Solubilization and adsorption behaviors of 2,4,6-trichlorophenol in the presence of surfactants

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HIGHLIGHTS

- The solubility of 2,4,6-trichlorophenol was enhanced 72 times by sodium deoxycholate at pH 7.5.
- NaDC demonstrated the best solubilization potential, followed by NaC, SDS and β -CD.
- The adsorption of 2,4,6-trichlorophenol was almost zero when NaC concentration was above CMC₂.

ARTICLE INFO

Article history:

Received 12 April 2013

Received in revised form 15 June 2013

Accepted 17 June 2013

Available online 28 June 2013

Keywords:

Solubilization

Adsorption

Surfactant

Sodium deoxycholate

2,4,6-Trichlorophenol

Soil remediation

ABSTRACT

The solubilization of 2,4,6-trichlorophenol (2,4,6-TCP) was studied in the presence of four different surfactants, namely sodium deoxycholate (NaDC), sodium cholate (NaC), sodium lauryl sulfate (SDS) and β -cyclodextrin (β -CD). The solubility of 2,4,6-TCP was enhanced a maximum of 72 times especially by NaDC at pH 7.5. In addition, other than great solubilization capacities, NaDC and NaC have the advantages of high biodegradability and biocompatibility as biosurfactants. The adsorption behaviors of 2,4,6-TCP on the surface of soil in the presence of these solubilizers were examined. The results showed that the adsorption isotherms for all studied surfactants matched the Henry adsorption isotherm well. The adsorption mechanisms were explored and the adsorption behaviors of 2,4,6-TCP were affected by different micelle forms of the surfactants based on their critical micelle concentration (CMC). The adsorption process was demonstrated by a redistribution procedure between surfactants in solution and surfactants adsorbed onto the soil surface. In particular, the adsorption of 2,4,6-TCP was almost zero when NaC concentration was above CMC₂. The results of our study have important implications for soil remediation and non-point source pollution control.

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1. Introduction

The contamination of soils and groundwater by toxic and/or hazardous organic compounds has become a widespread environmental problem, therefore the removal of hydrophobic organic compounds (HOCs) from them has received serious consideration [1,2]. In response to a growing need to address environmental contamination, many remediation technologies have been developed to treat soil [3,4]. Surfactant-enhanced soil remediation (SESR) has long been known as the most effective and promising technique for the removal of hydrophobic pollutants from soil and water [5–8]. The selection of suitable surfactants to be employed in soil washing is a very important task for the successful application of SESR technology [9–11].

There have been many published studies in the literature on the solubilization behaviors of surfactants [12–14]. It has been well

known that surfactants can remediate soils by solubilizing HOCs and then enhancing the desorption of HOCs from soils [15,16]. Even so, some research has indicated that the surfactants would also adsorb onto the soil matrix and thereby lead to HOCs partitioning into the immobilised adsorbed surfactants [17–20]. This would result in a rebound in HOCs adsorption capacity onto the soil [2]. Solubilization of HOCs into surfactant aggregates adsorbed on solid surfaces is sometimes referred to as “adsolubilization” [21]. Obviously, it is very important to find a suitable surfactant which has minimal adsorption onto the soil as well as an effective ability for solubilization.

To make the technology feasible and economical, the surfactant must be safe and effective. While traditional surfactants have the problems of low biodegradability and generation of toxic degradation products, they will also have certain detrimental effects on humans and animals [22]. Recently, biosurfactants have gained more attention compared to synthetic surfactants due to the environmentally compatible nature of those compounds [17]. Biosurfactants can be as effective as the highly used synthetic surfactants,

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and at the same time have some distinct advantages over synthetic surfactants, including high specificity, biodegradability and biocompatibility [22].

Initially in this research, sodium deoxycholate (NaDC) and sodium cholate (NaC) were chosen as representatives of biosurfactants. The solubilization capacities of NaDC and NaC were compared with β -cyclodextrin (β -CD) and Sodium Dodecyl Sulfate (SDS), two frequently used synthetic surfactants. Then, the adsorption behaviors of 2,4,6-trichlorophenol (2,4,6-TCP) in the presence of NaDC, NaC and SDS were studied. Third, to the best of our knowledge, little research had taken the CMC of surfactants into consideration during the adsorption experiments. Therefore, the effects of different micellar forms on adsorption behaviors were also studied, and the possible adsorption mechanisms were discussed. The objectives of this study were to find safe and efficient solubilizers to remove 2,4,6-TCP, a widespread environmental contaminant, from soils [23]. Meanwhile, the effects of different micellar forms on the adsorption behaviors were explored and the optimum concentration for each surfactant was discussed.

2. Materials and methods

2.1. Materials

2,4,6-TCP (98%), NaC (98%), NaDC (98%), β -CD (98%) and SDS ($\geq 99\%$) were purchased from the Aladdin chemical company. The chemical properties of the selected surfactants are shown in Table 1 (including Refs. [24–26]). The soil was stored in brown reagent bottles after sieving (200-mesh). Some characteristics of the soil are summarized in Table 2.

2.2. Methods

Solubilization studies were conducted by adding an excess amount of 2,4,6-TCP in 10 mL solution, with the initial concentration of surfactants spanned over a wide range of values below and above its CMC (0–100 mmol/L for NaDC, NaC and SDS, 0–10 mmol/L for β -CD due to the restriction of its own solubility). After 1-h heating in a water bath (at a temperature of 80 °C), the 2,4,6-TCP was dissolved to saturation. The bottles were put in a rotary shaker for 12 h at room temperature (15 °C) so that the excess dissolved

Table 2

Properties of soil sample.

Parameter	Soil sample
Specific surface area (m^2/g)	0.0031
Particle size (μm)	71.445
Iso-electric point	Around pH 10.5
X-ray fluorescence analysis (top 10)	O (48.1%), Si (25.2%), Al (8.87%), Fe (8.80%), S (3.93%), K (2.93%), Mg (0.639%), Ti (0.521%), Ca (0.326%), Na (0.209%)

2,4,6-TCP precipitated. Afterwards, samples were centrifuged at 8000 rpm for 10 min, and the supernatants were diluted 10 times to the range of the marking line. The detection was analyzed by high performance liquid chromatography (HPLC) and UV spectrophotometry as appropriate to the surfactant added. The HPLC analyses were performed isocratically using a mobile phase of 70% methanol, 1% glacial acetic acid and 29% water at a flow rate of 1.5 mL/min. The UV detection wavelength was 280 nm and the sample injection volume was 20 μL . Different pH effects were also explored in this solubilization research (pHs were adjusted by the addition of small amounts of dilute HCl and NaOH).

Adsorption studies were conducted by placing a constant ratio of soil (1 g/L) in 50 mL mixed solution at room temperature, with the concentration of 2,4,6-TCP varied from 0 to 200 mg/L. The concentration of surfactants varied according to their CMCs. The bottles were put in a shaker for 2.5 h to reach the adsorption equilibrium (preliminary experiments revealed that 2.5 h is long enough to reach equilibrium). The detection method was the same as above. Parallel tests were conducted in all cases with appropriate blanks.

3. Results and discussion

3.1. Solubilization of 2,4,6-TCP in the presence of NaDC, NaC, SDS and β -CD

3.1.1. Apparent solubility of 2,4,6-TCP in the presence of NaDC, NaC, SDS and β -CD

The solubilization potential of NaDC, NaC, SDS and β -CD was evaluated with 2,4,6-TCP at various pHs. Surfactants are

Table 1
Properties of surfactants used in this study.

Surfactant	Molecular formula	MW	Molecular structure	CMC (mM)	Refs.
NaDC	$\text{C}_{24}\text{H}_{39}\text{NaO}_4$	414.56		2.3 (CMC ₁) 6.1 (CMC ₂)	[24]
NaC	$\text{C}_{24}\text{H}_{39}\text{NaO}_5$	430.56		6.1 (CMC ₁) 12.3 (CMC ₂)	[24]
β -CD	$\text{C}_{42}\text{H}_{70}\text{O}_{35}$	1134.98		104–116	[25]
SDS	$\text{NaC}_{12}\text{H}_{25}\text{SO}_4$	288.38		8.2	[26]

amphiphilic compounds containing both hydrophilic head groups and hydrophobic tail groups [27]. The enhanced solubilization effects of surfactants for HOCs is usually used as an index in evaluating the capabilities of surfactants in removing HOCs from contaminated soils [1].

Fig. 1 compared the solubilization capacities of four studied surfactants. Symbols are experimental data with error bars expressing the standard deviations. According to Fig. 1, for all studied surfactants and pHs, the solubility of 2,4,6-TCP increased with increasing surfactant concentration in a linear pattern. Relevant solubilization of HOCs occurs when the CMC of surfactant is reached and the solubilization becomes proportional to the surfactant concentration above the CMC [9,28,29]. This phenomenon is called a “partition-like” interaction between the HOCs and the non-polar group of the dilute surfactant [7,30]. The result that the equilibrium of 2,4,6-TCP apparent solubility was increased in proportion to the surfactant concentrations was consistent with the research of Huang and Lee [27]. This article explained that surfactant monomers had the ability, related to the hydrophobicity of HOCs, to enhance aqueous concentrations. According to the research of Hofmann, the micelle of bile salts provides an amphipathic region in which water-insoluble substances can dissolve. The hydrophobic side of bile salts is believed to be adsorbed to HOCs, and the hydrophilic side of the bile acid faces outward, thus increases the solubility of HOCs [31]. However, there were some distinctions in the changing trend. For NaDC, the solubilization capacity was first increased then decreased with the increase in pH value, and the maximum solubility of 2,4,6-TCP was 42775.93 mg/L at the optimal pH 7.5. According to the research of Sobotka, the gelation of deoxycholic acid was observed between pH 6.4 and 7.8. The occurrence of gel at pH 7 and 7.5 may increase the solubility of 2,4,6-TCP, therefore the solubilization capacity of NaDC decreased at pH 8. However, no gelation is observed in the case of cholic acid

[32]. For NaC, The solubility of 2,4,6-TCP was generally showing a upward trend with the increase in pH value, and the maximum solubility of 2,4,6-TCP was 33585.36 mg/L at the optimal pH 8.0. The solubility of 2,4,6-TCP in the presence of NaDC and NaC depends on the pH. At pH 7, solubility of 2,4,6-TCP in the presence of NaC < solubility in the presence of NaDC, while at pH 8, solubility of 2,4,6-TCP in the presence of NaC > solubility in the presence of NaDC.

As to SDS, the solubility showed a descending trend with the increase in pH value. One possible explanation was that as the pH went up, more electrolyte was added to the solution, and these hydroxyl ions would reduce the electrical repulsion in the micelle as well as the thickness of the ionic layer surrounding the head-group [27]. This would reduce the size of the micelles, thus leading to a reduction of included 2,4,6-TCP, so that the solubility decreased.

On the other hand, the solubilization capacity of SDS was considerable, while the solubilization capacity of β -CD was not obvious. According to the results of a previous study [33], the molar efficiency of the surfactants was lower than that of the cyclodextrins. It was explained that surfactant-enhanced solubilization was based on the formation of micelles, while cyclodextrin-enhanced solubilization was based on one-to-one inclusion complexes. However, this result was contrary to ours, which showed that the efficiency of the surfactants was higher than that of β -CD. This was probably because the size of 2,4,6-TCP was bigger than the cavity of β -CD, therefore, it is hard for 2,4,6-TCP to enter the cavity. As a result, β -CD cannot significantly increase the solubility of 2,4,6-TCP.

3.1.2. Molar solubilization ratio (MSR) of NaDC, NaC, SDS and β -CD

MSR is an index often used to evaluate the effectiveness of a surfactant in solubilizing a given solute, and it was obtained in this study by the method of Edwards et al. [34].

Fig. 1. The solubilization of 2,4,6-TCP in the presence of surfactants at various pHs. (a) NaDC, (b) NaC, (c) SDS, (d) β -CD.

$$\text{MSR} = (S_{\text{mic}} - S_{\text{cmc}}) / (C_{\text{surf}} - \text{CMC}) \quad (1)$$

where S_{cmc} is the apparent solubility of 2,4,6-TCP in moles per liter at the CMC; S_{mic} is the total apparent solubility of 2,4,6-TCP in moles per liter in micellar solutions at a particular surfactant concentration greater than the CMC; and C_{surf} is the surfactant concentration at which S_{mic} is evaluated. The MSR can be obtained from the slope of the solubility curve above the critical micelle concentration [2].

The MSR values were obtained from slopes in Fig. 1 based on Eq. (1), and the maximum solubility and MSR value of studied surfactants were summarized in Table 3. We can conclude that the trends in MSR values were consistent with the trends in solubility changes at various pHs. The maximum MSR values for the studied surfactants were 428 ± 20 for NaDC at pH 7.5, 308 ± 3.2 for NaC at pH 8.0, 249 ± 8.5 for SDS at pH 7.0 and 18.1 ± 0.13 for β -CD at pH 7.0. From the MSR point of view, NaDC appeared to be the most efficient surfactant to increase the solubility of 2,4,6-TCP, followed by NaC and SDS, while the solubilization effect of β -CD was not obvious.

3.1.3. Micellar partition coefficient (K_{mic}) of 2,4,6-TCP in the presence of NaDC, NaC, SDS and β -CD

Solubilization of HOCs in surfactant micelles can be seen as an allocation process, and we can use K_{mic} to estimate the concentration of 2,4,6-TCP distributed into the micellar phase. It can be calculated with Eq. (2) by the method of Kile and Chiou [7]:

$$S_w^*/S_w = 1 + C_{\text{mn}}K_{\text{mn}} + C_{\text{mc}}K_{\text{mc}} \quad (2)$$

where S_w^* is the apparent solute solubility at the total stoichiometric surfactant concentration of C , S_w is the intrinsic solubility in “pure water”, C_{mn} is the concentration of the surfactant as monomers, and C_{mc} is the concentration of the surfactant in micellar form. The K_{mn} term is the partition constant of the solute between monomers and water and the K_{mc} term is the corresponding partition constant of the solute between micelles and water.

For a certain solute-surfactant system, when the surfactant concentration is above CMC, $C_{\text{mn}} = \text{CMC}$ and $C_{\text{mc}} = C_{\text{surf}} - \text{CMC}$, Eq. (2) can be simplified as:

$$S_w^*/S_w = C_{\text{surf}}K_{\text{mc}} + C_1 \quad (3)$$

where C_{surf} is the surfactant concentration at which S_{mic} is evaluated, and $C_1 = 1 + (K_{\text{mn}} - K_{\text{mc}}) \text{CMC}$, is a constant. K_{mc} can be

obtained from the slope of the solubilization multiples (S_w^*/S_w) curve above the CMC.

As to the calculation of NaDC and NaC, according to the research of Matsuoka and Moroi [24], there are three stages of micellization of sodium bile salts. As the concentration increases: monomer, primary aggregates and secondary aggregates of almost constant properties occur. Correspondingly, the first CMC (CMC_1) was defined as the critical micelle concentration at which primary aggregates begin to form, and the second CMC (CMC_2) was defined as the critical micelle concentration at which secondary aggregates begin to form [35–37]. Therefore, Eq. (2) could be modified into:

$$S_w^*/S_w = 1 + C_{\text{mn}}K_{\text{mn}} + C_{\text{mc1}}K_{\text{mc1}} + C_{\text{mc2}}K_{\text{mc2}} \quad (4)$$

where S_w^* is the apparent solute solubility at the total stoichiometric surfactant concentration of C , S_w is the intrinsic solubility in “pure water”, C_{mn} is the monomer concentration of surfactant, C_{mc1} is the primary aggregate concentration of surfactant, C_{mc2} is the secondary aggregate concentration of surfactant, K_{mn} is the partition constant of the solute between monomers and water, K_{mc1} is the partition constant of the solute between primary aggregates and water, K_{mc2} is the partition constant of the solute between secondary aggregates and water.

When the surfactant concentration is above CMC_2 , $C_{\text{mn}} = \text{CMC}_1$, $C_{\text{mc1}} = \text{CMC}_2 - \text{CMC}_1$, $C_{\text{mc2}} = C_{\text{surf}} - \text{CMC}_2$. Eq. (4) can be simplified as:

$$S_w^*/S_w = C_{\text{surf}}K_{\text{mc2}} + C_2 \quad (5)$$

where $C_2 = 1 + \text{CMC}_1 (K_{\text{mn}} - K_{\text{mc1}}) + \text{CMC}_2 (K_{\text{mc1}} - K_{\text{mc2}})$, is a constant. In this way, the K_{mc2} can be obtained from the slope of the solubilization multiples (S_w^*/S_w) curve above the critical micelle concentration.

Fig. 2 shows the S_w^*/S_w of 2,4,6-TCP at various pHs in the presence of surfactants. The values of K_{mic} (For SDS and β -CD, $K_{\text{mic}} = -K_{\text{mc}}$; For NaDC and NaC, $K_{\text{mic}} = K_{\text{mc2}}$) were calculated by Eqs. (2–5) and were obtained from slopes in Fig. 2. Obviously, the changing trends of S_w^*/S_w of 2,4,6-TCP were consistent with the trends of solubility of 2,4,6-TCP (Fig. 1). First, the S_w^*/S_w of 2,4,6-TCP increased linearly with increasing surfactant concentration for all pHs. Secondly, the S_w^*/S_w of 2,4,6-TCP was affected by the pH of the solution.

The solubilization multiples and K_{mic} of four surfactants are summarized in Table 4. For NaDC, the optimum pH was 7.5, and the maximum S_w^*/S_w was 71.63 in the presence of 100 mmol/L NaDC. For NaC, the optimum pH was 6.5, and the maximum S_w^*/S_w was 7.42 in the presence of 100 mmol/L NaC. For SDS, the optimum pH was 7.0, and the maximum S_w^*/S_w was 59.94 in presence of 100 mmol/L SDS. For β -CD, the optimum pH was 7.0, and the maximum S_w^*/S_w was 1.24 in presence of 10 mmol/L β -CD. The maximum K_{mic} values for the studied surfactants were 0.72 in the presence of NaDC at pH 7.5, 0.07 in the presence of NaC at pH 6.5, 0.60 in the presence of SDS at pH 7.0 and 0.02 in the presence of β -CD at pH 7.0. From the K_{mic} point of view, NaDC was the most efficient surfactant to increase the solubility of 2,4,6-TCP, followed by SDS and NaC, while the solubilization effect of β -CD was not obvious.

3.1.4. The effect of 2,4,6-TCP dissociation on solubilization

In principle, a given weak acid HA dissociates as follows in solution:

The acid dissociation constant K_a is given as follows:

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad (6)$$

Table 3
Maximum solubility and MSR values of 2,4,6-TCP in the presence of NaDC, NaC, SDS and β -CD.

Component	pH	S_{max}^a (mg/L)	MSR ^b	r^2 of MSR
NaDC	7.0	3.35×10^4	326 ± 11	0.996
	7.5	4.28×10^4	428 ± 20	0.994
	8.0	1.39×10^4	132 ± 0.41	0.992
NaC	6.0	7.41×10^2	6.62 ± 0.10	0.922
	6.5	3.71×10^3	33.7 ± 0.64	0.951
	7.0	1.09×10^4	88.1 ± 0.34	0.968
	8.0	3.36×10^4	308 ± 3.2	0.970
SDS	7.0	2.48×10^4	249 ± 8.5	0.998
	7.5	2.33×10^4	232 ± 4.4	0.995
	8.0	1.87×10^4	192 ± 1.6	0.987
β -CD	7.0	9.23×10^2	18.1 ± 0.13	0.901
	7.5	6.43×10^2	8.50 ± 0.27	0.941
	8.0	4.32×10^2	4.83 ± 0.68	0.878

^a S_{max} – maximum solubility (in the presence of maximum concentration of surfactants. 0–100 mmol/L for NaDC, NaC and SDS. 0–10 mmol/L for β -CD due to the restriction of its own solubility).

^b MSR – molar solubilization ratio.

Fig. 2. The solubilization multiples (S_w^*/S_w) of 2,4,6-TCP in the presence of surfactants at various pHs. (a) NaDC, (b) NaC, (c) SDS, (d) β -CD.

Table 4
Solubilization multiples (S_w^*/S_w) and K_{mic} of NaDC, NaC, SDS and β -CD.

Component	NaDC			NaC			SDS			β-CD			
pH	7.0	7.5	8.0	6.0	6.5	7.0	8.0	7.0	7.5	8.0	7.0	7.5	8.0
S_w^*/S_w^a	53.34	71.63	42.22	3.71	7.42	5.27	5.24	59.94	59.30	48.40	1.24	1.16	1.15
K_{mic}^b	0.52	0.72	0.40	0.03	0.07	0.04	0.05	0.60	0.59	0.50	0.02	0.02	0.01

^a S_w^*/S_w – solubilization multiples (in the presence of maximum surfactant concentrations. 0–100 mmol/L for NaDC, NaC and SDS. 0–10 mmol/L for β -CD due to the restriction of its own solubility).

^b K_{mic} – micelle–water partition coefficient (for SDS and β -CD, $K_{mic} = K_{mc}$; for NaDC and NaC, $K_{mic} = K_{mc2}$).

where $[H^+]$, $[A^-]$ and $[HA]$ are the equilibrium concentrations of H^+ , A^- and HA , respectively.

Assuming the total solubility is C_0 and the dissociation concentration is C_1 , the correlation of pK_a and pH can be easily reduced as follows:

$$pK_a = pH + \lg \frac{[HA]}{[A^-]} = pH + \lg \frac{C_0 - C_1}{C_1} \quad (7)$$

Dissociation rate δ can be calculated as:

$$\delta = C_1/C_0 = \frac{1}{10^{pK_a - pH} + 1} \quad (8)$$

According to the Report on Carcinogens, Twelfth Edition (2011) [38], the dissociation constant (pK_a) of 2,4,6-TCP is 6.23 at 25 °C. Therefore, δ is a constant at any particular pH. The calculation predicts that $\delta = 37.06\%$, 65.06% , 85.48% and 98.33% at pHs 6, 6.5, 7 and 8, respectively.

For any straight line in Fig. 1, the apparent solubilities of random two points, A and B, are a_0 and b_0 , and the dissociation concentrations of these two points at this very moment are a_1 and b_1 , respectively.

According to Eq. (8), $a_1/a_0 = C$, $b_1/b_0 = C$ (C is a constant).

$$S/S_0 = \frac{b_0 - b_1}{a_0 - a_1} = \frac{b_0 - b_0C}{a_0 - a_0C} = \frac{b_0}{a_0} \quad (9)$$

where S is the apparent solute solubility of 2,4,6-TCP at point B, S_0 is the apparent solute solubility of 2,4,6-TCP at point A. We can conclude that in the investigated pH range, the dissociation of 2,4,6-TCP increased with increasing pH, but the dissociation did not make any difference to the results of the solubilization multiple.

3.2. Sorption behaviors of 2,4,6-TCP onto the soil in the presence of NaDC, NaC and SDS

3.2.1. Sorption isotherms of 2,4,6-TCP in the presence of NaDC, NaC and SDS

The adsorption of 2,4,6-TCP onto the soil was evaluated in the presence of NaDC, NaC and SDS since they all have relatively good solubilization capacities. Fig. 3 shows the 2,4,6-TCP adsorption isotherms in the presence of surfactants at various concentrations. Symbols are experimental data with error bars expressing the standard deviations. According to Fig. 3a, the adsorption isotherm in

Fig. 3. Adsorption isotherm of 2,4,6-TCP in the presence of surfactant. (a) NaDC, (b) NaC, (c) SDS.

the presence of NaDC matched the Henry adsorption isotherm well. When the added NaDC concentration was 1 mmol/L, which was below CMC_1 , there was a substantial decline in the adsorption capacity. However, as more NaDC was added to the solution, 5 mmol/L for example, which was between CMC_1 and CMC_2 of NaDC, the adsorption capacity began to increase again. Once the added concentration of NaDC was more than CMC_2 , 10 mmol/L for example, the adsorption capacity of soil towards 2,4,6-TCP would increase to even higher levels than that in pure water. Thus, in order to remove 2,4,6-TCP to the maximum extent, the concentration of NaDC should be controlled below CMC_1 .

Fig. 3b shows the 2,4,6-TCP adsorption isotherm in the presence of NaC at various concentrations. There was a slight difference in the variation of adsorption capacity compared with NaDC. When the concentration was under CMC_1 , the adsorption capacity declined quickly. Then, as more NaC was added (between CMC_1 and CMC_2), the adsorption capacity began to increase again. At this

point, the adsorption capacity was close to the initial adsorption in pure water. The most notable phenomenon was that when the added concentration of NaC exceeded CMC_2 , the adsorption of 2,4,6-TCP dropped sharply to almost zero. Under these conditions, we can remove the contaminants in the soil completely.

Since the influence of NaDC or NaC on solubilization capacities of 2,4,6-TCP is different, it is possible that the influence of NaDC or NaC on the adsorption behavior of soil towards 2,4,6-TCP is different. It may be due to the difference in the structure of NaDC and NaC. According to the research of Sobotka, both sides of the molecule are spiked with methyl or hydroxyl groups in NaC, while in NaDC the “lower” side of the molecule has an unbroken frontage of methylene groups. Because the “lower” side of the molecule allows unhindered van der Waals attraction, this specific structure of NaDC results in the occurrence of gel. However, no gelation is observed in the case of NaC [32].

Fig. 3c shows the adsorption isotherm of 2,4,6-TCP in the presence of SDS at various concentrations. As for SDS, there is only one CMC and the situation is much simpler. Compared with the adsorption of 2,4,6-TCP in pure water, when the added SDS concentration was below the CMC (e.g. 5 mmol/L), the maximum adsorption declined slightly. When the added SDS concentration was above the CMC (e.g. 10 mmol/L), the adsorption capacity had a small rebound. However, neither of these concentrations made a huge reduction and the adsorption capacity remained at a high level.

3.2.2. Solubilization mechanism in the presence of surfactants

The adsorption process of 2,4,6-TCP in surfactant micelles can be seen as an allocation process [7], and the adsorption mechanism of 2,4,6-TCP in the presence of NaDC and NaC described above can be explained by Fig. 4. When no NaDC was added to the solution, there was a good deal of 2,4,6-TCP adsorbed onto the soil surface (Fig. 4a). When 1 mmol/L NaDC was added to the solution, since the added concentration was below CMC_1 , NaDC in the solution existed in monomeric form. 2,4,6-TCP began to redistribute between the soil surface and the NaDC monomers. The result was that 2,4,6-TCP was more inclined to be allocated in the solution, as shown in Fig. 4b. Therefore, the adsorption capacity of soil towards 2,4,6-TCP declined. As more NaDC was added to the solution, 5 mmol/L for example, between CMC_1 and CMC_2 , NaDC began to form primary aggregates, as shown in Fig. 4c. These small aggregates would cover the hydrophobic 2,4,6-TCP which would be inside the aggregate and therefore dissolved in the solution, further increasing the quantity of dissolved 2,4,6-TCP. However, as the primary aggregates adsorbed on the soil matrix, it would lead to 2,4,6-TCP partitioning into immobile adsorbed surfactants [17], so that the adsorption capacity had a small rebound. Once the added concentration of NaDC exceeded CMC_2 , the quantity of 2,4,6-TCP adsorbed onto the soil surface would increase substantially, as shown in Fig. 4d. This was because secondary aggregates began to form in the solution, and as the secondary aggregates adsorbed onto the soil matrix, the adsorption capacity increased further. This result was consistent with a previous study [39], where they observed that at low concentrations, surfactants are not likely to increase contaminant partitioning into the soil phase. However, the soil-water partition coefficient of the contaminant increased at higher nonionic surfactant doses.

In the case of NaC, the variation of adsorption capacity was similar with NaDC below CMC_2 (Fig. 4e–g). When the added concentration of NaC was below CMC_1 , the adsorption capacity decreased as 2,4,6-TCP redistributed into the solution. When the added concentration of NaC was between CMC_1 and CMC_2 , the adsorption capacity began to increase again and the adsorption capacity reached a relatively high level, as shown in Fig. 4g. In this case, it can be understood as there were two kinds of NaC micelles. One was the micelle phase dissolved in solution, and the other was

Fig. 4. Schematic diagram for the adsorption mechanism of 2,4,6-TCP in the presence of NaDC and NaC.

adsorbed on the soil surface. The latter would result in increased 2,4,6-TCP adsorption onto soil until 2,4,6-TCP solubilization by the micelle phase surfactant successfully competed with increased 2,4,6-TCP sorption onto surfactant-modified soil [2]. HOCs distributed between the mobile and immobile phases varied with surfactant dose due to competition between adsorbed and micelle phase surfactant [20]. In the case of Fig. 4g, since the concentration of primary aggregates in the solution was relatively low, the 2,4,6-TCP was more inclined to associate with the micelles adsorbed onto the soil surface, which led to a rebound in adsorption capacity. Then, with the increasing of NaC concentration, the micelle concentration increased. Once the NaC concentration exceeded CMC_2 , secondary aggregates began to appear. In the case of Fig. 4h, the concentration of NaC micelles was so large that almost all of the 2,4,6-TCP was redistributed into the solution and the quantity of 2,4,6-TCP adsorbed onto the soil surface was almost zero.

The adsorption mechanism of SDS can be explained as follows: When the added concentration of SDS was below CMC, some of the 2,4,6-TCP adsorbed onto the soil surface was desorbed and distributed into the monomers in solution, which led to a decrease in the adsorption capacity. Then, when the added concentration of SDS was above CMC, as more micelles were adsorbed on the soil surface, there was a small rebound in the adsorption capacity.

4. Conclusions

NaDC demonstrated the highest solubilization potential, followed by NaC, SDS and β -CD. The optimum pH for NaDC, NaC, SDS and β -CD were 7.5, 8, 7 and 7, respectively. The solubility of 2,4,6-TCP was enhanced a maximum of 72 times by NaDC at pH 7.5.

The adsorption behavior of 2,4,6-TCP was affected by the types of surfactant and its existing forms. The distinctions in adsorption behaviors in the presence of surfactants can be attributed to the

redistribution of 2,4,6-TCP between the micellar phase surfactant and the adsorbed surfactant. Compared with traditional surfactants, NaDC and NaC are more environmental friendly due to the superiority of biodegradability. Both of them can be used as outstanding surfactants for surfactant enhanced soil remediation.

Acknowledgement

This work is supported by Program for New Century Excellent Talents in University, Ministry of Education, China (NCET-12-0429).

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