



Enhanced soil retention for o-nitroaniline by the addition of a mixture of a cationic surfactant (Cetyl Pyridinium Chloride) and a nonionic surfactant (Polyethylene Glycol Mono-4-nonylphenyl Ether)

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ARTICLE INFO

Article history:

Received 12 January 2010

Received in revised form 22 May 2010

Accepted 23 June 2010

Available online 30 June 2010

Keywords:

o-Nitroaniline

Cationic surfactant

Nonionic surfactant

Sorption

Soil

Clay

ABSTRACT

The sorption enhancement of o-nitroaniline on a soil by the addition of a mixture of a cationic surfactant (Cetyl Pyridinium Chloride, CPC) and a nonionic surfactant (Polyethylene Glycol Mono-4-nonylphenyl Ether, P0707), as compared with that by individual CPC and P0707, was investigated to examine their potential application in soil retarding for organic contaminants. The maximum sorption coefficients (K_d^s) of o-nitroaniline on modified soils by individual CPC and P0707 were 110 mL g^{-1} at an added CPC dose of 6000 mg L^{-1} and 12.5 mL g^{-1} at an added P0707 dose of 7000 mg L^{-1} , respectively. They were approximately 78 and 8.87 times higher than the sorption coefficients (K_d) of o-nitroaniline on the unmodified soil (1.41 mL g^{-1}), suggesting that CPC and P0707 can enhance the sorptive capacity of soil for o-nitroaniline. The maximum K_d^s value of o-nitroaniline on modified soils by the mixture of CPC and P0707 was 144 mg L^{-1} (at CPC dose of $10,500 \text{ mg L}^{-1}$ and P0707 dose of 6000 mg L^{-1}), which is higher than that on the CPC (or P0707) modified soils and approximately 102 times higher than that on the unmodified soil. Therefore, mixed cationic–nonionic surfactants could be better than individual ones in soil modification to enhance retention of organic contaminants.

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1. Introduction

Contamination of soils and groundwater by organic compounds is of wide concerns because most of these compounds are persistent and toxic, and thus resulting in human health risks through bio-accumulation and bio-concentration in the food-chain system. Various physical, chemical, biological, and combined technologies have been developed to deal with the contamination [1–4]. Sorption of organic contaminants by soils is an important way to attenuate their mobility in the soil environment and thus decrease human health risks by decreasing the uptake and accumulation of organic contaminants in plants, microbes and animals [5–7]. Sorption of organic contaminants by soils is also important to avoid groundwater pollution, especially in the vadose zone [5–7].

It has been widely observed that sorption of organic contaminants by soils and clays depend almost exclusively on the solute water solubility [8–10] and the soil organic matter (SOM) content [10–13]. Therefore, it is now apparent that low organic matter soils and clays have little capacity for sorption of organic con-

taminants and thus are ineffective in retarding them, especially for those contaminants with high water solubility. However, the sorptive capacity of low organic matter clays and soils for organic contaminants can be greatly improved by modifying soils with organic cationic surfactants [5–7,14–17]. This simple modification resulted in significantly higher organic matter contents for sorption of organic contaminants. Moreover, the adsorbed surfactants on soils [5–7,14] and clays [15–17] were shown to be an effective organic medium for sorption of organic contaminants. For example, the organic phase derived from exchanged cationic surfactant (i.e., HDTMA) on soils was at least 10 times more effective than natural organic matter for removing organic contaminants from water [14]. It was suggested that such modified soils and clays may be used as clay landfill liners and slurry walls to improve the contaminant retardation and to avoid their dispersion [6]. Nonionic surfactants can also adsorb on soils and clays with a large quantity and act as the effective organic medium for sorption [18–23]. For example, Backhaus et al. [18] and Lee et al. [19,20] observed that the modification with nonionic surfactants can enhance sorption of organic contaminants on montmorillonite. In addition, Zhou and Zhu [23] demonstrated that the addition of nonionic surfactants can enhance the retardation capabilities of soils for polycyclic aromatic hydrocarbons (PAHs).

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A phenomenon unique to surfactants is the aggregation, i.e., the self-assembly of surfactant molecules (monomers) into dynamic clusters called micelle in solution when the surfactant concentration is higher than the critical micelle concentration (CMC) [1]. Surfactant aggregation may also occur at the solid–water interfaces. With increasing surfactant concentrations, surfactant monomers adsorbed on solid surface begin to aggregate and form micelle-like structures called hemi-micelles [1]. Surfactant micelles and hemi-micelles are an effective partition medium which is mainly responsible for the enhanced solubilization of organic contaminants in surfactant solution and for the sorption of organic contaminants by adsorbed surfactants respectively [5–7,14–20,23,24], while the solute partitioning into the surfactant monomers can be largely negligible. In the soil–water system in presence of surfactant, the distribution of organic contaminants is a competing result of sorption of organic contaminants by adsorbed hemi-micellar phase surfactant and solubilization of organic contaminants by micellar phase surfactant [4,14,19,20,23,24]. The following equation has been used to evaluate the apparent soil–water distribution of organic contaminants in presence of surfactant [4,19]:

$$K_d^* = \left(\frac{f_{oc}K_{oc} + f_{sf}K_{sf}}{1 + K_{mn}X_{mn} + K_{mc}X_{mc}} \right) \quad (1)$$

where K_d^* (mL g^{-1}) is the apparent soil–water distribution coefficient in presence of surfactants, which can also be calculated from the compound concentrations in solid phase (K_d^* , $\mu\text{g g}^{-1}$) and the equilibrium concentration of compound in aqueous phase (C_e , mg L^{-1}) with the equation of $K_d^* = C_s^*/C_e$. f_{oc} is the organic carbon content of soil derived from SOM (g g^{-1}); K_{oc} ($K_{oc} = K_d/f_{oc}$) is the f_{oc} normalized solute distribution coefficient between SOM and water (mL g^{-1}). The distribution coefficient of solute between SOM and water in absence of surfactants, K_d (mL g^{-1}), is calculated from the compound concentrations in solid phase (C_s , $\mu\text{g g}^{-1}$) and the equilibrium concentration of compound in aqueous phase (C_e , mg L^{-1}) in absence of surfactants with the equation of $K_d = C_s/C_e$. f_{sf} is the organic carbon content of soil derived from adsorbed surfactants (g g^{-1}); K_{sf} is the f_{sf} normalized solute distribution coefficient between adsorbed surfactants and water (mL g^{-1}). X_{mn} is the concentration of surfactant monomers in water (mg L^{-1}); X_{mc} is the concentration of surfactant micelles in water (mg L^{-1}); K_{mn} is the partition coefficient of a solute between surfactant monomers and water, and K_{mc} is the solute partition coefficient between the aqueous micellar phase and water. $f_{oc}K_{oc}$ and $f_{sf}K_{sf}$ describe the sorption capability of SOM and soil adsorbed surfactants respectively for organic contaminants, while $(1 + K_{mn}X_{mn} + K_{mc}X_{mc})$ describes surfactant solubilization for organic contaminants [4,19]. Prior to micellization ($X_{mn} = X_{mc} = 0$), K_d^* values were seen to increase with increasing surfactant concentrations because the adsorbed surfactant was effective medium for partitioning of organic contaminants while the solute partitioning into the surfactant monomers in solution can largely be negligible.

Though single surfactants can be used to enhance the sorption of low organic matter clays and soils for organic contaminants [5–7,14–20,23,24], no studies have been concerned with investigating the interactive and/or synergistic effect of multiple surfactants on promoting sorption of organic contaminants by soil. Adsorption of cationic surfactants on soils and clays was mainly attributed to the ion-exchange reactions of surfactant cations with soil/clay metal-exchanged cations [5,6,14–16], while adsorption of nonionic surfactants was mainly attributed to hydrogen bonding [21,22,25]. Giving consideration to the different adsorption mechanisms of cationic and nonionic surfactants on soils and clays, cationic and nonionic surfactants can be expected to adsorb on soils and clays simultaneously without sorptive competition and thus to

provide higher organic matter content for sorption. Moreover, in the mixed cationic–nonionic surfactant systems, mixed micelles might form, which may differ significantly from the micelles of individual surfactant and exhibit a number of synergistic advantages over the use of a single surfactant type [26–31]. For example, mixed micelles of cationic–nonionic surfactant mixtures may be more effective for partition of organic contaminants than the micelles of individual surfactants [26–28]. If mixed micelle-like structures (mixed hemi-micelles) formed on soil/clay surface, it can be expected that the organic phase derived from the soil adsorbed mixed hemi-micelles may be more effective for sorption of organic contaminants than the organic phase derived from the adsorbed single surfactant. In other mixed surfactant systems, mixed surfactants might not adsorb on soils and clays simultaneously and thus cannot provide higher organic matter content than single surfactants for sorption because of: (1) the possible sorptive competition of cationic–cationic, nonionic–nonionic or anionic–anionic surfactant mixtures due to the same adsorption mechanisms of them on soils and clays; (2) the precipitation of anionic–cationic surfactant mixtures in solution [1]. For anionic–nonionic surfactant mixtures, they were observed to adsorb on soils and clays less than single ones and thus to enhanced the desorption but not sorption of organic contaminants [4,22]. Therefore, in this study, a cationic surfactant (Cetyl Pyridinium Chloride, CPC), a nonionic surfactant (Polyethylene Glycol Mono-4-nonylphenyl Ether, P0707), and especially their mixtures were employed to examine their influences on the sorption of o-nitroaniline by soil and their capabilities to enhance the retardation of organic contaminants in soils. o-Nitroaniline is an environmentally relevant contaminant, and has been widely found in the effluents from pesticides, dyestuffs, pharmaceuticals, petrochemicals and other industries. Because of its relatively high solubility (1260 mg L^{-1}), o-Nitroaniline is expected to be adsorbed less by soils [8–10] and thus have higher mobility than other organic contaminants such as PAHs.

2. Materials and methods

2.1. Materials

The cationic surfactant, Cetyl Pyridinium Chloride (CPC) with a formula of $\text{C}_{21}\text{H}_{38}\text{ClN}\cdot\text{H}_2\text{O}$ was purchased from China Medicine Group Shanghai Chemical Reagent Corporation. Its average molecular weight, carbon content and CMC are 358 g mol^{-1} , 70.4% and 350 mg L^{-1} , respectively. The CMC value was obtained in this study by measuring the CPC surface tension using a reported method [4]. The nonionic surfactant, Polyethylene Glycol Mono-4-nonylphenyl Ether (P0707) with a formula of $(\text{C}_9\text{H}_{19}\text{C}_6\text{H}_4(\text{CH}_2\text{CH}_2\text{O})_{10}\text{OH})$ was purchased from Tokyo Chemical Industry Corporation. Its average molecular weight, carbon content and CMC are 780 g mol^{-1} , 69.2% and 480 mg L^{-1} [21], respectively. Surfactants were used without further purification. o-Nitroaniline with a purity of +98.5% was purchased from China Medicine (Group) Shanghai Chemical Reagent Corporation. The water solubility, molecular weight, pK_a and octanol–water partition efficient ($\text{Log } K_{ow}$) of o-nitroaniline are 1260 mg L^{-1} , $138.13 \text{ g mol}^{-1}$, -0.29 , and 1.85 , respectively [10]. Soil sample was collected from the 0–10 cm upper layer of the horizon in Hangzhou, air dried and sieved to obtain particles of less than 100 meshes in all experiments. The soil contains 1.43% organic carbon (i.e., 0.0143 g g^{-1}), 47.8% clay, and had a cation-exchange capacity (CEC) of 0.19 mmol g^{-1} . The clays and their relative contents of the soil are montmorillonite (41%), kaolinite (26%), illite (15%) and others (18%). These soil properties were measured using methods described in previous studies [24,32].

2.2. Sorption experiments

Sorption experiments were conducted using duplicate samples by the batch equilibration technique at $25 \pm 1^\circ\text{C}$ in 20 mL glass centrifuge tubes. Two grams of soil was added into 20 mL solutions which contained 400 mg L^{-1} of o-nitroaniline and various concentrations of CPC, P0707 or their mixtures in the tubes. Initial CPC and P0707 concentrations are ranged from 0 to $30,000\text{ mg L}^{-1}$ and 0 to $20,000\text{ mg L}^{-1}$ respectively in both individual and binary surfactant systems. Then, the tubes were sealed and mixed for 24 h to reach apparent equilibrium. After centrifugation ($3000 \times g$ for 20 min), an appropriate aliquot of the supernatant was removed for the analysis of o-nitroaniline concentration by a UV-spectrometer at a wavelength of 420 nm. Three groups of controlled experiments respective to three surfactant systems (i.e., CPC, P0707 and their mixtures) were conducted. In these controlled groups, no o-nitroaniline was added into the solutions, i.e., controlled experiments were conducted by mixing 2 g soil with 20 mL solutions of CPC, P0707 or their mixtures. The supernatant of controlled samples were analyzed at the UV-wavelength of 420 nm as the background concentrations of o-nitroaniline to amend the equilibrium concentrations of o-nitroaniline because surfactants have a little UV-absorbance at wavelength of 420 nm. Experimental uncertainties of o-nitroaniline were evaluated in tubes without sorbents and surfactants, which is less than 4% of the initial o-nitroaniline concentrations. Therefore, adsorbed o-nitroaniline amounts were calculated directly through the mass difference of o-nitroaniline between in the initial and equilibrium solutions.

The supernatant of controlled samples were analyzed at UV-wavelengths of 259 and 275 nm for the equilibrium concentrations of individual CPC and P0707, respectively. In binary systems of CPC and P0707, the dissolving equation group with the dual-wavelength spectrophotometry, expressed by the following equations (Eqs. (2) and (3)), was employed to analyze and calculate the equilibrium concentrations of CPC and P0707 in the supernatant of controlled samples:

$$A_{\text{CPC}} = \varepsilon_{\text{cpc}1} C_{\text{cpc}} + \varepsilon_{\text{P0707}1} C_{\text{P0707}} \quad (2)$$

$$A_{\text{P0707}} = \varepsilon_{\text{cpc}2} C_{\text{cpc}} + \varepsilon_{\text{P0707}2} C_{\text{P0707}} \quad (3)$$

where A_{CPC} and A_{P0707} are the absorbance of CPC and P0707 at the wavelengths of 259 and 275 nm, respectively; $\varepsilon_{\text{cpc}1}$ and $\varepsilon_{\text{P0707}1}$ are the mole absorbance ratios of CPC and P0707 respectively at the wavelength of 259 nm; $\varepsilon_{\text{cpc}2}$, $\varepsilon_{\text{P0707}2}$ are the molar absorbance ratios of CPC and P0707 respectively at the wavelength of 275 nm; C_{cpc} and C_{P0707} are the equilibrium concentrations of CPC and P0707, respectively. The adsorbed amounts of CPC and P0707 were calculated by the difference from initial and equilibrium surfactant concentrations.

3. Results and discussion

3.1. Sorption of o-nitroaniline by soil in presence of individual CPC and P0707

The measured sorption coefficients (K_d^*) of o-nitroaniline by soil in presence of individual CPC and P0707 are shown in Figs. 1 and 2, respectively. In absence of surfactants, the measured sorption coefficient (K_d) of o-nitroaniline by soil was approximately 1.41 mL g^{-1} . According to the organic carbon content (f_{oc}) derived from SOM, $f_{oc} = 1.43\%$, the normalized sorption coefficient (K_{oc} , $K_{oc} = K_d/f_{oc}$) was 98.6 mL g^{-1} .

With the addition of CPC, sorption coefficients (K_d^*) of o-nitroaniline increased dramatically and then reached a plateau at an approximate CPC dose of 6000 mg L^{-1} (Fig. 1). When the added dose of CPC was higher than an approximate value of $21,000\text{ mg L}^{-1}$,

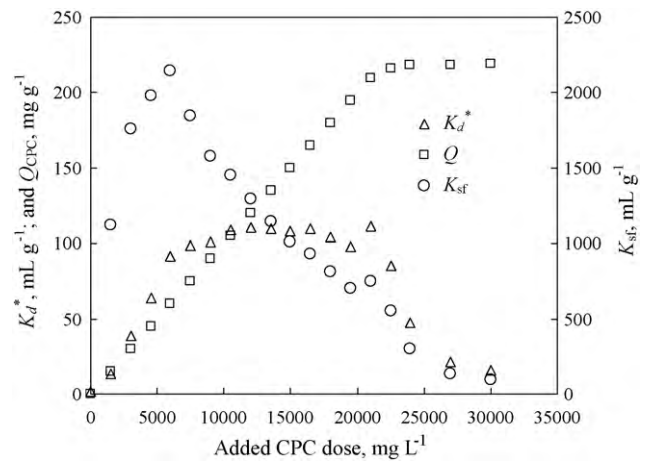


Fig. 1. The measured apparent sorption coefficients (K_d^*), adsorbed CPC amounts (Q_{CPC}), surfactant carbon content normalized sorption coefficients (K_{sf}) of o-nitroaniline versus the added CPC dose.

K_d^* values decreased steeply (Fig. 1). The plateau K_d^* value for o-nitroaniline in presence of CPC was approximately 110 mL g^{-1} (Fig. 1), which is 78 times higher than that of soil (1.41 mL g^{-1}), suggesting that CPC can be used to modify soils to enhance their retardation capabilities for organic contaminants. The dramatic increase of K_d^* by CPC at added CPC dose below 6000 mg L^{-1} could be attributed to both of the CPC adsorption on soils and the partitioning of o-nitroaniline into the soil adsorbed CPC. The surfactant carbon content normalized sorption coefficients (K_{sf}), $K_{\text{sf}} = (K_d^* - K_d)/f_{\text{sf}}$ and $f_{\text{sf}} = Q \times 70.4\%/1000\text{ g g}^{-1}$, is a parameter to describe the partition abilities of adsorbed surfactants for organic compounds, where Q is the adsorbed surfactant amounts (mg g^{-1}). With the added CPC dose increased to 6000 mg L^{-1} , the adsorbed CPC amounts (Q_{CPC}) and K_{sf} increased to 60 mg g^{-1} and 2140 mL g^{-1} , respectively (Fig. 1). K_{sf} reached the maximum value of 2140 mL g^{-1} at the added CPC dose of 6000 mg L^{-1} , and then decreased when more CPC were added (Fig. 1). The maximum partition ability of adsorbed CPC ($K_{\text{sf}} = 2140\text{ mL g}^{-1}$) was 21.7 times higher than the partition ability of soil organic matter ($K_{oc} = 98.6\text{ mL g}^{-1}$). In the added dose range of CPC from 6000 to $21,000\text{ mg L}^{-1}$, however, the adsorbed CPC amounts (Q_{CPC}) increased continually from 60 mg g^{-1} to reach a plateau value of 216 mg g^{-1} while the K_d^* values were in a plateau of 110 mL g^{-1} (Fig. 1). Therefore, the additional adsorbed CPC at added CPC dose above 6000 mg L^{-1} is not an effective medium for o-nitroaniline partition, which results in

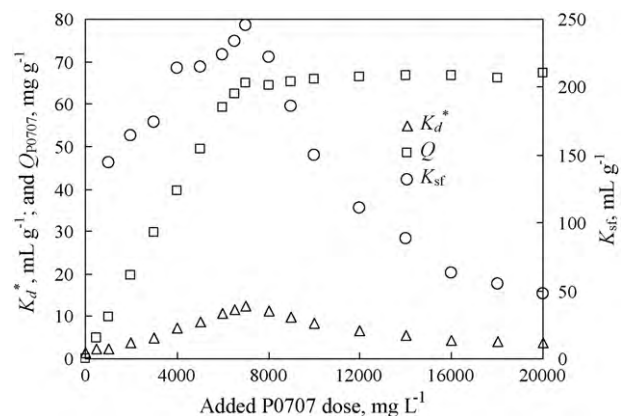


Fig. 2. The measured apparent sorption coefficients (K_d^*), adsorbed P0707 amounts (Q_{P0707}), surfactant carbon content normalized sorption coefficients (K_{sf}) of o-nitroaniline versus the added P0707 dose.

the dramatic decrease of calculated K_{sf} values (Fig. 1). It has been observed that cationic surfactants prefer to adsorption on soils and clays with the ion-exchange reactions of surfactant cations with soil/clay metal-exchanged cations [5,6,14–16]. According to the soil CEC value of 0.19 mmol g^{-1} , the adsorbed CPC amounts (i.e., $60 \text{ mg g}^{-1} = 0.17 \text{ mmol g}^{-1}$) at added CPC dose of 6000 mg L^{-1} , could be mainly attributed to the ion-exchange reactions of CPC cations with soil exchanged cations. Additional adsorption of CPC on soil at added CPC dose above 6000 mg L^{-1} could be attributed to other mechanisms such as hydrophobic effects [14–17]. At the added CPC dose of $21,000 \text{ mg L}^{-1}$, the measured equilibrium concentration of CPC in solution was 40 mg L^{-1} , which is lower than the CMC value (350 mg L^{-1}) of CPC. At the added CPC dose of $22,500 \text{ mg L}^{-1}$, however, the measured equilibrium concentration of CPC in solution was 863 mg L^{-1} , which is higher than the CMC value of CPC, indicating that CPC micelles are formed in solution. At the added CPC dose above $22,500 \text{ mg L}^{-1}$, therefore, significant partitioning of *o*-nitroaniline into aqueous CPC micelles may occur [4,19], which can remain *o*-nitroaniline in surfactant solution and is responsible for the steep decrease in K_d^* values as well as K_{sf} values (Fig. 1).

With the addition of P0707, both K_d^* and K_{sf} of *o*-nitroaniline increased dramatically to reach a maximum value at an approximate P0707 dose of 7000 mg L^{-1} , and then decreased steeply when more P0707 were added (Fig. 2). The maximum K_d^* value was 12.5 mL g^{-1} , which is 8.87 times higher than that in absence of surfactants (1.41 mL g^{-1}). Thus, P0707 can also be used to modify soils to enhance their retardation capabilities for organic pollutants. However, this enhancement by P0707 was lower than that by CPC (the maximum $K_d^* = 110 \text{ mL g}^{-1}$), which could be mainly attributed to the lower K_{sf} values of adsorbed P0707 ($<244 \text{ mL g}^{-1}$) than that of adsorbed CPC for *o*-nitroaniline (Figs. 1 and 2). Adsorbed amounts of P0707 (Q_{P0707}) on soil increased dramatically to reach a plateau value of 65 mg g^{-1} at the approximate P0707 dose of 7000 mg L^{-1} , too (Fig. 2). At the added P0707 dose of 7000 mg L^{-1} , the measured equilibrium concentration of P0707 in solution was 498 mg L^{-1} , which is slightly higher than the CMC value (480 mg L^{-1}) of P0707, indicating that P0707 micelles begin to form in solution. At the added P0707 dose below 7000 mg L^{-1} , therefore, the increase in K_d^* values could be attributed to the adsorption of P0707 on soil and the consequently significant partitioning of *o*-nitroaniline into soil adsorbed P0707. At the added P0707 dose above 7000 mg L^{-1} , however, significant partitioning of *o*-nitroaniline into aqueous P0707 micelles may occur [4,19], which may remain *o*-nitroaniline in surfactant solution and is responsible for the steep decrease in K_d^* values.

3.2. Sorption of *o*-nitroaniline by soil in presence of the mixture of CPC and P0707

The measured sorption coefficients (K_d^*) of *o*-nitroaniline onto soil in presence of the mixture of CPC and P0707 are shown in Fig. 3. In this system containing the mixture of CPC and P0707, K_d^* values of *o*-nitroaniline increased clearly with the added CPC dose to reach a maximum value at the added dose of $10,500 \text{ mg L}^{-1}$ and then decreased at the added dose above $10,500 \text{ mg L}^{-1}$. At an added dose of CPC below $15,000 \text{ mg L}^{-1}$, K_d^* values of *o*-nitroaniline also increased with the added P0707 dose to reach a maximum value and then decreased if more P0707 was added. However, at an added dose of CPC above $15,000 \text{ mg L}^{-1}$, the added P0707 continually decreased the K_d^* values of *o*-nitroaniline. As described in equation 1, the decrease of K_d^* values of *o*-nitroaniline could be attributed to the forming of mixed micelles in solution, which remains *o*-nitroaniline in solution by solubilization [26–28]. The maximum K_d^* value of *o*-nitroaniline is approximately 144 mL g^{-1} ,

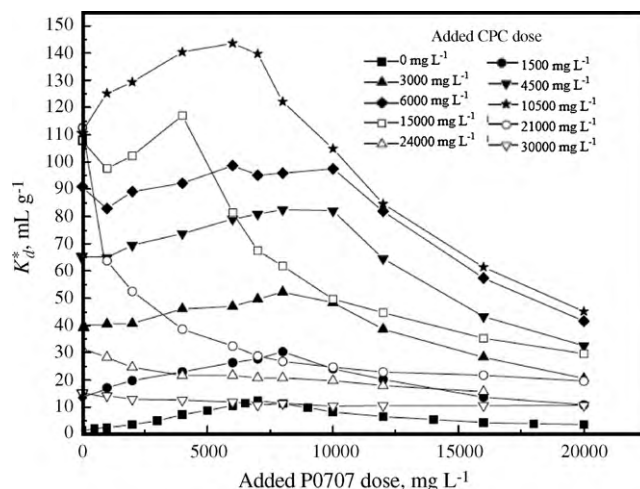


Fig. 3. The measured sorption coefficients (K_d^*) of *o*-nitroaniline by soil in presence of the mixture of CPC and P0707.

which is appeared at the added P0707 and CPC dose of 6000 and $10,500 \text{ mg L}^{-1}$ respectively (Fig. 3). This maximum K_d^* value is 102 times higher compared to that of *o*-nitroaniline onto soil in absence of surfactants (1.41 mL g^{-1}). It is also higher than the observed maximum K_d^* values of *o*-nitroaniline in presence of individual CPC ($K_d^* = 110 \text{ mL g}^{-1}$) and P0707 ($K_d^* = 12.5 \text{ mL g}^{-1}$). Therefore, the mixture of P0707 and CPC can be added (as better alternative than individual P0707 and CPC) into soils to enhance soil retardation capabilities for organic pollutants.

According to equation 1, the higher soil retardation capabilities (identified by the K_d^* value) for *o*-nitroaniline by the mixture of P0707 and CPC than that by the individual ones, as an example at the added P0707 and CPC dose of 6000 and $10,500 \text{ mg L}^{-1}$, respectively, could possibly be a result of (i) a higher f_{sf} value for the mixture of P0707 and CPC than the individual ones (i.e., the adsorbed amounts of the mixture of P0707 and CPC onto soil are more than that of the individual ones), or (ii) a higher K_{sf} value for the mixture of P0707 and CPC than the individual ones, i.e., the partitioning ability, described by the K_{sf} value, of adsorbed surfactants on the soil is higher for the mixture of P0707 and CPC compared to the individual ones, or (iii) both of them. At both added CPC dose below $10,500 \text{ mg L}^{-1}$ and P0707 dose below 6000 mg L^{-1} , CPC and P0707 did not change their adsorption on soil each other (Figs. 4 and 5), i.e., CPC and P0707 can adsorb on soil simultaneously without sorptive competition in mixed CPC and P0707 system to result in more

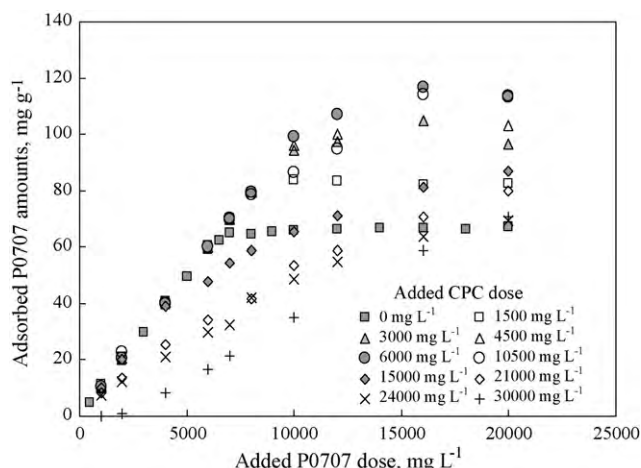


Fig. 4. Adsorbed P0707 amounts versus added P0707 dose in presence of CPC.

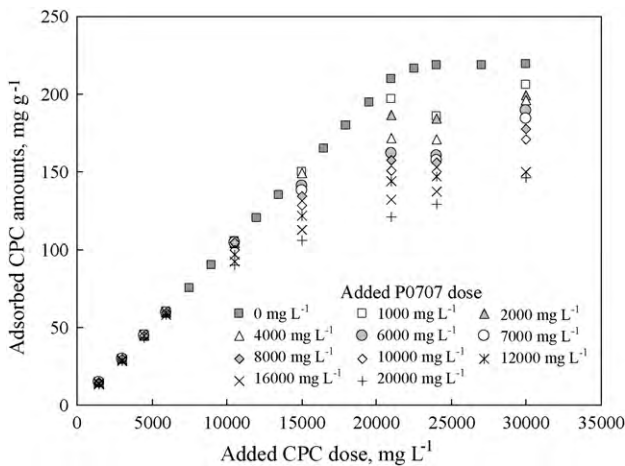


Fig. 5. Adsorbed CPC amounts versus added CPC dose in presence of P0707.

adsorbed surfactants and higher f_{sf} value for the mixture of P0707 and CPC than the individual ones. Therefore, higher f_{sf} value for the mixture of P0707 and CPC on soil should be an explanation for its higher ability to retard o-nitroaniline in soil as compared with that of individual P0707 and CPC. For example, at the added CPC dose of 10,500 mg L⁻¹, the increase of K_{sf} with added P0707 dose below 6000 mg L⁻¹ can be at least partly attributed to the increase of f_{sf} derived from soil adsorbed P0707 amounts (Fig. 6). No sorptive competition of CPC and P0707 adsorbed on soil in mixed system, at the added dose of CPC and P0707 below 10,500 and 6000 mg L⁻¹ respectively, could be attributed to their different adsorption mechanisms (i.e., ion-exchange reactions for cationic surfactants, while hydrogen bond interactions for nonionic surfactants) [5,6,14,15,21,22,25]. The sum of K_{sf} values of o-nitroaniline at added CPC dose below 10,500 mg L⁻¹ and P0707 dose below 6000 mg L⁻¹ in individual surfactant system (Figs. 1 and 2) can be employed to represent the ideal K_{sf} values of o-nitroaniline in the binary surfactant system since CPC and P0707 did not change their adsorption on soil each other in these dose ranges of CPC and P0707 (Figs. 4 and 5). In binary surfactant system, the measured K_{sf} values of o-nitroaniline onto soil are higher than the ideal K_{sf} values if the added CPC and P0707 dose are below 10,500 and 6000 mg L⁻¹ respectively. The measured and ideal K_{sf} values of o-nitroaniline in binary surfactant system at the added CPC dose of

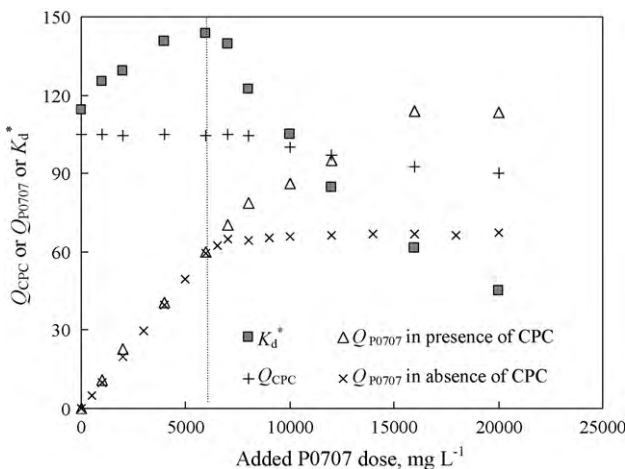


Fig. 6. The measured K_d^* (mL g⁻¹) values of o-nitroaniline as well as adsorbed CPC amounts (Q_{CPC} , mg g⁻¹) and P0707 amounts (Q_{P0707} , mg g⁻¹) versus the added P0707 dose at the added CPC dose of 10,500 mg L⁻¹.

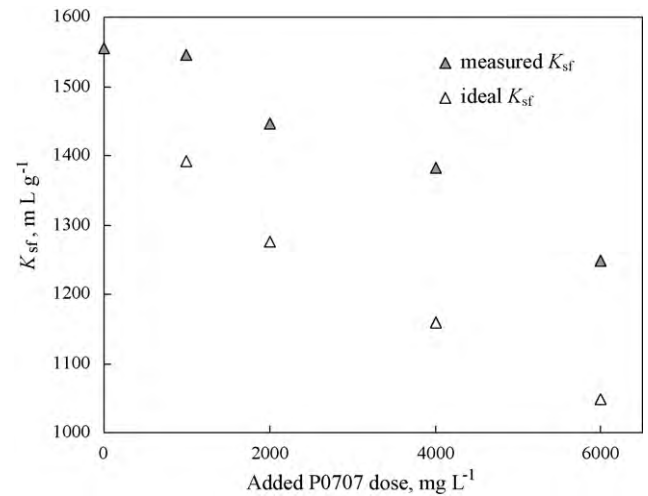


Fig. 7. The measured and ideal K_{sf} values of o-nitroaniline versus the added P0707 dose below 6000 mg L⁻¹ at the added CPC dose of 10,500 mg L⁻¹.

10,500 mg L⁻¹ and P0707 dose below 6000 mg L⁻¹, as an example, are showing this deviation of measured K_{sf} values from the ideal ones clearly (Fig. 7). Therefore, higher partitioning ability and K_{sf} value of the adsorbed mixture of P0707 and CPC on soil than that of the adsorbed individual ones should be the additional explanation for the higher o-nitroaniline retardation in soil by the mixture of P0707 and CPC. The deviation of measured K_{sf} values from the ideal ones for the mixture of P0707 and CPC can be interpreted by the formation of mixed micelle-like structures (mixed hemi-micelles) of adsorbed mixture of CPC and P0707 on soil surface because (i) mixed micelles of cationic–nonionic surfactant mixtures are more effective for partition of organic contaminants than the micelles of individual surfactants [26–28] and (ii) mixed micelles differ significantly from the micelles of individual surfactant and generally exhibit synergistic advantages (i.e., deviations of measured values of property parameters of mixed surfactants from their ideal ones) over the use of a single surfactant type [26–31].

At the added dose above 10,500 mg L⁻¹, CPC decreased the P0707 adsorption on soil (Fig. 4). Meanwhile, CPC adsorption at the added CPC dose above 10,500 mg L⁻¹ was decreased by the added P0707 (Fig. 5). The decreased adsorption of both CPC and P0707 on soil at the added CPC dose above 10,500 mg L⁻¹ and the subsequent decrease of f_{sf} value, as described in equation 1, are therefore responsible for the decrease of K_d^* value of o-nitroaniline at the added CPC dose above 10,500 mg L⁻¹ (Fig. 3). At the added CPC dose below 10,500 mg L⁻¹ and P0707 dose above 6000 mg L⁻¹, CPC increased the P0707 adsorption on soil (Figs. 4 and 6), while P0707 did not change the adsorption of CPC (Figs. 5 and 6). Therefore, the f_{sf} value should be increased due to the increased adsorption of P0707. However, K_d^* value of o-nitroaniline decreased with the added P0707 dose (Figs. 3 and 6). A possible reason for these phenomena, as described in Eq. (1), is that micelles or mixed micelles formed in solution to enhance the solubilization of o-nitroaniline and remain o-nitroaniline in solution due to the partition of o-nitroaniline into micelles [4,19].

3.3. Environmental application of mixed cationic–nonionic surfactants in soil modification to enhance soil retardation capabilities for organic pollutants

The higher soil retardation capabilities for o-nitroaniline by the mixture of P0707 and CPC than that by the individual ones, observed and discussed in above, give an encouragement for the application of mixed cationic–nonionic surfactants in soil modifica-

tion to enhance retention of organic contaminants in soils. Several aspects that need more detailed investigations should be emphasized for their potential applications in soil modification. Firstly, the added dose of mixed surfactants should be optimized for both soil and surfactant specifics because (i) adsorption amounts of surfactants on soils depend on the structural and composition properties of both soil and surfactant and (ii) over dose of surfactants added into soil can decrease the soil retention of organic contaminants due to the solubilization as observed in this study (Figs. 3 and 6). Adsorption of nonionic surfactants by soils depends on both the types and contents of soil/sediment clay minerals following a type order of montmorillonite > organic carbon > illite > 1.4 nm minerals (vermiculite + chlorite + 1.4 nm intergrade mineral) » kaolinite [32]. Adsorption of cationic surfactants by soils/sediments also depends on both the types and contents of soil/sediment clay minerals because clay minerals have different cation-exchange capacities for cationic surfactant adsorption [5,6,14–16]. Soils containing more clay minerals with 2:1 structure such as montmorillonite generally have high adsorption for both cationic and nonionic surfactants [5,6,16,32], and thus, may be modified well with mixed cationic–nonionic surfactants to enhance retention of organic contaminants. Moreover, both of cationic and nonionic surfactants with longer aliphatic chains have more adsorption on soils/clays and higher partition ability for organic contaminants [1,5,6,15,21,25], and thus, should be better alternatives than their analogues for the application in soil modification. In addition to the optimization of the added dose of mixed surfactants, the designing and selection of surfactants for their applications in soil modification to enhance retention of organic contaminants should be environmentally friendly to avoid the possible environmental risks of surfactants themselves [1,2,4,22]. Biosurfactants might be the environmentally friendly ones for designing and selection in application of soil modification [1].

4. Conclusions

In this study, it was observed that both CPC and P0707 can enhance the sorptive capacity of soil for o-nitroaniline. The partition abilities of adsorbed surfactants for o-nitroaniline depend on the adsorbed amounts of surfactants. Mixed cationic–nonionic surfactants may be applied in soil modification to enhance retention of organic contaminants. The maximum enhancement of o-nitroaniline sorption by the mixture of CPC and P0707 is approximately 102 times relative to that of soil in absence of surfactants, and higher than that of single CPC (78 times) and P0707 (8.87 times). The higher enhancement of the mixture of CPC and P0707 for soil retardation capabilities for o-nitroaniline, compared to that of individual ones, could be attributed to (1) more surfactants adsorbed on soil for partition of o-nitroaniline because CPC and P0707 adsorb on soil simultaneously in the mixed surfactant system, and (2) higher partition ability of adsorbed mixture of CPC and P0707 for o-nitroaniline sorption because of the formation of mixed micelle-like structures (mixed hemi-micelles) of the adsorbed mixture of CPC and P0707 on soil surface. In addition, the designing and selection of surfactants for their applications in soil modification to enhance retention of organic contaminants should be environmentally friendly and with an optimization of their added dose for both soil and surfactant specifics.

Acknowledgements

This work was in part supported by National Science Foundation of China (20737002, 40973065 and 20777065), the Program for New Century Excellent Talents in University of China (NCET-08-493), and Zhejiang Provincial Natural Science Foundation of China (Z507093).

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