Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Soil Cleanup by In-Situ Surfactant Flushing. VIII. Reclamation of Multicomponent Contaminated Sodium Dodecylsulfate Solutions in Surfactant Flushing

Julie L. Underwood[a]; Kenneth A. Debelak[a]; David J. Wilson[b]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE [b] DEPARTMENT OF CHEMISTRY, VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE

To cite this Article Underwood, Julie L. , Debelak, Kenneth A. and Wilson, David J.(1995) 'Soil Cleanup by In-Situ Surfactant Flushing. VIII. Reclamation of Multicomponent Contaminated Sodium Dodecylsulfate Solutions in Surfactant Flushing', Separation Science and Technology, 30: 11, 2277 — 2299

To link to this Article: DOI: 10.1080/01496399508013112

URL: http://dx.doi.org/10.1080/01496399508013112

SEPARATION SCIENCE AND TECHNOLOGY, **30**(11), pp. 2277–2299, 1995

Soil Cleanup by In-Situ Surfactant Flushing. VIII. Reclamation of Multicomponent Contaminated Sodium Dodecylsulfate Solutions in Surfactant Flushing

JULIE L. UNDERWOOD and KENNETH A. DEBELAK
DEPARTMENT OF CHEMICAL ENGINEERING

DAVID J. WILSON
DEPARTMENT OF CHEMISTRY

VANDERBILT UNIVERSITY
NASHVILLE, TENNESSEE 37235

ABSTRACT

Solvent extraction with hexane has been studied for use in reclaiming contaminated surfactant solutions for reuse in remediation of hazardous sites. The hexane flow rate, sodium dodecylsulfate (SDS) concentration, and contaminant mixture were varied to determine their effects on the removal of multicomponent mixtures of phenanthrene, naphthalene, and biphenyl. Hexane flow rates greater than 60 mL/min were found to remove greater than 80% of phenanthrene and naphthalene after 1.5 hours of extraction time. The mass transfer rate increased until a hexane flow rate of about 60 mL/min was reached and then remained essentially constant. In experiments in which the SDS concentration was varied from 10 to 100 mM in aqueous solutions of mixtures of phenanthrene and naphthalene, the removal percentages for naphthalene were 98, 91, and 82, respectively, for 10, 50, and 100 mM SDS solutions after 2 hours of extraction, and for phenanthrene were 94, 88, and 75%. The mass transfer rates in these experiments increase with increasing SDS concentration. Mixtures of phenanthrene and biphenyl, naphthalene and biphenyl, and phenanthrene, naphthalene, and biphenyl were all removed at rates similar to the removal rates of the individual compounds. Initial mass transfer rate studies and sodium chloride (NaCl) experiments were conducted to investigate which mechanism better described the extraction process, a five-step adsorption/desorption model similar to the Langmuir–Hinshelwood mechanism for catalysis or a diffusion model in which solubilized contaminants in micelles diffuse through an aqueous boundary layer to the hexane drop. Experiments with phenanthrene in 10, 25, 50, 75, and 100 mM SDS were conducted in the extraction column, and the initial rate of mass transfer was calculated for each run. The results were inconclusive as to which step in the mechanism (adsorption, surface exchange of solubilized pollutants, or desorption) was the rate-limiting step. The NaCl experiments showed that increasing the salt concentration in SDS solutions did not increase the mass transfer rate of a mixture of phenanthrene and naphthalene, suggesting that the micelles may not have to actually adsorb onto the hexane drops to transfer material, as in the diffusion model.

INTRODUCTION

The contamination of soils and groundwater with volatile and/or nonvolatile organics from underground storage tanks, spills, and improper waste disposal presents a major remediation problem in the United States and other industrial nations. The removal/destruction of organics either in the absorbed state or present as dense nonaqueous phase organics (DNAPL) has been approached using several technologies: pump and treat, soil vapor stripping, in-situ biodegradation, in-situ heating using radio frequencies, surfactant flushing, and others. This paper is concerned with surfactant flushing. Ellis, Payne, and McNabb (1) were among the first to publish results of a lab-scale study on surfactant flushing. Nash (2) performed a field study of surfactant flushing on a small scale. Vigon and Rubin (3) examined surfactant selection and optimal dosage requirements. Our group has published several experimental and theoretical studies of surfactant flushing (4–11). Workers at Eckenfelder, Inc., have carried out pilot-scale studies of the surfactant washing of soils contaminated with toluene and biphenyl (12–14). The surfactant used was sodium dodecylsulfate (SDS, an anionic surfactant). The pilot study also included the development of a method for the reclaiming and recycling of the SDS solution.

Surfactant flushing removes organic contaminants from soil and groundwater by solubilizing them within micelles in the surfactant solution. This solubilization makes surfactant flushing much more efficient than flushing with water alone when one is attempting to remove hydrophobic organic contaminants; in an earlier paper (11) we focused on the problems associated with spent surfactant treatment and surfactant recycle. An anionic surfactant (sodium dodecylsulfate, SDS) was chosen so that solvent extraction could be used to remove the contaminants and reclaim the surfactant solution for reuse. We believed that anionic surfactants would be much less soluble in nonpolar solvents than nonionic surfactants, making solvent extraction possible. Gannon et al. (6) showed that gentle extraction of *p*-dichlorobenzene (DCB) and naphthalene from SDS solution into hexane without emulsion formation was possible. Underwood et al.'s (11) results showed that extraction of contaminated SDS solutions with hexane was an effective method for cleaning up these solutions for recycle. The next step in the development of a reclamation process for the recycle of surfactant solutions is the development of design and scale-up information. In this work we examine some of the kinetics, the effect of solvent flow rate, and surfactant concentrations on an extraction process used to reclaim the surfactant solution and remove the contaminants.

Mechanism for Extraction

Two models of the mass transfer process occurring during solvent extraction of SDS solutions are presented here. The first model involves diffusion of solubilized material through an aqueous boundary layer to a hexane drop. The second model is similar to the one proposed by Shaeiwitz et al. (15) and Carroll (16) involving diffusion of a mixed micelle, adsorption, surface exchange of solubilized material from a micelle to a hexane drop, desorption, and diffusion of a "clean" micelle back into the bulk surfactant phase.

Diffusion Model

Figure 1 illustrates the diffusion process thought to be occurring in the first model. Micelles containing solubilized organic pollutants are con-

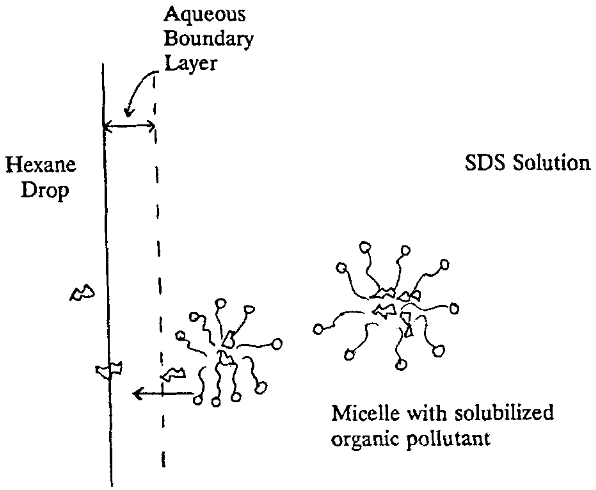
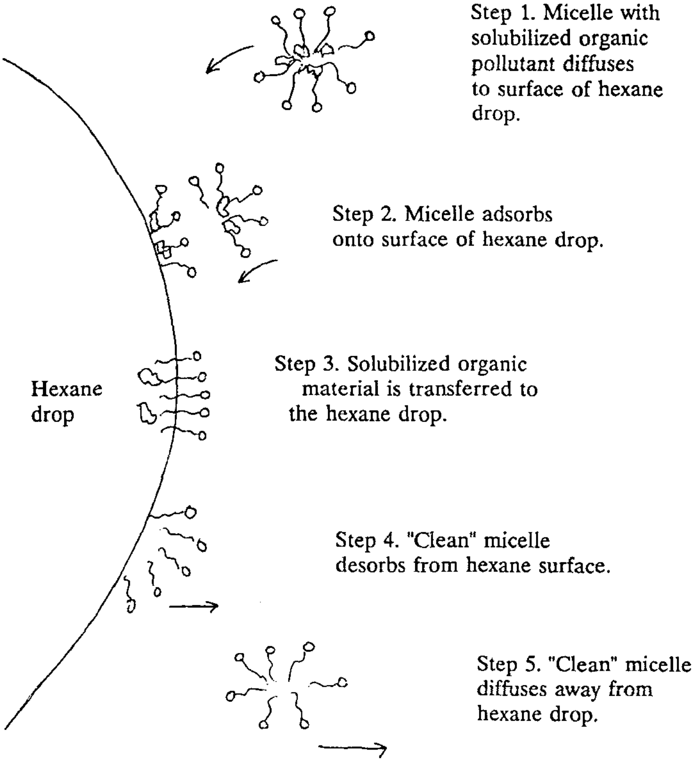


FIG. 1 Diffusion model for hexane extraction of organic pollutants.

tained in the surfactant solution. As hexane drops rise by the mixed micelles, the solubilized material diffuses from the micelles through an aqueous boundary layer and into the hexane drops. The micelles remain intact; they do not adsorb onto the hexane drops.

Adsorption/Desorption Model

An alternative model to the diffusion-only model is one similar to the Langmuir–Hinshelwood mechanism for gas–solid catalysis. The model is depicted in Fig. 2. The first step involves the diffusion of a micelle containing solubilized organic material to the surface of a hexane drop. Chan et al. (17) state that micelles are typically 40 Å in diameter and contain approximately 100 surfactant molecules or ions. A hexane drop with a diameter of 0.25 cm would then be 6.25×10^5 times larger than a typical



Step 1. Micelle with solubilized organic pollutant diffuses to surface of hexane drop.

Step 2. Micelle adsorbs onto surface of hexane drop.

Step 3. Solubilized organic material is transferred to the hexane drop.

Step 4. "Clean" micelle desorbs from hexane surface.

Step 5. "Clean" micelle diffuses away from hexane drop.

FIG. 2 Adsorption–desorption model for hexane extraction of organic pollutants.

micelle. A micelle would see a hexane drop as a liquid hexane phase. The diffusion of a micelle to the surface of a hexane drop can be written as

$$MO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MO_i \tag{1}$$

where MO symbolizes a micelle containing organic material and i denotes the micelle at the interface.

In the second step the micelle adsorbs onto the surface of the hexane drop as given by the equation

$$MO_i + S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MOS \tag{2}$$

The micelle probably disperses into individual surfactant molecules which are singly charged and require only a small free surface for adsorption (15).

Next, the solubilized organic compound(s) within the micelle become solubilized within the hexane drop. This reaction is given by

$$MOS \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} MS \tag{3}$$

After the mass transfer takes place, the micelles desorb from the surface of the hexane drop:

$$MS \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} M_i + S \tag{4}$$

and then diffuse away from the drop, back into the bulk surfactant solution:

$$M_i \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} M \tag{5}$$

EXPERIMENTAL

Chemicals and Apparatus

The SDS (Fluka) used in the experiments was 98% pure. Other chemicals employed were hexane (Fisher, certified and spectranalyzed), phenanthrene (Eastman and Fluka), naphthalene (Fisher), biphenyl (Aldrich), sodium chloride (Fisher), and toluene (Fisher). All chemicals were used as received.

The apparatus used in the extraction studies involving a distributor is shown in Fig. 3. The glass column was 122 cm long with an inner diameter

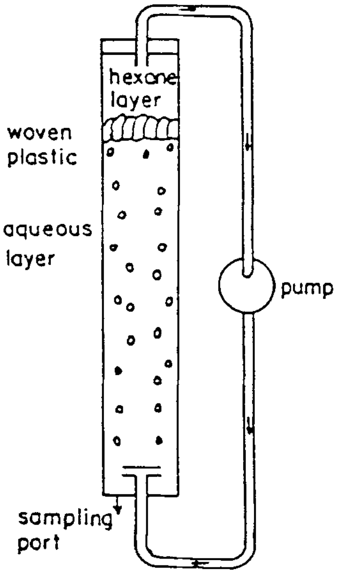


FIG. 3 Apparatus for the extraction experiments using a distributor (12).

of 4.4 cm. The column was fitted with rubber stoppers at both ends. The top stopper contained a glass tube for pumping hexane. The bottom stopper had a glass sample tube that was clamped off and a glass funnel with a fused glass plate on top with nine approximately 0.25 cm diameter holes for distributing the hexane drops. A Cole-Parmer Masterflex peristaltic pump was used to pump the hexane from the top of the column to the bottom. A 7-cm sheet of woven, knitted plastic was placed at the organic–aqueous interface to help the hexane drops coalesce into a layer of hexane.

Extraction Studies with a Distributor

Experiments were conducted in the glass column shown in Fig. 3. The procedure for an experiment began by filling the column with SDS solution contaminated with mixtures of phenanthrene, naphthalene, and biphenyl to a volume of about 1700 mL. About 200 mL of hexane was added on top of the SDS layer, and a 7-cm layer of plastic woven material (pot scrubber) was placed at the aqueous–organic interface to promote hexane drop coalescence. The peristaltic pump was started, signifying the start of the experiment. Samples of SDS solution (5 mL) were taken every 5 minutes for the first 20 minutes, then every 15 minutes until 1 hour, and then every 30 minutes until the end of the run. Hexane samples (2 mL) were taken every 15 minutes for the first hour and every 30 minutes afterward until the end of the run. Each run lasted from 2 to 3 hours. Samples were analyzed on a Hitachi UV spectrophotometer (10).

The hexane flow rate, SDS concentration, contaminant mixture, and NaCl concentration were varied to determine their effects on contaminant

TABLE 1
Extraction Experiments with a Distributor

Experimental variable	Contaminant and mole fraction	Hexane flow rate (mL/min)	SDS concentration (mM)	NaCl concentration (M)
Hexane flow rate	0.4 Phenanthrene 0.6 Naphthalene	15	50	0
	0.4 Phenanthrene 0.6 Naphthalene	40	50	0
	0.4 Phenanthrene 0.6 Naphthalene	60	50	0
	0.4 Phenanthrene 0.6 Naphthalene	80	50	0
	0.4 Phenanthrene 0.6 Naphthalene	120	50	0
SDS concentration	0.4 Phenanthrene 0.6 Naphthalene	80	10	0
	0.4 Phenanthrene 0.6 Naphthalene	80	50	0
	0.4 Phenanthrene 0.6 Naphthalene	80	100	0
Contaminant mixture	0.4 Phenanthrene 0.6 Naphthalene	80	50	0
	0.4 Phenanthrene 0.6 Biphenyl	80	50	0
	0.4 Naphthalene 0.6 Biphenyl	80	50	0
	0.333 Phenanthrene 0.333 Naphthalene 0.333 Biphenyl	80	50	0
NaCl concentration	0.4 Phenanthrene 0.6 Naphthalene	40	50	0.05
	0.4 Phenanthrene 0.6 Naphthalene	40	50	0.1

removal. The hexane flow rates used were 15, 40, 60, 80, and 120 mL/min. SDS concentrations of 10, 50, and 100 mM were investigated. Runs were performed with the contaminant combinations phenanthrene/naphthalene, phenanthrene/biphenyl, naphthalene/biphenyl, and phenanthrene/naphthalene/biphenyl. Two sodium chloride concentrations were explored, 0.05 and 0.1 M. Some initial rate studies were conducted with phenanthrene in 10, 25, 50, 75, and 100 mM SDS to investigate the adsorption/desorption model for extraction. The experimental conditions are summarized in Table 1.

RESULTS

Effect of Hexane Flow Rate

Experiments were performed using an extraction column equipped with a distributor head to determine the effect of varying the hexane flow rate on the removal of mixed phenanthrene and naphthalene from 50 mM SDS solutions. Figures 4 and 5 show the phenanthrene and naphthalene concentrations in the aqueous SDS solutions as functions of time for hexane flow rates of 15, 40, 60, 80, and 120 mL/min. The percentages of phenanthrene and naphthalene removed after 1.5 hours of extraction time are given in Table 2. All removal percentages are in the 80% range with the exception of the slowest hexane flow rates of 15 and 40 mL/min.

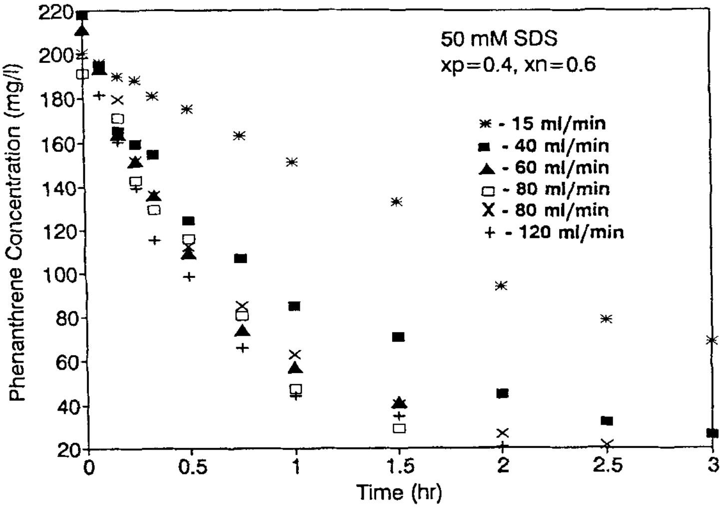


FIG. 4 The effect of hexane flow rate on the removal of phenanthrene from 50 mM SDS.

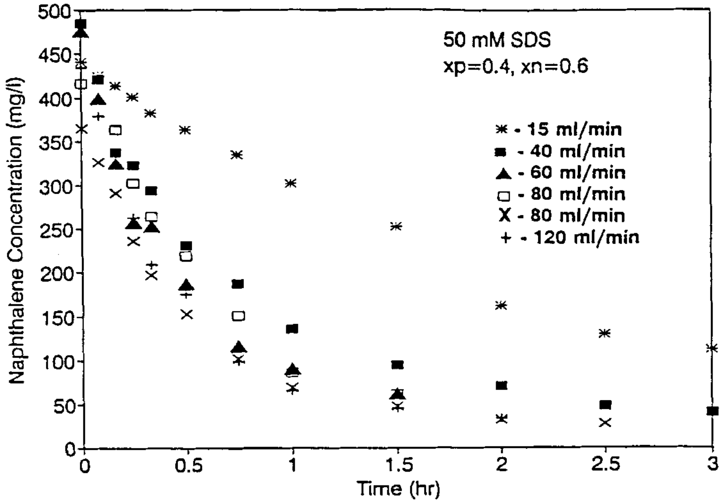


FIG. 5 The effect of hexane flow rate on the removal of naphthalene from 50 mM SDS.

The initial mass transfer rates were calculated for each hexane flow rate by fitting the first 20 minutes of concentration versus time data to a line by linear regression and taking the derivative of the equation $C = at + b$. The mass transfer rate, dC/dt, is the slope of the best-fit line, a. The mass transfer rates for phenanthrene and naphthalene are plotted as functions of hexane flow rate in Fig. 6. The mass transfer rates increase initially until a hexane flow rate of about 60 mL/min is reached and then appear to reach a constant value.

TABLE 2
Effect of Hexane Flow Rate on the Removal of Phenanthrene and Naphthalene

Hexane flow rate (mL/min)	% Removed after 1.5 hours	
	Phenanthrene	Naphthalene
15	33.7	43.0
40	67.6	80.5
60	80.4	87.0
80	84.7	85.2
80	81.6	86.8
120	82.4	89.6

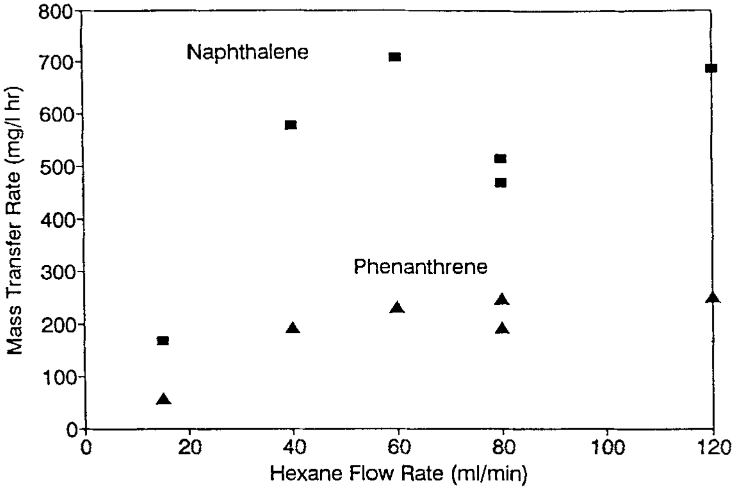


FIG. 6 Mass transfer rates of naphthalene and phenanthrene as functions of hexane flow rate.

Effect of SDS Concentration

Another set of experiments was conducted with the mole fraction of phenanthrene (x_p) equal to 0.4 in the solid phase and naphthalene (mole fraction $x_n = 0.6$) as the other component in the mixture. Figures 7 and 8 are graphs of the phenanthrene and naphthalene concentrations in the SDS phase versus time for SDS concentrations of 10, 50, and 100 mM. Increasing the SDS concentration increases the initial phenanthrene and naphthalene concentrations so that a longer extraction time is required to achieve the same percent removal. The removal percentages of naphthalene after 2 hours of extraction are 98, 91, and 82, respectively, for 10, 50, and 100 mM SDS solutions. For phenanthrene the percentages are 94, 88, and 75 for 10, 50, and 100 mM SDS solutions after 2 hours of contacting in the column. Mass transfer rates were calculated for the three SDS concentration runs as previously described for the hexane flow rate runs. Figure 9 shows the mass transfer rates of naphthalene and phenanthrene from initially saturated solutions as functions of SDS concentration. The mass transfer rate increases with increasing SDS concentration.

An experiment was also performed in which a 50-mM SDS solution was initially saturated with phenanthrene and naphthalene and then SDS was added to the solution to make the concentration 100 mM. This solution was treated in the extraction column, and the mass transfer rates were

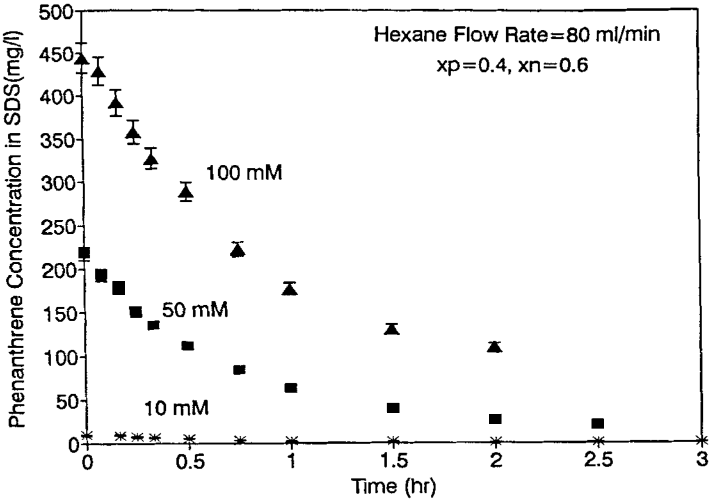


FIG. 7 The effect of SDS concentration on the removal of phenanthrene from SDS solutions.

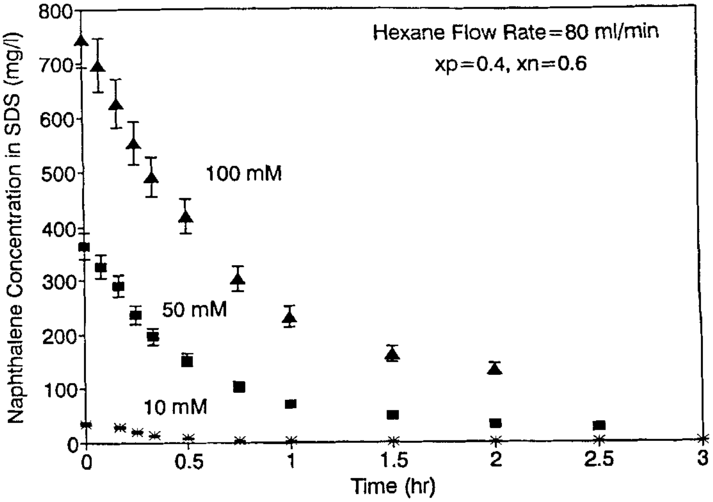


FIG. 8 The effect of SDS concentration on the removal of naphthalene from SDS solutions.

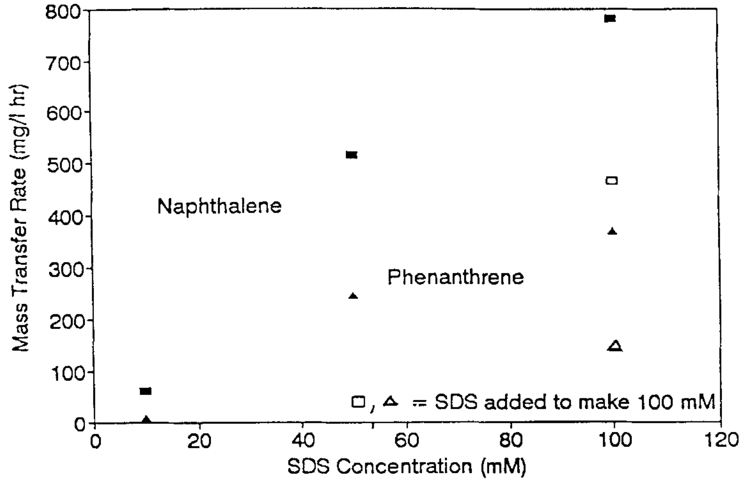


FIG. 9 Mass transfer rate of phenanthrene and naphthalene as a function of SDS concentration (□ and △ = saturated 50 mM SDS solution to which SDS was added to make a 100-mM SDS solution).

calculated. These rates also appear on Fig. 9. The rates (144 mg/L·h-phenanthrene, 464 mg/L·h-naphthalene) are about half those for saturated 100 mM SDS (368 mg/L·h-phenanthrene, 782 mg/L·h-naphthalene), as expected.

Effect of Contaminant Mixture

The removal rates of other mixtures of the three organic compounds were observed and compared to the removal rates of the single compounds. Figure 10 shows the removal of phenanthrene (x_p = 0.4) and biphenyl (x_b = 0.6) from a 50-mM SDS solution. The two compounds in the mixture are removed from SDS at about the same rate as if they were each separately extracted from the SDS solution. Similar results were found for a mixture of naphthalene (x_n = 0.4) and biphenyl (x_b = 0.6) in 50 mM SDS; these are pictured in Fig. 11. The percent removal after 2 hours of extraction is 92% for both compounds, similar to the removal percentages of the individual compounds from SDS solutions. The build-up of naphthalene and biphenyl in hexane during this same experiment is shown in Fig. 12. Figures 13 and 14 depict the removal of phenanthrene (x_p = 0.333), naphthalene (x_n = 0.333), and biphenyl (x_b = 0.333) from 50 mM SDS and their build-up in the hexane, respectively. The percent

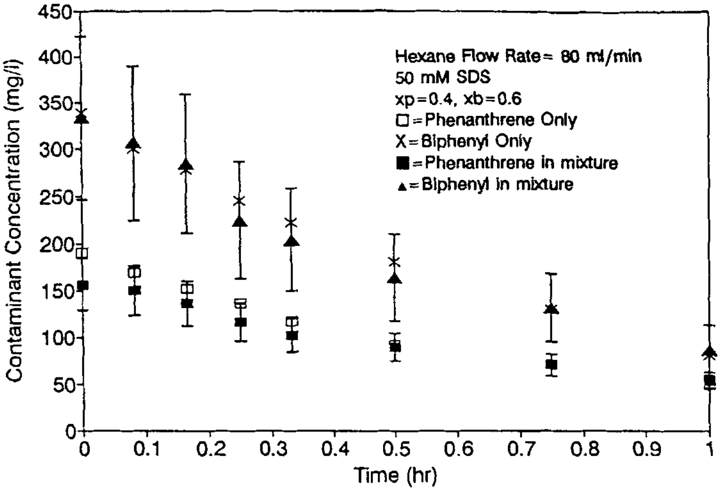


FIG. 10 Removal of phenanthrene and biphenyl from 50 mM SDS.

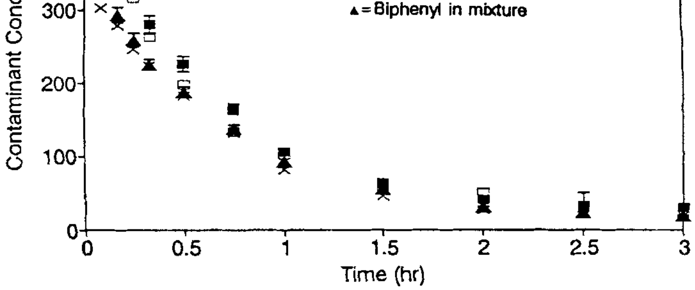


FIG. 11 Removal of naphthalene and biphenyl from 50 mM SDS.

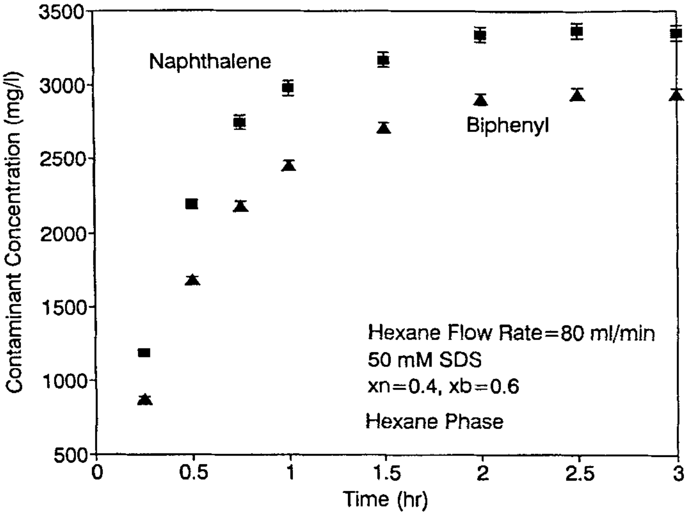


FIG. 12 The accumulation of naphthalene and biphenyl in hexane.

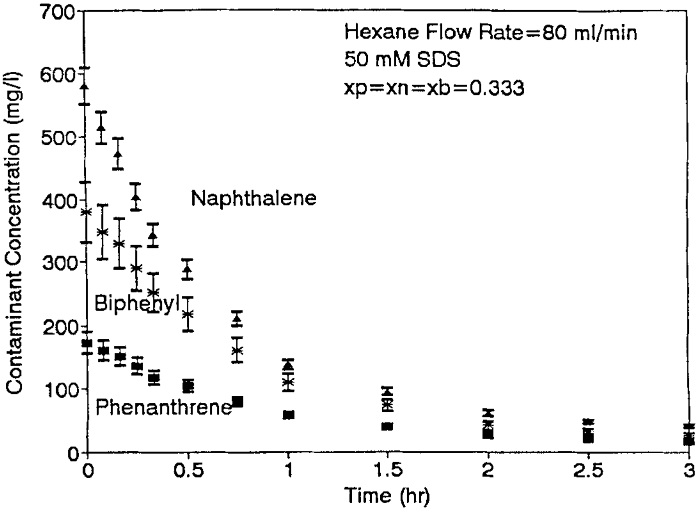


FIG. 13 The removal of phenanthrene, naphthalene, and biphenyl from 50 mM SDS.

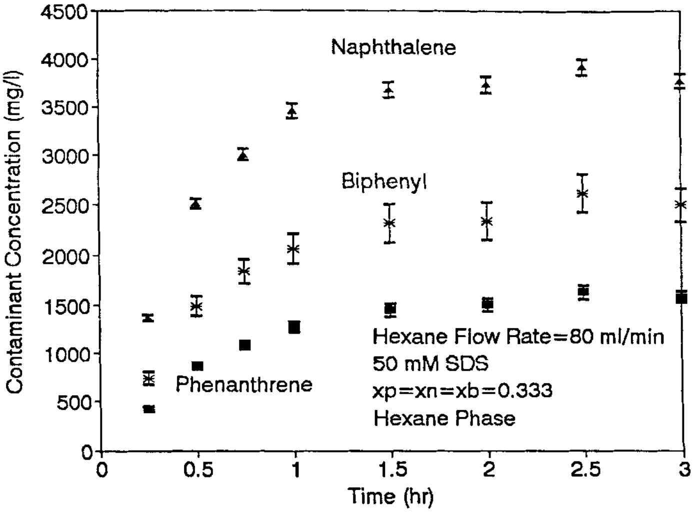


FIG. 14 The extraction of phenanthrene, naphthalene, and biphenyl from 50 mM SDS into hexane.

removals are 84% for phenanthrene, 89% for naphthalene, and 89% for biphenyl after 2 hours of extraction.

Material balances on each component were done to account for all the material transferred between SDS and hexane in the column runs. The percent differences between the mass of pollutant transferred from SDS and the mass extracted by hexane range from 2 to 20% for the concentrations shown in Figs. 11–14.

Effect of Sodium Chloride

The influence of sodium chloride (0.05 and 0.1 M) on the removal of phenanthrene ($x_p = 0.4$) and naphthalene ($x_n = 0.6$) from 50 mM SDS solutions is shown in Figs. 15 and 16. The presence of NaCl in the SDS solutions increases the initial concentrations of phenanthrene and naphthalene by about 10–20% over their initial concentrations in SDS with no NaCl. The removal of the compounds does not seem to be influenced by sodium chloride, as seen in Table 3. Initial mass transfer rates were determined for the sodium chloride experiments and are depicted in Fig. 17 as a function of NaCl concentration. The mass transfer rate does not seem to vary significantly with increasing NaCl concentration.

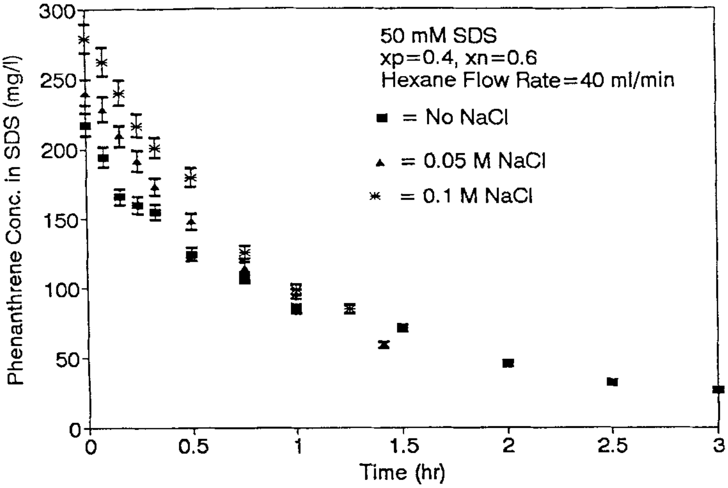


FIG. 15 The effect of sodium chloride on the removal of phenanthrene from 50 mM SDS.

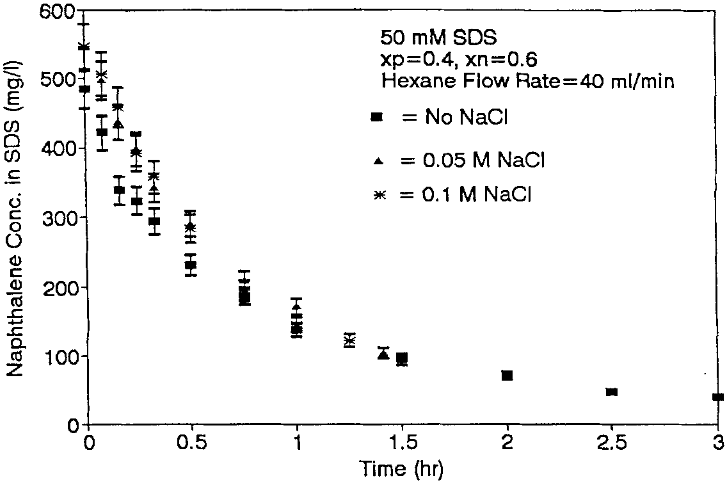


FIG. 16 The effect of sodium chloride on the removal of naphthalene from 50 mM SDS.

TABLE 3
Comparison of the Removal of Phenanthrene and Naphthalene from SDS Solutions Containing NaCl

NaCl concentration (M)	% Removed after 1 hour	
	Phenanthrene	Naphthalene
0	60.9	71.9
0.05	60.4	66.9
0.1	64.7	73.6

Initial Rate Studies

Experiments were conducted in the extraction column using a hexane flow rate of 80 mL/min and SDS concentrations of 10, 25, 50, 75, and 100 mM to determine the initial mass transfer rate of phenanthrene. The purpose of these experiments was to help determine if the adsorption/desorption model was a viable mechanism for the mass transfer occurring during extraction. The first 30 minutes of concentration versus time data were fitted to a line, the slope of which was the initial rate of mass transfer. Figure 18 shows the initial rate of mass transfer as a function of initial concentration of phenanthrene in the SDS phase. The rate increases as

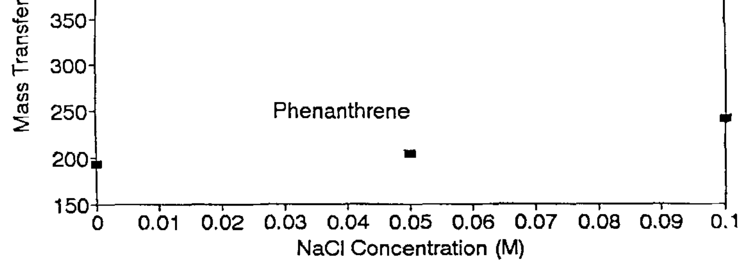


FIG. 17 Mass transfer rates of phenanthrene and naphthalene as functions of sodium chloride concentration.

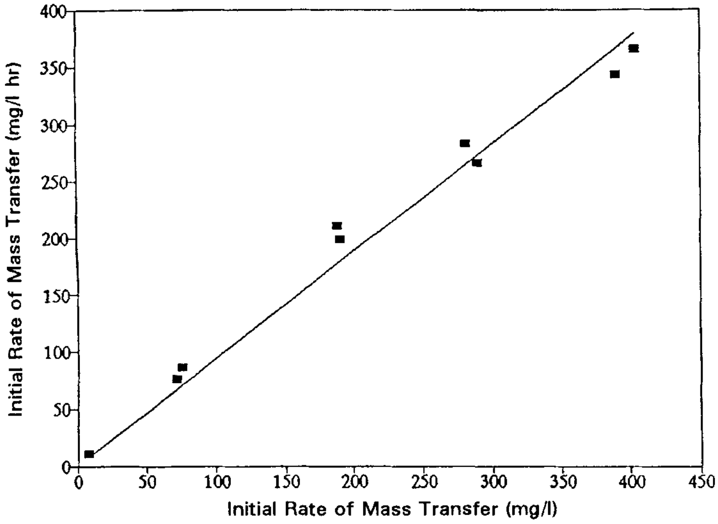


FIG. 18 Variation of initial rate of mass transfer of phenanthrene with initial phenanthrene concentration in the SDS phase.

the initial concentration increases. The best-fit line has a correlation coefficient of 0.98.

DISCUSSION

The extraction experiments in which a distributor was used to produce many hexane drops at a time explored the effect of the hexane flow rate, SDS concentration, contaminant mixture, and NaCl concentration on the removal of pollutant compounds from SDS solutions. The results of these studies were used to propose a model for the mass transfer occurring between hexane drops and SDS micelles.

Effect of Hexane Flow Rate

The concentration profiles of phenanthrene and naphthalene in the SDS phase for various hexane flow rates are given in Figs. 4 and 5. Flow rates of 60 mL/min or greater all appear to remove contaminants at about the same rate, as seen in Table 2. With the slower flow rates of 15 and 40 mL/min, fewer hexane drops are present in the column at any one time, and the result is a slower mass transfer rate, as seen in Fig. 6.

The hexane flow rate experiments indicate that there may be two different factors controlling mass transfer during extraction. At the slower flow rates, the limiting factor is the presence of drops or surface area for mass transfer. At the higher hexane flow rates (80 and 120 mL/min), mass transfer could be limited by the axial mixing occurring which causes larger drops to break up into smaller ones and eventually leads to emulsions forming between SDS and hexane. The higher hexane flow rates result in more hexane drops in the column, but the drops may actually be spending less time in the column due to an "eddy" effect created by the axial dispersion in which drops in the center of the column are pushed upward by swirling aqueous phase near the walls of the column.

Effect of SDS Concentration

The removal of mixtures of phenanthrene and naphthalene from 10, 50, and 100 mM SDS solutions is shown in Figs. 7 and 8. The initial concentration of each of the compounds increases with increasing SDS concentration. The percentage of the compounds removed during the experiments decreases somewhat with increasing SDS concentration (98→82% for naphthalene, 94→75% for phenanthrene) but is still acceptable for the solutions to be reused. The reason that both of these phenomena occur has to do with the increased number of micelles and the increased size of micelles at higher SDS concentrations, which results in a larger volume of micellar phase per liter of solution. Offen, Dawson, and Nicoli (18) and Valenzuela, Abuin, and Lissi (19) found that increasing the SDS concentration increased micellar size. This increase in micellar phase volume increases the amount of solute that can be solubilized by the micelles.

The mass transfer rates for the experiments represented in Figs. 7 and 8 are shown in Fig. 9. The increased number of micelles at higher SDS concentrations leads to increased micellar phase surface area per liter of solution, resulting in increased bulk aqueous phase solute concentrations. The increased concentration difference between the bulk aqueous phase and the hexane phase results in increased mass transfer rates of solutes.

An experiment was performed in which a 50-mM SDS solution was saturated with phenanthrene and naphthalene and then the SDS concentration was increased to 100 mM. The mass transfer rates of the compounds during extraction for the 100-mM solution were about half the mass transfer rates of the 50-mM solution. This result suggests that concentration differences are the driving force for the mass transport. When more SDS is added to a solution previously saturated in phenanthrene and naphthalene, the concentrations of the solutes in the micelles are decreased by an amount proportional to the amount of added SDS. The SDS solution of phenanthrene and naphthalene is "diluted" by increasing the size and number of micelles. The corresponding mass transfer rate during extraction is reduced due to the decrease in solute concentration in the micellar phase.

Effect of Contaminant Mixture

The effect of different mixtures of organic pollutants on their removal from 50 mM SDS solutions was investigated, and the concentration profiles of the contaminants are shown in Figs. 10, 11, 13, and 14. About 90% of all of the compounds in each mixture are removed after 2 hours of extraction. The removal rates of the compounds in the mixtures are very similar to the removal rates of the individual compounds from 50 mM SDS. The removal rates are similar because the compounds are apparently not soluble in each other at the temperature of the experiments. The presence of a second compound in the mixture does not have a strong influence on the removal of the first compound, as indicated by the solubility results previously (10). This is true for phenanthrene, naphthalene, and biphenyl, but may not be the case for other mixtures of compounds such as an alcohol and naphthalene [Kolthoff and Graydon (20)] or two organic liquids [Chaiko, Nagarajan, and Ruckenstein (21) and Valenzuela, Abuin, and Lissi (19)] in which the solubility of each compound is influenced by the other compound. The solubility differences could lead to removal rates that are somewhat different than the removal rates of the individual compounds. Solubility data on mixtures of pollutants at a hazardous waste site may help indicate the removal behavior of the pollutants during recovery of the SDS solutions.

Mechanism for Extraction

Two models of the mass transfer occurring during solvent extraction of SDS solutions were proposed. The diffusion model, pictured in Fig. 1, suggested that the solubilized material in the SDS micelles diffused through an aqueous boundary layer and into the hexane drops. The second model, illustrated in Fig. 2, was a five-step model involving diffusion of micelles to the hexane drop surface, adsorption of micelles on the hexane drop, transfer of solubilized material, desorption of micelles, and diffusion of "clean" micelles back into the bulk SDS solution.

Two sets of experiments were performed to gain insight into which model better described the extraction process: initial rate studies and sodium chloride studies. The initial rate studies were conducted in the extraction column with a distributor. The initial rates of mass transfer were determined for phenanthrene in each SDS solution and plotted as a function of initial SDS concentration (see Fig. 18). The adsorption/desorption model was tested by assuming that the diffusion steps occur rapidly and that each of the three steps, adsorption (Eq. 6), surface exchange of material (Eq. 7), and desorption (Eq. 8), in turn are rate-limiting in the extraction process. Expressions relating the initial rate of mass transfer, r_0, to the initial phenanthrene concentration, C_0, are

$$r_0 = k_2 S_0 C_0 \qquad \text{(adsorption)} \tag{6}$$

$$r_0 = \frac{k_3 K_2 S_0 C_0}{1 + K_2 C_0} \qquad \text{(surface exchange)} \tag{7}$$

$$r_0 = \frac{k_4 K_3 K_2 S_0 C_0}{1 + (K_3 K_2 + K_2) C_0} \qquad \text{(desorption)} \tag{8}$$

in which the k's are rate constants and S_0 is the total number of adsorption sites on the hexane drop (a constant). If either surface exchange or desorption is rate-limiting, a graph of r_0 versus C_0 should increase initially and then become essentially constant. If the adsorption step is rate-limiting, r_0 vs C_0 should be a straight line with a positive slope. A best-fit line was determined for the data in Fig. 14; the correlation coefficient of the line was 0.98. The data do appear to be slightly curved, however. The results are inconclusive as to which step could be rate-limiting in the adsorption/desorption model.

The experiments with NaCl in the SDS solutions were conducted to further examine the mass transfer process going on during extraction. Two salt concentrations were used, 0.05 and 0.1 M. A mixture of phenanthrene ($x_p = 0.4$) and naphthalene ($x_n = 0.6$) was removed in the experiments from 50 mM SDS solutions. The concentration profiles are shown in Figs. 15 (phenanthrene) and 16 (naphthalene). The initial mass transfer rates were determined and are plotted versus NaCl concentration in Fig. 17. The presence of salt does not appear to affect the mass transfer rate of either compound. Since the salt, which probably decreases the coulombic repulsions between micelles and hexane drops, does not improve mass transfer, this result suggests that perhaps the micelles do not actually have to adsorb onto the hexane drops in order to transfer solubilized pollutants. Instead, the solubilized material may diffuse through an aqueous layer to the hexane drop, as in the diffusion model.

CONCLUSIONS

The extraction studies with a distributor focused on three areas: the effect of hexane flow rate, the effect of SDS concentration, and the effect of contaminant mixture, on the removal of mixtures of pollutants from SDS solutions. The hexane flow rate experiments show that increasing the flow rate increases the mass transfer rate up to a flow rate of about 60 mL/min; the mass transfer rate remains essentially constant beyond this point. At the slower hexane flow rates, the limiting factor appears to be surface area for mass transfer, and, at higher flow rates, the mass transfer is limited by another factor. Over 80% of the contaminants were removed after 1.5 hours of extraction at hexane flow rates greater than 60 mL/min.

Mixtures of phenanthrene and naphthalene in 10, 50, and 100 mM SDS were removed by extraction with hexane. Increasing the SDS concentration increases the initial phenanthrene and naphthalene concentrations so that a longer extraction time is required to achieve the same percent removal. The mass transfer rate increases with increasing SDS concentration due to the increased micellar phase–aqueous phase interfacial area.

Other mixtures of naphthalene and biphenyl, phenanthrene and biphenyl, and phenanthrene, naphthalene, and biphenyl in 50 mM SDS were all removed to the extent of about 90% after 2 hours of extraction. The removal rates of the compounds in the mixtures are similar to the removal rates of the single compounds from 50 mM SDS because the compounds are not soluble in one another, nor are they influenced to a great extent by each other.

The 50- and 100-mM SDS solutions were found to contain a considerable amount of solubilized hexane if mixed to equilibrium with hexane. The concentration of solubilized hexane in the SDS solutions reclaimed by extraction is about one-third to one-sixth of that found at equilibrium.

The initial rate data and the sodium chloride experiments favor the diffusion model over the five-step adsorption/desorption model as a possible mechanism for the extraction process. The initial rate experiments were inconclusive as to whether the adsorption, surface exchange, or desorption step was rate-limiting. The NaCl experiments showed that the addition of salt to SDS solutions had little effect on the mass transfer rate, indicating that the SDS micelles may not have to actually adsorb on the hexane drops to transfer solubilized pollutants.

REFERENCES

1. W. E. Ellis, J. R. Payne, and G. D. McNabb, *Treatment of Contaminated Soils with Aqueous Surfactants*, US EPA Report EPA/600/2-85/129, PB 86-122561 (February 1985).
2. J. H. Nash, *Field Studies of In-Situ Soil Washing*, US EPA Report EPA/600-2-85/110, PB 88-146808 (February 1987).
3. B. W. Vigon and A. J. Rubin, *J. Water Pollut. Control Fed.*, *61*, 1233–1240 (July 1989).
4. D. J. Wilson, *Sep. Sci. Technol.*, *24*, 863 (1989).

5. H. J. Wayt and D. J. Wilson, *Ibid.*, *24*, 905 (1989).
6. O. K. Gannon, K. Bibring, K. Raney, J. A. Ward, D. J. Wilson, J. L. Underwood, *Ibid.*, *24*, 1073–1094 (1989).
7. J. L. Underwood, "Reclamation of Sodium Dodecyl Sulfate Solutions for Re-Use in In-Situ Surfactant Flushing of Contaminated Soils," Masters Thesis, Vanderbilt University, Nashville, Tennessee, August 1990.
8. A. N. Clarke, P. D. Plumb, T. K. Subramanayan, and D. J. Wilson, *Sep. Sci. Technol.*, *26*, 301 (1991).
9. D. J. Wilson and A. N. Clark, *Ibid.*, *26*, 1177 (1991).
10. J. L. Underwood, K. A. Debelak, D. J. Wilson, and J. M. Means, *Ibid.*, *28*, 1527 (1993).
11. J. L. Underwood, K. A. Debelak, and D. J. Wilson, *Ibid.*, *28*, 1647, 1993.
12. A. N. Clark, K. H. Oma, M. M. Megehee, and D. J. Wilson, *Ibid.*, *28*, 2103 (1993).
13. K. H. Oma, A. N. Clark, M. M. Megehee, and D. J. Wilson, *Ibid.*, *28*, 2319 (1993).
14. K. H. Oma, A. N. Clark, M. M. Megehee, and D. J. Wilson, *Ibid.*, *28*, 2507 (1993).
15. J. A. Shaeiwitz, A. F-C. Chan, E. L. Cussler, and D. F. Evans, *J. Colloid Interface Sci.*, *84*, 47 (1981).
16. B. J. Carroll, *Ibid.*, *79*, 126 (1981).
17. A. F. Chan, D. F. Evans, and E. L. Cussler, *AIChE J.*, *22*, 1006–1012 (1976).
18. H. W. Offen, D. R. Dawson, and D. F. Nicoli, *J. Colloid Interface Sci.*, *80*, 118–122 (1981).
19. E. Valenzuela, E. Abuin, and E. A. Lissi, *Ibid.*, *102*, 46–50 (1984).
20. I. M. Kolthoff and W. F. Graydon, *J. Phys. Colloid Chem.*, *55*, 699–712 (1951).
21. M. A. Chaiko, R. Nagarajan, and E. Ruckenstein, *J. Colloid Interface Sci.*, *99*, 168–182 (1984).

Received by editor October 17, 1994