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RESEARCH ARTICLE

Adsorptive removal of naphthalene induced by structurally different Gemini surfactants in a soil-water system

Jia Wei[1] · Jun Li[1] · Guohe Huang[2] · Xiujie Wang[1] · Guanghui Chen[1] · Baihang Zhao[1]

Abstract A new generation of surfactant, Gemini surfactants, have been synthesized and have attracted the attention of various industrial and academic research groups. This study focused on the use of symmetric and dissymmetric quaternary ammonium Gemini surfactants to immobilize naphthalene onto soil particles, and is used as an example of an innovative application to remove HOC in situ using the surfactant-enhanced sorption zone. The sorption capacity of modified soils by Gemini surfactant and natural soils was compared and the naphthalene sorption efficiency, in the absence and presence of Gemini surfactants with different alkyl chain lengths, was investigated in the soil-water system. The results have shown that the increased added Gemini surfactant formed admicelles at the interface of soil/water having superior capability to retard contaminant. Symmetric and dissymmetric Gemini surfactants have opposite effect on the aspect of removing of PAH attributing to their solubilization and sorption behavior in soil-water system. Compared with the natural soil, sorption of naphthalene by Gemini-modified soil is noticeably enhanced following the order of $C_{12-2-16} < C_{12-2-12} < C_{12-2-8}$. However, the symmetric

Gemini surfactant $C_{12-2-12}$ is the optimized one for in situ barrier remediation, which is not only has relative high retention ability but also low dosage.

Keywords Gemini surfactant · Naphthalene · Soil-water system · Remediation

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Introduction

Widespread contamination of soil and groundwater by polycyclic aromatic hydrocarbons (PAHs) and other hydrophobic organic compounds (HOCs) has emerged as one of the most concerning issues worldwide (Chibwe et al. 2015; Li et al. 2016; Maliszewska-Kordybach et al. 2008; Nemr and Abd-Allah 2003). Knowledge of the transport and fate of these contaminants and novel remediation strategies are therefore of great interest to related fields. Sorption and desorption are well-known fundamental processes in controlling the fate and transport of organic contaminants in the environment (Huang et al. 2003; Lamichhane et al. 2016; Yang et al. 2014). In some circumstances, contaminants are removed via an enhanced desorption. In other circumstances, contaminants can be prevented from a point source of pollution by improving the sorption ability of sorbate. Surfactants are valuable products possessing both of the capabilities which have been widely used in the fields of water, soil, and sediment remediation technology (Agnello et al. 2016; Uhmann and Aspray 2012). Surfactant-aided soil washing has been widely used to treat HOCs contaminated soil and sediment ex situ (López-Vizcaíno et al. 2012; Ye et al. 2015), because surfactant may enhance the solubility of HOCs in water which contributes to the removal of organic contaminants from soil or sediment. Recently,

many researchers began to employ surfactants to modify solids in order to remove contaminants from aqueous media or inject them into an aquifer to create an in situ enhanced sorption zone which would intercept a migrating HOCs plume, significantly retarding the transport of these contaminants (Guzel et al. 2016; Rodríguez-Cruz et al. 2007). For instance, conventional cationic surfactant can be retained by both the outer and inner layer surfaces of clay via an ion exchange process in aqueous systems and are not easily displaced by smaller cations such as H^+, Na^+, or Ca^{2+} (Karapanagioti et al. 2005). Cationic-surfactant-modified sorbent were assessed and proposed for the retardation of a variety of compounds. The systems demonstrated chemical and biological stability and were pilot tested as a permeable barrier for groundwater remediation (Li and Bowman 1998). This suggests the potential utility of the modified soils for treatment of contaminated waters and as components of containment barriers, that is, in slurry walls, hazardous waste landfills, and petroleum. However, most investigated surfactants are conventional surfactants, which consist of single monomers with a single hydrophobic core and a single hydrophilic shell.

Presently, a new generation of surfactant, called "Gemini surfactants," has been synthesized and has attracted the attention of various industrial and academic research groups (Shukla and Tyagi 2006). They form micelles at much lower concentrations than the conventional surfactants and also tend to aggregate at interfaces far more readily (Khan et al. 2014). They have been shown to be more surface active than monomeric surfactants at the same molar mass concentration. The application of Gemini surfactants has been extensively explored. The most notable application is their modification function in the remediation of contaminated water, soil, or sediment. Neupane et al. (Neupane and Park 2000) have proposed the use of anionic Gemini surfactant to treat alumina for the removal of HOCs from the aqueous phase. Adsorption of some cationic Gemini surfactants onto silica has been investigated (Prarat et al. 2013; Zheng et al. 2012). Moreover, studies relating to HOCs partitioning into modified soil particles, formed by cationic Gemini surfactant, are rather few at this time.

This study focused on the use of Gemini cationic surfactants to immobilize polycyclic aromatic hydrocarbons onto soil particles, and is used as an example of an innovative application to remove HOCs in situ using the surfactant-enhanced sorption zone. In this endeavor, three symmetric and dissymmetric Gemini surfactants and one organic contaminant naphthalene were used, and specific work was undertaken in detail, as follows: (1) The sorption behavior of selected surfactant was evaluated; (2) The sorption capacity of modified soils and natural soils was compared; and (3) The PAH sorption efficiency, in the absence and presence of Gemini surfactant, was investigated. By evaluating Gemini surfactant with different alkyl chain lengths and by looking at both solubilization and sorption behavior, this work attempts to provide a broader analysis of Gemini surfactant-modified soil sorbent.

Materials and methods

Materials

The PAH employed was naphthalene, with a purity >98 % (Aldrich products). Its octanol/water partition coefficient (Log K_{ow}) and water solubility are 3.36 and 34 mg L^{-1}, respectively. Gemini cationic surfactants C_{12-2-8}, $C_{12-2-12}$, and $C_{12-2-16}$ were obtained from Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Science, having a purity of 95 %. Selected physicochemical properties of surfactant are included in Table 1. Concentrated PAH stock solutions were prepared in HPLC-grade methanol and stored in the dark at 4 °C in an amber borosilicate bottle to minimize photodegradation and/or volatilization. Fresh Gemini surfactant stock solutions were prepared by dissolving the relevant surfactants in deionized water at room temperature. Then, desired mole fractions were obtained by mixing precalculated volumes of the stock solutions and the following experimental procedures were performed.

The soil sample of this study was a natural soil and was collected from the top (0–25 cm) layer of a contamination free area in Saskatchewan, Canada. It was transported back to the laboratory in coolers, air-dried, crushed, and passed through 2 mm mesh to remove surface plant remains and coarse materials and was stored in closed containers in the darkness of refrigerator. The soil pH value was measured in slurries made up at a 1:2.5 soil/water ratio. The cation exchange capacity (CEC) was analyzed employing a method reported by Gao et al. (2001). The organic carbon of soil was determined using a LECO TruPec CN determinator at the condition of 50 % relative humidity and 25 °C. The main soil properties were tabularized in Table 2.

Methods

Solubilization measurement

Solubilization of naphthalene by Gemini surfactants was subsequently carried out in batch mode. For each test, an excess amount of naphthalene was separately spiked into each vial containing a series of 10 mL surfactant solutions having a range of concentrations below and above the CMC to ensure maximum solubility. The sample vials were sealed with a screw cap fitted with a Teflon-lined septum to prevent any volatilization loss of naphthalene from surfactant. Triplicate samples were prepared for each surfactant concentration. The

Table 1 Formula and experimental critical micelle concentration (CMC) of the selected Gemini surfactants

Surfactant	Molecular formula	Molecular weight (g M^{-1})	CMC[a] (mM)
C$_{12-2-8}$	C$_{12}$H$_{25}$N^{+}(CH$_3$)$_2$ (CH$_2$)$_3$-N^{+}(CH$_3$)$_2$ C$_8$H$_{17}$·2Br-	558.67	1.5
C$_{12-2-12}$	C$_{12}$H$_{25}$N^{+}(CH$_3$)$_2$ (CH$_2$)$_3$-N^{+}(CH$_3$)$_2$ C$_{12}$H$_{25}$·2Br-	614.79	0.87
C$_{12-2-16}$	C$_{12}$H$_{25}$N^{+}(CH$_3$)$_2$ (CH$_2$)$_3$-N^{+}(CH$_3$)$_2$ C$_{16}$H$_{35}$·2Br-	672.03	0.2

[a] Data for Gemini surfactants reported by Wei et al. (2011)

samples were then mechanically shaken end-over-end for a period of 24 h in a thermostatic chamber maintained at a temperature of 25±0.5 °C. Following this step, the samples were subsequently centrifuged at 5000 rpm for 30 min to fully separate the undissolved naphthalene, at the same temperature. An appropriate aliquot of the supernatant was then carefully withdrawn with a volumetric pipet and diluted to 10 mL in flasks with 1 mL methanol and the rest with the corresponding surfactant-water solution for naphthalene analysis.

Surfactant and PAHs sorption

Sorption of Gemini surfactants, as well as naphthalene onto soil from water in the presence or absence of surfactants was conducted using a batch equilibration technique at different aqueous surfactant concentrations. A soil sample of 0.1 g was weighed into 20 mL capped glass vials, to which 10 mL of distilled water or a given concentration of Gemini solution was added (based upon the estimated adsorption amount of surfactant on the soil). A 0.01 M CaCl$_2$ background electrolyte was used to minimize ionic strength change. To inhibit microbial growth, 0.01 M NaN$_3$ was used in all cases. The initial surfactant concentration spanned a large range of values below and above the nominal CMC of Gemini surfactant. Then, the samples were spiked with a known mass of naphthalene prepared in methanol, and ensured to be lower than their water solubilities. The content in methanol was about 2 % in volume so that it could not have an effect upon adsorption (Lee et al. 2004). Next, the capped tubes were placed in a reciprocating chamber for 24 h at 25±0.5 °C. Preliminary experiments showed the sorption equilibrium of both surfactant and naphthalene were reached less than 24 h later. The aqueous phase was separated by centrifugation at 5000 rpm for 30 min in the HERAEUS Multifuge X1R High Speed centrifuge after equilibration. Subsequently, an appropriate aliquot of the supernatant was sampled for naphthalene and Gemini surfactants analysis.

Table 2 Selected properties of the soil sample

Solid	CEC (cM kg^{-1})	f_{oc} (%)	pH	Sand (%)	Silt (%)	Clay (%)
Soil	15.8	13.3	8.8	39.96	27.26	32.79

Analytical method

Cationic Gemini surfactant analysis was carried out, at room temperature, using a G20 automatic titrator furnished with a 20 mL autoburet, a stirrer, a surfactant sensitive electrode, and a reference electrode. A 1 mL surfactant sample was added to 20 mL distilled water and then was placed in a 100 mL titration vessel. The solution was titrated with 4 mM SDS dropwise added from the buret at a rate of 10 mL min^{-1}. The intersection point in a titration was automatically distinguished by the titrator. The concentration of naphthalene was detected by a Varian UV spectrophotometer (Cary 300) using the peak at 220 nm. The typical error was less than 5 % for solubilization determination and 10 % for adsorption determination.

The equilibrium concentration of surfactant and solute in solution was analyzed. The amount of surfactant adsorbed onto the soil solid or the amount of pollutant adsorbed onto the surfactant-treated soil solid is determined based upon the difference between the initial mass added and the mass remaining in the solution and is given by:

$$Q_s = \frac{(C_i - C_s) \times M \times V}{G} \quad (1)$$

where

Q_s concentration of sorbed adsorbate (surfactant or pollutant) per gram of adsorbant, in milligram per gram

C_i initial concentration of adsorbate, in molar

C_s equilibrium concentration of adsorbate, in molar

M molecular weight, in gram per molar

V volume of solution, in liter

G weight of soil solid, in gram

As controls, duplicate blank samples were analyzed for each surfactant concentration. The sorption of surfactant and naphthalene on the tubes was examined and found to be negligible, and the amount of surfactant and naphthalene blank (with no soils) did not show any significant change before and after mixing. Owing to the method's high sensitivity, all solute samples had to be diluted in order to obtain readings within the linear calibration range. All data in the figures are presented as an average of the two replicates.
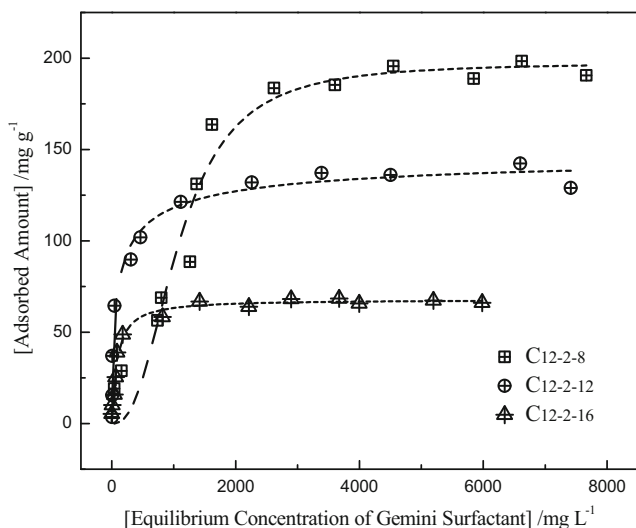
Fig. 1 Surfactant sorption isotherms (*Symbols*, experimental data; *dotted lines*, fitted Langmuir isotherms)

Results and discussion

Sorption of Gemini surfactant

Adsorption of three Gemini surfactants onto soil from double distilled water solution is shown in Fig. 1. Langmuir isotherms were used to interpret surfactant sorption on selected soil. The equation (Karapanagioti et al. 2005) used is:

$$Q_e \ = \ Q_{emax}K_LC_e(1 + K_LC_e)^{-1} \qquad (2)$$

where Q_e is the amount of surfactant sorbed per unit mass of sorbent at equilibrium, C_e is the surfactant equilibrium concentration in solution, Q_{emax} is the amount of surfactant required to saturate the sorbent, and K_L is the Langmuir constant.

The lines in Fig. 1 present the fitted Langmuir surfactant isotherms (Eq. 2) for all surfactant-sorbent systems studied in the present work. All three selected Gemini surfactants exhibit similar sorption behavior with sorption on the soils increasing sharply with aqueous surfactant concentrations, until a plateau value is reached, and then stays constant with further increases of the surfactant concentration in solution. As for the three Gemini surfactant systems, different levels of surfactant are loaded onto the soil surface in terms of surfactant mass adsorbed to the external surface area due to their different CMC and molecular structures.

Table 1 presents the plateau values for the amount of surfactant sorbed (Q_{emax}) and the surfactant concentration in solution at which this plateau value (C_{emax}) is first observed. The sorption saturation of all studied Gemini surfactants occurs when the aqueous concentrations are at or a little above their CMC, manifesting that Gemini monomers are mainly sorbed components on a solid surface.

It is well known that cationic surfactants are sorbed onto soil particles predominantly through cation exchange interactions (Zhu et al. 2003). In this study, the maximum amount (in mg g^{-1}) of surfactant at the soil/aqueous solution interface, C_{emax}, increases with the decreased length of one hydrophobic chain. The plateau values of three isotherms correspond to 154.83, 119.47, and 50.62 mequiv kg^{-1}, respectively, all below the CEC of the soil (158 mequiv kg^{-1}), indicating that not all CEC sites of selected soil are available for cationic exchange. In this study, three Gemini surfactants, C_{12-2-8}, $C_{12-2-12}$, and $C_{12-2-16}$ monomers occupied approximately 97.99, 75.61, and 32.04 % of the total CEC soil sites.

The equilibrium surfactant concentration values, C_e, in the aqueous phase, required to reach C_{emax} of the three Gemini surfactants are, respectively, much higher than their individual CMC, almost double, indicating that some adsorption via the hydrophobic group interaction also exists except for cation exchange mechanisms. The maximum adsorption value for the three selected Gemini surfactants is in the order of $C_{12-2-8} > C_{12-2-12} > C_{12-2-16}$ because more Q_{emax} is reached when high C_{emax} is exhibited, as it has a greater CMC value. Obviously, it is easier for $C_{12-2-16}$ to attain equilibrium with a relatively small amount of added surfactant, while the amount of adsorbed $C_{12-2-16}$ is minute. Although $C_{12-2-12}$ reaches its Q_{emax} at lower C_e compared with C_{12-2-8}, the adsorbed amount seems to occur at higher concentrations in comparison with $C_{12-2-16}$. Therefore, the amount of surfactants in both solid and solution significantly influences their mobilization and immobilization effect on organic contaminant.

Solubilization of naphthalene by Gemini surfactants

As well known, an important property of surfactants is their ability to enhance the solubility of water-insoluble molecules by trapping them in energetically favorable microenvironments which also decides the application of surfactant in soil and water remediation. To better understand the effect of selected Gemini surfactants on the sorption of contaminant in the soil-water system, their solubilization capacity towards naphthalene must be examined.

The apparent water solubility of a solute in surfactant solution has been expressed as (Kile and Chiou 1989):

$$\frac{S_w^*}{S_w} \ = \ 1 \ + \ K_{mn}X_{mn} \ + \ K_{mc}X_{mc} \qquad (3)$$

where S_w^* is the apparent solute solubility at a surfactant total concentration of X; S_w is the intrinsic solute solubility in "pure water"; X_{mn} is the concentration of the surfactant as monomers in water (if $X \leq CMC$, $X_{mn} = X$; if $X > CMC$, $X_{mn} = CMC$); X_{mc} is the concentration of the surfactant as micelle in water ($X_{mc} = X - CMC$); K_{mn} is the partition
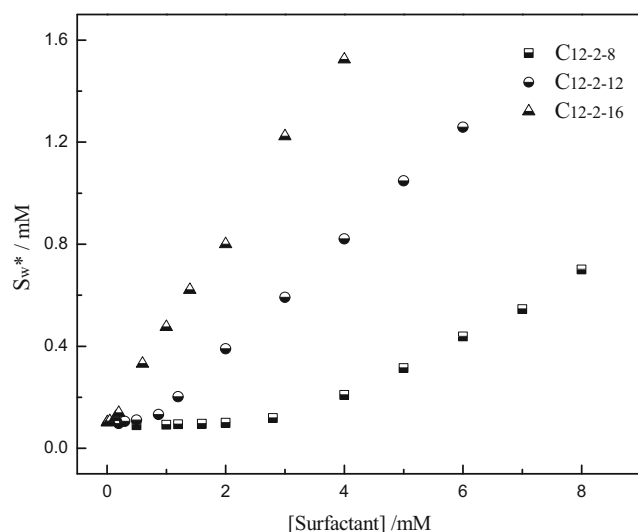
Fig. 2 Water solubility enhancement of naphthalene as a function of the concentration of the selected Gemini surfactants at 25 °C

coefficient of the solute between the surfactant monomer and water; and K_{mc} is the solute partition coefficient between the aqueous micellar phase and water (Kile and Chiou 1989).

Figure 2 shows the apparent solubility of naphthalene in the presence of three selected Gemini surfactants. Clearly, there is little or no solubility enhancement for naphthalene below the CMCs of surfactants because monomers exist in solution under this concentration forming a weak organic environment to facilitate the partition of HOCs. While the obviously increased solubility of naphthalene begins with each Gemini's CMC, respectively, indicating that formed Gemini micelle has strong solubilizing power. The molar solubilization MSR is characterized as the number of moles of compound solubilized by one mole of micellized surfactant. It denotes the effectiveness of a particular surfactant in solubilizing a given solute and can be expressed as follows (Edwards et al. 1991):

$$MSR = \frac{S_{ac} - S_{cmc}}{C_{ac} - CMC} \quad (4)$$

where S_{ac} is the total apparent solubility of solute in given surfactant solution at a specified surfactant concentration C_{ac} (the surfactant concentration above CMC at which S_{ac} is evaluated) and S_{cmc} is the apparent solubility of solute at CMC. In the presence of excess naphthalene, MSR values of three selected Gemini surfactants could be obtained from the slope of

the linear fitted line in which the concentration of solute is plotted against surfactant concentration above the CMC (surfactant concentration in mM vs. phenanthrene concentration in mM) given in Fig. 2. MSR signifies the extent of solubility enhancements for naphthalene at all Gemini surfactant concentrations above their CMCs following the order of $C_{12-2-16}$ > $C_{12-2-12}$ > C_{12-2-8}, which reverse the order of their monomer adsorption abilities. It is interrelated to the hydrocarbon chain length of different Gemini surfactants.

Simultaneously, the micelle-water partition coefficient (K_{mc}, L M^{-1})(Jafvert et al. 1994) also calculated from the S_w and the obtained MSR values using the following formula:

$$K_{mc} = \frac{MSR}{S_w} \quad (5)$$

The calculated K_{mc} of naphthalene by three Gemini surfactants are presented in Table 3. The larger value of K_{mc} indicates that the surfactant has greater tendency to dissolve organic compound in micellar phase. In this study, the $C_{12-2-16}$ micelle possesses the superior solubilization capability compared with other two studied Gemini surfactants as demonstrated by K_{mc} values.

Mobilization and immobilization of naphthalene with Gemini surfactant in soil-water-Gemini surfactant systems

Dependence of the naphthalene concentrations on the total concentration of the selected Gemini surfactants in the mobile phase, e.g., aqueous phase, is presented in Fig. 3, describing the mobility of the naphthalene within the soil-water-Gemini surfactant systems. It is clear that the amount of aqueous naphthalene decreased dramatically with the increasing amount of aqueous surfactant before the surfactants reach their CMCs, respectively. Within this range of surfactant concentrations, the surfactants exist as monomers in solutions which have less solubilization capabilities for solute and easy to adsorb onto solid surface. Therefore, the residual surfactant monomers in solutions have weak interaction with naphthalene compared with increased organic matter formed by sorbed surfactant onto soil particles, which act as strong sorption media for naphthalene.

Along with the added cationic surfactant, new surfactant molecules could be retained by a tail-to-tail interaction

Table 3 Parameters of selected Gemini surfactants and the distribution of PAHs in the presence or absence of Gemini surfactant systems

Surfactant	CMC (mg L^{-1})	Q_{emax} (mg g^{-1})	C_{emax} (mg L^{-1})	K_{mc} (L M^{-1})	K_d^* (mL g^{-1})
C_{12-2-8}	838.01	197.26	1640.72	456.03	491.22
$C_{12-2-12}$	535.37	150.04	1114.14	880.75	380.17
$C_{12-2-16}$	134.13	67.82	177.06	1453.32	275.04

The average errors in the Q_{emax}, C_{emax}, K_{mc}, and K_d^* are ±7.3, ±5.9, ±2.8, and ±8.1 %, respectively
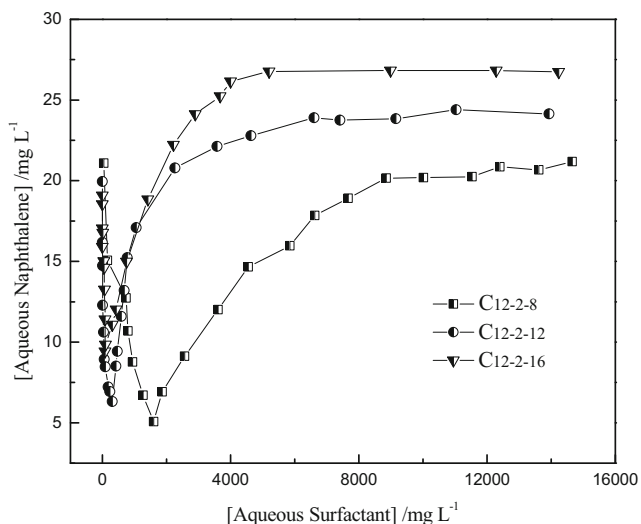
Fig. 3 Amount of naphthalene solubilized as a function of amount of Gemini surfactant in solution

mechanism leading to a more dense coverage named admicelles (Brown and Burris 1996) than the monolayer which has inferior capability to retard contaminant as Fig. 4(a) illustrated. Consequently, the increased added surfactant concentration contributes to high sorbed surfactant concentration resulting in unfavorable mobility of contaminant. As Fig. 4(b) shown, after the CMC, with the increasing added surfactant concentrations, the adsorption reaches saturation and the excess monomers begin to form micelles in the aqueous solution which has powerful solubilization ability towards naphthalene. In couple with the gradually decreased surfactant sorption, thus more naphthalene molecules partition into the micelles within the aqueous phase.

Obviously, the higher CMC values of surfactant, the more amount of surfactant need to improve the mobility of

contaminant. Therefore, the optimized surfactant for desorption of organic compounds should not only have low CMC value but also possess inferior adsorption capability. Among all three selected Gemini surfactant, $C_{12\text{-}2\text{-}16}$ has been determined to be the most effective surfactant to mobilize PAHs due to its powerful solubilizing capability towards solute and the least dosage, which is also indicated by its solubilization data.

As expected, both natural and modified soils displayed sorption of naphthalene from water. Compared with the natural soil, sorption of naphthalene by Gemini-modified soil is noticeably enhanced. The following equation can be employed to describe naphthalene partitioning within the soil-water-Gemini surfactant system(Lee et al. 2000):

$$K_d^* = \frac{K_{oc}f_{oc} + f_{soc}K_{ss}}{1 + K_{mn}X_{mn} + K_{mc}X_{mc}} \qquad (6)$$

where K_d^* is the ratio of sorbed naphthalene to naphthalene in aqueous solution (mL g^{-1}); f_{oc} is the natural organic-carbon fraction (NOC) in the soil (0.0133 g g^{-1}); f_{soc} is the surfactant-derived organic-carbon (SOC) fraction in the soil; K_{oc} and K_{ss} are the carbon-normalized naphthalene distribution coefficient with the NOC and the SOC, respectively (mL g^{-1}); X_{mn} and X_{mc} are the surfactant monomer and micellar concentrations in water, respectively (g L^{-1}); and K_{mn} and K_{mc} are the naphthalene partitioning coefficients with the surfactant monomer and micellar phases, respectively (mL g^{-1}); K_d is the solute sorption coefficient with the soil in absence of surfactant, which equals to $f_{oc}K_{oc}$ in case of $X_{mn}K_{mn} + X_{mc}K_{mc} = 0$ (Zhu et al. 2003). This equation implies competitive interactions of contaminants between total organic matter and aqueous surfactant micelles. Therefore, the potential existing of surfactant with different dosage may either promote or impede remediation

Fig. 4 Schematic sorption and desorption process for Gemini surfactant and naphthalene in soil-water system
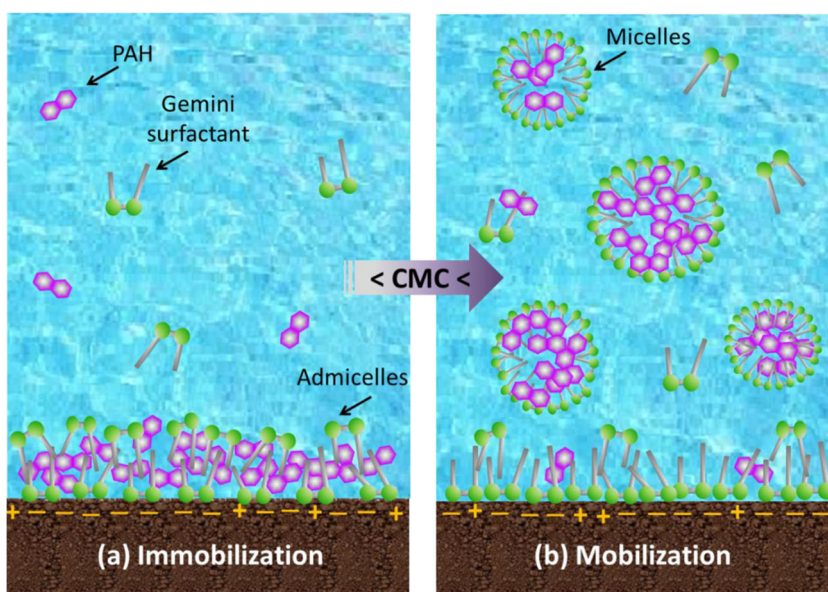
Table 4 Equilibrium Gemini surfactant concentrations and calculated surfactant-derived organic carbon contents (f_{soc}) in soils

$C_{12\text{-}2\text{-}8}$			$C_{12\text{-}2\text{-}12}$			$C_{12\text{-}2\text{-}16}$		
Initial concn, (mM)	Equiv concn, (mM)	f_{soc}, %	Initial concn, (mM)	Equiv concn, (mM)	f_{soc}, %	Initial concn, (mM)	Equiv concn, (mM)	f_{soc}, %
0.415	0.072	1.073	0.255	≈ 0	0.975	0.082	≈ 0	0.335
0.794	0.279	1.611	0.601	0.012	2.192	0.163	≈ 0	0.665
2.332	1.322	3.157	1.096	0.050	3.893	0.232	0.015	0.884
2.660	1.428	3.850	1.362	0.135	4.569	0.271	0.070	0.820
3.844	2.259	4.954	1.782	0.369	5.259	0.547	0.119	1.748
5.825	2.858	9.271	2.203	0.662	5.735	0.705	0.124	2.372
6.589	3.337	10.161	2.706	0.931	6.606	0.992	0.144	3.459
7.976	4.590	10.582	3.021	1.073	7.251	1.423	0.455	3.953
9.768	6.449	10.372	3.300	1.234	7.689	1.643	0.635	4.116

efforts depending on the magnitude of interaction between contaminant and surfactant monomers or micelles.

Based on the surfactant properties, the surfactant-derived organic carbon contents on the solid (f_{soc}) could be calculated as listed in Table 4. After modification, the organic matter content of soil increases dramatically.

The apparent solute soil-water distribution coefficients, K_d^* as a function of Gemini surfactant equilibrium concentration in the aqueous phase are shown in Fig. 5. All systems share a similar sorptive behavior pattern and K_d^* values are significantly affected by the addition of Gemini surfactants demonstrating a strong and nonlinear uptake of naphthalene from water. The amount sorbed by $C_{12\text{-}2\text{-}8}$ modified soil is 1.4–17.3 times of the natural soil, respectively, at original naphthalene concentration of 30 mg L^{-1}. For $C_{12\text{-}2\text{-}12}$, the highest amount sorbed by modified soil is 13.2 times of the natural soil. For $C_{12\text{-}2\text{-}16}$, modified soil sorbed as many as 7.2 times as the natural soil. This is reflected in the dramatic increase in the slopes of isotherms shown in Fig. 5. The increase in K_d^* is obviously caused by the strong sorption of Gemini monomers on soil. These results show that Gemini surfactant-modified soils can be used as good sorbents to sorb naphthalene from water.

Hence, the adsorbed surfactant seemed to create a more hydrophobic environment for the solutes than that created by surfactant micelle in solution. Several explanations have been proposed for this observation. This may result from geometric differences between sorbed and dissolved surfactant aggregate structures (Sun et al. 2009) and the differences in surfactant packing density seem to support this hypothesis. Danzer and Grathwohl (1998) reported that there is a larger hydration layer surrounding the hydrophilic exterior of the micelle, which will become thickness when the surfactant is sorbed to the solid. This might favor the hydrophobic interactions of sorbed surfactant with HOC molecules. Zhu et al. (2003)

also proposed that the conformation of surfactant onto solid may rearrange and have higher packing density corresponding to a more hydrophobic phase for PAHs.

Both the increased extent in K_d^* at lower Gemini surfactant concentration (before CMC) and decreased extent in K_d^* at higher Gemini surfactant concentration (after CMC) appeared to be positively related to the hydrophobic chain length of Gemini surfactant, that is, in the order of $C_{12\text{-}2\text{-}8} < C_{12\text{-}2\text{-}12} < C_{12\text{-}2\text{-}16}$. A possible explanation may be found in the different nature of CMC values. As for $C_{12\text{-}2\text{-}16}$, its minor CMC values make it reach equilibrium saturation at a quite short range.

However, the adsorption of naphthalene onto soil in the presence of Gemini surfactant is ranked as $C_{12\text{-}2\text{-}16} < C_{12\text{-}2\text{-}12} < C_{12\text{-}2\text{-}8}$. The greatest retardation of naphthalene is observed using $C_{12\text{-}2\text{-}8}$ modified soil due partially to the highest organic matter derived from $C_{12\text{-}2\text{-}8}$ and almost 100 % surface
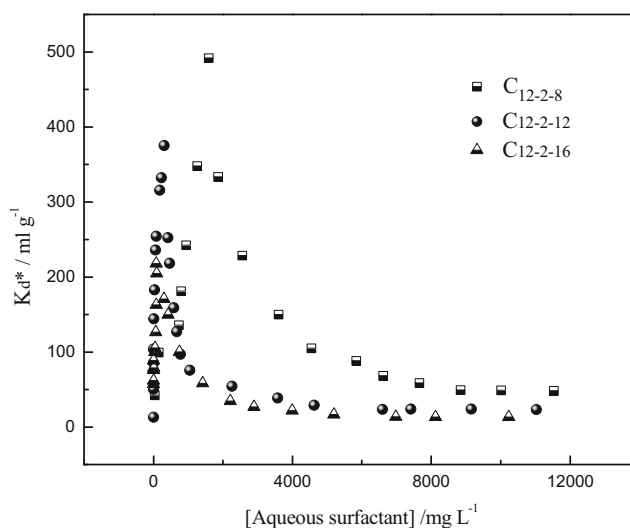

Fig. 5 Apparent partition coefficients of naphthalene in relation to the Gemini surfactants concentration

coverage in the form of a monolayer is formed as demonstrated by displacing 97.99 % soil exchange cations as mentioned before. The more sorbed surfactant, the larger area of monolayer is formed and greater organic matter is obtained. Consequently, more naphthalene molecular can be intercepted by modified soil particles. Correspondingly, the dosage of C_{12-2-8} is as well the highest among them in order to attain elevated immobilization effect. Therefore, although C_{12-2-8} has the greatest immobilization capability for naphthalene, its dosage is the highest among all three studies Gemini surfactants in order to achieve the same retardation goal. Taking all factors into consideration, $C_{12-2-12}$ is the optimized Gemini surfactant for in situ barrier remediation, which is not only has relative high retention ability but also low dosage.

Conclusions

The binding of Gemini surfactant onto soil particles and the distribution of naphthalene between the solid phase and the aqueous phase were investigated. Symmetric and dissymmetric Gemini surfactants with different hydrophobic chain lengths were studied for the purpose of comparison. The presence of all selected cationic Gemini surfactant increased naphthalene retardation, with this increase being dependent upon surfactant CMC and available ion exchange sites on soil. The amount of sorbed naphthalene by selected Gemini surfactant modified soil is 17.3, 13.2, and 7.2 times of the natural soil, decreasing with the increased length of hydrophobic chain of Gemini surfactant. However, due to the results of the solubilization and partition experiment, a conclusion can be formed that the symmetric Gemini surfactant $C_{12-2-12}$ is preferred to form an in situ immobile zone within an aquifer to restrict contaminants due to its relatively high retention ability but also its low dosage. Additional studies would be required when various contaminants are present, since the adsorption and desorption behavior may depend upon the characteristics of organic compounds.

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