.998	2.41 ± 0.06	0.970 ± 0.040	0.995
2 mmol L^{-1} NaCl	240.0 ± 16.5	0.942	2.37 ± 0.09	1.137 ± 0.065	0.974
10 mmol L^{-1} NaCl	272.2 ± 10.9	0.992	2.47 ± 0.08	0.962 ± 0.063	0.982
100 mmol L^{-1} NaCl	222.8 ± 10.6	0.989	2.36 ± 0.04	0.958 ± 0.036	0.994
2 mmol L^{-1} NaCl + SDBS	433.5 ± 19.7	0.992	2.64 ± 0.04	0.996 ± 0.027	0.997
10 mmol L^{-1} NaCl + SDBS	518.6 ± 30.4	0.986	3.05 ± 0.04	0.740 ± 0.025	0.999
100 mmol L^{-1} NaCl + SDBS	338.6 ± 10.4	0.995	2.51 ± 0.03	0.770 ± 0.022	0.999

[a]Sodium dodecylbenzene sulfonate.

aqueous solution, and K_d values in saline water were always greater than that in freshwater. As NaCl concentration elevated, the enhancement in K_d value first increased to reach its maximum but was followed by a decrease at 100 mmol L^{-1} NaCl, and the enhancements were 18.7, 34.6 and 10.2% for 2, 10 and 100 mmol L^{-1}, respectively. The promoting effect of salinity on sorption has been widely reported before, and the reduction in PHE solubility at elevated salinity, i.e., the well-known salting out effect, accounts for sorption enhancement (Oh *et al.* 2013).

However, the salting out effect on solubility seems not to be the only reason for K_d variation (Xiao *et al.* 2011). It has been suggested that SOM itself could also be salted out at elevated salinity, resulting in a more compressed and hydrophobic conformation, which exhibited high affinity with PHE and further favoured PHE sorption (Luo *et al.* 2008).

Furthermore, SOM releasing ubiquitously occurs in a sediment-water system (Kaiser & Kalbitz 2012; Mukherjee & Zimmerman 2013). It not only lowers the content of SOM, but also produces dissolved organic matter (DOM) in aqueous solution with potential solubilization for PHE, thus exhibiting inhibitory effects on sorption, which was systematically studied in our previous report (Zhang *et al.* 2014). Hence, DOM concentrations in solution containing 0–100 mmol L^{-1} NaCl were also determined by a total organic carbon (TOC) analyzer (TOC-V$_{CPH}$, Shimadzu, Japan), and the relationships between DOM concentration and the corresponding K_d value are illustrated in Figure 3. Obviously, the K_d value was negatively correlated with DOM concentration examined in the range 9.60–12.50 mg L^{-1} ($r = -0.722$). Gao *et al.* (2007) found that SOM releasing with subsequent DOM solubilization impeded PHE sorption, and resulted in greater K_d values on deionized water-eluted soils than that on control soils. Similar observations were also reported by Yu *et al.*
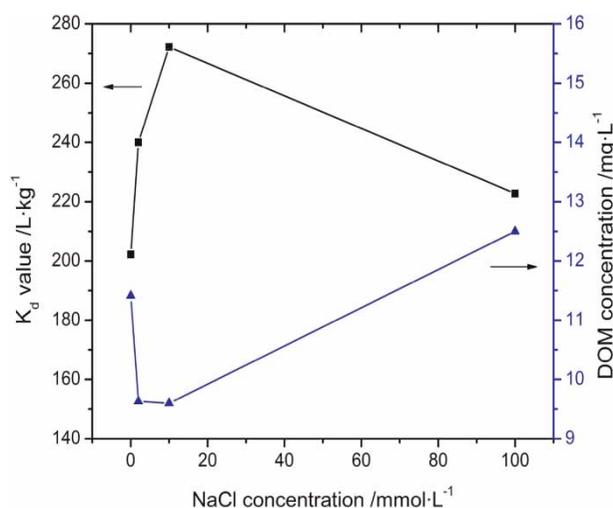
Figure 3 | Relationships between K_d values and aqueous DOM concentrations.

(2011). Consequently, as NaCl concentration increased ($\leq$10 mmol L^{-1}), the salting out effects on PHE solubility and SOM conformation, along with the decrease in DOM solubilization, led to an obvious enhancement in K_d value. With NaCl concentration continuously increased (100 mmol L^{-1}), although the salting out effect would be strengthened, the substantial increase in DOM solubilization drove an evident decline in the K_d value. Therefore, SOM releasing with subsequent DOM formation in solution, would play an important regulatory role in PHE removal, which is noteworthy and should be addressed in future studies.

Combined effects of SDBS and NaCl on PHE removal

SDBS (2 mmol L^{-1}) and NaCl (2–100 mmol L^{-1}) may function together in combination and consequently be more

efficient for PHE removal due to the separate mechanisms for PHE removal enhanced by their individual addition. As presented in Table 2, partition is the main removal mechanism, and K_d values in the combined system were generally greater than those in freshwater, or in the systems with only SDBS or NaCl. Moreover, the combined effect appeared to be synergistic, since the enhancement calculated as ΔK_d (after subtracting the K_d value in freshwater) at elevated salinity was much higher than the sum of the individual values, and increased by a factor of 3.4, 3.2 and 2.7 (for 2, 10 and 100 mmol L^{-1} NaCl, respectively). The comparison results are shown in Figure 4.

As presented in Table 2, K_d value first increased with increasing salinity, but then decreased at an NaCl concentration of 100 mmol L^{-1}. DOM is a surface-active substance similar to surfactants, and SDBS added with a concentration much higher than that of the aqueous DOM would eliminate the regulatory effect of DOM solubilization on sorption. Consequently, the K_d variation tendency could not be explained by the change in DOM solubilization. It has been indicated that an elevated salinity could decrease the CMC of a surfactant (Alam et al. 2012), and a surfactant with a concentration below its CMC generally enhances PHE sorption, while with a concentration above the CMC would in turn inhibit sorption, due to the sorbed surfactant contributing to sorption and the solute surfactant mobilizing PHE (Pan et al. 2009). In the present test conditions, the CMCs of SDBS in saline water decreased with increasing salinity, and were 3.8, 2.6 and 1.7 mmol L^{-1} (for 2, 10 and 100 mmol L^{-1} NaCl, respectively). Hence, the experimental concentration of 2 mmol L^{-1} SDBS was only enough for SDBS monomers to aggregate in solution to form micelles

at an NaCl concentration of 100 mmol L^{-1}. The micelles with a hydrophobic core inside and a hydrophilic shell outside could compete with the native SOM for PHE partition, thus the K_d value decreased at 100 mmol L^{-1} NaCl.

The synergistic effect on PHE removal achieved in the combined system was mainly attributed to both the amount and the conformation of sorbed SDBS influenced by salinity. The introduced NaCl weakened electrostatic repulsions between SDBS monomers, as well as between SDBS and sediment particles, which induced SDBS to be sorbed on sediment and resulted in an increase in the sorbed amount (Paria 2008). The salting out effect would also act on the sorbed SDBS and create a high packing conformation. In addition, the hydrophilic head groups of SDBS were neutralized by either the sediment surface or salt ions when SDBS was sorbed on sediment, and the thickness of the hydration layer was reduced, which enhanced the hydrophobic interactions between sorbed SDBS and PHE, hence being favourable for sorption (Sun et al. 2009). Change in the synergistic effect was not obvious when increasing NaCl concentration from 2 to 10 mmol L^{-1}, with a similar factor of 3.4 and 3.2, indicating that the combination of 2 mmol L^{-1} SDBS and 2 mmol L^{-1} NaCl was the optimum for economic and efficient PHE removal. At NaCl concentration of 100 mmol L^{-1}, SDBS micelles had already formed in solution, whereas the combined effect still expressed as synergism, was ascribed to the fact that sorbed SDBS with a close packing conformation outcompeted aqueous micelles for PHE partition.

CONCLUSIONS

The combined effects of SDBS (2 mmol L^{-1}) and NaCl (2–100 mmol L^{-1}) on PHE removal via sorption on sediment were investigated by batch method, and the following conclusions can be derived.

In all cases, PHE sorption followed the linear equation, and partition is the main mechanism for PHE removal from aqueous solution. Individual addition of SDBS and NaCl moderately enhanced PHE removal, while the enhancement was substantial with their combined addition, and PHE removal efficiency achieved a peak of 92.8%.

The combined effect appeared to be synergistic, and the sorption enhancement increased by a factor of 3.4, 3.2 and 2.7 with increasing salinity (with 2, 10 and 100 mmol L^{-1} NaCl, respectively) when compared with the sum of the individual additions. With an increasing amount and a high packing conformation at elevated salinity, the sorbed SDBS outcompeted aqueous SDBS for PHE partition. The
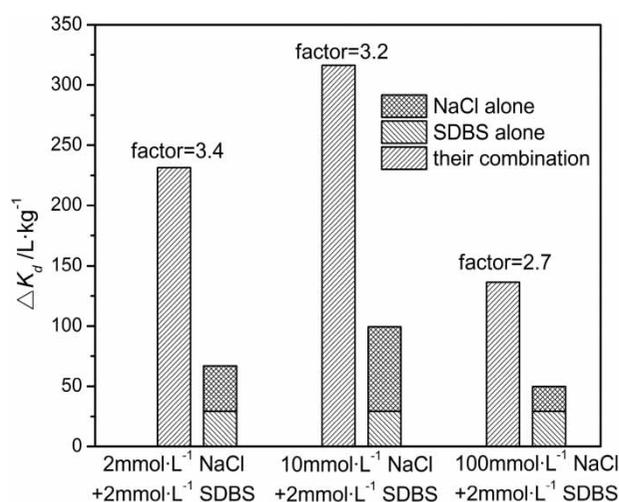

Figure 4 | Sorption enhancements (ΔK_d) with the addition of NaCl, SDBS and their combination.

combination of 2 mmol L^{-1} SDBS and 2 mmol L^{-1} NaCl was the optimum for PHE removal.

Therefore, SER seems more effective and economic for PHE removal in a saline environment than in freshwater, since surfactant applied with a reduced dose could also achieve high removal efficiency in a saline environment. Additionally, preliminary water quality monitoring is essential for economic and efficient SER application.

ACKNOWLEDGEMENTS

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