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Cover Page Footnote

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Chapter 3

APPLICATION OF MICROEMULSION TO REMEDIATE ORGANOCHLORINE PESTICIDES CONTAMINATED SOILS

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ABSTRACT

Microemulsion, a system containing water, surfactant, cosurfactant and oil phase, has the potential to enhance the solubility and bioavailability of hydrophobic organic compounds (HOCs). The aim of this study is to develop microemulsion which could enhance the bioremediation of organochlorine pesticides (OCPs) contaminated soils. After screening four surfactants and two plant oils, Triton X-100 and linseed oil were selected for microemulsion formation because of their respective instinctive higher solubilizing capacity over other candidates. Microemulsions formed with Triton X-100 and linseed oil could effectively enhance the aqueous solubility of 1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane (DDT), and the enhancement was much higher than that achieved by Triton X-100 solution alone. Besides, the solubilization capacity of Triton X-100-linseed oil system was positively influenced by both cosurfactant (C/S ratios) and oil (O/S ratios) contents of the microemulsions. Desorption tests reveal that this microemulsion system is more effective than its counterpart Triton X-100 solution to desorb DDT from contaminated soil.

Keywords: remediation, microemulsion, organochlorine pesticides (OCPs), surfactant

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1. INTRODUCTION

Organochlorine pesticides (OCPs) have been used worldwide since 1940s due to their low cost and high effectiveness. However, most OCPs, e.g., lindane (γ -HCH) and 1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane (DDT), are persistent, bioaccumulated, semivolatile, and highly toxic, which led to growing concerns on their potential contamination on the environment, and associated adverse effects on human health and wildlife (Kannan et al., 1992, Kucklick and Baker, 1998; Walker et al., 1999; Meijer et al., 2001). Both DDT and HCHs are still detectable in sediments and soils throughout the world due to their heavy utilization and high environmental persistence (Meijer et al., 2001, Nakata et al., 2002). Owing to the serious health risks associated with even extremely low levels of such pollutants, increasing attention has been paid recently for developing innovative technology to prevent accumulation of organochlorine pesticides from soil to food. To date, the remediation options for soil contaminated by organochlorine pesticides include low temperature thermal desorption (Percin, 1995), incineration, bioremediation (Dua et al., 2002), photodegradation (Chu, 1999) and phytoremediation (Lunney et al., 2004; White et al., 2007). Among the various technologies, bioremediation is known to be advantageous for the environmental and economic reasons (Guerin, 1999).

Generally, soil pollutants are mainly degraded in solution as they are more available for microbial action (Harms and Bosma, 1997). However, most organochlorine pesticides are poorly soluble in water, and adhere tightly with soil particles through adsorption, electrostatic interaction and covalent bonding (Bollag et al., 1992). Therefore, the degradation of organochlorine pesticides in soils is usually slow and frequently unsatisfactory. To facilitate the degradation of organochlorine pesticides by microorganisms in soils, some surface-active agents (Quintero et al., 2005; Walters and Aitken, 2001; Kommalapati et al., 1997; Mulligan, 2005; Kantachote et al., 2004) have been employed to enhance the solubility and bioavailability of hydrophobic organic pollutants in soils. Nevertheless their effects on the degradation of pollutants still remain controversial since some of them may exert inhibitory effects on the degradative microorganisms. Microemulsion, consisting of surfactants, co-surfactants and oil, might be another potential candidate for remediation of soils due to its high solubilization capacity relative to the surfactant micellar solutions (Rosen, 1989).

Different from surfactant solutions, microemulsion are thermodynamically stable, isotropic, and macroscopically homogeneous dispersions of two immiscible fluids, generally oil and water, stabilized by surfactant molecules either alone or mixed with a cosurfactant, and the droplets of microemulsions are nanometer-sized (Kahlweit, 1988). Due to their special structure, microemulsions

exhibit good wetting ability, moderate viscosity, low interfacial tensions and high solubilization for both hydrophilic and hydrophobic compounds. As a novel emulsifying agent, microemulsions have been successfully used in soil washing and exhibit high efficiency in enhancing the solubility of some hydrophobic organic pollutants (Dierkes et al., 1998; Ying et al., 2002; Bragato et al., 2004). However, there is no application of microemulsions for remediating organochlorine pesticides contaminated soil.

Therefore, the objectives of the present study are to: (1) explore the feasibility of forming microemulsion using non-ionic surfactants and plant oils with the help of 1-pentanol as a cosurfactant; (2) investigate the effect of cosurfactant or oil content on the solubilizing capacity of a specific microemulsion system; and (3) preliminarily elucidate the effect of microemulsion system on the transfer of DDT from soil phase to aqueous phase.

2. MATERIALS AND METHODS

2.1 Materials

Triton X-100, Tween 80 and Brij 35 were the non-ionic surfactants tested in the present study because of their prevailing use in soil washing, and one biosurfactant, bile salt, is also tested in the present study. The three non-ionic surfactants and bile salt were purchased from Sigma Chemical Co., and all surfactants (purity >98%) were used as received from supplier without purification. The formula and properties of the surfactants are listed in Table 1. Two plant oils, soybean oil and linseed oil, were tested to check their suitability as the oil phase in this study because soybean oil is the most commonly produced vegetable oil worldwide and linseed oil is the most widely used vegetable oil in industry. These two plant oils (Sigma Chemical Co.) and 1-pentanol (purity >98%, Fluka Chemical Co.) were used without any further purification. n-hexane and acetone used were of analytical grade, while double deionized water was used for all tests.

Table 1 Characteristics of selected surfactants

Surfactant	Structure ^a	CMC (mg L ⁻¹)	MW	HLB ^b
Tween 80	C ₁₈ S ₆ E ₂₀	11	1310	15.0
Brij 35	C ₁₂ E ₂₃	76	1198	16.9
Triton X-100	C ₈ PE ₁₀	131	625	13.5
Bile salts				

^a C represents alkyl chain length (CH₂), P represents a phenol ring (C₆H₆), E represents an etgoxylate group (C₂H₄O), and S₆ represents a sorbitan ring.
^b Hydrophile-lipophile balance

DDT used in this study was purchased from Sigma Chemical Co., and was 99% pure. It was used without any further purification.

2.2 Screening the suitability of surfactants for the formation of microemulsions with plant oils

Surfactants solutions at 10, 25, 50, 100 and 200 CMC (critical micelle concentration) were prepared individually with distilled water. 1-pentanol was added to each surfactant solution as a co-surfactant with a cosurfactant to surfactant ratio (C/S ratio) of 0.5:1, 1:1 or 1.5:1. For each solution, 2 g/L soybean oil or linseed oil was added, gently mixed and aged for 12-15 h at ~ 25 °C before subjected to stability evaluation.

In this study, the stability of microemulsions was checked by both visual transparency check and centrifugation. The homogeneity and optical isotropy of microemulsions were examined by visual examination at room temperature. Then the stabilities of all samples were tested by carrying out centrifugation at 100 x g for 5 min (Prince, 1977). Samples without any phase separation were subjected to visual inspection and centrifugation again after 7 days. Three microemulsion systems without phase separation were identified as stable microemulsions.

2.3 Solubilization Study

Preparation of microemulsion: To determine the effect of C/S ratios on the solubilization of DDT by microemulsions, 1-pentanol, as cosurfactant was mixed with the Triton X-100 at the ratios of 1:3 and 1:6, to form the surfactant/cosurfactant phases. Then, the surfactant/cosurfactant phases were mixed with linseed oil according to the oil to surfactant ratio (O/S ratio) of 1:20 to obtain microemulsion precursors containing surfactant, cosurfactant and oil. The precursors were subsequently diluted with water to obtain microemulsions formed with various concentrations of surfactants and different C/S ratios. To study the effect of O/S ratio on the solubilizations of DDT by microemulsions, microemulsion precursors formed with a constant C/S ratio of 1:3 and three different O/S ratios, 1:20, 1.5:20 and 2:20, were prepared according to the procedures described above. Then, the precursors were diluted with water to obtain microemulsions formed with various concentrations of surfactants and different O/S ratios.

Appropriate amount of DDT dissolved in acetone was carefully added to the bottom of 20 mL glass vials, and the amount of added DDT was well in excess of its aqueous saturation. After the acetone was evaporated, 10 mL microemulsions or surfactant solution prepared as described before were added into each vial. Duplicate tests were prepared for each microemulsion or surfactant solution.

These vials were capped with aluminium-lined cap and then shaken on a rotary shaker at 250 rpm at 25 °C for an equilibrium period of 72 h as determined from our preliminary study. After equilibrium was reached, the samples were filtered through a glass column packed with glass wool to remove any undissolved DDT particles. A 1-mL aliquot of the filtered solution was then carefully withdrawn with a volumetric pipette and extracted in n-hexane; dilutions were done in n-hexane as needed to bring the solute to a detectable concentration range. Analysis of DDT was carried out in an Agilent Gas Chromatography 7890 equipped with a Nickel 63 electron capture detector (μ ECD) and a HP-5 column (30 m \times 0.32 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 programmed to increase from 100 °C 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.

Dilution effect on the solubilizing capacity of microemulsion system was also studied. Firstly, microemulsion precursor containing Triton X-100, 1-pentanol (with C/S=1:3) and linseed oil (with O/S=2:20) were prepared as described above. Then, the precursor was diluted carefully with water to obtain microemulsions formed with a wide range of Triton X-100 concentration from 10 mg/L to 5000 mg/L. And the solubilization of DDT in these diluted microemulsions was investigated according to methods described above.

2.4 Batch Desorption Study

0.5 g DDT spiked soil was added to 20 mL glass vials for studying desorption of DDT in soil-water system under the influence of microemulsions and surfactant solutions. 10 mL of surfactant solutions or microemulsion covering a wide range of surfactant concentrations from 40 mg/L to 5000 mg/L were added to the vials. 0.02% NaN₃ was added to the mixture as microbial growth inhibitor (Wong et al., 2004). The samples were shaken on a rotary shaker at 250 rpm under dark at ambient temperature (25-28°C). After an equilibrium period of 96 h as determined from preliminary study, duplicate samples were sacrificially collected and were centrifuged for 5 min at 3000 \times g to separate the aqueous phase from the soil particles. DDT concentration of the aqueous phase was quantified by GC/ECD as described above.

3. RESULTS AND DISCUSSION

3.1 Formation of stable microemulsions

As shown in Figure 1, 21 stable microemulsions were obtained from combinations of four surfactants and two plant oils. Among these 21 microemulsions, 10 were formed with Tween 80, 6 were formed with Brij 35 and 5 were formed with Triton X-100. However, no stable microemulsion was formed with bile salts. Both soybean oil and linseed oil could be used as the oil phase to achieve stable microemulsions with Tween 80, Triton X-100 and Brij 35. In fact, Zhao et al., (2006) has suggested that the tail length of the nonionic surfactant should be close to the carbon chain length of the fatty acid compositions in oil, and the size of head group in nonionic surfactant should not be too small (less than 5) or too large (larger than 40) in order to obtain stable microemulsions. In this study, Tween 80 could form more stable microemulsions than both Brij 35 and Triton X-100 that may be attributed to its special chemical structure containing 18 CH₂, close to the carbon chain length of the fatty acid compositions in both soybean oil and linseed oil having 23 ethoxylate groups (Warisnoicharoen et al., 2000). On the other hand, the HLB values of Tween-80, Brij 35 and Triton X-100 indicate that all microemulsions formed are oil-in-water microemulsions (Ying et al., 2002), in which vegetable oils are emulsified by surfactants and cosurfactant.

While studying the microemulsion formation, the solubility of DDT in the proposed surfactants and oils were also investigated as the second parameter to select suitable surfactant and plant oil. As shown in Table 2, among the three surfactants which could form stable microemulsions with the two plant oils, Triton X-100 exhibited the highest solubilization capacity. Between the two plant oils, linseed oil exhibit 36.4% more solubilization than soybean oil, indicating that Triton X-100 and linseed oil would be a better candidate for the solubilization of DDT over other candidates.

Table 2. Solubility of DDT in surfactants or plant oils

Solution (wt %)	DDT solubilized (mg/L)
1% Triton X-100	134.7
1% Tween 80	112.3
1% Brij 35	42.6
Linseed oil	1.2×10 ⁵
Soybean oil	8.8×10 ⁴

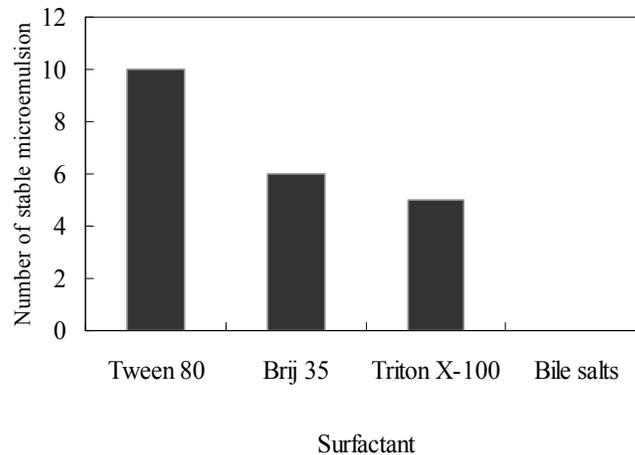


Figure 1. Number of stable microemulsion formations obtained with the three non-ionic surfactants and one biosurfactant

3.2 Factors influencing the solubilizing capacity of microemulsion formed with Triton X-100 and Linseed oil

In microemulsions, oil and water microdomains are separated by surfactant/cosurfactant interface (Kahlweit, 1988). When a hydrophobic solute is solubilized in a microemulsion, it may exist either in the oil volume fraction or in the volume fraction corresponding to the interfacial layer (Testard and Zemb, 1998). Thus, in addition to the surfactant content, both cosurfactant and oil fractions will also influence the solubilizing capacity of a microemulsion system. In this study, to elucidate the effect of cosurfactant content on the solubilizing capacity of microemulsions, the aqueous solubility of DDT in microemulsions formed with Triton X-100 and linseed oil, at different C/S ratios (1:3 and 1:6), and a constant oil to surfactant ratio of 1:20, was examined. Plots of the aqueous solubility of DDT as a function of surfactant concentrations used in microemulsions are shown in Figure 2A. As presented, all the microemulsions formed could markedly increase the aqueous solubility of DDT within the concentration range of 1% (w/w) to 30% (w/w). At the same C/S ratio, DDT solubility increased linearly with an increase in surfactant concentrations of the microemulsions. Compared to treatment with Triton X-100 only, the microemulsions were more effective. As shown in Figure 2B, increasing the O/S ratios from 1:20 to 2:20 at a constant C/S ratio of 1:3 also resulted in an increase in the solubilization of DDT, indicating the positive effect of oil in the solubilization of DDT by microemulsions.

Solubilization capacity of a surfactant could be commonly quantified by the weight solubilization ratio (WSR) (Li and Chen, 2002), which is defined as the mass of HOCs solubilized by unit weight of surfactants above its CMC and can be calculated as follows:

$$WSR_{surf} = (S_{Surf*} - S_{CMC}) / (C_{surf} - CMC)$$

where S_{Surf*} is the apparent solubility of solute at surfactant concentration of C_{surf} and S_{CMC} is the apparent solubility of certain compounds at CMC. Therefore, WSR can be obtained from the slope of solubilization curve in the range of surfactant concentrations above the CMC. In contrast to the surfactants solution, the WSR of solutes in microemulsion systems was proposed to be expressed as (Zhao et al., 2005):

$$WSR_{\mu E} = (S_{\mu E*} - S_{int}) / C_{\mu E}$$

where, $C_{\mu E}$ is the microemulsion concentration at which $S_{\mu E*}$ is evaluated; S_{int} is the intrinsic water solubility of the solutes; and $S_{\mu E*}$ is the apparent solubility of solute in microemulsions. In the present study, the concentration of microemulsion is termed as total weight of surfactant, cosurfactant and oil present. Similar to that of surfactant solution, $WSR_{\mu E}$ could be calculated from the slope of the solubilization curve.

The calculated values of WSR_{surf} , $WSR_{\mu E}$ of DDT Triton X-100 solution or in microemulsion systems are listed in Table 3. WSR of DDT in Triton X-100 solution was only 0.0131. However when Triton X-100 was employed to emulsify linseed oil and form microemulsions, the WSR of DDT has increased to 0.0214-0.0283, which was about 63.3-116.0% higher compared with Triton X-100 only. Besides, it could also be observed that increasing C/S ratios from 1:6 to 1:3 has led to 10.7% increase of WSR, and increasing O/S ratios from 1:20 to 2:20 resulted in 19.4% increase of WSR, indicating that both cosurfactant and oil content can positively influence the solubilizing capacity of microemulsion systems. Such a high enhancement of solubilizing capacity of Triton X-100 obtained through emulsifying alcohol and plant oil is reported for the first time. For instance, previous study on the solubilization of PAHs in microemulsion system based on sodium castor oil sulfate showed that the solubilizing capacity of microemulsion was only 14.6% higher than Triton X-100, and 40.2% higher than Tween 80 (Zhao et al., 2005).

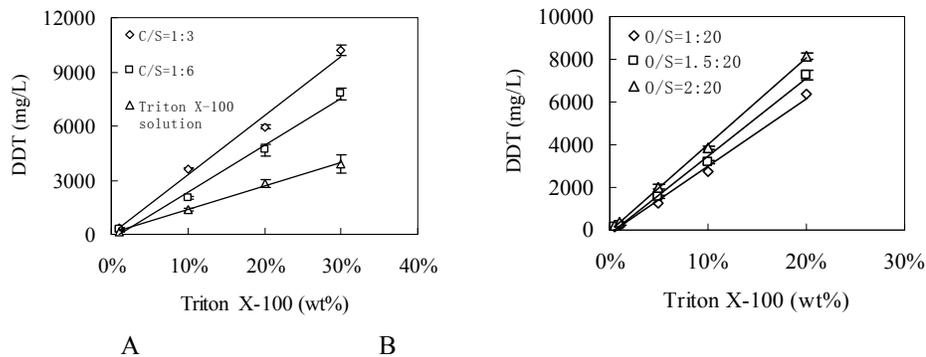


Figure 2. Effect of cosurfactant (C/S ratios) and oil (O/S ratios) content on the solubilizing capacity of microemulsion system based on Triton X-100 and linseed oil

Table 3 Weight solubilization ratios (WSR) of DDT in Triton X-100 solution and microemulsion systems formed with different C/S ratios and O/S ratios

	Triton X-100	Microemulsion (with fixed O/S=1:20)		Microemulsion (with fixed C/S=1:3)		
		C/S=1:6	C/S=1:3	O/S=1:20	O/S=1.5:20	O/S=2:20
WSR	0.0131	0.0214	0.0237	0.0237	0.0258	0.0283
R ²	0.997	0.991	0.988	0.994	0.996	0.999

3.3 Dilution effect on the solubilization capacity of microemulsion system formed with Triton X-100 and Linseed oil

It is well known that particle sizes or microdomain structures of microemulsions can be changed when diluted by water (Lawrence and Rees, 2000), and transfer of W/O microemulsion to O/W microemulsion can also be induced by dilution process (Constantinides and Yiv, 1995). Therefore, the best microemulsion (with C/S=1:3 and O/S=2:20) obtained in previous experiment was diluted to study whether the dilution of microemulsion could influence the solubilization of DDT. As shown in Figure 3, the solubilizing capacity of microemulsion system (with C/S=1:3 and O/S=2:20) decreased linearly with the decreasing concentration of Triton X-100 during dilution. However, at the same concentration of Triton X-100, microemulsion system always exhibited higher solubilizing capacity for DDT than Triton X-100 solution alone. When the Triton X-100 concentration was <1 CMC, both surfactant solution and microemulsion system did not solubilize the DDT due to the lack of micelle formation (Kile and Chiou, 1989). For example, about 39.7 mg/L DDT could be solubilized by microemulsion comprising 1000 mg/L of Triton X-100, while only 12.9 mg/L DDT was

solubilized by the same concentration of Triton X-100. This stable and higher solubilizing capacity of microemulsion over its counterpart surfactant solution above the CMC of surfactant imply that microemulsion can be a potential candidate to desorb HOCs from contaminated soils.

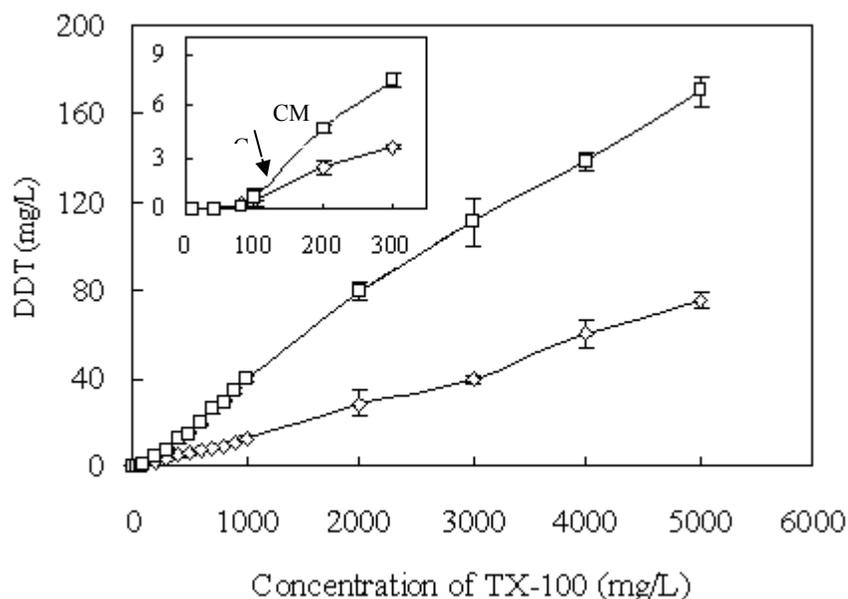


Figure 3. Dilution effect on the solubilizing capacity of both surfactant solution (◇) and microemulsion based on Triton X-100 and Linseed oil (□)

3.4 Desorption efficacy of DDT from sandy loamy soil by Triton X-100 solution and microemulsions formed with Triton X-100

Desorption rate of DDT in soil-water systems by surfactant solution or microemulsions at a wide concentration range from 0 to 5000 mg/L Triton X-100 are shown in Figure 4. The desorption rates of DDT were about 0.052% by water without surfactant or microemulsion due to the higher octanol-water partition coefficient, $\text{Log } K_{ow}$, of DDT. With an increase in surfactant concentration in surfactant solution and microemulsions, no significant increase of desorption of DDT was observed until the Triton X-100 concentrations exceeded about 200 mg/L (Figure 4, subset). This was probably ascribed to the fact that a portion of surfactant monomers were being lost from aqueous phase as the result of surfactant sorption on soil particles (Zhu et al., 2003, Cheng and Wong, 2005; Wang and Keller, 2008). Also, most studies indicated that the amount of surfactants required to desorb HOCs in soil- and sediment-water systems is considerably greater than the CMC in water (Zheng and Obbard, 2002; Cheng and Wong, 2006). In some studies, this concentration was described as critical

desorption concentrations (CDC), above which desorption process was sharply accelerated with increasing surfactant concentration (Yang et al., 2006, Zhou and Zhu, 2007). In the present study, the desorption rate of DDT from soil increased drastically when the concentrations of Triton X-100 exceeded 200 mg/L; and no differences of CDC were observed between surfactant solution and microemulsion up to 400 mg/L of Triton X-100. Above this concentration, the microemulsions achieved higher desorption than their corresponding surfactant solution. For example, with 1000 mg/L of Triton X-100, the desorption rates of DDT achieved by microemulsion and surfactant solution were 66% and 55%, respectively. However, the desorption enhancement achieved by microemulsion in water/soil system was much lower than the slouabilization enhancement achieved in aqueous solutions, implying the potential sorption of different components of microemulsions on soil particles.

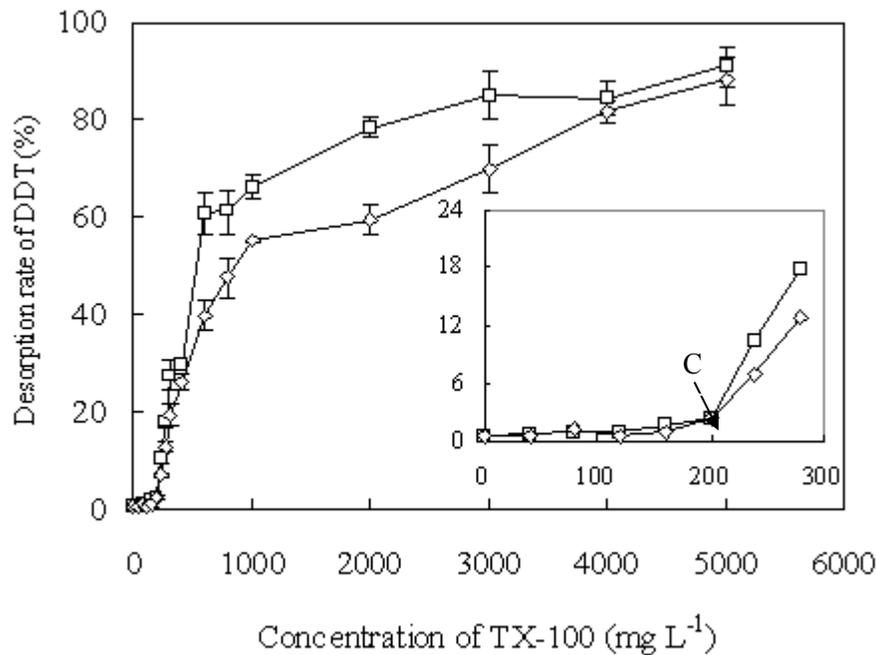


Figure 4. Desorption of DDT from loamy sandy soil by surfactant solution (◇) and microemulsion based on Triton X-100 and Linseed oil (□)

4. CONCLUSION

Four surfactants and two plant oils were tested for the possibility of forming stable microemulsions. Except the bile salt, other non-ionic surfactants formed stable microemulsions. Among these, Triton X-100 and linseed oil were selected

for further studies because of their respective higher DDT solubilizing capacity over other candidates. Microemulsions formed with Triton X-100 and linseed oil could effectively enhance the aqueous solubility of DDT, and the enhancement was 63.3-116.0% more than that achieved by Triton X-100 solution only. Besides, the solubilization capacity of Triton X-100-linseed oil system was positively influenced by both co-surfactant (C/S ratios) and oil (O/S ratios) contents of microemulsions. Similar to the aqueous system, desorption capacity of microemulsions was higher than the surfactant alone in water/soil system. Therefore, the microemulsion system is a potential candidate for the remediation of OCPs contaminated soil due to its higher solubilizing and desorbing capacity, though further studies are needed to investigate the detailed behavior of microemulsion in soil matrix and their effect on the biodegradation of OCPs by microorganisms.

6. ACKNOWLEDGMENT

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