Bioremediation of Organochlorine Pesticides Contaminated Soil
with Microemulsions

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Abstract

Bioremediation is advantageous to remediate organochlorine pesticides (OCPs) contaminated soil because of its relative low cost and environmental safety. However, most OCPs, such as dichloro-diphenyl-trichloroethane (DDT) and gamma-hexachlorocyclohexane (γ-HCH), are poorly soluble in water, and contact tightly with soil particles through adsorption, electrostatic interaction and covalent bonding. Therefore, the degradation of OCPs in soils is usually slow and frequently unsatisfactory due to the difficulties in their transfer from soil particles to aqueous phase where degradative microorganisms could metabolize these compounds. As an alternative to synthetic surfactants, which are usually introduced into bioremediation processes to enhance the bioavailability of OCPs, microemulsion, which is a combination of surfactants, cosurfactants and oil phase, might be a potential candidate due to its much higher solubilization capacity than surfactant micelles.

The first experiment of this study investigated the suitability of four surfactants, Tween 80, Triton X-100, Brij 35 and Bile slats, for forming microemulsions with two vegetable oils: soybean oil and linseed oil. It was found that Tween 80, Triton X-100 and Brij 35 formed stable microemulsions with the two vegetable oils, whereas no stable microemulsion could be formed with bile salts. Almost all formed microemulsions exhibited higher solubilizing capacities than their respective surfactant solutions and the two vegetable oils selected were good candidates for the oil phase of microemulsions. Microemulsions based on Tween 80 exhibited the highest solubilizing capacities for both DDT and γ-HCH, and the solubilizing capacities of microemulsions decreased in the following order: Tween 80>Triton X-100>Brij 35.

To reveal potential factors influencing the solubilizing capacities of microemulsions for OCPs, microemulsion systems formed with both Tween 80 and Triton X-100 were studied in detail. These microemulsion systems effectively enhanced the solubilities of both DDT and γ-HCH and exhibited higher solubilizing capacities than their respective surfactant solution alone. With an increase of either cosurfactant to surfactant ratio (C/S ratio, w/w) or oil to surfactant ratio (O/S ratio, w/w), the solubilizing capacities of microemulsion systems increased remarkably. Between the two factors, O/S ratio played a more significant role than C/S ratio to increase the solubilizing capacities of microemulsions, indicating that the oil phase was more influential than cosurfactant in enhancing the solubilization of hydrophobic organic compounds in microemulsions. Among the microemulsion systems developed, the system formed with Triton X-100 or Tween 80, linseed oil as oil phase, the C/S ratio of 1:3 and O/S ratio of 1:10 exhibited the maximum solubilizing capacity for the two pesticides.

Sorption of components forming microemulsions and the effect of microemulsions on the desorption of the two OCPs in soil-water systems were investigated to reveal the feasibility of applying microemulsions to enhance the bioavailability of OCPs in soil environment. The effect of microemulsions formed with Tween 80 and Triton X-100, or also called oil-swollen micelles, on the solubilization and desorption of DDT and γ-HCH from both loam soil and clay soil were investigated. Results showed that the solubilizing capacities of microemulsions depend on the critical micelle concentration (CMC) of surfactant employed. Once the concentration of surfactants present in microemulsions exceeded their respective CMC, the microemulsions exhibited much higher solubilizing capacities than their counterpart surfactant solutions. Desorption tests revealed that microemulsions formed with either Tween 80 or Triton X-100 significantly enhanced the desorption of OCPs from both loam soil and clay soil.
However, compared with the efficiencies achieved by surfactant solutions only, microemulsions exhibited their superiority over their counterpart surfactants to desorb OCPs only in loam soil-water system while they were less effective in clay soil-water system, indicating that the presence of 1-pentanol and linseed oil might negatively influence the partition of OCPs into surfactant micelle cores in clay soil-water system. Further studies focusing on the distribution of Tween 80, 1-pentanol and linseed oil in soil-water system revealed that the difference in the sorption of linseed oil onto the two soils resulted in the different effects of microemulsions formed with Tween 80 on the desorption of OCPs in loam soil and clay soil systems. Therefore, microemulsions formed with Tween 80 and Triton X-100 are better candidates over conventional surfactants solutions to desorb OCPs from loam soil, which would consequently enhance the bioavailability of OCPs as well as other hydrophobic organic contaminants (HOCs) in soil environment during bioremediation processes of contaminated soil.

Three Sphingobium strains including S. indicum B90A, S. japonicum UT26 and S. francense Sp+ were screened for their abilities to degrade γ-HCH. Both S. indicum B90A and S. japonicum UT26 rapidly degraded γ-HCH at low temperature (4°C), while the degradation capability of S. francense Sp+ was relatively low. During the biodegradation at 4 °C, γ-HCH was converted to extremely low amounts of 1,2,4-trichlorobenzene (1,2,4-TCB) and 2,5-dichlorophenol (2,5-DCP), whereas most of γ-HCH was transformed to 2,5-Dichloro-2,5-cyclohexadiene-1,4-diol (2,5-DDOL) by S. japonicum UT26. It was therefore concluded that haloalkane dehalogenases in some Sphingobium strains were still very active at temperature as low as 4 °C and S. indicum B90A might be a good candidate for developing novel bioremediation techniques suitable for cold regions to decontaminate γ-HCH from soils or water systems. Furthermore, the biodegradation of γ-HCH by S. indicum B90A at 30°C was accelerated by the addition of both Tween 80 and microemulsions formed with Tween 80. Microemulsions formed with Tween 80 were much more effective than Tween 80 only; while microemulsions formed with Triton X-100 totally inhibited the biodegradation of γ-HCH by S. indicum B90A due to the toxicity of Triton X-100 for the bacteria.

Microemulsions formed with Tween 80 effectively enhanced the biodegradation of DDT by Phanerochaete chrysosporium, and the enhancement efficacy was about 2 times of Tween 80 solution. However, both Triton X-100 solution and microemulsions formed with Triton X-100 could not facilitate the biodegradation of DDT due to the intrinsic toxicity of Triton X-100 for P. chrysosporium. Further studies revealed that microemulsions formed with Tween 80 enhanced the biodegradation of DDT through transporting DDT from crystalline phase to mycelium of P. chrysosporium as well as their positive effect on the growth of P. chrysosporium. Therefore, microemulsions formed with Tween 80 are good candidates over conventional non-ionic surfactants to enhance the biodegradation of DDT by the white rot fungi like P. chrysosporium.

The addition of microemulsions enhanced the bioremediation efficiency of γ-HCH contaminated soils; in this process, microemulsions enhanced both the bioavailability of γ-HCH and the growth of the degradative bacteria. After 21 days incubation, 50 mg/kg soil of γ-HCH was effectively removed from contaminated soil. However, the addition of microemulsions did not significantly enhance the removal rate of DDT when the initial concentration of DDT was 2 mg/kg soil, and enhanced the removal rate from 42.5% to 62.3% when the initial concentration of DDT was 25 mg/kg. These results revealed that although microemulsions could enhance the bioavailability of DDT during the bioremediation of soils contaminated with relatively high concentration of DDT, the relatively lower biodegradation ability of P. chrysosporium for DDT still severely restricted the bioremediation efficacy.
Therefore, it is concluded that microemulsions formed with Tween 80 are promising alternatives to synthetic surfactants in enhancing the bioremediation efficiency of OCPs contaminated soils. This innovative technique combining microemulsions and bioremediation expands the scope of soil bioremediation and provides an efficient and safe way for the remediation of soil contaminated by organochlorine pesticides.
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