

THE FATE OF A SURFACTANT DURING BIOLOGICAL TREATMENT OF CONTAMINATED SOILS

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INTRODUCTION

Bioremediation is a very versatile technology that utilizes microbial agents to degrade contaminants to nonhazardous or less hazardous states. This is not a new technology. It has existed since life began on earth and is the principal method used in recycling various hydrocarbons which comprise the mass of the biosphere (Schneider and Billingeley 1990). Bioremediation can and has been applied in the treatment of wastewater, groundwater, and soils contaminated with various organic compounds. By supplying nutrients, electron acceptors, and other factors that are limited in the natural environment, biodegradation rates of organics are accelerated. This technology offers a cost-effective, environmentally safe, and field-available remediation alternative when compared to pump and treat methods for remediation of contaminated sites.

The most common biological treatment is *in-situ* bioremediation. *In-situ* bioremediation involves stimulating indigenous microorganisms to degrade the pollutant or contaminant which is adsorbed onto soils within the saturated zone of a site (Ryan et al. 1991). In order for bioremediation to be more effective, additives such as surface active agents or surfactants may be used to increase the bioavailability of contaminants to the microorganism. These surface active agents, such as soaps or detergents, are favorable chemicals in remedial processes due to their ability to be transported through porous media. However, issues pertaining to the ultimate fate of dosed surfactants within the sub-surface remain unknown.

During bioremediation treatment there has been concerns about the interaction of surfactants in soil and soil/aqueous systems. Although these chemicals have been introduced into the environment as a basis for remedial action at the contaminated region, there is still relatively little known as to the fate of surfactant within the biological active zone. This study uses the nonionic

surfactant, Tween 80, to evaluate the fate mechanisms of the surfactant within the soil systems. Surfactants are suitable additives for remediation purposes because of their amphiphilic characteristics. These amphiphilic molecules exhibit polar as well as nonpolar qualities (Pennell et al 1993). In polar solvents such as water, the polar end of the molecule has an affinity for water and other polar substances. The nonpolar end of the surfactant molecule is hydrophobic forming structured aggregates referred to as micelles. The cluster of hydrophobic groups provide an ideal environment for hydrophobic contaminants which may otherwise have a low solubility in polar environments.

This study is designed to determine the fate of a nonionic surfactant in heterogeneous subsurface environments. Because soil is one of the most poorly defined variables that affect *in-situ* bioremediation rates, this study will be performed on six different soil-types designed to represent the diversity of soils found in nature. It is anticipated that the behavior of Tween 80 in soil is strongly related to soil-type. By adding a surfactant to the soils or subsurface surroundings, this addition enhances the biodegradation process by increasing the bioavailability of the contaminants to the microorganisms.

MATERIALS AND METHODS

The analytical approach of this study include two different methods for determining the fate of the surfactant in soil and soil/aqueous systems: total organic carbon and spectrophotometry. The first method allows the measurement of surfactant in soils and the supernatant of the soil/aqueous systems. The Analytical Laboratory of the Environmental Chemistry Division at Waterways Experiment Station will conduct the total organic carbon analysis. The second method measures the amount of surfactant in the supernatant of the soil/aqueous systems directly without a calorimetric dye as an indicator for the surfactant. Both measurements

permit the measurement of aqueous-phase surfactant concentrations above and below the critical micelle concentration.

The nonionic surfactant used is polyoxyethylene (20) sorbitan monooleate commercially known as Tween 80. Tween 80 was purchased from Sigma Chemical Company without further purification.

Soil Characterization

The five soils were collected from different regions of the United States. They are: (1)Crot (AZ): high pH; (2)Alligator clay (MS): high cation exchange capacity; (3) Tellico loam (TN): high extractable iron content; (4) WES reference (MS): high in organic matter; (5) Gessie (IN): high calcium; and (6) sand. The sand was purchased from USA Silica Co., Ottawa, IL. The Petrography and Chemistry Branch at Waterways Experiment Station determined the mineralogy, chemical, and physical properties present in the soils by X-ray diffraction (XRD) analysis. For XRD analysis, a portion of each soil sample was ground in a mortar and pestle to pass through a 45 μ m (No.325) mesh sieve. The data is summarized in Tables 1, 2, and 3.

Total Organic Carbon Measurements

In this technique, each test sample was prepared in 250 ml nalgene centrifuge bottles with 60 g of soil and 140 ml precalculated surfactant solution. The surfactant solution concentrations range from 0 to .01%. The centrifuge bottles were sealed with polypropylene screw caps. The samples were equilibrated for 24 hours on reciprocating shaker (bottles aligned with the direction of the stroke) at 120 strokes/min. The supernatant solution was filtered through a 47mm glass fiber filter and analyzed for surfactant using the total organic carbon method, ASTM D4779-88.

Spectrophotometry

Samples were also analyzed on the UV spectrophotometer. The test samples were prepared by the procedure described previously except that the supernatant was filtered through a 0.45 μ m and 0.22 μ m filter also. The surfactant solution range from 0 to 0.1%. The filtrate was placed in the spectrophotometer for absorbance measurement at 230 nm. Readings were also made for reference samples with the supernatant of the soil-aqueous systems without the surfactant to permit correction for background absorbance. The absorbance values were employed in creating calibration curves.

RESULTS AND DISCUSSION

The appropriate method needed to evaluate the amount of surfactant sorbed on soil and in soil-aqueous systems may depend on the type of surfactant tested and the concentrations of the surfactant. The spectrophotometric method in this study was found to be an effective method for measuring the surfactant's concentration in aqueous systems. The surfactant, Tween 80, appears at a wavelength of 230 nm. Tween 80 has also been known to peak at 210 nm and 280 nm. The various concentrations of Tween 80 were used to show that the concentrations are directly proportional with absorbance (Figures 1 and 2). This preliminary study determined the wavelength of the surfactant and also indicated that the UV detector is able to detect the surfactant without a color indicator, such as azo dye or tungstophosphoric acid. Presently, at this phase of the study, there is no data available for comparing the total organic carbon technique with spectrophotometry. Additional work will be conducted to understand the underlying process affecting the nonionic surfactant sorption onto natural materials, including adsorption/desorption equilibrium isotherm, adsorption kinetics, and biological uptake of surfactant. Such information will aid the quantification and prediction of the behavior of nonionic surfactant in soils and soil-aqueous systems.

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Table 1. Soil Solids Characterization							
		<i>Ottawa</i>	<i>WES</i>	<i>Tellico</i>	<i>Gessie</i>	<i>Alligator</i>	<i>Crot</i>
TEST	(UNIT)	Sand	Clay	Sandy Clay	Sandy Clay	Clay	Sandy Clay
[Ca]	mg/kg	<20.0	1440	416	13300	2560	59500
[Fe]	mg/kg	103	21100	51600	17900	16400	13500
[Mg]	mg/kg	<25.0	2090	1050	7920	2850	15000
[Mn]	mg/kg	<0.500	449	3850	647	462	255
[K]	mg/kg	<100	1140	580	983	1560	4470
[Na]	mg/kg	22.5	29	21.5	41.4	7503	5570
[SO ₄]	mg/kg	<50	<55	<53	<51	<51	166
[Cl]	mg/kg	<30	33.4	<32	<31	<31	249
CEC	meq/kg	0.42	10.8	10.5	15.3	16.7	13.6
TKN	mg/kg	5.33	537	455	1090	557	224
NH ₃ -N	mg/kg	3.05	15	6.67	6.83	15.1	4.7
NO ₂ /NO ₃	mg/kg	10.6	6.77	7.85	12.1	10.3	5.84
TP	mg/kg	25.9	606	671	655	514	354
OPO	mg/kg	<0.20	1.38	6.48	2.34	1.37	6.01
TOC	mg/kg	1385	5320	6033	14296	7227	4746
Z poten'l	milli-volts	-84.3	-51.1	-44.2	-75.2	-29.0	-43.2
Plastic index		NA	16	14	12	25	45
Surface area	m ² /g	<1.0	22.68	31.655	12.762	28.87	34.68
Total Intrus. volume	ml/g	0.279	0.397	0.4301	0.378	0.260	0.257
Total Pore Diam. area	m ² /g	0.058	7.641	15.155	5.887	7.81	9.016

Table 1. Soil Solids Characterization (cont.)

Pore Diam. (vol.)	m ^{*c-6}	97.142	13.45	23.443	12.866	1.274	71.854
Medium Pore Diam. (area)	m ^{*c-6}	0.0215	0.013	0.0164	0.015	0.0153	0.0123
Average Pore Diam.	m ^{*c-6}	19.334	0.208	0.1135	0.257	0.133	0.114

Large bold print represents maximum concentrations, small bold print represents minimum concentrations.

Table 2. Soil samples with the soil type I.D.#, particle size distribution, and selected biological and chemical properties.

Soil	Samp. I.D.#	Particle size distribution ¹			microbial density ² (AODC)	Remarks	pH
		%Sand	%Silt	%Clay			
Sand	S1	96	4	0	$(3.4 \pm 0.16) \times 10^6$		6.8
Tellico Loam	S2	38	40	22	$(7.0 \pm 0.04) \times 10^6$	51600 mg/kg Fe 3850 mg/kg Mn 671 mg/kg K 6.48 mg/kg OPO	6.6
Gessie	S3	48	46	6	$(1.4 \pm 0.01) \times 10^7$	1090 mg/kg TKN 14296 mg/kg TOC	7.2
A. Clay	S4	13	65	22	$(2.0 \pm 0.01) \times 10^7$	7503 mg/kg Na 16.7 meq/100g CEC 15.1 mg/kg NH ₂ N	5.5
WES Ref	S5	8	76	16	$(2.1 \pm 0.01) \times 10^7$		5.3
Crot	S6	56	24	20	$(14.0 \pm 0.01) \times 10^7$	59500 mg/kg Ca 15000 mg/kg Mg 4470 mg/kg K 166 mg/kg SO ₄ 249 mg/kg Cl	10

¹The particle sizes are defined as follows: sand = 2 to 0.05 mm, silt = 0.05 to 0.002 mm and clay = <0.002 mm. ²Data given in colony forming units per milliliter solution (cfu/ml). AODC = Acridine Orange Direct Count of microorganisms.

Table 3. Mineralogic composition of 5 soil samples. In this analysis, Major indicates >20%, Minor indicates <10%, and Trace indicates <5% of a given phase. The upper portion of the table includes the non-clay minerals, and the lower portion includes the phyllosilicates and a zeolite.

Sample	Quartz	Na Feldspar	K Feldspar	Hematite	Amphibole	Calcite	Dolomite
WES	Major	Minor	Minor	-	-	-	-
Tellico	Major	-	Trace	Minor	-	-	-
Gessie	Major	Minor	Major	-	-	Trace	Minor
Alligator	Major	Minor	Minor	-	-	-	-
Crot	Major	Minor	Minor	-	Minor	Major	-
Sample	Kalinite	Illite/Mica	Chlorite	Smectite	Hydroxy-Interlayered Smectite	Analcime	
WES	Trace	Minor	Trace	-	Trace	-	
Tellico	-	Trace	Trace	-	-	-	
Gessie	Trace	Trace	-	-	Trace	-	
Alligator	Minor	Minor	Trace	-	Minor	-	
Crot	Minor	Minor	-	Trace	-	Minor	

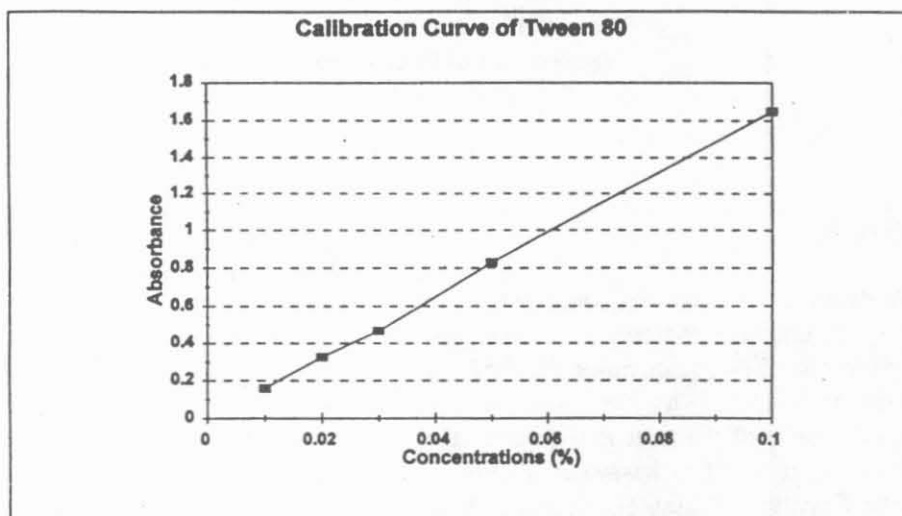


Figure 1. Shows the correlation between the observed absorbance at 230.1nm and percent concentration.

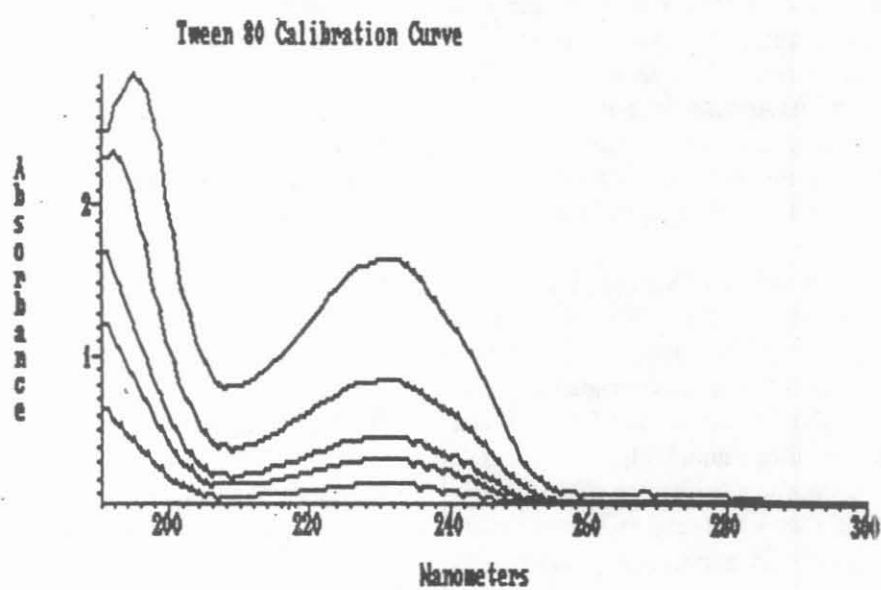


Figure 2.