

마이크로이멀전을 이용한 유기오염물로 오염된 지반의 정화 Remediation of Contaminated Soil with Organic Contaminants using Microemulsion

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SYNOPSIS : In the soil washing process, the contaminants are usually removed by abrasion from soil particles using mechanical energy and water. However, organic contaminants with low water solubility like polycyclic aromatic hydrocarbons (PAH) are remained on soil particles. Previous studies have shown that surfactant possessing amphipathic activity enhances the solubility of organic materials. For this reason solutions with surfactants have been used to improve removal of organic contaminants on soil washing process. But, in this manner, many problems were found like complete loss of surfactants and additional contamination by surfactant. The remediation method using microemulsion has been introduced to overcome these disadvantages. In this case, surfactants are recycled by phase separation of microemulsion after remediation. In microemulsion process, the surfactant will be recycled by phase separation of the microemulsion into a surfactant-rich aqueous phase and an oil phase after extraction. That is why remediation concept applying microemulsion as washing media has been introduced. Suitable microemulsion have to be used in order to have the chance of refilling the soil after decontamination and to avoid any risk due to toxicity. The purpose of this research is to evaluate effect of microemulsion to remediation of contaminated soil. We performed test with various organic contaminants like Pyrene and BTEX, also compared efficiency of remediation in microemulsion process with soil washing

Key words : soil washing process, microemulsion, non-ionic surfactant, extraction test.

1. Introduction

Surfactants are referred to as amphiphilic molecules because the polar group has a large affinity for polar solvents, such as water, whereas the nonpolar group has a large affinity for nonpolar or hydrophobic solvents, which include most organic contaminants. Surfactants lower interfacial tension between organic contaminants and water, thereby decrease capillary forces within the porous media. For this reason solutions with surfactants have been used to improve removal of organic

contaminants on soil washing process. However, the main problem involved in this procedure is the loss of the surfactant and additional contamination during subsequent wastewater treatment.

In microemulsion process, the surfactant can be recycled by phase separation of the microemulsion into a surfactant-rich aqueous phase and an oil phase after extraction. Suitable microemulsion have to be used in order to have the chance of refilling the soil after decontamination and to avoid any risk due to toxicity. Using properties of microemulsion in terms of high solubility, recycling of surfactants, we will have many advantages in soil remediation compared with soil washing.

This research is focused on the possibility of application of microemulsion in soil remediation. This study is divided into two categories. The one is to confirm the efficiency of microemulsion as extraction media through extraction results. The other is comparison of remediation in microemulsion process with soil washing and recycling of microemulsion in extraction process.

2 Microemulsion as Extraction Media

2.1 Properties of Microemulsion

At the constant pressure and temperature, the phase behavior of the ternary system is described by a Gibbs triangle showing the regions depending on composition. The perpendicular cut through the surfactant corner at a fixed oil/water-ratio, α , shows the dependence of the phase behavior upon temperature (Fig. 1). At low temperatures, the nonionic surfactant forms micelles in the water and stabilizes an o/w emulsion in the two-phase area. Oil solubilization increases when the temperature is raised and then the three-phase area is reached in which a microemulsion forms. At low surfactant concentration, the system separates into three phase. The three-phase area forms the body of the so-called Kahlweit-fish. At higher surfactant concentrations, in the tail of fish, the surfactant phase can solubilize the entire oil and water quantity. The point where body and tail of the fish meet indicates content required to form a single-phase microemulsion. The system directly undergoes the three-phase to one-phase transition only at a one single temperature. Thus it is measure for the solubilization capacity of the surfactant used. Once one-phase microemulsion is formed, it can be separated into two phases just by temperature variation.

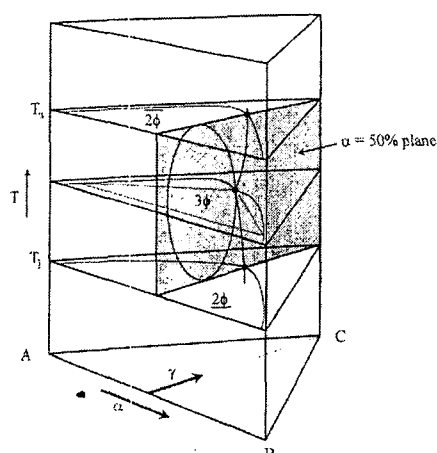


Fig.1. Prismatic Diagram Nonionic Surfactant/Water/Oil System

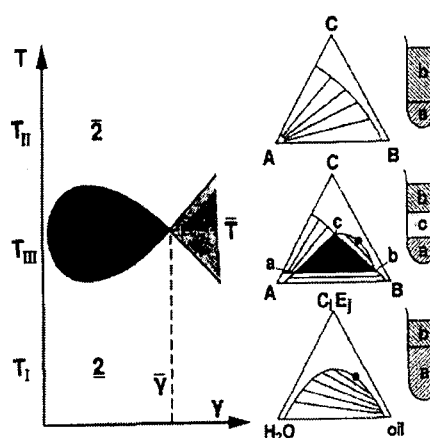


Fig.2. Macroscopic Appearance of a Ternary Surfactant/Oil/Water System

The extension of three-phase is described by an upper temperature T_u and a lower temperature T_l . The mean temperature

$$T_{mean} = \frac{T_u + T_l}{2} \quad (\text{Eq. 1})$$

characterizes the position of three-phase.

2.2 Soil Remediation Process using Microemulsion

Another important property for soil remediation achieved by microemulsion system is their great solubilization capacity. But the most important medium is its temperature-dependent phase behavior. As shown in Fig. 3, 1-phase can be left simply by temperature decrease from extraction temperature $T_{ex}(P)$ to the splitting temperature $T_{sp}(p)$. In this mechanism, phase separation can be achieved after extraction process. By lowering the temperature, the 1-phase system splits into a lower aqueous surfactant-rich phase and an upper oil-rich phase containing most of contaminants extracted.

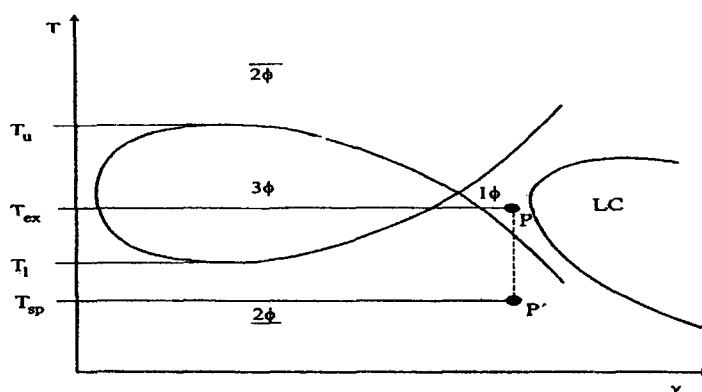


Fig. 3. The Vertical Section of Fig. 1 at Constant α

3 Testing Procedure

3.1 Testing Materials

Pyrene was applied as the polycyclic hydrocarbons (PAH). The other contaminants used in this study are Benzene, Toluene, Ethylbenzene. These compounds are a major constituent of petroleum and related products. Alkylpolyethoxylate (C_iE_j ; i = chain length, j =degree of ethoxylation) was used as the surfactant. C_4E_1 (2-butoxyethanol) was purchased from Aldrich company with a purity >99%. $C_{10}H_{22}$ (Decane, a purity >99%) was used as a oil component. Kaolinite doped with contaminants was used a soil component. The material was air-dried, yielding a particle size of < $74\mu\text{m}$.

3.2 Testing Method

3.2.1 Preparation of Contaminated Soil with Pyrene

Kaolinite(200g) was suspended on 2.8 l of a water-acetone mixture(l/l). A solution of 50mg pyrene in 200ml acetone was added. The whole suspension was stirred for 72hours. It was air-dried at room temperature for 1 week.

3.2.2 Blank Test with BTEX

Blank test was performed for volatilization of BTEX and the quantity sorbed on tube during test procedure. It should be identical in mass balance through the test. After 8day, solutions were sampled and extracted with hexane and finally analyzed with GC(gas chromatography).

Table 1. Blank Test

Time	8day	
Ce / C ₀	Bezene	0.914
	Toluene	0.922
	Ethylbenzene	0.941

3.2.3 Sorption Equilibrium Test

Solutions(BTE, 50ppm) were mixed with soil(kaolinite) in the tube without headspace and shaken with rotary shaker. After 2, 4, 6, 8, 16, 24, 36, 48, 72hr, solutions were extracted with hexane, filled in 2ml vials with supernatant and the concentration of solutions were measured with GC.

3.2.4 Sorption Isotherm Test

Sorption isotherm tests were performed to verify properties of each contaminants. Multi solute system which contained Benzene, Toluene, Ethylbenzene in one time was applied. Experiment in large concentration range (20ppm, 50ppm, 100ppm, 150ppm, 200ppm, 250ppm)was performed.

Table 2 Oven Temperature Program of GC for Analysis of BTE

Oven Ramp	°C/min	Next °C	Hold Min	Run Time
Initial		40	7	7.00
Ramp 1	30	150	5	12.83
Post Run		40	5	17.83

3.2.5 Extraction Test

The systems used for extraction are shown in Table 3. Extraction with system 1, 2, 3, 4 performed at 35°C. Soil was stirred at 200rpm with 60ml of microemulsion in shaking incubator at 35°C. For kinetic studies, the extraction time was varied from 10min to 4hr. To achieve liquid-solid separation, filtration through a membrane filter with pores of 0.45µm was used. Extraction tests of recycling microemulsion were performed through 3times(S-1, S-2, S-3).

Table 3 Surfactant/Oil/Water Composition of Extraction Test

System	C4E1(wt%)	Decane(wt%)	Water(wt%)	α (Oil/Water ratio)	Extraction time
1	55	15	30	50	30min-4hr
2	55	15	30	50	10min-2.5hr
3	55	0	45	0	10min-2.5hr
4	0	0	100	0	10min-2.5hr

4 Results

4.1 Sorption Isotherm Test

4.1.1 Linear Sorption Isotherm

$$K_p = \frac{C_s}{C_e} \quad (\text{Eq. 2})$$

Where, K_p = linear equilibrium partition coefficient

Figure 4 and Table 4 show the result of sorption isotherm test

Table 4 Linear Distribution Coefficient of BTEX

	Benzene	Toluene	Ethylbenzene
K_p	2.11	4.35	8.92

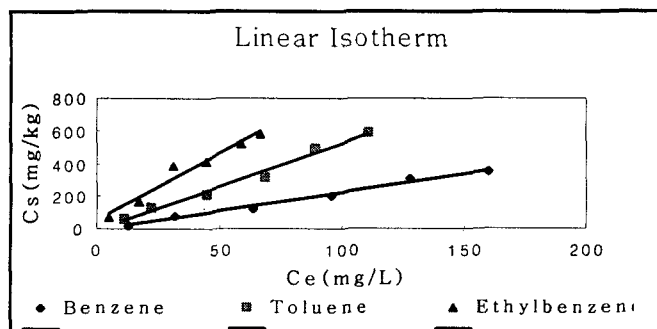


Fig. 4. Linear Sorption Isotherm test

4.1.2 Freundlich Sorption Isotherm

In sorption models, Freundlich isotherm model is adapted when the relationship of C_e and C_s is non-linear. Freundlich isotherm model is acceptable until sorption reaches equilibrium.

$$C_s = K_{fr} C_e^N \quad (\text{Eq. 3})$$

$$\log C_s = \log K_{fr} + N \log C_e \quad (\text{Eq. 4})$$

Where, K_{fr} : Freundlich partition coefficient ($[L^3/M]^N$)

N : Freundlich exponent coefficient

Table 5 Parameters for Freundlich Isotherm

	Benzene	Toluene	Ethylbenzene
N	0.75	0.80	0.89
K_{fr}	2.78	4.22	7.73

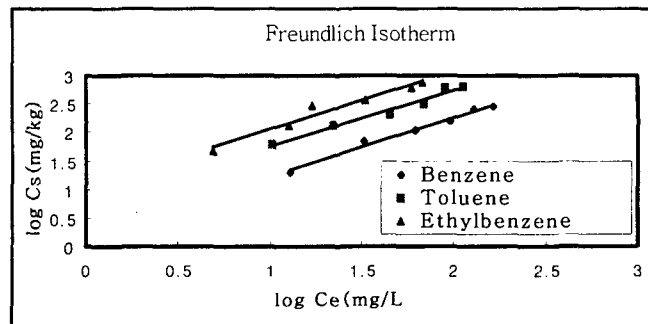


Fig. 5. Freundlich Sorption Isotherm for BTEX

4.2 Extraction Test

4.2.1 Pyrene Extraction Test

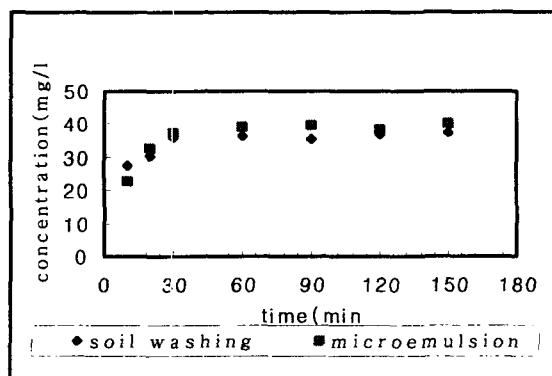


Fig. 6. Comparison of Extraction Result between System 2 and 3.

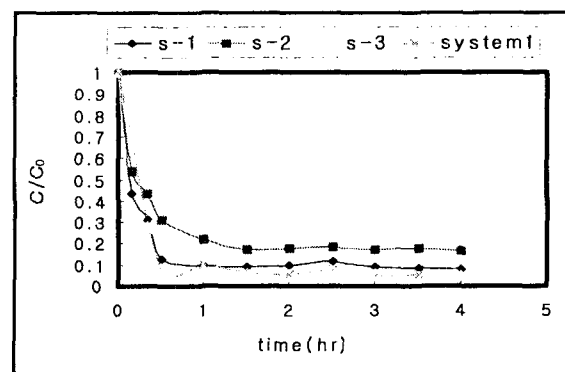


Fig. 7. Comparison of Recycled Microemulsion with system 1.

The extracted concentrations of pyrene in system 2,3 show that in the early stage of extraction soil washing process has a little bit more efficient than microemulsion process. However, the extraction efficiency of microemulsion as extraction medium is proved to be better as approaching equilibrium. In the soil washing process, about 89% pyrene was removed and reach equilibrium at 60min. In the soil washing process, about 92% pyrene was removed and reach equilibrium at 30min.

4.2.2 Benzene Extraction Test

Figure 8 shows extraction result of system 2. The extracted concentrations of benzene in system 2 shows rapid removal of contaminant by microemulsion. About 85% benzene was removed and reach equilibrium at 30min. Figure 9 shows differences between microemulsion and soil washing process. Like result of pyrene extraction test, soil washing with surfactant has similar removal efficiency compared with microemulsion process. However, soil washing process without surfactant is lower than that of microemulsion in removal efficiency.

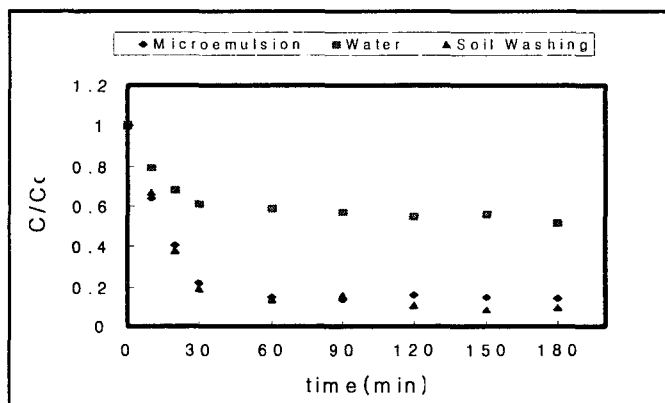


Fig. 8. Comparison between Microemulsion and Soil Washing Process(Benzene)

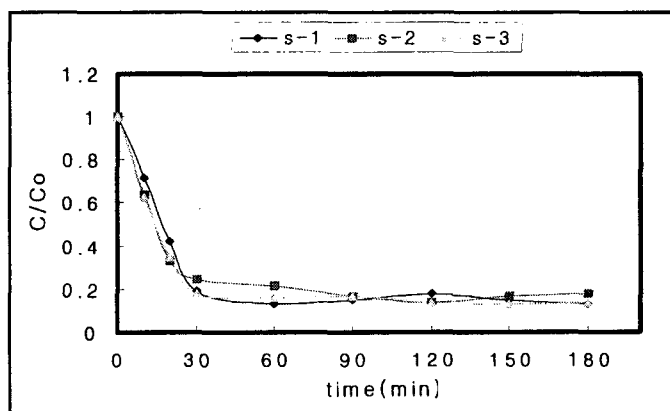


Fig. 9. Removal Efficiency of Recycled Microemulsion (Benzene)

5 Conclusion

Microemulsions are formed on a range of 22 and 48°C at surfactant contents $\alpha = 55\text{wt}\%$. Appropriate microemulsions such as C₄E₁/Decane/Water were found for application in soil remediation. C₄E₁/Decane/Water microemulsion is a good extraction media for removing organic contaminants like pyrene and BTEX as a representative contaminant from the soil. The extraction rates are higher than that of soil washing process and contaminants can be easily dissolved in microemulsion. Separation of microemulsion with the oil phase was performed successfully. Results of extraction test show excellent removal efficiency of contaminants on a range of 80 to 90%. In recycling extraction test, recycled microemulsion shows little difference in removal efficiency.

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