A Study on the Surfactant-Enhanced Desorption of Organic Contaminants from Soil Particles

계면활성제를 이용한 지반 오염물질의 탈착 연구

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요 지

계면활성제를 이용하여 흙입자에 흡착된 유기오염물질을 탈착시키는 실험을 실시하였다. 용매로는 중성 세제와 음이온성 세제가 사용되었으며 이를 이용하여 흙으로부터 퀴놀린 및 2-나푸톨을 분리하였다. 음이온성 세제로 퀴놀린은 약 80%, 2-나푸톨은 90% 가량 탈착되었으며, 중성 세제보다 음이온성 세제가 위의 두 오염물질에 대하여는 더 효과가 좋은 것으로 나타났다. 이온이 제거된 물로 두 오염물질에 대한 탈착실험을 행하여 계면활성제의 탈착능을 물과도 비교하여 보았다.

Abstract

Laboratory tests were performed to desorb organic contaminants spiked onto soil particles by using surfactants. Nonionic and anionic surfactants were tested as potential desorbing solvents for extracting quinoline and 2-napthol adsorbed on soil particles. Anionisc surfactant remediated approximately 80% and 90% of quinoline and 2-napthol respectively and appeared to be more effective than nonionic surfactant in remediating those compounds. Comparison between simple deionized water washing of the organic contaminated soil and a given surfactant technique evaluated the improvement by the application of a surfactant to the promotion of desorption.

Keywords : Surfactants, Desorption, Organic contaminants, In-situ soil remediation

1. Introduction

In a number of places of the world, soil has been contaminated with a wide variety of

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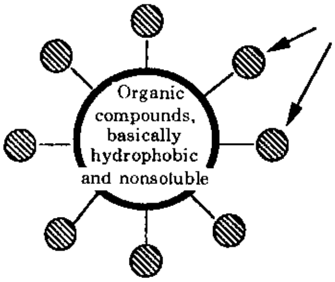
hazardous organic chemical contaminants originating from numerous sources that are associated with industrial, agricultural, or commercial human activities. Organic contaminants can be incorporated with soil particles by physico-chemical interactions between the contaminants and the soil. Once the contamination plume is developed in the soil mass over a period of time, it is sometimes very hard to treat the subsurface to a health-based standard cleanup level due to the difficulty of removing absorbed organic contaminants on soil particles.

For the recovery of contaminated soil, surfactants(surface-active agents) have become potentially attractive flushing agents because as they are injected into a contaminated site they can dislocate weakly sorbed materials through competition for adsorption sites and enhance the solubilization of organic compounds, such that the desorbed contaminants can be degraded by native soil microbs or transported and captured for wastewater treatment porcessing. Basically, surfactants are compounds that have one polar(water soluble, hydrophilic) end, while the other end is nonpolar(organic soluble, hydrophobic). As a result of its amphiphilic nature, they promote aqueous dissolution of hydrophobic organic compounds by forming micelle(Fig.1).



Surfactants make organic compounds water soluble by forming micelle with its hydrophobic head oriented toward the organic compounds and its hydorphilic head away from the organics.

Fig 1. Micelle forming of surfactants

A number of successful uses of surfactants(surface-active agents) for remediation of contaminated soil have been performed. Exner et. al.(1984) reported experiments on the in-place detoxification of dioxin-contaminated soil by spraying the soil with 0.5~3.0% w/w of organic surfactants followed by irradiation with a mercury vapor lamp, which reduced the dioxin concentration in the soil from 671ng/g to 11ng/g, a 98% reduction, within 31 hours. McDermott et al.(1989) used sodium dodecylbenzenesulfonate(anionic surfactant) for extracting PCB from soils. The PCB was recovered from the surfactant solution by precipitation with calcium chloride, reducing the mass of contaminated material to 3% of the original soil mass. Edwards et al.(1991) presented experimental data on the enhanced apparent solubilities of naphthalene, phenanthrene, and pyrene resulting from solubilization in aqueous solutions of commercial, nonionic surfactants. The solubilization of anthracene, phenanthrene and pyrene was also evaluated in soil-water suspensions with several nonionic and anionic surfactants(Liu et al. 1991). Lewis et al.(1992) performed surfactant screening test of diesel contaminated soil. Twenty-two surfactants were screened for their effectiveness in mobilizing the organics from the contaminated soil prior to bioremediation. Overall removal of total petroleum hydrocarbon(THP) generally exceeded 60% for those surfactants showing an enhancement in THP removal over that of water alone. The anionic surfactants performed best in removing the diesel components from the soil, with the remediation percentage approaching 80~90%.

The literature review suggests that the remediation of contaminated soil is feasible by surfactant extraction. However, appropriate methods that can quantify the desorbing potential of surfactants by simple contact shaking of the contaminated soil with a surfactant have not been developed. Thus, the objective of the study is to develop a quick laboratory test to assess the effectiveness of the desorbing solution for contaminants adsorbed on soil particles by physico-chemical processes.

2. Test Materials

Natural silty clay of low plasticity recovered from University of Houston (Fig. 2) was prepared to blend with uniform, fine siliceous Gulf of Mexico sand (100% sand) to make 65% sand, 20% silt, and 15% clay mixture. By unified soil classification system, the original Houston soil was shown to have 15% sand, 48% silt, and 37% clay, while the Gulf of Mexico soil is wholey composed of 100% sand. Native organic content of the test soil is 1.2% and cation exchange capacity is 12.6meq/100g. Atterberg limit tests showed that the liquid limit of the test soil was 22.3%, plastic limit was 17.7%, thus the plasticity index was 4.6%. The void ratio e of the test soil was approximately 0.55.

Two organic contaminats were chosen for testing: quinoline, and 2-napthol. quinoline is representative of fused ring heterocyclic amines; and 2-napthol is a double ring structure phenol compound. Phenolic compounds are important aromatic compounds. These two compounds are U.S.EPA priority pollutants classified as acute toxic wastes. The chemical and physical properties of the contaminants are described in the literature (Lide 1993-1994, and Verschueren 1977).

Nonionic and anionic surfactants were selected as aqueous solutions for extraction tests. Cationic surfactant were not used as decontaminant solutions because (1) the cationic syndets are noted for their disinfecting (bactericidal) properties, thus the surfactant can eliminate the native bacteria which can naturally degrade the contaminants; and (2) cationic surfactants can modify soil surfaces to promote sorption and retard migration of hydrophobic organic compounds. As the nonionic surfactant, Neodol Ethoxylate® 25-3 from Shell Chemical Company was used. Witcolate™ SE-5® from Witco Corporation was used as the anionic surfactant. Both surfactants are biodegradable in soil-water systems. The concentration of the surfactants is 1.0% by weight, which is well above the critical micelle concentration. The critical micelle concentrations for the nonionic and anionic surfactants are

0.001% and 0.01%, respectively. Deionized water was also used as an extraction solution. Comparison between simple water washing of the contaminated soil and a given surfactant technique evaluates the improvement by the application of a chemical solution to promote desorption.

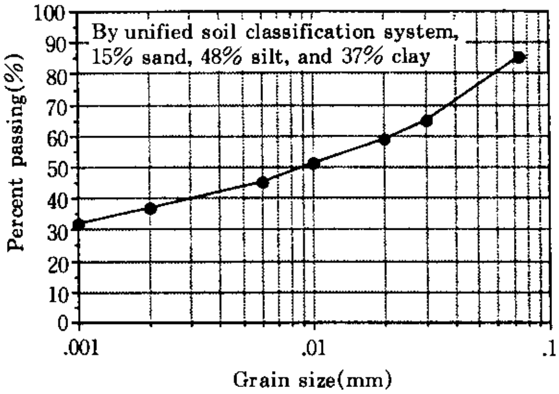


Fig 2. Particle size distribution of University of Houston soil

3. Desorption Studies by Successive Reverse Isotherm Method

As a preliminary test for desorption tests, quinoline and 2-napthol were analyzed for their adsorption characteristics onto the test soil through the adsorption rate tests. Batch adsorption rate experiments were carried out in establishing the adsortption equilibrium time required for adsorption of each contaminant onto the test soil. Test procedures were as follows: (1) Test soil was autoclaved to prevent undersirable biodegradation, which affects the remediation test results. Biodegradation checks were perfomed even though the soil was autoclaved. Autoclaving was performed for an hour at 250℃ and 139kPa, (2) Ten accurately weighed(±1.0mg) 6g samples of autoclaved and dried test soil were place in clean autoclaved 8 mL Pyrex® vials and mixed with 5 mL of aqueous contaminant solution at a concentration of 50.0 mg/L. The vials were sealed with Teflon® lined caps, (3) The vials were stored in the refrigerator at 4℃ in a shaking position(with Fisher Shaking Water Bath Model 129®). Physical shaking or agitation can keep mixing the contaminants with soil particles homogeneously, so that the soil particles can be more exposed to the contaminants and the rate of adsorption will increase, (4) Two mixture samples were withdrawn after every 24 hours of contact time and centrifuged at 2500 rpm for a period of 15 minutes in a refrigerated centrifuge (Damon Model CRU 5000 Centrifuge®) in order to separate the solid from the liquid phase. Supernatant liquid of 4.2 mL from each sample was extracted with syringes and analyzed for the concentration of organic compound on a gas chromatography(GC).

The results of the adsorption rate tests shown in Fig. 3 demonstrate that equilibrium of each organic compound was closely approached within 24 hours. The initial aqueous solution concentration of quinoline reaches equilibrium at 23.0mg/L, and 2-napthol at 24.9 mg/L within 24 hours. Based on this result, an equilibrium time of 24 hours was selected for further testing of these organic compounds. A 24-hour contact period is a conservative period to reach equilibrium. For organic compounds, no evidence of biodegradation existed because equilibrium concentrations were well maintained after equilibrium was established.

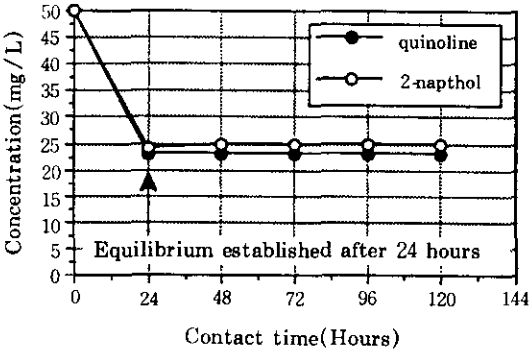


Fig 3. Adsorption rate test for organic compounds

As a major test of the study, desorption tests were conducted for those contaminants by simple contact shaking of the contaminated soil with an aqueous surfactant solution of the extracting agent, primarily to assess the effectiveness of the surfactants, termed here the successive reverse isotherm, or "SRI," procedure. Successive washing of the contaminated soils by a surfactant was performed, and the amount of extracted organic contaminant was analyzed by gas chromatography.

The following procedure was used to study the desorption potential of the various desorption compounds on the test soil.

(1) Based on the adsorption rate studies, each contminant was mixed thoroughly with initially dry, powdered and autoclaved test soil for 24 hours on a shaking table at 4℃. Approximate sample sizes were 6 g of test soil and 5 mL of contaminant solution at a concentration of 50mg/L.

(2) Sample vials were centrifuged at 2500 rpm for at least 15 minutes in a refrigerated centrifuge (Damon Model CRU 5000 Centrifuge®) in order to separate the solid from the liquid phase, and approximately 2.5 mL of the clear supernatant solution was decanted. The concentration of the contaminant in the supernatant solution was then determined by gas chromatography. The detector used was a flame ionization detector.

(3) An aqueous solution of the surfactant equal to the volume of liquid decanted was then added to the sample, and the resulting soil/liquid mixture was agitated gently by hand in

the vial at room temperature for a period of time necessary to reach equilibrium (approximately 5 minutes). Preliminary tests were conducted to establish agitation time to reach equilibrium for the desorption process.

(4) The sample vials were again centrifuged, and approximately 2.5 mL of the clear supernatant solution was again decanted. Because this supernatant solution contained contributions from both the initial contaminant and contaminant removed from the soil during Step 3, keeping track of the weight of contaminant adsorbed on the soil solids at the end of Step 1 and Step 3, comparison, as indicated below, was necessary to compute the degree of desorption or remediation.

(5) The process was then repeated several times, decanting half of the supernatnat after agitation and adding back an equal volume of decontaminant solution until no further removal of contaminant could be observed. SRI tests were always conducted on replicate samples. Calculations of desorption are as folows:

The amount of contaminant loaded on soil after adsorption equilibrium is calculated as

$$\alpha = \frac{(X - Y)Z}{1000\ \mathrm{mL/L}}, \tag{1}$$

in which

α=amount of contaminant contained in the soil in Step 1, in mg,

X=initial concentration of the contaminant in aqueous solution in mg/L,

Y=concentration of contaminant remanining in solution after equilibrium, as measured by gas chromatography in the decanted supernatant solution, in mg/L, and

Z=volume of contaminant solution, in mL.

Furthermore, we have

$$\beta_o = \frac{Y(Z-\delta)}{1000\ \mathrm{mL/L}}, \tag{2}$$

in which

β_o=amount of contaminant, in mg, still in solution after decanting δ mL of supernatant liquid.

Then, we get

$$\beta_f = \frac{Y'(Z-d)}{1000\ \mathrm{mL/L}}, \tag{3}$$

in which

β_f=amount of comtaminant, in mg, in solution after adding back δ mL of the decontaminating solution, shaking until a new equilibrium condition is reached, an decanting δ mL again, and

Y'=new concentration of contaminant remaining in solutionf after equilibrium, as measured in the decanted supernatant solution, in mg/L.

Finally, the quantity of contaminant removed in each step, in mg, is $\beta_o - \beta_f$. Since the process is progressive, the amount of contaminant removed, ρ, as a percentage by weight of the initial contaminant applied after i washing cycles with the decontaminant solution was given by (4), where i was the washing cycle number,

$$\rho(\%) = \frac{\sum_{i=1}^{I} (\beta_o - \beta_f)_i}{\alpha} \times 100 \tag{4}$$

The results of SRI tests on quinoline and 2-napthol are shown in Figs. 4 through 7. Anionic surfactant desorbed quinoline almost up to 80% while nonionic surfactant and deionized water desorbed 55% and 28% of quinoline from the soil, respectively. Anionic surfactant at 1% concentration desorbed quinoline almost three times as much as deionized water. Anionic surfactants have sodium ions in their structures and ionize to yield Na^+ and a negatively charged surfactant ion that is resistant to sorption on the negatively charged soil particles because of charge repulsion. This can be an advantage of the surfactant. It should not adsorb significantly to sedimentary materials compared to cationic or nonionic surfactants. Quinoline is hydrophobic compound, and the anionic surfactant makes the surface of the contaminant hydrophilic (water-wettable). This altering of the surface chemistry apparently results in an increase of the water solubility and improves the remediation process. For 2-napthol, anionic surfactant desorbed more effectively than nonionic surfactant and deionized water did since it makes the surface of the 2-napthol hydrophilic. This reaction results in a remediation percentage of up to 90% in the SRI test, while nonionic surfactant and deionized water worked 40% and 45%, respectively. Generally, most of the anionic surfactants do not adsorb onto the soil surface because the face surface of clay soil particles is negativley charged. However, some portion of the anionic surfactants can

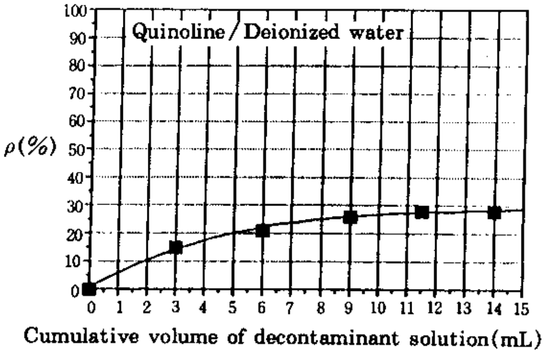


Fig 4. Successive reverse isotherm test for quinoline with deionized water

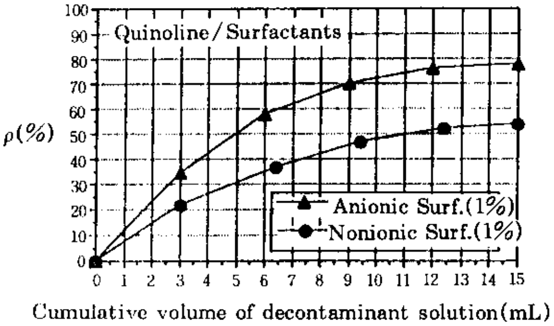


Fig 5. Successive reverse isotherm test for quinoline with surfactants

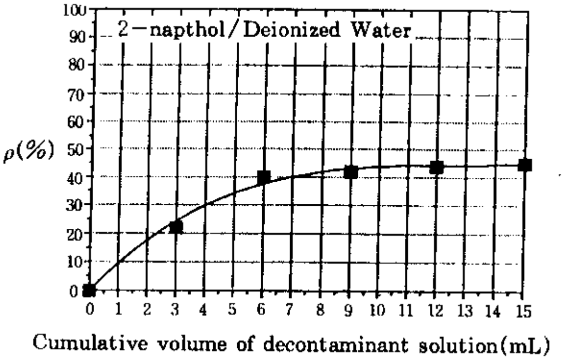


Fig 6. Successive reverse isotherm test for 2−napthol with deionized water

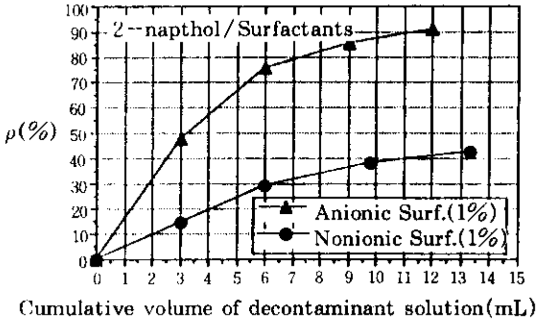


Fig 7. Successive reverse isotherm test for 2−napthol with deionized water

Table 1. Summary of SRI tests (Remediation percentage)

	Quinoline	2-napthol
Deionized Water	28%	45%
Anionic Surfactant(1%)	80%	90%
Nonionic Surfactant(1%)	55%	40%

still adsorb on to the edge surface of the clay particle when it is positively charged. But nonionic surfactants might adsorb onto the soil surface, releasing contaminants which adsorb mainly onto soil particles. Thus, anionic surfactants seem to be more effective for poly-aromatic hydrocarbons like quinoline and 2-napthol that adsorb on the organic matter in soil rather than onto soil particles. Table 1 summarizes the results of the SRI tests.

4. Conclusions

(1) The SRI(Successive Reverse Isotherm) test was developed as a screening technique for estimating the desorption potential of a given decontaminant solution such as surfactants. The SRI test consists of simple contact shaking of the contaminated soil with an aqueous extracting solution, primarily to assess the effectiveness of the extracting solution.

(2) Quinoline and 2-napthol were desorbed well by anionic surfactant. Eighty and ninety percent of quinoline and 2-napthol were recovered from the soil respectively, while deionized water remediated the contaminants less than 50%. This ensures comparison between

simple deionized water washing of the organic contaminated soil and a given surfactant technique evaluated the improvement by the application of a surfactant to promote desorption. For the contaminated soils by poly aromatic hydrecarbons like quinoline and 2-napthol, anionic surfactant washing seemed to work more effectively than nonionic surfactant which remediated the contaminants less than 60%.

Acknowledgments

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