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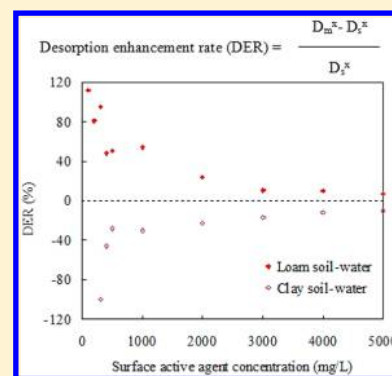
Enhanced Solubilization and Desorption of Organochlorine Pesticides (OCPs) from Soil by Oil-Swollen Micelles Formed with a Nonionic Surfactant

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S Supporting Information

ABSTRACT: The effect of oil-swollen micelles formed with nonionic surfactant polyoxyethylene sorbitan monooleate (Tween 80), cosurfactant 1-pentanol, and linseed oil on the solubilization and desorption of organochlorine pesticides (OCPs) including DDT and γ -HCH from both loam soil and clay soil were investigated. Results showed that the solubilizing capacities of oil-swollen micelles were dependent on the critical micelle concentration (CMC) of Tween 80. Once the concentrations of oil-swollen micelles exceeded the CMC of Tween 80, the oil-swollen micelles exhibited much higher solubilizing capacity than empty Tween 80 micelles for the two OCPs. Desorption tests revealed that oil-swollen micelles could successfully enhance desorption of OCPs from both loam soil and clay soil. However, compared with the efficiencies achieved by empty Tween 80 micelles, oil-swollen micelles exhibited their superiority to desorb OCPs only in loam soil–water system while was less effective in clay soil–water system. Distribution of Tween 80, 1-pentanol and linseed oil in soil–water system revealed that the difference in the sorption behavior of linseed oil onto the two soils is responsible for the different effects of oil-swollen micelles on the desorption of OCPs in loam soil and clay soil systems. Therefore, oil-swollen micelles formed with nonionic surfactant Tween 80 are better candidates over empty micelle counterparts to desorb OCPs from soil with relatively lower sorption capacity for oil fraction, which may consequently enhance the availability of OCPs in soil environment during remediation processes of contaminated soil.



INTRODUCTION

The contamination of soils and sediments by organochlorine pesticides (OCPs) is an environmental concern due to high chronic toxicity of OCPs to both animals and humans.^{1,2} Most of the OCPs are strongly and long-lastingly sorbed to soils and sediments, making them unavailable for the remediation processes.³ Nevertheless, surfactants can act as an agent for the remediation of OCPs contaminated soils through either surfactant-aided soil washing or surfactant-enhanced biodegradation because they could enhance the water solubility and mobility of OCPs in soil environment and thus increase their desorption or biodegradation efficiency.^{4–6}

Surfactants are present as dispersed molecules (monomers) at low concentrations, while above their critical micelle concentration (CMC) the monomers aggregate in solution to form micelles consisting of a hydrophobic core and a hydrophilic shell.^{7–11} Hence, in a soil–water–surfactant system, molecules of hydrophobic organic compounds (HOCs) exist mainly in the following forms: solubilized in surfactant micelles, dissolved in the surrounding solution, sorbed directly on the soil particles, or sorbed in association with sorbed surfactants.¹² The solubilizing capacities of surfactant micelles and the amounts of sorbed surfactants are the two major factors influencing desorption of HOCs from soil particles during surfactants-aided remediation processes.^{9,10,13}

Thus, the efficacy of surfactants-aided remediation might be increased through either increasing the hydrophobicity of surfactant micelles cores to enhance the solubilizing capacities of surfactant micelles, or decreasing the sorption loss of surfactant molecules onto soil particles to lower the interaction of HOCs with sorbed surfactants. Cheng and Wong¹⁴ indeed found that the desorption of phenanthrene and pyrene from soil by polyoxyethylene sorbitan monooleate (Tween 80) can be enhanced by the addition of dissolved organic matter (DOM) derived from pig manure compost and pig manure probably due to the formation of surfactant–DOM complex. Besides, Chu and Kwan¹⁵ found that solvent (acetone/triethylamine)-incorporated surfactant micelles could improve the performance of conventional soil-washing. All these results have illuminated that increasing the hydrophobicity of surfactant micelle core is a feasible approach to enhance the performance of surfactant in surfactant-aided remediation processes. However, few researchers studied this issue and more effective ways of enhancing the hydrophobicity of surfactant micelle cores warrant further study.

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Micelles of surfactant usually solubilize only tiny amount of oil molecules until a pure oil core is formed. After that, additional oil molecules will stay in the oil phase because no longer energy is gained due to the vanishing entropy of mixing between the oil molecules and the surfactant tails.^{11,16,17} However, an enhanced solubilization of oil is possible in the presence of cosurfactant. The cosurfactant molecules provide additional entropy of mixing and additional stabilizing area between the surfactant tails and oil molecules, both effects allowing further growth of the oil-swollen micelles that have more hydrophobic cores than empty micelles.^{17–21} Therefore, the oil-swollen micelles formed with the aid of cosurfactant can provide us with a new approach to increase the hydrophobicity of surfactant micelles. Previous researchers have revealed that some oil-swollen micelles, also called as oil-in-water (O/W) microemulsions, can be used as emulsifying agents for some hydrophobic organic pollutants in soil washing,^{22–24} and both the oil solubilized in the core and the cosurfactants in the interface between the surfactant tails and oil molecules can provide solubilizing spaces for hydrophobic compounds.^{25,26} However, the influence of soil properties on the solubilization or desorption of HOCs from contaminated soils by oil-swollen micelles consisting of surfactant, cosurfactant and oil, is still unclear, although it is revealed that the sorption of surfactants onto soil particles is particle-size dependent.^{9,10} Besides, very little information is available on the sorption of cosurfactant and oil onto soil particles and the consequential influence on remediation processes of contaminated soils by oil-swollen micelles.

Previous studies have found that nonionic surfactants are more suitable for soil remediation than either anionic or cationic surfactants,^{8,9,14} since anionic surfactants could be precipitated with divalent cations in soil^{9,27} while cationic surfactants can be sorbed onto soil due to their positive charges.^{10,28} Therefore, the aims of the present study are to (1) investigate the solubilization of OCPs including dichlorodiphenyl-trichloroethane (DDT) and gamma-hexachlorocyclohexane (γ -HCH), which are extremely stable in the environment and hard to be degraded,^{4–6} in oil-swollen micelles formed with nonionic surfactant Tween 80, cosurfactant 1-pentanol and linseed oil; (2) study the effect of oil-swollen micelles on the mass transfer of OCPs from two different soil matrices, loam soil and clay soil, and compare their efficiency with that of empty micelle counterparts; and (3) elucidate the effect of surfactant, cosurfactant and oil on the transfer of OCPs by oil-swollen micelles in soil–water systems.

MATERIALS AND METHODS

Chemicals. Polyoxyethylene sorbitan monooleate (Tween 80) was the nonionic surfactant used in this study because of its ability in forming oil-swollen micelles, or called oil-in-water microemulsions, with 1-pentanol (cosurfactant) and linseed oil (oil phase) as studied previously,²⁹ and linseed oil is the most widely used vegetable oil in industry while 1-pentanol is extensively used together with surfactants in soil flushing.^{24,29} Tween 80 (purity >98%) was purchased from Sigma Chemical Co.. 1-pentanol (purity >98%) and linseed oil were obtained from Fluka Chemical Co. and Sigma Chemical Co., respectively, and used without any further purification. *n*-Hexane and acetone were obtained as analytical grade solvent. Double deionized water was used for all tests. Two organochlorine pesticides, dichloro-diphenyl-trichloroethane (DDT) and gamma-hexachlorocyclohexane (γ -HCH), were purchased

from Sigma Chemical Co. (both 99% pure) and their representative physicochemical properties can be found in our previous publication.²⁹

Preparation of DDT/ γ -HCH Contaminated Soils. A loam soil and a clay soil collected from two abandoned farmlands in the New Territories, Hong Kong were air-dried at ambient temperature (25–28 °C) for two weeks. The physicochemical properties of the soils were determined according to standard methods³⁰ and listed in the Supporting Information (SI) Table S1. The soils used in the subsequent experiments were passed through a 1 mm sieve in order to improve the homogeneity of the soils. DDT and γ -HCH were dissolved in acetone and then separately spiked into the two soils to obtain two loam soils contaminated with 50 mg/kg of DDT or γ -HCH, and two clay soils contaminated with 50 mg/kg of DDT or γ -HCH. These artificially contaminated soils were then stirred vigorously for 30 min to promote homogeneous distribution of pesticide. The acetone in the mixture was allowed to evaporate for one week at 30 °C under a fume hood, and the contaminated soils were aged for 2 month at room temperature before desorption experiments. The concentrations of DDT and γ -HCH in the spiked soils were redetermined after 2-month aging period to reveal their real concentrations.

Preparation of Oil-Swollen Micelles and Solubilization

Tests. First, 3.33 g of 1-pentanol serving as a cosurfactant was mixed with 10 g of Tween 80 at a cosurfactant to surfactant ratio (C/S ratio) of 1:3 (w/w) to form the surfactant/cosurfactant phase, which was then mixed with 1 g of linseed oil according to the oil to surfactant ratio (O/S ratio) of 1:10 (w/w) to obtain oil-in-water microemulsion precursors containing surfactant, cosurfactant and oil.²⁹ The precursors were subsequently diluted with distilled water to obtain oil-swollen micelles formed with various concentrations of surfactants, and all these procedures were preformed at 25 °C. For the various oil-swollen micelles obtained, the C/S ratio and O/S ratio were always 1:3 (w/w) and 1:10 (w/w), respectively. Thus, the surface active agent concentration in oil-swollen micelle, or called oil-swollen micelle concentration, herein below is termed as total weight of Tween 80, 1-pentanol, and linseed oil present, while the surface active agent concentration in empty micelle, or called empty micelle concentration, means the concentration of Tween 80 in the solution because of the absence of 1-pentanol and linseed oil.

An appropriate amount of DDT or γ -HCH dissolved in acetone was carefully added to the bottom of 20-mL glass vials, and the amount of added DDT or γ -HCH was well in excess of its aqueous saturation. After the acetone was evaporated, 10 mL of oil-swollen micelles or surfactant solution (or called empty micelles) prepared as described before were added into each vial. Duplicate tests were prepared for each treatment. These vials were capped with aluminum-lined caps and were shaken on a rotary shaker at 250 rpm at 25 °C for an equilibration period of 96 h as determined from a preliminary study. After equilibrium was reached, the samples were filtered through a glass column packed with glass wool to remove any undissolved DDT or γ -HCH particles. A 1 mL aliquot of the filtered solution was then carefully withdrawn with a volumetric pipet and extracted in *n*-hexane and the concentration of DDT or γ -HCH was determined using an Agilent Gas Chromatography 7890 equipped with a Nickel 63 electron capture detector (μ ECD) and a HP-5 column (30 m \times 0.25 mm ID, 0.25 μ m film thickness). An injection volume of 1 μ L was used (splitless

injection) and the injector temperature was maintained at 220 °C. The oven temperature was programmed to increase from 100 to 180 °C at 15 °C/min, held for 1 min, increased to 270 °C at 10 °C/min, and then held for 5 min. The ECD was maintained at 300 °C, and nitrogen was used as makeup gas at 60 mL/min.

Batch Desorption Study. Desorption of DDT or γ -HCH in soil–water systems was performed in 20-mL glass vials. 0.5 g of either loam soil spiked with DDT or γ -HCH or clay soil spiked with the two pesticides was added to each vial. Ten mL of empty micelles or oil-swollen micelles covering a wide range of concentrations from 10 to 5000 mg/L were added to the vials. 0.02% of NaN_3 was added to the mixture as a microbial growth inhibitor.⁹ The samples were shaken on a rotary shaker at 250 rpm under dark at 25 °C. After an equilibration period of 96 h as determined from a preliminary study, duplicate samples were sacrificially collected, centrifuged for 5 min at 3000g, and then filtered through 0.22 μm glass fiber filter paper to separate the aqueous phase from the soil particles. DDT and γ -HCH in the aqueous phase was extracted and quantified using GC/ECD as described previously. The concentrations of Tween 80, 1-pentanol, and linseed oil in the aqueous phase were also determined to reveal their distribution in soil–water systems. Tween 80 concentration in the filtrate was determined using Waters model 2690 chromatographic system (Milford, MA). Separation of Tween 80 from bulk solution was achieved at ambient temperature using a Waters MS column (50 \times 2.1 mm internal diameter) packed with a 3.5- μm octadecyl stationary phase, and protected by a stainless steel guard. The mobile phase used for the chromatographic separation was composed of acetonitrile/water (70/30, v/v) and delivered isocratically at a flow rate of 0.25 mL/min. The column effluent was monitored using a Micromass Quattro LC tripe-quadrupole MS detector equipped with an electrospray interface. The samples were analyzed using an electrospray probe (300 °C). The spectrometer was programmed to allow the $[\text{MH}]^+$ ions of Tween 80 at m/z 653.3 to pass through the first quadrupole (Q1) and into the collision cell (Q2). The collision energy was set at 35 eV and the product ions for Tween 80 (m/z 419.4) were monitored through the third quadrupole (Q3). Argon was used as collision gas at pressure of 0.0027 mBar, and the dwell time per channel was between 0.3 and 0.5 s. Analysis of 1-pentanol in the filtrate was carried out using an Agilent Gas Chromatography 5890 equipped with a flame ionization detector (FID) and a EC-1000 column (15 m \times 0.52 mm ID, 12 μm film thickness). An injection volume of 1 μL was used (splitless injection) and the injector temperature was maintained at 200 °C. The oven temperature programmed to increase from 50 to 110 °C at 10 °C/min, held for 1 min, increased to 160 °C at 10 °C/min, and then held for 5 min. The FID was maintained at 250 °C, and hydrogen gas was used as makeup gas at 50 mL/min. Extraction of linseed oil from the filtrate was carried out following the method described by Neves et al.³¹ Determination of linseed oil was carried out with a Hewlett-Packard 6890 series gas chromatograph fitted with a mass detector (Hewlett-Packard MDS 5973) and a HP-5 column (30 m \times 0.25 mm ID, 0.25 μm film thickness). The injector temperature was 220 °C and the flow rate of helium was 1.0 mL/min. The column temperature was set at 60 °C for 3 min, increased at a rate of 10 °C/min to 200 °C, then switched to a rate of 4 °C/min, finally heated up to 260 °C and maintained isothermally for 10 min. Electron impact mass

spectrometry with a 70- eV ionization potential, 300 μA trap current, and 200 °C ion source temperature was used.

RESULTS AND DISCUSSION

Solubilization of DDT and γ -HCH in Oil-Swollen Micelles Formed with Tween 80. The changes in apparent solubilities of both DDT and γ -HCH as a function of surface active agents, empty Tween 80 micelles or oil-swollen micelles formed with Tween 80, 1-pentanol and linseed oil (with C/S = 1:3 and O/S = 1:10), concentrations are shown in Figure 1. An

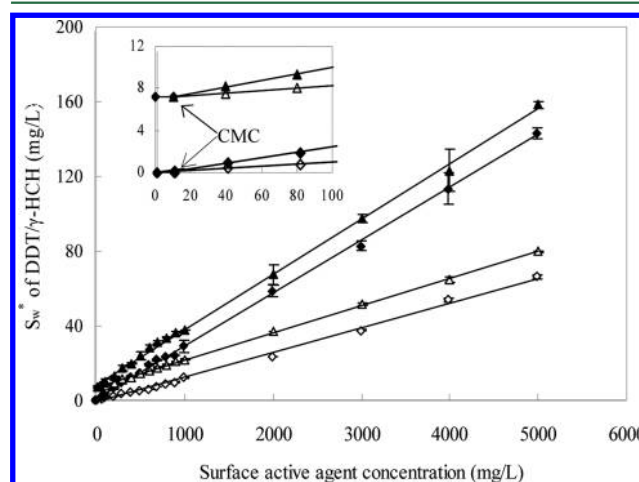


Figure 1. Changes in apparent solubilities of both DDT and γ -HCH as a function of surface active agent concentrations below and above the CMC: DDT in empty micelles (\diamond) and oil-swollen micelles (\blacklozenge); γ -HCH in empty micelles (\triangle) and oil-swollen micelles (\blacktriangle).

extremely slight (for DDT) or no (for γ -HCH) increase in the slope was observed when the concentration of empty micelles or oil-swollen micelles was below 10 mg/L which is very close to the critical micelle concentration of Tween 80,^{7,8,29} indicating the weak (for DDT) or no (for γ -HCH) interaction between the surfactant monomers and the pesticides. However, a linear solubility increase of both pesticides was observed when the concentrations of empty micelles and oil-swollen micelles exceeded 10 mg/L, indicating that the solubilizing capacity of oil-swollen micelles may also dependent on the critical micelle concentration (CMC) of Tween 80, being similar with that of empty micelles.^{7,8}

Previous studies have revealed that the apparent water solubility of a hydrophobic organic compound (HOC) in a surfactant solution can be expressed as follows:^{7,12,13}

$$S_w^*/S_w = 1 + X_{mn}K_{mn} + X_{mc}K_{mc}$$

where S_w^* is the apparent HOC solubility at a total stoichiometric surfactant concentration of $X = X_{mn} + X_{mc}$; S_w is the intrinsic solute solubility in pure water; X_{mn} is the concentration of surfactant as monomer in water ($X_{mn} = X$, if $X \leq \text{CMC}$; $X_{mn} = \text{CMC}$, if $X \geq \text{CMC}$); X_{mc} is the concentration of the surfactant in micellar form ($X_{mc} = X - \text{CMC}$); K_{mn} and K_{mc} are the partition coefficients of the solute between the surfactant monomers and water, and micelles and water, respectively. The values of K_{mn} , K_{mc} , and CMC for empty micelles and oil-swollen micelles can be calculated from the solubility slopes and are shown in SI Table S2.

The calculated CMC for oil-swollen micelles is 0.014–0.015 g/L, which is almost the same as the values of empty micelles.

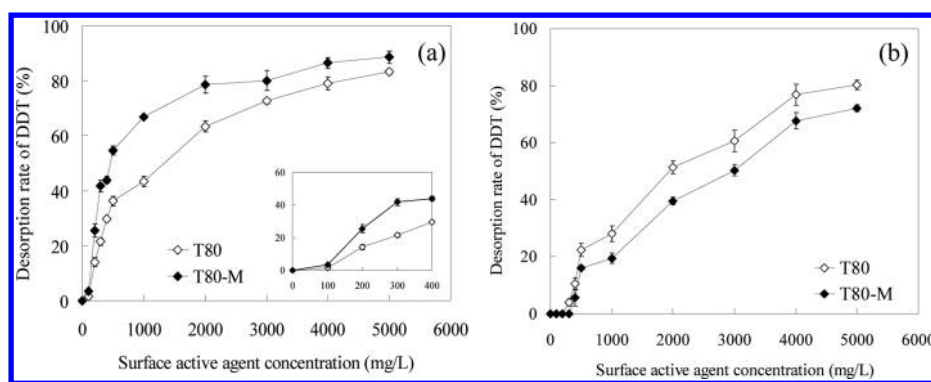


Figure 2. Desorption of DDT from loam soil (a) and clay soil (b) as a function of surface active agent (T80: empty micelles; T80-M: oil-swollen micelles) concentrations.

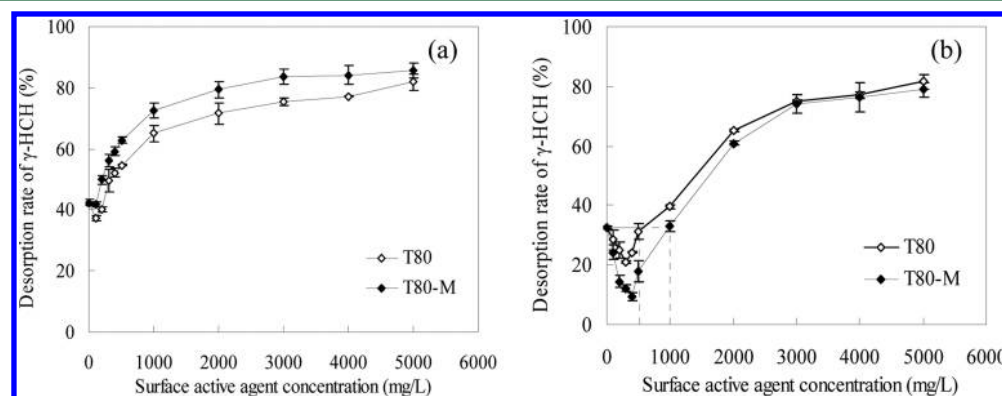


Figure 3. Desorption of γ -HCH from loam soil (a) and clay soil (b) as a function of surface active agent (T80: empty micelles; T80-M: oil-swollen micelles) concentrations.

The presence of 1-pentanol and linseed oil does not increase the interaction between surfactant monomers and pesticides molecules, as it is shown that the K_{mn} values of oil-swollen micelles are very close to that of empty micelles. After micelle formation, molecules of 1-pentanol and linseed oil can penetrate into the surfactant micelles, where 1-pentanol mainly exists in the interface between the hydrophobic tails of surfactants and hydrophobic cores of micelles, whereas oil molecules mainly exist in the hydrophobic cores of micelles.^{25,26} On the other hand, the dissolving of alcohol and oil molecules might enlarge the effective core size and advance the hydrophobic contaminant partitioning capacity of the micelles as its nonpolar organic content was increased and the emulsion lifetime was changed.^{15,32} Therefore, the K_{mc} of both DDT and γ -HCH in the oil-swollen micelles was about 2 times higher than that in empty micelles, indicating the superior solubilizing capacity of oil-swollen micelles for the two pesticides over empty micelles.

Desorption of DDT and γ -HCH from Soils by Oil-Swollen Micelles Formed with Tween 80. Desorption of DDT from both loam soil and clay soil as a function of surface active agent, either empty micelles or oil-swollen micelles, concentrations are displayed in Figure 2. Almost no desorption was observed when no or relatively low concentration of either empty micelles or oil-swollen micelles was present in the soil–water system due to the extremely high octanol–water partition coefficient of DDT ($\log K_{ow} = 6.29$),²⁹ and the fact that a portion of surfactant monomers in aqueous phase was lost as the result of surfactant sorption onto soil.^{9,13,33} Also, most studies indicated that the amount of surfactants required to

desorb HOCs in soil/sediment–water systems is considerably greater than the CMC in clear water, and this concentration was described as critical desorption concentration (CDC), above which desorption process was sharply accelerated with increasing surfactant concentration.^{13,34,35} In the loam soil–water system, the CDC for both empty micelles and oil-swollen micelles were very similar, about 100 mg/L, after which DDT desorbed remarkably and sharply, and the desorption rates achieved by oil-swollen micelles were always much higher than that achieved by the same concentrations of empty micelles, implying that oil-swollen micelles are superior over empty micelles only to desorb DDT from loam soil. For instance, $66.9 \pm 1.7\%$ of DDT was successfully desorbed from the contaminated loam soil by 1000 mg/L of oil-swollen micelles and the desorption rate achieved by 1000 mg/L of empty micelles was only $43.5 \pm 2.8\%$. However, in the clay soil–water system the CDCs for empty micelles and oil-swollen micelles were 300 mg/L and 400 mg/L, respectively, which were much higher than that in loam soil–water system. It is probably due to the fact that the clay soils have much higher sorption capacity than loam soil for both HOCs and surfactants due to the small particle size of clay, and the desorption process of HOCs from the clay fraction is usually slower than that from sandy fraction or others.⁹ Interestingly, the desorption rates achieved by oil-swollen micelles were always lower than that achieved by the same concentrations of empty micelles in clay soil–water system, contrary to their effect in loam soil–water system. These results revealed that above their respective CDCs, the effects of oil-swollen micelles on desorption of DDT

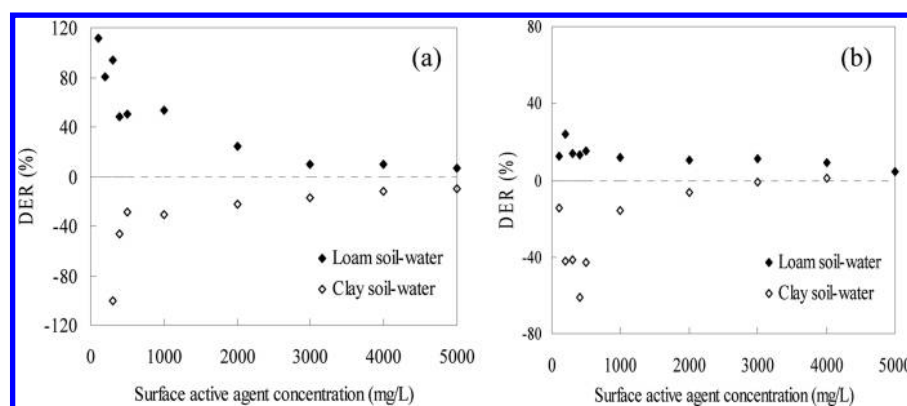


Figure 4. Desorption enhancement rates (DER) during DDT (a) and γ -HCH (b) desorption as a function of surface active agent concentrations in loam soil–water (◆) and clay soil–water (◇) systems.

might be either superior or inferior to the same concentrations of empty micelles, depending on the properties of soils treated.

Figure 3 shows the desorption efficacies of γ -HCH from either loam soil or clay soil by empty or oil-swollen micelles at a wide concentration range from 0 to 5000 mg/L. About $42.4 \pm 2.5\%$ and $32.5 \pm 1.3\%$ of γ -HCH could be desorbed from loam soil and clay soil, respectively, without the addition of any surface active agent. No enhanced desorption but slightly increased retardation of γ -HCH in the two soils was observed at relatively low concentrations of empty micelles and oil-swollen micelles, since the sorbed surfactant or components forming oil-swollen micelles might serve as extra sorbing sites to enhance the sorption of γ -HCH.⁹ However, the desorption rate increased sharply with an increase in the concentrations of empty micelles or oil-swollen micelles after saturating all the extra absorbent sites.

To clarify the effect of the two types of micelles on desorption of γ -HCH, a break-even concentration (BEC) was defined as the concentrations of empty micelles or oil-swollen micelles at which the desorption rate of γ -HCH in the presence of these micelles is equal to that in the absence of any micelle.⁹ As an example, the determination of BECs for empty micelles or oil-swollen micelles in clay soil–water system is depicted in Figure 3b. BECs for empty micelles and oil-swollen micelles in loam soil–water system were 240 mg/L and 110 mg/L, respectively, indicating that oil-swollen micelles could commence the desorption of γ -HCH from contaminated loam soil at a much lower concentration than that of empty micelles. Furthermore, the desorption rates achieved by oil-swollen micelles at a concentration above BECs were always higher than that achieved by the same concentration of empty micelles. However, the BEC for oil-swollen micelles in clay soil–water system was 1000 mg/L, which is higher than 520 mg/L for empty micelles, and the efficiency of oil-swollen micelles to desorb γ -HCH from contaminated clay soil were always lower than that of empty micelles at the same concentrations.

To compare the effect of oil-swollen Tween 80 micelles against its counterpart of empty micelles on desorption of the two pesticides in these two soil–water systems, desorption enhancement rates (DER) at X mg/L of surface active agent were calculated as following:

$$\text{desorption enhancement rate (DER)} = \frac{D_m^x - D_s^x}{D_s^x}$$

where D_m^x represents desorption rate achieved by X mg/L of oil-swollen micelles, and D_s^x represents desorption rate achieved by X mg/L of empty micelles only.

The calculated DERs were plotted as a function of surface active agent concentrations present in the soil–water system and displayed in Figure 4. In loam soil–water system, the DERs for both DDT and γ -HCH are always positive, ranging from less than 5% to as high as 112%, whereas they are always negative in clay soil–water system. These results indicate that soil property plays an important role in the desorption of DDT and γ -HCH from contaminated soils by oil-swollen micelles, and only in the loam soil–water system oil-swollen micelles are superior over empty micelles to desorb the two OCPs from soil.

Distribution of Tween 80, 1-Pentanol and Linseed Oil in Soil–water System during Oil-Swollen Micelle Enhancement of the OCPs Desorption Process. It is well-known that during surfactant-enhanced remediation processes, surfactants could sorb onto soil particles to a certain extent,^{9,10,36,37} resulting in a loss of surfactants in the aqueous phase that results in a reduced solubilization of HOCs as well as an increase in sorbing sites for HOCs.^{9,13,38} Other studies also revealed that the addition of 1-decanol or 1-dodecanol into nonionic surfactants solutions could enhance the adsorption of nonionic surfactants to silica.³⁹ Since the oil-swollen micelles employed in the present study are composed of Tween 80, 1-pentanol and linseed oil, sorption of any of these three components onto soil particles may lead to a reduced solubilization of these two OCPs and a consequential enhanced sorption of these pesticides to soil particles.

Figure 5a presents the Tween 80 sorption isotherms from either empty micelles or oil-swollen micelles onto the two soils, and in both loam soil and clay soil typical Langmuir isotherms were observed, which is consistent with other research.^{40–42} In the loam soil–water system, the presence of 1-pentanol and linseed oil increased the saturation sorption capacity of Tween 80 by 10% compared with the presence of Tween 80 only in the system, from 1960.8 mg/kg to 2158.4 mg/kg. In clay soil, the saturation sorption capacity of Tween 80 was about 3 times that of loam soil due to the much higher sorption capacity of clay soil than that of loam soil,⁹ and the presence of 1-pentanol and linseed oil only enhanced the saturation sorption capacity of Tween 80 by 8.6%, from 6847.6 mg/kg to 7436.5 mg/kg. As shown in Figure 5b, sorption of 1-pentanol onto the two soils first increased with increasing aqueous 1-pentanol concentration until a saturation sorption capacity was reached, but its

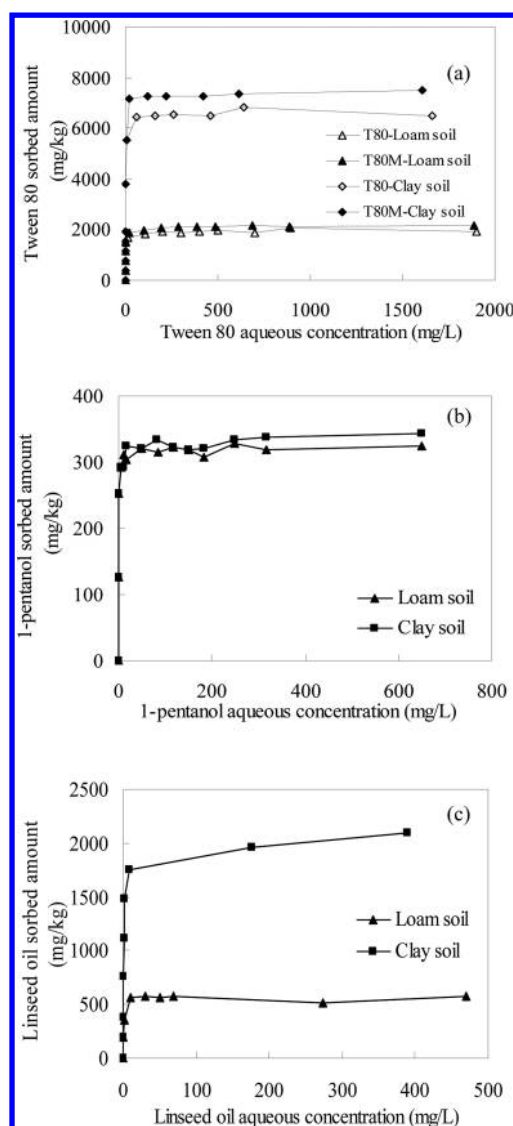


Figure 5. Sorption isotherm (a) of Tween 80 from empty micelles (T80) or oil-swollen micelles (T80-M) onto loam soil and clay soil at 25 °C; and sorption isotherms of 1-pentanol (b) and linseed oil (c) from oil-swollen micelles onto loam soil and clay soil at 25 °C.

saturation sorption amount was an order of magnitude less than that of Tween 80 and no significant differences of 1-pentanol sorption were observed in loam soil–water and clay soil–water systems. However, the sorption of linseed oil on the two soils was significantly different (Figure 5c), as shown that the saturation sorption capacity of linseed oil onto clay soil was about 2100 mg/kg soil which is about 4 times of that onto loam soil.

Our experiments revealed that oil-swollen micelles exhibited their superiority over counterpart empty micelles to desorb both DDT and γ -HCH in only loam soil–water system while they were less effective than empty micelles in clay soil–water system. It is presumable that the much higher sorption capacity of clay soil for Tween 80, 1-pentanol and/or linseed oil forming oil-swollen micelles may result in the phenomenon. The loss of Tween 80 from oil-swollen micelles was only less than 10% higher than from empty micelles in both loam soil–water and clay soil–water systems, and the sorption of 1-pentanol onto the two soils from oil-swollen micelles was extremely weak and with similar amounts. Therefore, the different sorption behavior

of linseed oil onto the two soils may be mainly responsible for the different effects of oil-swollen micelles on the desorption of these two OCPs in the two soil–water systems.

ENVIRONMENTAL IMPLICATIONS

Oil-swollen micelles can be applied in soil-washing processes to remove HOCs from soil matrices or employed to enhance the biodegradation of DDT.⁴³ The oil phase plays a very important role since it provides more hydrophobic micelle cores compared to empty micelles. However, the sorption of oil molecules, cosurfactant and surfactant onto soil particles would result in the decreased solubilizing capacity of oil-swollen micelles and increase the sorption of HOCs because of extra sorbing sites provided, in which the sorption of oil seems to be the most influential. Although oil-swollen micelles possess much higher solubilizing capacity for OCPs over counterpart empty micelles, their advantages in solubilization could not guarantee consequential advantages in desorption of OCPs in soil–water system. The application of oil-swollen micelles in soil-washing or bioremediation may be advantageous over empty micelles only in loam soil or sandy soil environments which have low sorption capacity for oil molecules, and not for clay soil possessing much higher sorbing capacity for oil molecules. Although the present study only focuses on DDT and γ -HCH, these results may be applicable to many other HOCs such as polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) that strongly sorb onto soils and sediments. Further research is needed to study the binding mechanisms between oil molecules and soil particles to expand the usage of oil-swollen micelles in remediation processes.

ASSOCIATED CONTENT

Supporting Information

Two tables showing detailed properties of the two soils and the solubilization data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The authors declare no competing financial interest.

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