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Soil Clean Up by *in-situ* Surfactant Flushing. VI. Reclamation of Surfactant for Recycle

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ABSTRACT

Solvent extraction has been studied for use in reclaiming contaminated surfactant solutions for reuse in soil surfactant flushing in the remediation of hazardous waste sites. Hexane was used as the solvent to extract *p*-dichlorobenzene (DCB), naphthalene, and biphenyl from 25, 50, and 100 mM sodium dodecylsulfate (SDS) solutions in a continuous countercurrent flow column. The contaminant concentration in the aqueous SDS was followed with time, and the removal was modeled using an unsteady-state model which included diffusion kinetics. The mass transfer time constant was approximately 2 hours. The percent removal of DCB increased with increasing hexane flow rate and decreased with both increasing SDS flow rate and increasing SDS concentration. The concentrations of all three contaminants were reduced by about 90% or better. Extraction of contaminated SDS solutions with hexane appears to be an effective method for cleaning up these surfactant solutions for recycle.

INTRODUCTION

Contamination of groundwater with organic chemicals from underground storage tanks, spills, and waste disposal has become a major problem in the United States. Cleanup procedures can be expensive and slow, may not result in a permanent solution to the problem, and may have substantial negative environmental impact. Development of less expensive and more efficient methods for cleaning up groundwater and soil would have quite substantial benefits.

In-situ methods of cleanup, which treat the contaminated material on site and in place, have a number of attractive features. Clarke and Mutch

(1) and Ghassemi (2) reviewed the field of *in-situ* remediation techniques. *In-situ* soil vapor extraction is an efficient and cost effective method for removing volatile organics from the vadose zone. It cannot, however, be used to remove less volatile compounds, nor can it remove dense nonaqueous phase liquids (DNAPLs) in the zone of saturation.

Surfactant flushing, an *in-situ* technique for removing both nonvolatile and volatile organics from soil and groundwater, may be the solution for cleaning up some waste sites. Surfactant flushing (surfactant flooding or washing, micellar solution flooding) has been used in the petroleum industry for tertiary oil recovery (3, 4). Ellis, Payne, and McNabb were among the first to apply surfactant flushing to hazardous waste cleanup (5); they carried out laboratory studies. Nash (6) carried out field work on a small scale. Vigon and Rubin (7) investigated surfactant selection and dosage optimization parameters. Surfactant flushing has also been studied in the laboratory by our group (8).

Surfactant flushing removes organic contaminants from soil and groundwater by solubilizing them within aggregates (micelles) in the surfactant solution. Surfactants consist of a hydrophobic portion (often a long hydrocarbon chain) and a hydrophilic portion (an ionic or polar head or polyethoxyethylene chain). At concentrations above the critical micelle concentration (cmc), surfactant molecules/ions cluster together to form micelles, generally spherical in dilute solution, with the hydrocarbon tails of the surfactant molecules in the interior of the micelles. Trapped or adsorbed hydrophobic organics can dissolve in the nonpolar micellar interiors, being thereby mobilized for removal. This solubilization makes surfactant flushing much more efficient than flushing with water alone when one is dealing with hydrophobic organic contaminants.

Ellis, Payne, and McNabb (5) used aqueous solutions of nonionic surfactants to flush PCBs, petroleum hydrocarbons, and chlorinated phenols from soils. Removals of over 90% were found with 1.5% surfactant solutions. These removals were orders of magnitude greater than those obtained by flushing with water alone. This group also worked on treating the contaminated surfactant solutions resulting from surfactant flushing. They noted that reuse of the surfactant would greatly improve the economics of surfactant flushing. They were, however, unable to find a successful technique for recovering the surfactant solution.

We were prompted by their work (5) to pursue surfactant flushing on a laboratory scale (8). Our efforts focused primarily on overcoming the problems associated with spent surfactant treatment and surfactant recycling. Ellis et al. (5) used nonionic surfactants because of their small cmcs. We chose to use an anionic surfactant (sodium dodecylsulfate, SDS) so that solvent extraction could possibly be used to reclaim the surfactant solutions. We thought that anionic surfactants would have much lower solubilities in nonpolar solvents than nonionic surfactants, thus making solvent extraction a possibility.

The problem of surfactant recycling was investigated by Gannon et al. (8) who used a gentle extraction technique to remove *p*-dichlorobenzene (DCB), biphenyl, and naphthalene from SDS solutions into hexane. They found that vigorous shaking or mixing of the hexane and SDS phases resulted in stable emulsions. They then tried slowly stirring the solutions so that the hexane–water interface was not disturbed. Gannon et al. found that approximately 90–95% of all three of the contaminants were removed after about 24 hours. The removal was acceptable, but the rate of removal was too slow to be practical.

Preliminary results of a bench-scale spray column operating in semi-batch mode were reported previously (8). Hexane was used to extract DCB in that study. Removals of 95% or better were attained in as little as 45 minutes of treatment for a 25-mM SDS solution and a hexane flow rate of 90 mL/min.

At field scale, a continuous countercurrent flow of hexane and contaminated SDS solutions in an extraction column would probably be much more efficient than a batch technique. The present work focuses on continuous countercurrent extraction in a spray column. In the following we first discuss the theory behind the diffusion of organic contaminants from SDS solution into hexane drops. Then we describe an unsteady state model of the extraction process. The operation of the extraction column is described, including the effects of hexane and SDS solution flow rates, SDS concentration, and contaminant identity on contaminant removal. The ability of recycled SDS to remove contaminants from soil is evaluated. Finally, the conclusions drawn from the work are summarized.

THEORY

Diffusion Model

A model describing the diffusion of a contaminant through an aqueous boundary layer into a droplet of organic liquid was described earlier (10). The boundary layer and drop can be divided into two regions described by two mass flux equations, as shown in Fig. 1. Region I is the organic liquid drop, of radius a. Region II is an aqueous boundary layer of thickness $b - a$ through which contaminants must diffuse to get to the organic layer.

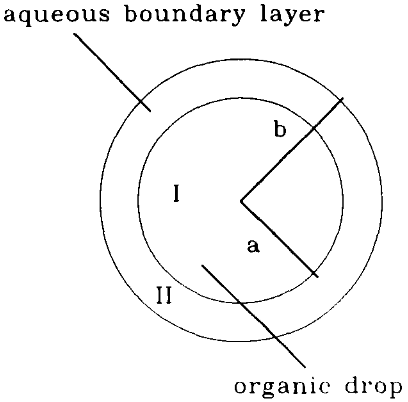

FIG. 1 The two regions of diffusion: an organic liquid drop (Region I) and an aqueous boundary layer (Region II).

The simplified species continuity equations for Regions I and II are (10)

$$\frac{\partial C_A}{\partial t} = D_I\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_A}{\partial r}\right)\right] \quad \text{(Region I)} \qquad (1)$$

$$\frac{\partial C_A}{\partial t} = D_{II}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_A}{\partial r}\right)\right] \quad \text{(Region II)} \qquad (2)$$

in which C_A is the concentration of contaminant A, and D_I and D_{II} are the diffusion coefficients for A in Regions I and II, respectively. The assumptions are made that the droplets of organic liquid are spherical, density and diffusion coefficients are constant, no reactions take place, and there is no flux of A due to bulk flow of liquid.

The boundary conditions at the interface are

$$\lim_{\delta \to 0^+}[C_A(a - \delta, t)] = \lim_{\delta \to 0^+}[KC_A(a + \delta, t)] \qquad (3)$$

$$\lim_{\delta \to 0^+}\left[D_I\frac{\partial C_A}{\partial t}(a - \delta, t)\right] = \lim_{\delta \to 0^+}\left[D_{II}\frac{\partial C_A}{\partial t}(a + \delta, t)\right] \qquad (4)$$

where δ is some small distance $\ll$ the drop radius a, and K is the distribution coefficient for the contaminant between the two liquid phases. The conditions as $t \rightarrow \infty$ are

$$\lim_{t\to\infty} C_A(r, t) = KC_{AO} \qquad \text{(Region I)} \tag{5}$$

$$\lim_{t\to\infty} C_A(r, t) = C_{AO} \qquad \text{(Region II)} \tag{6}$$

where C_{AO} is the concentration of the contaminant in the aqueous bulk phase. The contaminant concentration at the edge of the boundary layer that is in contact with the bulk phase is assumed to be C_{AO}. The concentration of contaminant at $r = 0$ and time t must be finite.

The differential Eqs. (1) and (2) are solved by the method of separation of variables (11). The solution in Region I (the droplet) is

$$C_A(r, t) = \sum_{\lambda} \frac{A_\lambda}{r} \sin\left(\sqrt{\frac{\lambda}{D_I}}\, r\right) \exp(-\lambda t) + KC_{AO} \tag{7}$$

The solution to Eq. (2) in the aqueous boundary layer (Region II) is

$$C_A(r, t) = \sum_{\lambda} \left[\frac{B_\lambda}{r} \cos\left(\sqrt{\frac{\lambda}{D_{II}}}\, r\right) + \frac{C_\lambda}{r} \sin\left(\sqrt{\frac{\lambda}{D_{II}}}\, r\right)\right] \exp(-\lambda t) + C_{AO} \tag{8}$$

The boundary condition

$$C_A(b, t) = C_{AO} \tag{9}$$

along with Eqs. (3) and (4) can be applied to Eqs. (7) and (8) to give three linear homogeneous equations in A_λ, B_λ, and C_λ. Since the equations are homogeneous, to avoid having all three constants equal to zero, it is required that the determinant of the coefficients of A_λ, B_λ, and C_λ be equal to zero (12). This yields an eigenvalue equation which must be solved for the system, as shown previously (10). Zero is the smallest eigenvalue corresponding to equilibrium. The rate-limiting (largest) time constant for diffusion is the reciprocal of the least positive eigenvalue, $\lambda_1 \equiv \lambda$. An upper bound for λ is given by $\pi^2 D_I/a^2$, the reciprocal of the time constant for mass transfer when no boundary layer is present. A lower bound for λ is $\pi^2 D_{min}/b^2$, where D_{min} is the lesser of D_I and D_{II}. A small value of λ results in a large time constant. The diffusion of the contaminant from the surfactant solution through the aqueous boundary layer into a hexane droplet is limited by the largest time constant. A larger time constant means that contaminant takes longer to diffuse into the droplet. This rate-limiting time constant, $\tau = \lambda^{-1}$, may be determined by using a simple search algorithm to find the desired root of the eigenvalue equation (10).

Time-Dependent Column Model

A compartment model is used to simulate the unsteady-state behavior of the countercurrent extraction column (10). Figure 2 shows the column partitioned mathematically into N compartments. The rate of change of solute mass in the ith compartment is given by

$$dm_i/dt = R(C^R_{i-1} - C^R_i) + E(C^E_{i+1} - C^E_i) \qquad (10)$$

where C^R_i = concentration of solute in the aqueous phase in the ith compartment
C^E_i = concentration of solute in the organic phase in the ith compartment
m_i = mass of solute in the ith compartment
R = raffinate (aqueous) mass flow rate
E = extract (organic phase) mass flow rate

The changes in concentration in the two phases due to advection are

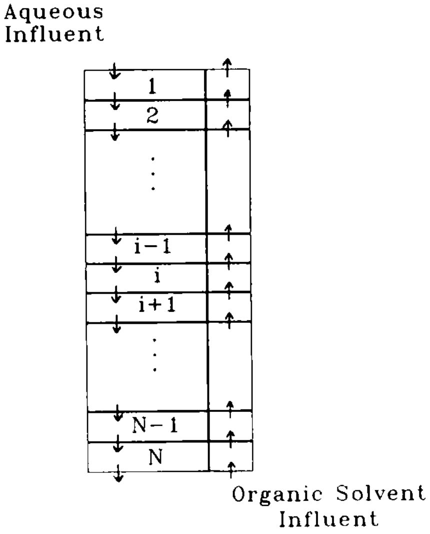

FIG. 2 Compartment model of a countercurrent extraction column.

described by the equations

$$\frac{dC_i^R}{dt} = \frac{R}{V_R}(C_{i-1}^R - C_i^R) \tag{11}$$

$$\frac{dC_i^E}{dt} = \frac{E}{V_E}(C_{i+1}^E - C_i^E) \tag{12}$$

where V_E and V_R represent the volumes of the extract and raffinate in the volume element. Equations (11) and (12) do not allow for mass transport between the aqueous and organic phases. The total solute mass balance (Eq. 10) accounts for the overall change in solute mass with time.

A linear equilibrium distribution is assumed to apply; this is given by

$$C_{ei}^E = KC_{ei}^R \tag{13}$$

where the subscript e denotes equilibrium and K is the distribution coefficient for the solute between the organic and aqueous phases. In the ith compartment we have

$$m_i = V_E C_{ei}^E + V_R C_{ei}^E \tag{14}$$

The following two equations are derived from Eqs. (13) and (14):

$$C_{ei}^R = \frac{m_i}{V_E K + V_R} \tag{15}$$

$$C_{ei}^E = \frac{Km_i}{V_E K + V_R} \tag{16}$$

The following procedure is used to model the change in contaminant concentration in both phases (10). Equations (10)–(12) are integrated forward one time increment Δt to give $m_i(t + \Delta t)$, $C_{0i}^R(t + \Delta t)$ (initial concentration of contaminant in the aqueous phase at $t + \Delta t$), and $C_{0i}^E(t + \Delta t)$ (initial concentration of contaminant in the organic phase at $t + \Delta t$). The concentrations of contaminant in the aqueous and organic phases are then allowed to relax toward their equilibrium values via an exponential decay, resulting in

$$C_i^R(t + \Delta t) = C_{0i}^R \exp\left(-\frac{\Delta t}{\tau}\right) + C_{ei}^R\left[1 - \exp\left(-\frac{\Delta t}{\tau}\right)\right] \tag{17}$$

$$C_i^E(t + \Delta t) = C_{0i}^E \exp\left(-\frac{\Delta t}{\tau}\right) + C_{ei}^E\left[1 - \exp\left(-\frac{\Delta t}{\tau}\right)\right] \tag{18}$$

Equations (17) and (18), along with $m_i(t + \Delta t)$ provide the initial concentrations for each compartment for the next integration step forward in time. Equations (10)–(12) are then integrated forward another time increment Δt, and the concentrations in both phases in each compartment are computed again using Eqs. (17) and (18). This procedure is continued until simulation of the run is complete.

The boundary conditions at the top and bottom of the column must be treated separately. The mass balances at the top of the column are

$$dm_1/dt = R(C^R_{\text{infl}} - C^R_i) + E(C^E_2 - C^E_1) \tag{19}$$

$$\frac{dC^R_1}{dt} = \frac{R}{V_R}(C^R_{\text{infl}} - C^R_1) \tag{20}$$

$$\frac{dC^E_1}{dt} = \frac{E}{V_E}(C^E_2 - C^E_1) \tag{21}$$

where C^R_{infl} is the influent raffinate concentration. At the bottom of the column, the following equations apply:

$$dm_N/dt = R(C^R_{N-1} - C^R_N) - EC^E_N \tag{22}$$

$$\frac{dC^R_N}{dt} = \frac{R}{V_R}(C^R_{N-1} - C^R_N) \tag{23}$$

$$\frac{dC^E_N}{dt} = -\frac{E}{V_E}C^E_N \tag{24}$$

The concentration profiles in the column are obtained by integrating Eqs. (11), (12), (20), (21), (23), and (24) forward in time and solving the

TABLE 1
Default Parameters Used in the Column Model Program

Water density	1.0 g/mL
Organic solvent density	0.66 g/mL
Water viscosity	0.01 poise
Organic solvent drop diameter	0.25 cm
Flow rate of organic phase	1.5 mL/s
Flow rate of aqueous phase	0.167 mL/s
Column radius	2.2 cm
Column length	122 cm
Column partitioning	7 compartments
Mass transfer time constant	7,200 s
Influent contaminant concentration	280 mg/L
Pulse concentration	280 mg/L
Pulse starts at	100 s
Pulse ends at	200 s
Distribution coefficient	150
Δt	0.1 s
Duration of run	15,000 s

mass transport equations (Eqs. 17 and 18) for each compartment. This was done on a microcomputer running MS-DOS and using a program written in BASICA. Parameters used in the program are given in Table 1. Most of the parameters relate to an experimental quantity such as the flow rates and column length. The adjustable parameters are the number of compartments into which the column is divided and the mass transfer time constant, τ. A first approximation to τ is $1/\lambda$ from the diffusion model for a single droplet of hexane. The number of compartments necessary to represent the mass transfer taking place in the column can be varied as appropriate to represent axial dispersion in the column. Considering the column as one compartment is equivalent to viewing it as a completely mixed tank. Axial dispersion in the column model decreases as the number of compartments is increased. With an infinite number of compartments there is no axial dispersion, and the column acts as a plug flow device in both directions.

Experimental

Materials

The sodium dodecylsulfate (SDS) was from Fluka Chemical Co., and was stated to be 99% pure. The *p*-dichlorobenzene (DCB) was Baker reagent grade from J. T. Baker Chemical Co. The naphthalene and the certified and spectranalyzed hexanes were from Fisher Scientific. Reagent-grade biphenyl from Aldrich Chemical Co. was used. All chemicals were used as received.

Analysis of Samples

The absorbances of the organic compounds in the SDS solutions were determined by ultraviolet spectrophotometry on a Hitachi 100-40 UV-VIS instrument. The spectrophotometer was calibrated with hexane solutions of known concentrations for each organic compound. Beer's law extinction coefficients were determined for each compound at a characteristic wavelength. The extinction coefficients were 0.002585 absorbance units per mg/L at 282 nm for DCB, 0.001609 at 311 nm for naphthalene, and 0.1059 at 252 nm for biphenyl. The Beer's law calibration lines were then used to convert absorbance readings to concentrations.

Spray Extraction Column

The continuous countercurrent extraction column is shown in Fig. 3. The cylindrical Pyrex glass column is 122 cm long with an inner diameter of 4.4 cm. At the top of the column is a rubber stopper with glass tubes

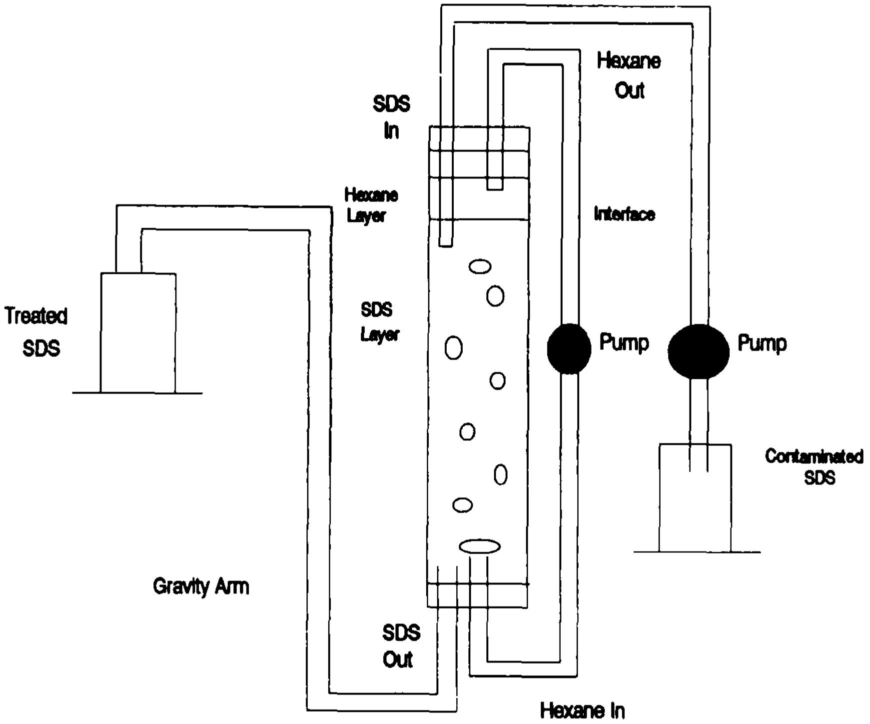

FIG. 3 Apparatus for continuous countercurrent flow extraction.

for inflow of SDS solution and outflow of hexane. The bottom of the column is equipped with another stopper with a glass tube for the SDS solution effluent and a glass funnel with a fused glass plate on top with nine holes (approximately 0.25 cm diameter) for distributing the hexane droplets. A 7-cm sheet of plastic woven material is placed at the aqueous–organic interface. The SDS effluent tube is attached to Tygon tubing which leads to a glass jar to catch the effluent. Contaminated SDS solution is pumped by a Cole-Parmer Masterflex peristaltic pump to the top of the column. Another Masterflex pump moves the hexane from the top of the column to the bottom for another pass through the column.

Preparation of SDS Solutions

The contaminated SDS solutions were made by adding the appropriate amount of SDS to 2 L of deionized water. The mixture was stirred to dissolve the SDS completely. Then DCB, naphthalene, or biphenyl was added so that the bottom of the flask showed a substantial solid residue of crystals. The flask was then closed and placed on a magnetic stirrer for 3 days to saturate the solution with the organic compound. For most of the continuous flow experiments, 4 L total of the contaminated solution was used. In those experiments in which the SDS solution flow rate was varied, 8 L of SDS solution were made up.

Column Operating Procedure

The procedure for making a run began with gravity filtration of the saturated SDS solution to remove any suspended crystals. The column was aligned as vertically as possible with a level and a plumb bob on a string. The column was then filled with the contaminated SDS solution to a volume of about 1600 mL. Approximately 300 mL hexane was added on top of the SDS solution, and a 7-cm layer of plastic woven material was placed at the aqueous–organic interface to assist the coalescence of the hexane droplets.

A glass jar was used to collect the SDS solution effluent, which left the column through a tubing "gravity arm." The jar and tubing on the gravity arm were positioned high enough from the floor while the column was initially filled to prevent any solution from flowing from the column. Contaminated SDS solution was pumped from a beaker reservoir to the top of the column while hexane was pumped around in a continuous loop from the top to the bottom of the column.

The height of the gravity arm was changed during the run to maintain a constant liquid level at the top of the column. Twenty-milliliter samples of the SDS effluent were taken from the gravity arm tubing every 15 minutes. Fifty milliliters of the hexane in the column was removed, and 50 mL of fresh hexane was added every hour to prevent saturation of the hexane with the organic contaminants. Each run lasted about 4 hours. Samples were analyzed on the Hitachi UV spectrophotometer described above.

Experiments Conducted

The hexane flow rate, SDS flow rate, and SDS concentration were varied in the DCB experiments only. Hexane flow rates used were 20, 50, and 90 mL/min. SDS flow rates were 10, 18, and 26 mL/min. SDS concentrations varied from 25 to 100 mM. Two experiments with saturated solutions of naphthalene and biphenyl in SDS were conducted. An experiment using recycled SDS solution (treated by this solvent extraction procedure) was conducted by Susan Burchfield (personal communication) and is included here to show that recycled SDS can be used in the surfactant flushing of soils.

RESULTS AND DISCUSSION

Diffusion Model

The hexane droplet rise velocity relative to the surrounding aqueous phase was determined from an equation given by Fair, Geyer, and Okun (13):

$$v = \frac{2\Delta\rho g r^2}{9\mu_w\left[1 + \frac{1}{4}\left[\frac{\rho_w r v}{2\mu_w}\right]^{1/2} + 0.34\,\frac{\rho_w r v}{12\mu_w}\right]} \tag{25}$$

in which v is the hexane droplet rise velocity, ρ_w is the density of the aqueous phase, ρ_0 is the density of hexane, $\Delta\rho = \rho_w - \rho_0$, μ_w is the dynamic viscosity of the aqueous phase, r is the drop radius, and g is the gravitational constant. Figure 4 shows the relationship between drop rise velocity and drop radius. The drop rise velocity increases with increasing drop radius.

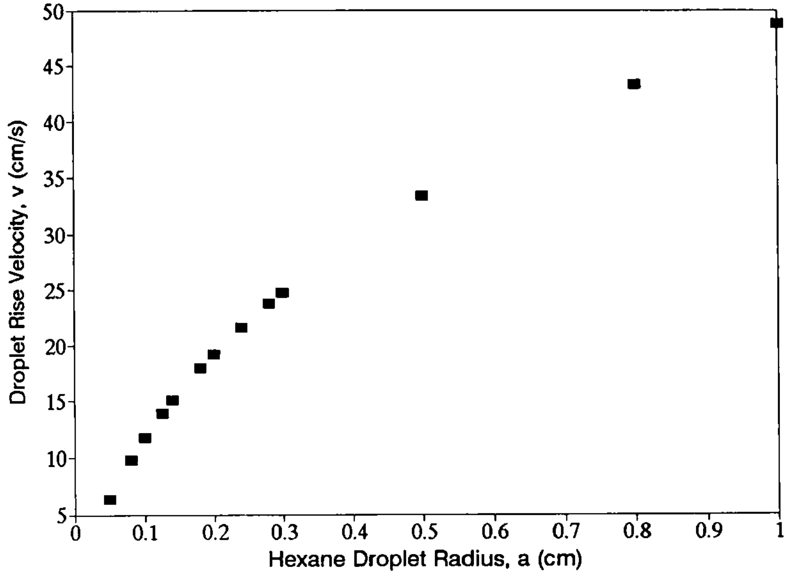

FIG. 4 Plot of hexane droplet rise velocity versus droplet radius.

The Reynolds number, Re, of a hexane drop rising in water is given by

$$Re = 2\rho_w v r/\mu_w \tag{26}$$

Figure 5 is a plot of Reynolds number as a function of hexane droplet radius. Reynolds number increases as the drop radius increases. A faster rise velocity is desirable on the one hand because the aqueous boundary layer around the drop is thinner due to the drop "flattening out" as it rises through the aqueous phase. The thinner boundary layer makes diffusion of organic contaminants into the drops easier and reduces the contact time required in the extraction column. On the other hand, contact times decrease with increasing rise velocity, and the surface-to-volume ratio of the droplets also decreases, since larger rise velocities are associated with larger droplets. Also, excessive turbulence is undesirable because the high velocities of the hexane droplets could cause them to break off smaller droplets which could form a stable emulsion with the aqueous SDS phase.

The dispersion head in the extraction column was designed to produce hexane droplets with a diameter of 0.25 cm. In fact, the droplets ranged in size from 0.2 to 0.3 cm in diameter, with the average value being about 0.25 cm. Drop sizes were determined from photographs taken with a millimeter ruler in the background. The calculated rise velocity of a drop with radius 0.125 cm is 13.97 cm/s, and the Reynolds number is 349. This

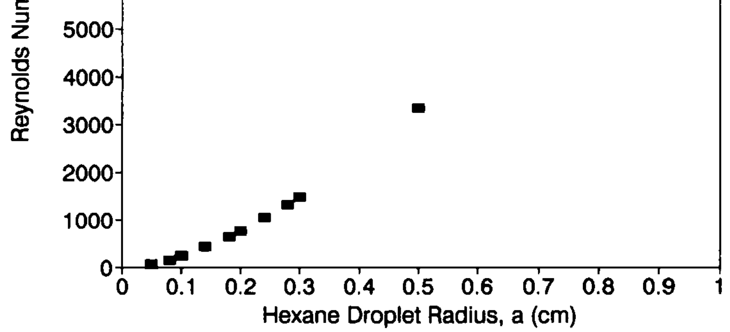

FIG. 5 The relationship between Reynolds number and hexane droplet radius.

velocity is not in the turbulent range, and the droplets showed no tendency to break up as they rose through the column.

Turbulence, boundary layer thickness, and column height all affect the diffusion process. The hexane flow rate should be fast enough to remove contaminants from the surfactant solution, but not so fast that the droplets tend to break up. Ideally, drop contact time should be comparable to the diffusion time constant. Boundary layer thickness should be small to enhance mass transport of the contaminant into the organic droplet. The extraction column should be of a height and diameter that allow a sufficient volume of contaminated SDS solution to be treated in an acceptably short time. Larger columns allow more solution to be reclaimed at a time; longer columns give each drop a longer transit time through the column.

The eigenvalue equation (determinant of the coefficients of A_λ, B_λ, and C_λ set equal to zero; see Eqs. 7 and 8) was solved using a computer program to find the mass transfer time constant ($1/\lambda$) for various distribution coefficients (K), hexane droplet radii (a), and diffusion coefficients of the contaminant in the hexane drop (D_I) and in the aqueous boundary layer (D_II). D_I was estimated as 3.08×10^{-5} cm^2/s by using the Scheibel relation for organic solutes diffusing into organic solvents (14). The Wilke–Chang correlation (14) was used to estimate the diffusion coefficient for DCB in the aqueous boundary layer around the hexane drop, D_II, as 7.95×10^{-6} cm^2/s. Figure 6 shows the relationship between the mass transfer time constant and distribution coefficient for $a = 0.125$ cm, $b = 0.135$ cm, $D_\text{I} = 3.08 \times 10^{-5}$ cm^2/s, and $D_\text{II} = 7.95 \times 10^{-6}$ cm^2/s. The time constant increases linearly with increasing K from 282 seconds at $K = 5$ to 10,000 seconds at $K = 200$. The time constant at $K = 150$ is 7200 seconds or 2 hours.

The relationship between mass transfer time constant and hexane droplet radius is depicted in Fig. 7 for $K = 150$, $D_\text{I} = 3.08 \times 10^{-5}$ cm^2/s, and $D_\text{II} = 7.95\ 10^{-6}$ cm^2/s. The time constant increases linearly with increasing drop radius over the range 0.05 to 0.14 cm.

Figure 8 shows the mass transfer time constant as a function of diffusion coefficient of the contaminant in hexane for $a = 0.125$ cm, $b = 0.135$ cm, $D_\text{II} = 7.95 \times 10^{-6}$ cm^2/s, and $K = 150$. The time constant decreases from 7460 seconds for $D_\text{I} = 5 \times 10^{-6}$ cm^2/s to 7040 seconds for $D_\text{I} = 1 \times 10^{-4}$ cm^2/s.

The mass transfer time constant as a function of diffusion coefficient of the contaminant in the aqueous boundary layer is shown in Fig. 9. Parameter values are $a = 0.125$ cm, $b = 0.135$ cm, $K = 150$, and $D_\text{I} = 3.08 \times 10^{-5}$ cm^2/s; the time constant decreases with increasing D_II, as expected.

Figures 6 through 9 show the effects of varying distribution coefficient, drop radius, and diffusion coefficients in hexane and in the aqueous layer

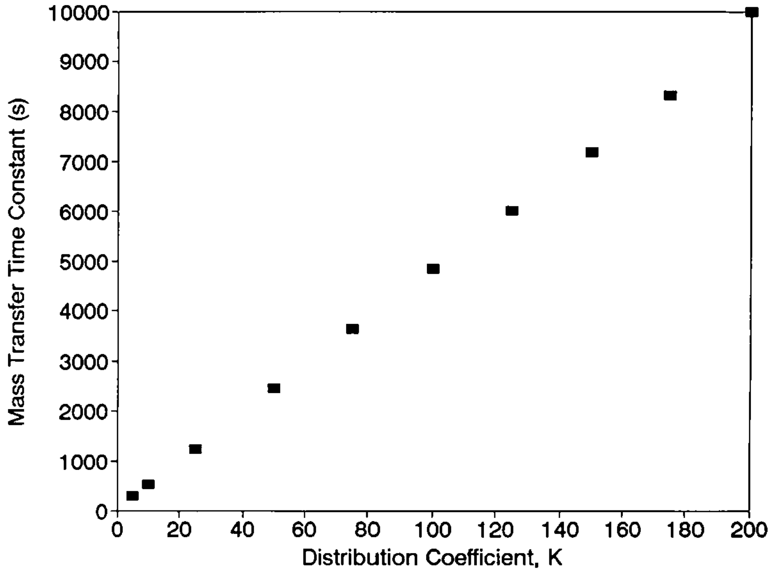

FIG. 6 Mass transfer time constant as a function of distribution coefficient K. $a = 0.125$ cm, $b = 0.135$ cm, $D_{\mathrm{I}} = 3.08 \times 10^{-5}$ cm^2/s, $D_{\mathrm{II}} = 7.95 \times 10^{-6}$ cm^2/s.

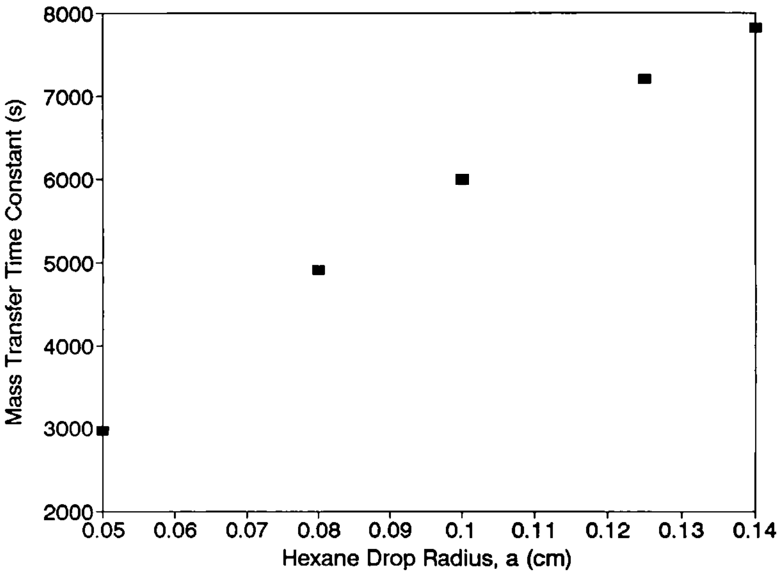

FIG. 7 The effect of hexane droplet radius on the mass transfer time constant. $K = 150$, $D_{\mathrm{I}} = 3.08 \times 10^{-5}$ cm^2/s, $D_{\mathrm{II}} = 7.95 \times 10^{-6}$ cm^2/s.

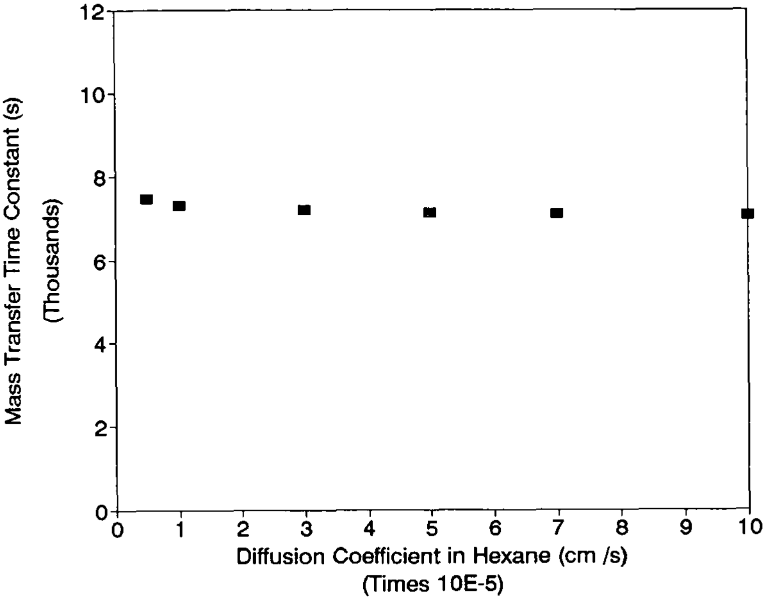

FIG. 8 Relationship between mass transfer time constant and diffusion constant in hexane. $a = 0.125$ cm, $b = 0.135$ cm, $K = 150$, $D_{II} = 7.95 \times 10^{-6}$ cm^2/s.

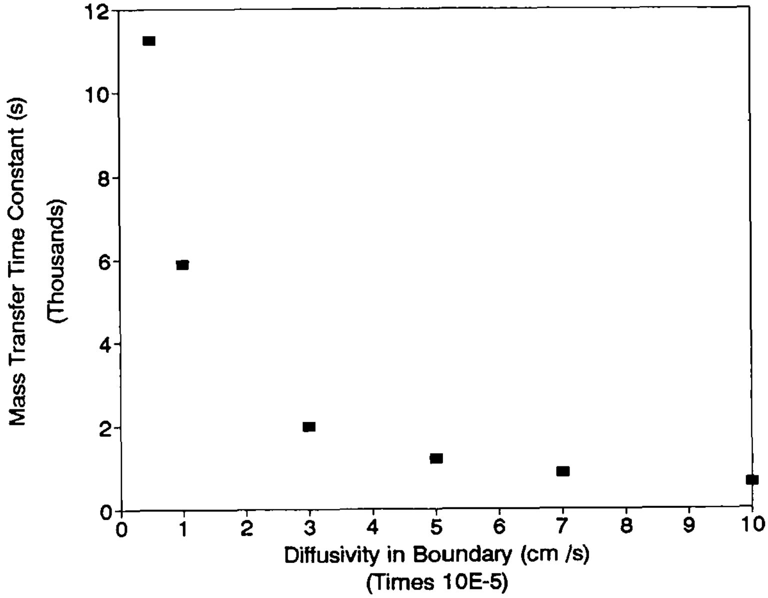

FIG. 9 Mass transfer time constant as a function of diffusion coefficient in the aqueous boundary layer. $a = 0.125$ cm, $b = 0.135$ cm, $K = 150$, and $D_I = 3.08 \times 10^{-5}$ cm^2/s.

on the mass transfer time constant. The time constant is an indication of the time necessary for the hexane drops to remove the contaminant. Smaller distribution coefficients, drop radii, and boundary layer thicknesses result in smaller time constants. Larger diffusion coefficients also result in smaller time constants.

The values of K, D_I, and D_{II} used for this system (DCB, 25 mM aqueous SDS, hexane) are 150, 3.08×10^{-5} cm^2/s, and 7.95×10^{-6} cm^2/s, respectively. These parameters correspond to a mass transfer time constant of 7200 seconds or 2 hours for the system studied.

The distribution coefficient K was estimated from equilibrium data (15). A large value of K implies that at equilibrium a large fraction of the contaminant is in the organic solvent phase. This is desirable, since the major objective of using solvent extraction is to remove at least 80–90% of the contaminant from the SDS solution. A large value of K, however, also means that the mass transfer time constant will be larger, and a longer period of time will be required to equilibrate the droplet with the aqueous phase, so that more droplet contact time will be required to take full advantage of the higher carrying capacity of the droplet.

The compartment model prediction of the DCB concentration profile is shown in Fig. 10. The parameters used to calculate the curves are $K = 150$, τ $(1/\lambda) = 7200$ seconds, and N (the number of compartments

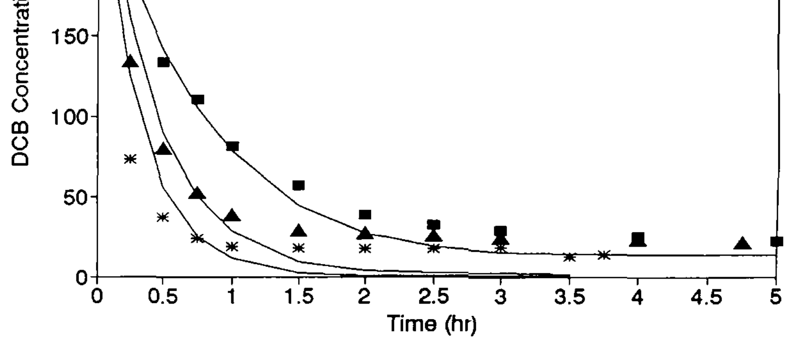

FIG. 10 Effect of hexane flow rate on DCB removal: (■) 20 mL/min; (▲) 50 mL/min; (*) 90 mL/min; (——) model.

representing the column) = 7. The model is fairly good at predicting the unsteady-state behavior of the process, but gives lower DCB concentrations at steady state than were found experimentally. The model does not assume that the hexane is passed through the column more than once, as was done in the experiments, so one expects the calculations to overestimate removal, as was found.

The parameters N and τ turn out to be related when one is fitting the time-dependent column model to the data. As N is increased, the optimal mass transfer time constant τ is decreased. The time constant determined from the diffusion model for a single hexane drop (7200 seconds) was used in the time-dependent column model, since 80–90% of the DCB was removed in the experiments after 2 hours. The removal of DCB was best represented by dividing the column into 7 compartments when one sets τ = 7200 seconds.

Effect of SDS Flow Rate

The removal of DCB with a hexane flow rate of 50 mL/min and an SDS concentration of 25 mM is shown in Fig. 11 for SDS flow rates of 10, 18, and 26 mL/min. The best removal (86% after 1 hour) is obtained with the

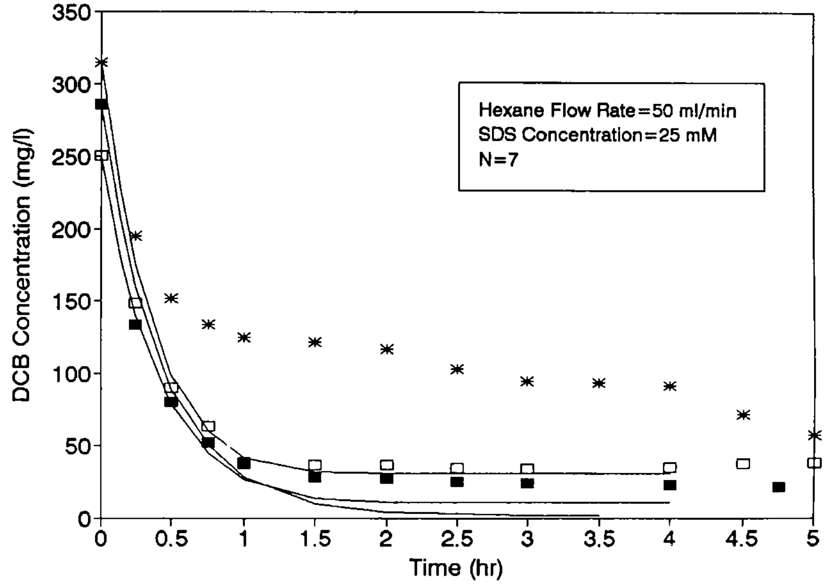

FIG. 11 Effect of SDS flow rate on the removal of DCB: (■) 10 mL/min; (□) 18 mL/min; (*) 26 mL/min; (——) model.

slowest SDS flow rate, 10 mL/min. The removals after 1 hour for SDS flow rates of 18 and 26 mL/min are 85 and 60%, respectively. The lower SDS flow rates allow the SDS solution a longer contact time with the hexane droplets, so that more of the contaminant can be extracted from the SDS solution before the solution exits the column.

The DCB concentration profiles predicted by the compartment model are also shown in Fig. 11. The parameters used are $N = 7$, $K = 150$, and $\tau = 7200$ seconds. Again, the curves predict the time-dependent behavior fairly well, but the steady-state concentration of contaminant in the SDS solution is too low, again due to the hexane being recycled back through the column in the experiments.

Effect of SDS Concentration

The results of varying the SDS concentration on the removal of DCB are shown in Fig. 12 for a hexane flow rate of 90 mL/min and an SDS flow rate of 10 mL/min. The removal of DCB after 1 hour is 93% for 25 mM SDS, 85% for 50 mM SDS, and 73% for 100 mM SDS. The higher SDS concentrations have a greater DCB residual at steady state, but, even at these higher concentrations, the percent removal is good. Therefore 100

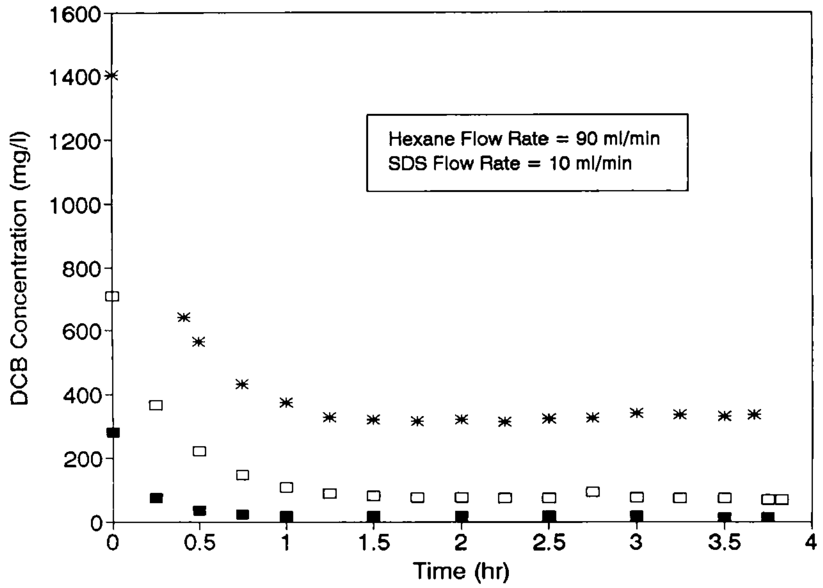

FIG. 12 Removal of DCB as a function of SDS concentration: (■) 25 mM; (□) 50 mM; (*) 100 mM.

mM SDS solutions, capable of solubilizing roughly four times the amount of contaminant as 25 mM solutions, can be used without causing problems in recycling.

Removal of Other Contaminants

Figure 13 compares the removals of three contaminants (DCB, naphthalene, and biphenyl) under the same extraction conditions: hexane flow rate = 90 mL/min, SDS flow rate = 10 mL/min, and SDS concentration = 25 mM. Concentrations of all three of the contaminants are reduced by about 90% or better. Figure 13 shows that the extraction process should be useful for most hydrophobic organics, presumably including PCBs, solvents, and chlorinated pesticides.

Effectiveness of Recycled SDS Solutions

The performance of SDS solution reclaimed by the extraction process described here in removing contaminants from soil in flushing columns was examined. Figure 14 shows plots of SDS effluent naphthalene concentration versus volume of effluent for fresh and recycled SDS solutions.

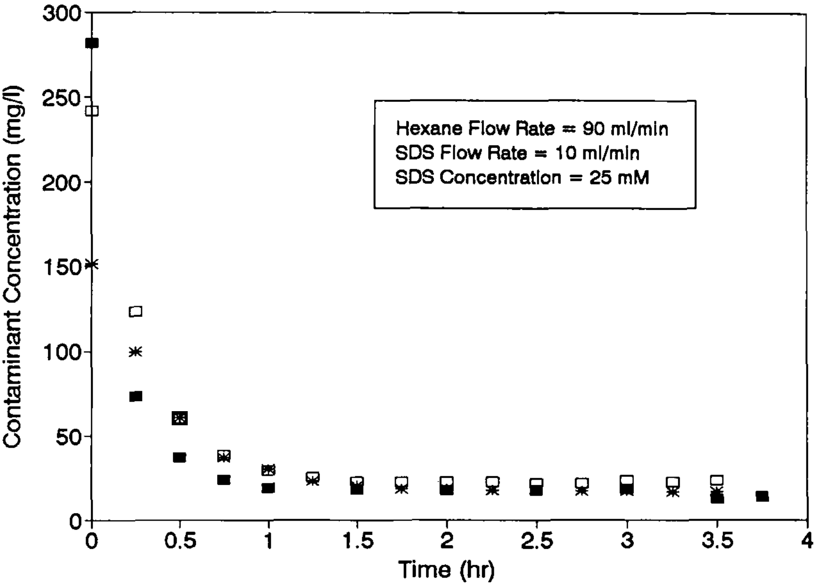

FIG. 13 A comparison of the removals of three organic contaminants: (■) DCB; (□) naphthalene; (*) biphenyl.

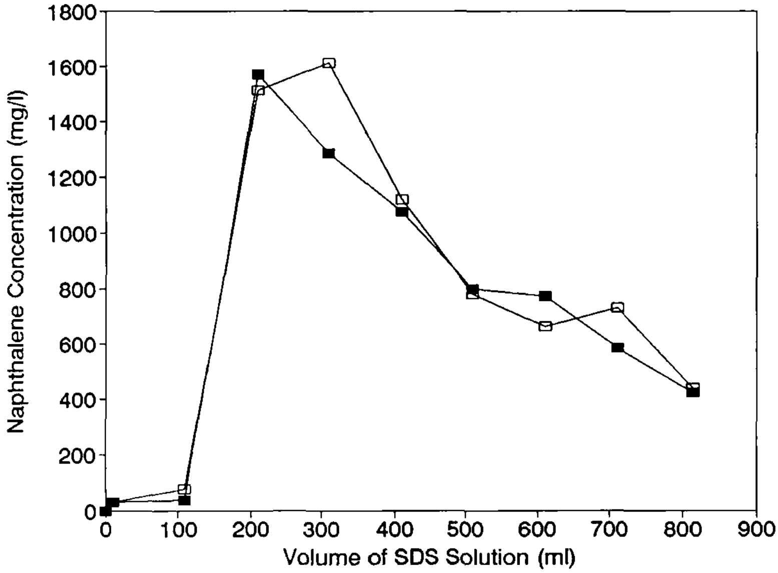

FIG. 14 Comparison of the performance of fresh and recycled 100 mM SDS solution in soil columns for naphthalene removal: (■) fresh SDS; (□) reclaimed SDS.

The results are not significantly different. This experiment was carried out by Susan Burchfield with recovered 100 mM SDS and columns filled with naphthalene-spiked sandy red clay of a type common in middle Tennessee. The batch column previously described (8) was used with a hexane flow rate of 20 mL/min to treat the SDS solution. Batch extraction was carried out for 10 hours to give a residual naphthalene concentration in the SDS solution of 90 mg/L. It appears that extraction is a suitable method for surfactant solution reclamation.

CONCLUSIONS

Our results show that extraction of contaminated SDS solutions with hexane is effective in cleaning them up for recycle. Reuse of surfactant should add substantially to the economic viability of surfactant flushing. Solvent extraction also concentrates the hazardous material that must be incinerated or otherwise disposed of. Normally this solvent would be purified for recycle by distillation.

The model calculations lead to several conclusions. The rise velocity of a hexane drop increases as the drop radius increases, as does the Reynolds number. Faster rise velocities mean thinner aqueous boundary layers around the drops and faster diffusion of organic contaminants into the drops; they also mean shorter drop contact times and smaller droplet surface-to-volume ratios, however. Drop velocities in the turbulent range can lead to the breakup of drops and formation of undesirable emulsions.

The mass transfer time constant $\tau = 1/\lambda$ is a measure of the time required for the hexane drops to approach equilibrium with respect to the surrounding aqueous phase in the partitioning of organic contaminants. Smaller distribution coefficients, drop radii, and boundary layers give smaller time constants. Larger diffusion coefficients result in smaller time constants, also.

The mass transfer time constant for $K = 150$, $D_{\mathrm{I}} = 3.08 \times 10^{-5}$ cm²/s, $D_{\mathrm{II}} = 7.95 \times 10^{-6}$ cm²/s, $a = 0.125$ cm, and $b = 0.135$ cm is 7200 seconds (2 hours). This time constant is an estimate for τ in the time-dependent model, and a rough measure of how long it should take the system to reach steady state.

Experiments with the spray column operating in the continuous countercurrent flow mode establish several points. Faster hexane flow rates give faster removals of contaminants, within limits. The aqueous effluent DCB concentration at steady state was found to increase with increasing SDS concentration. The percent removals of DCB decreased somewhat with increasing SDS concentration, but were still acceptable (80–90+%). More complete removals of DCB were found to occur with slower SDS flow rates, which provide longer contact times of the solution with the hexane. The mass transfer time constant of 2 hours, predicted from the diffusion model, is too long for the higher SDS flow rates; the contact time of the SDS with the hexane under these conditions is insufficient. The compartment model seems to predict the time-dependent behavior of the extraction process fairly well, but gives steady-state aqueous DCB concentrations which are low, since the model does not allow for hexane recycle. The number of compartments the column is partitioned into (N) and the mass transfer time constant (τ) are adjustable parameters in the model. The values $N = 7$, $\tau = 7200$ seconds, and $K = 150$ provide the best fit to the data. Three organic compounds (DCB, naphthalene, and biphenyl) were all removed at about the same rate by using the same hexane and SDS flow rates and SDS concentrations. Recycled SDS solution seemed to perform as well as fresh SDS in removing naphthalene from red clay in soil column experiments.

ACKNOWLEDGMENTS

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