



AQUEOUS SOLUBILITY ENHANCEMENT AND DESORPTION OF HEXACHLOROBENZENE FROM SOIL USING A PLANT-BASED SURFACTANT

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(First received March 1996; accepted in revised form February 1997)

Abstract—A plant-based surfactant extracted from fruit pericarps of *Sapindus mukorossi* (Ritha) is proposed for remediation of contaminated soil from a local hazardous waste site. Natural surfactants can be prepared using a very simple water extraction of fruit pericarp powder. Natural surfactant solutions are employed to enhance the aqueous solubility of a hydrophobic organic compound, hexachlorobenzene (HCB), and to desorb HCB from soils in batch and one-dimensional flow-through soil column experiments. The solubility of HCB in natural surfactant solutions increased linearly with surfactant concentration beyond the critical micelle concentration. The mass of dry Ritha powder required to solubilize 1 mg of HCB in 1 liter of water was comparable to sodium dodecylsulfate solution and other commercial surfactants. HCB concentration in the aqueous solutions approached 90% of the HCB solubility in the respective natural surfactant solutions when soils contaminated to high levels were used for desorption. HCB recovery was up to 90% of the total HCB for soils contaminated with lower levels. Desorption behavior observed for natural surfactant solutions was similar to SDS solutions. Natural surfactant solutions performed more efficiently than a simple water flood in recovering HCB from one-dimensional soil columns. The HCB concentration in the effluent was found to be as high as 80% of the surfactant-enhanced HCB solubility in respective solutions. The results of this study provide a strong case for pursuing natural surfactant solutions in further research. © 1997 Elsevier Science Ltd

Key words—hexachlorobenzene, solubility, desorption, plant-based surfactant, natural surfactant, soil flushing, *Sapindus mukorossi* (Ritha)

INTRODUCTION

Contamination of subsurface soils and ground-water formations by organic solvents and petroleum products is a significant problem. Conventional pump-and-treat technologies are most widely used for the remediation of contaminated groundwater. However, these methods require long times to make significant reductions in the quantity of organic contaminants (Mackay and Cherry, 1989). The removal of hydrophobic organic compounds (HOCs) from contaminated soils is hindered by very low solubility in water and high interfacial tension (Hunt and Sitar, 1988). In recent years there has been an increasing interest in using surfactant solutions to enhance the performance of the existing pump-and-treat facilities.

Surfactant molecules tend to concentrate at the interfaces and lower the interfacial tension. They also form aggregates known as micelles at concentrations beyond the critical micelle concentration (CMC). The micelles can dissolve appreciable quantities of non-polar solutes which are virtually insoluble in normal aqueous solutions depending on the type of surfactant, hydrophobicity of the compounds and their interactions (Rosen, 1989). Considerable research has been done on the use of aqueous surfactant solutions for remediation of contaminated soils (Ellis *et al.*, 1985; Abdul *et al.*, 1990, 1992; Edwards *et al.*, 1991, 1994; Liu *et al.*, 1991; Jafvert *et al.*, 1994; Roy *et al.*, 1995a, b).

The ability of a surfactant to solubilize a hydrophobic compound from soil is dependent on (i) interaction of the compound with the surfactant, (ii) sorption of the compound on soil, (iii) sorption of surfactant on soil and its effect on increasing the wettability of soil and (iv) partitioning of the compound with the surfactant micelle (Liu *et al.*,

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1991). The soil does adsorb the surfactant to some extent and hence the effective CMC will be greater than the aqueous phase CMC (Vigon and Rubin, 1989; Liu *et al.*, 1991; Edwards *et al.*, 1994). Non-ionic and anionic surfactants undergo less significant adsorption on soil than cationic surfactants, although they may still be substantial.

Although some commercial surfactants have shown good potential in terms of recovery of contaminants from soil columns, their fate in the subsurface is still unknown. The surfactants left in the subsurface may have a negative or positive influence on the biodegradation of the organic compounds (Breuil and Kushner, 1980; Oberbremer *et al.*, 1990; Laha and Luthy, 1991; Rouse *et al.*, 1994). Surfactant recycle is recommended and technologies need to be refined for complex wastes at hazardous waste sites (Abdul *et al.*, 1992; Underwood *et al.*, 1993). Another alternative may be biosurfactants, produced by microorganisms (Wilson, 1986; Desai and Desai, 1993). Studies indicate that these biosurfactants improve hydrocarbon dispersion and bacterial attachment to hydrophobic contaminants and, therefore, they enhance solubility and increase the biodegradation rates of hydrophobic compounds. Major classes of biosurfactants include glycolipids, phospholipids and fatty acids, lipopeptide/lipoproteins and polymeric surfactants.

One of the plant-based natural surfactants derived from *Sapindus mukorossi*, commonly known as "Soapnut" or "Ritha" in the Indian subcontinent, has been tested to remediate contaminated soils (Kommalapati, 1995). Dry powder from the fruit pericarp is extracted into water and used as a detergent and in folk medicine (Sarin and Beri, 1939; Gedeon, 1954). The recorded use of this product as common soap does not cite any toxic effects on human skin and eyes (Windholz, 1983). Some work has been done on isolation and identification of the constituent chemical compounds of this fruit extract (Row and Rukmini, 1966; Kimata *et al.*, 1983). Preliminary experiments conducted in the present authors' laboratory using natural surfactant solutions for remediation of contaminated soils indicated that these solutions can desorb and solubilize significant amounts of hydrophobic compounds (Mandava, 1994). Natural surfactant solutions were prepared by extracting fruit pericarp with water for 3 h at ambient temperature and filtering the resultant solution through a series of filters (Roy *et al.*, 1997). The empirical formula for the natural surfactant was determined using oxidation stoichiometry and found to be $(C_{26}H_{31}O_{10})_n$, where n is a variable which needs to be estimated (Kommalapati, 1995). The value of n was found to be about 2 by Row and Rukmini (1966) for an isolated saponin fraction. The percent carbon in the natural surfactant solution was found to be 60.6% (Kommalapati, 1995) compared to the 57.8% determined by Row and Rukmini (1966). Natural surfactant solutions supported microbial growth and

degraded considerably under both aerobic and anaerobic conditions in 15 and 45 days, respectively (Kommalapati and Roy, 1996, 1997).

The objective of this paper is to evaluate the suitability of a plant-based surfactant to solubilize a HOC (hexachlorobenzene, HCB) in water and to desorb it from soil using batch and column studies. Surfactant solutions made from the fruit pericarps of *S. mukorossi*, commonly known as Ritha, are used in this research. The results of the study are crucial for determining the potential of this surfactant in remediation of contaminated soils.

MATERIALS AND METHODS

Materials

Dry fruits of *S. mukorossi* were procured from India. These fruits are golden brown in color and globular in shape, with a diameter between 1 and 3 cm. After removing the seed the outer pericarps were dried in an oven at 50°C for about 2 days. The fruit pericarps were ground and sieved through a US standard No. 20 sieve (840 μ m). Some properties of the natural surfactant are listed in Table 1. Sodium dodecylsulfate (SDS), an anionic and biodegradable surfactant with a 12-carbon straight chain, was used for comparison. SDS was purchased from Life Technologies (Gaithersburg, MD) with 99.5% purity and used as supplied. The molecular weight of SDS is 288.38 and the CMC is 8.08 mm. HCB, an aromatic chlorinated hydrocarbon, was used as a test compound. The chemical was obtained from Aldrich Chemical Co. (Milwaukee, WI) with 99% purity and was used as supplied. Reported solubility of HCB is in the range of 4.7–110 μ g/l, the log octanol/water partition coefficient is 5.31 and molecular weight is 284.8 (Montgomery and Welkm, 1990).

An uncontaminated soil received from a Superfund site north of Baton Rouge, LA, was air-dried, homogenized and kept in an oven overnight at 105°C for drying. The soil was ground and the fraction passing US Standard No. 10 (2 mm) sieve was used. This soil is classified as a sandy loam with a clay content of about 10% and very low organic matter content (0.2%).

Preparation of natural surfactant solutions

A method developed by Kommalapati (1995) was used. Dry fruit pericarp powder was added to deionized (DI) water (10 g per 100 ml water to make a 10% solution) and stirred for 3 h at room temperature. The mixture was centrifuged at 10,000 rpm (14,087 g) for 45 min and the supernatant was filtered through a 0.44-mm pre-filter followed by a Metrical 0.45- μ m membrane filter (Gelman Scientific, Ann Arbor, MI). The resulting solution was a 10% solution used as the stock for all studies. Natural surfactant solutions with concentrations higher than 10% were prepared in the same manner, except that a higher amount of fruit pericarp powder (20 g per 100 ml for a 20% solution) was used. It should be noted that about 70% of the fruit pericarp is soluble, and the remaining portion was discarded.

Table 1. Properties of natural surfactant (Kommalapati, 1995)

Empirical formula ^a	$(C_{26}H_{31}O_{10})_n$
TOC ^a	41 g/l
COD ^a	124 g/l
Nitrogen and phosphorus ^a	Not detected
CMC	0.1%
pH (1% solution)	4.5

^aFor 10% solution.

Solubility experiments

Solubility experiments were performed in 250-ml Erlenmeyer flasks without any added soil using 100 ml of surfactant solution in the presence of excess quantities of pure HCB crystals. The flasks were equilibrated for about 36 h on a mechanical shaker. The samples were centrifuged in Teflon™ tubes for 15 min at 15,000 rpm (25,155 g) and the supernatant was extracted and analyzed for HCB using a gas chromatograph. Several concentrations of natural surfactant (0.1–25%) and SDS concentrations in the range of 0.09% (3 mM) to 2.9% (100 mM) (w/w) were used.

Effect of natural surfactant sterilization on HCB solubility

A study was conducted with five concentrations of natural surfactant and three different types of treatments to study the effect of sterilization. In the control, natural surfactant solutions were used without any treatment and the samples were steam-sterilized or autoclaved for the second treatment. The third set was prepared in autoclaved glassware using filter-sterilized natural surfactant. The last two methods were designed to prevent microbiological growth.

Soil contamination

The soil fraction passing US Standard No. 10 sieve (2 mm) was spiked with HCB to study the performance of natural surfactant solutions in desorption and soil flushing. HCB was dissolved in petroleum ether, and soil was added slowly with continuous mixing. The solvent was allowed to evaporate for 2 h before transferring into a glass bottle and tumbling for about a week to simulate long-term adsorption found at actual waste sites.

Desorption experiments

Contaminated soil (5 g) was weighed and added to several 125-ml Erlenmeyer flasks. Surfactant solution (50 ml) of different concentrations above and below the CMC was added to each flask. The concentrations of natural surfactant used were in the range of 0.05–2.5% (w/w) and SDS in the range of 0.14 (5 mM) to 1% (35 mM) (w/w) in addition to water. The flasks were shaken at room temperature for about 36 h on a mechanical shaker. The samples were withdrawn and centrifuged to separate the soil particles before analyzing for HCB.

One-dimensional soil flushing experiments

Glass columns 10 cm long and 5.75 cm in diameter with a stainless-steel top and bottom were used to pack the contaminated soil for the soil flushing experiments (Kommalapati, 1995; Roy *et al.*, 1995a). To prevent soil from being washed out of the column and to distribute the flow uniformly, the outlet and inlet ends of the column were fitted with fine wire mesh sandwiched between two coarse wire meshes. A soil packing procedure was used to achieve a bulk density similar to field conditions (Roy *et al.*, 1995a). The packed contaminated soil column was saturated with DI water. Experiments were conducted in the downflow mode with water and natural surfactant solutions at a flow rate of 2.5 ml/min (pore water velocity = 0.24 cm/min). The effluent collected in each pore volume (~105 ml) was analyzed for HCB in duplicate.

Analysis of hexachlorobenzene

Commercially available Sep Pak C₁₈ cartridges (Waters Corp., Milford, MA) were used for extracting HCB from aqueous surfactant solutions. The cartridges were activated by passing 5 ml DI water, 5 ml methanol and 5 ml DI water again. The sample was eluted through the cartridge at a rate of 5 ml/min followed by 5 ml DI water. The cartridge was then eluted with 5 ml hexane, which was collected and analyzed for HCB on an HP 5890 Series II gas chromatograph (GC) fitted with an HP 7673 auto sampler and Ni⁶³ electron capture detector (Hewlett-Packard Co.,

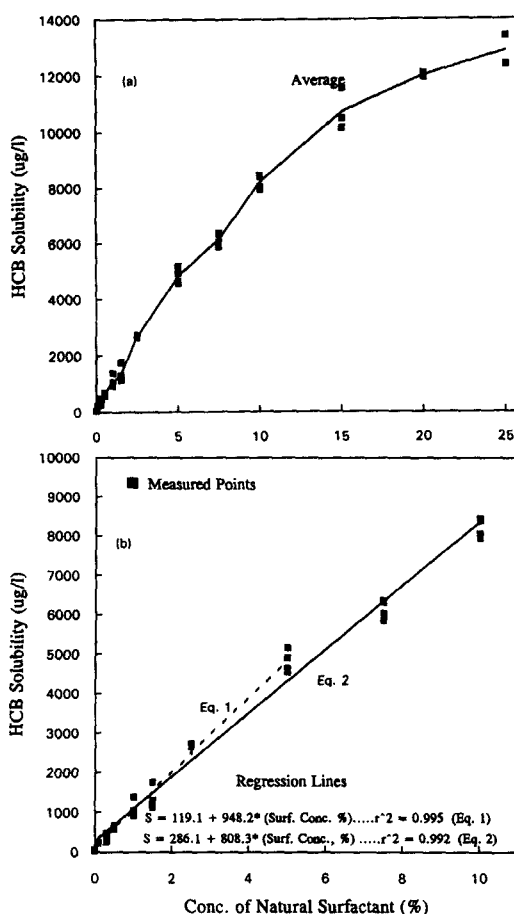


Fig. 1. Variation of hexachlorobenzene solubility with natural surfactant concentration: (a) concentration up to 25% and (b) regression lines for the ranges 0.1–5% and 0.1–10%.

Wilmington, DE). The GC was fitted with a 30-m PTE-5 capillary column, with 0.32 mm internal diameter and 1.0 μ m film thickness (Supelco, Bellefonte, PA). The chromatographic conditions were as follows: 1 μ l splitless injection, injection temperature 275°C, temperature program –50°C (initial for 1 min) to 270°C at 10°C per minute and hold for 3 min, total run time 26 min, and ECD temperature 325°C. Minimum detection limit for the method was 1 pg. The extraction efficiency for HCB with this method was 93.7% with a standard deviation of 2.2%, and no interference was noted due to the presence of the two surfactants used in the study. HCB sorbed on soil was extracted using acetone:hexane (1:1) mixture and analyzed on GC. The extraction efficiency was 86% with a standard deviation of 7% using this procedure.

RESULTS AND DISCUSSION

HCB solubility in surfactant solutions

Natural surfactant. The results of the solubility experiments are summarized in Fig. 1(a). The variation of HCB solubility in natural surfactant solutions in the concentration range of 0.1–25% by weight is presented in the graph. It is apparent from the figure that the solubility of HCB increased by 300-fold when 25% natural surfactant solution was

used. Aqueous solubility of HCB is about 50 $\mu\text{g/liter}$, which is in the range suggested in the literature (Montgomery and Welkm, 1990). The solubility of HCB in natural surfactant solution of 25% concentration was about 13,000 $\mu\text{g/liter}$. There appears to be a linear relationship between solubility and surfactant concentration up to about 10% by weight. Mandava (1994) used naphthalene as a test organic compound in her work on natural surfactant solutions and reported that naphthalene solubility increased linearly with concentration in the range of 0.25–10%. Such a linearity between the hydrophobic compound solubility and surfactant concentration beyond CMC has been well established for commercial surfactants (Rosen, 1989; Edwards *et al.*, 1991; Jafvert *et al.*, 1994). The solubility of HCB in surfactant solutions above 10% does not linearly increase with concentration but approaches a saturation value. The possible reason for this asymptotic value in solubility could be that the maximum capacity of the micelles for HCB or the surfactant was not extracted from the pericarp efficiently at higher surfactant concentration. For example, the surfactant is probably not extracted from pericarp for a 25% solution as efficiently as for a 10% solution. This was verified by determining the weight of the residue remaining after extracting the surfactant from the pericarp.

The CMC of natural surfactant solutions was determined to be 0.1% from surface tension and viscosity measurements (Roy *et al.*, 1997). Regression analysis was performed between the HCB solubility and natural surfactant concentration in the ranges of 0.1–5% and 0.1–10% and the regression lines are shown in Fig. 1(b) along with the regression equations. Equation (1) was obtained using the solubility data in the range of 0.1–5% and equation (2) from the data in the range of 0.1–10%. Equation (2) overestimates HCB solubility at low surfactant concentrations, but equation (1) describes the solubility variation better in this range. The slope of the regression line represents the maximum amount of HCB per mass of surfactant in equilibrium with solid-phase HCB at standard temperature and pressure. The slope of the solubility curve can be used to calculate the solubilization ratio (SR), defined as

$$SR = \frac{C_o - C_o^*}{C_s - C_s^*}$$

Where C_o and C_o^* are the concentrations of organic in a surfactant solution at any surfactant concentration and at CMC (in g/g), respectively, and C_s and C_s^* are the concentrations of surfactant and the CMC of the surfactant (in g/g), respectively. One could also use molar concentrations and calculate the molar solubilization ratio (Edwards *et al.*, 1991). Since the surfactant concentration is expressed as percent w/w, the solubility units are converted from $\mu\text{g/liter}$ to g/g and the solubilization ratio is calculated. For natural

surfactant the solubilization ratio is found to be 0.0948×10^{-3} .

Effect of sterilization on HCB solubility. The results of preliminary experiments with HCB and the work of Mandava (1994) indicated a significant increase in solubility of hydrophobic compounds in sterilized natural surfactant solutions. Ritha, being a fruit extract, is prone to biodegradation, and the degradation of the constituent compounds of the natural surfactant may decrease the HOC solubilizing capacity of the surfactant solution. Also, high temperature and pressure treatment during sterilization may break down natural surfactants into compounds that may be more or less effective in solubilizing hydrophobic compounds.

The results of the study are summarized in Fig. 2. The figure shows that the results of preliminary work and the observations of Mandava (1994) are probably not true in this case. There is no significant difference in HCB solubility at the 95% confidence level between steam-sterilized and non-sterile natural surfactant solutions, even though the autoclave sterilized samples have solubilities lower than non-sterile samples (Tukey, 1953). The filter-sterilized samples have solubilities lower than both the autoclaved and non-sterile samples. The differences are significant only between the non-sterile and filter-sterile samples. The reason for this may be the adsorption of surfactant by the filter which may reduce the effective concentration of the surfactant. However, about 100 ml of the sample was filtered and the adsorption should not be a significant factor for such large volume of surfactant.

SDS solutions. SDS is a very common surfactant being studied in the laboratory for remediation of soils contaminated with hazardous wastes (e.g. Jafvert *et al.*, 1994; Roy *et al.*, 1995a, b). Solubility of HCB in SDS solutions of several concentrations below and above CMC was measured in duplicate. Figure 3 shows the variation of HCB solubility with

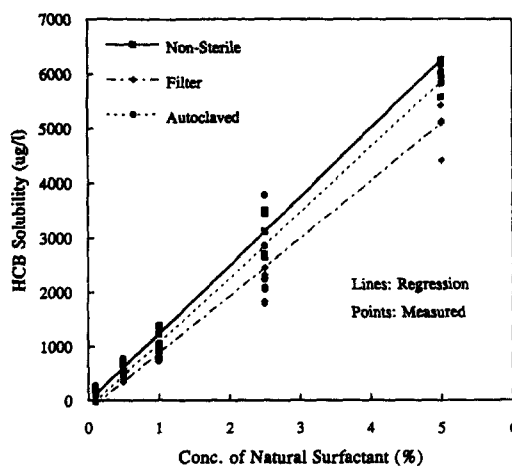


Fig. 2. Effect of sterilization of natural surfactant on hexachlorobenzene solubility.

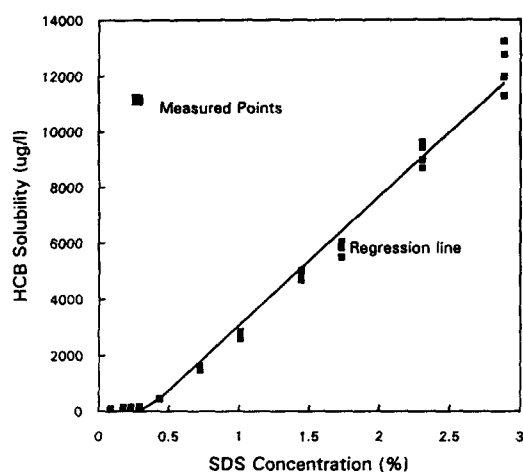


Fig. 3. Solubility of hexachlorobenzene in sodium dodecyl sulfate solutions.

SDS concentration. There is a linear relationship between SDS concentration and HCB solubility beyond the CMC, which is 8 mM. A linear regression performed between the HCB solubility and SDS concentration beyond CMC yielded a high coefficient of determination ($r^2 = 0.990$). Maximum solubility obtained with a 100-mM SDS solution (28.8 g/liter or 2.9% w/w) was about 12 mg/liter, which is about 250 times the water solubility. The solubilities obtained in the present studies at lower SDS concentrations are similar to those reported by Jafvert *et al.* (1994), within the experimental error. It should be noted that they used only three concentrations, with the highest concentration being only 3.5 g/liter. However, SDS concentrations as high as about 30 g/liter were used in this study and 11 concentrations were employed. The solubilization ratio as defined earlier for SDS was determined to be 0.472×10^{-3} .

Comparison between natural surfactant solutions and commercial surfactants. The maximum solubility of HCB (13 mg/liter) for natural surfactant solutions was with 25% natural surfactant. The maximum SDS concentration used (100 mM, 2.88% w/w) solubilized about 12 mg/liter HCB. Natural surfactant solutions behaved similarly to SDS solutions in terms of the linear relationship between surfactant concentration and solubility. The comparison between SDS and natural surfactant was done on the basis of surfactant required to be added in 1 liter of water to solubilize 1 mg HCB. About 10.5 g fruit pericarp and about 5.5 g SDS were required to solubilize 1 mg HCB. It should be noted that only 70% of fruit pericarp was extracted into water, which makes the net amount to be about 7.5 g. This shows that natural surfactant solutions are only 26% less efficient than SDS solutions in solubilizing a chlorinated hydrophobic organic compound, HCB. Jafvert *et al.* (1994) used about 10 surfactants to solubilize HCB in aqueous solutions and determined solubility parameters (mmol HCB per mol of surfactant). Solubility data

obtained in the present study for natural surfactant are compared with data of 10 commercial surfactants. Only a fraction of a gram of surfactant was needed to solubilize 1 mg HCB in 1 liter of water for Brij 30 and Tween 85. About 2–3 g Brij 35, Tween 20, Tween 80 and Exxal F 5715 were sufficient to do the same job. Triton X-705 and Pluronic P-65 in large quantities (51 and 83 g, respectively) were required to solubilize 1 mg HCB in 1 liter solution. Comparison can also be made based on solubilization ratios. Table 2 shows the solubilization ratios for 10 commercial surfactants calculated using the data presented by Jafvert *et al.* (1994). From this discussion, it is apparent that the performance of natural surfactant solutions is superior to that of Triton X-705 and Pluronic P-65 and comparable to SDS, whereas the other surfactants listed above performed better than natural surfactant, particularly the non-ionic surfactants, Brij 30 and Tween 85. It should also be noted that natural surfactants have other advantages, such as simple preparation technique, no toxic by-products, and enhancement of microbial growth, a critical factor in bioremediation.

Batch desorption studies

Desorption studies were used to evaluate the efficiency of natural surfactant solutions to desorb HCB from soil. SDS solutions were also employed in desorption studies to compare the performance of natural surfactant solutions. The amount of HCB desorbed from soil and solubilized by natural surfactant and SDS solutions were estimated as a percentage of HCB initially present in the soil and are reported as percent recoveries.

Natural surfactant solutions. Figure 4(a) shows the plot between the aqueous phase HCB concentration and natural surfactant concentration, and Fig. 4(b) shows the percent HCB desorbed from soil by natural surfactant solutions for different soil contamination levels. For a higher contamination level, about 90 mg HCB per kg soil, the aqueous phase HCB concentration approached the solubility of HCB in the respective surfactant solution. For soil contamination of 30 mg/kg, HCB concentration approached

Table 2. Solubilization ratios for several commercial surfactants and natural surfactant

Surfactant	Molecular weight	Solubilization ratio ($\times 10^{-3}$)
Natural surfactant*	N/A	0.095
Sodium dodecylsulfate*	288.34	0.472
Sodium dodecylsulfate	288.34	0.372
Brij 30	362	2.06
Brij 35	1198	0.295
POE 10-LE	626	0.924
Tween 20	1225	0.372
Tween 80	1310	0.376
Tween 85	1840	1.13
Triton X-705	3286	0.019
Exxal F 5715	640	0.503
Pluronic P-65	3518	0.012

*Determined in this study.

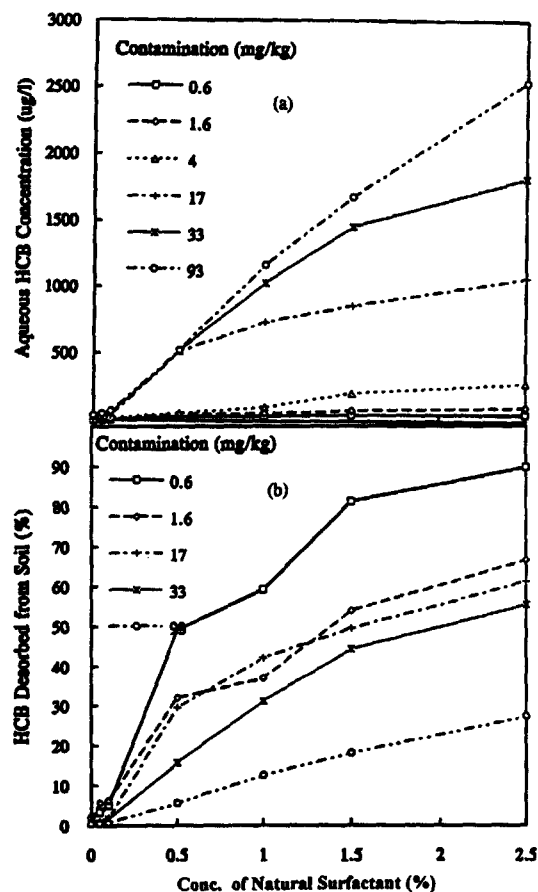


Fig. 4. Desorption of hexachlorobenzene from soil with natural surfactant solutions: variation of (a) aqueous-phase hexachlorobenzene and (b) percent desorbed.

the solubility of HCB for natural surfactant concentrations up to 1.5%. For lower contamination levels, about 90% of total HCB was removed from the soil. It seems that the solubility of HCB in natural surfactant solution limits the extent of desorption, and by repeating the washing process one would be able to clean the soil to a desired level. For the lowest contamination level employed (0.6 mg/kg) about 90% of HCB was recovered from soil. Even though the contamination level was less than what could have been solubilized by the natural surfactant concentrations, only 90% of HCB was desorbed. Irreversible adsorption of HCB with soil is believed to be mainly responsible for the remaining 10% HCB on the soil. For other contamination levels (1.6, 17 and 33 mg/kg) about 70, 60 and 50% of HCB, respectively, was recovered from the soil. For the highest contamination level used (90 mg/kg), the percent recovery varied linearly with natural surfactant concentration. This variation was very similar to the one observed in solubility studies. These aqueous-phase HCB concentrations were within 10–15% of the HCB solubility in the respective natural surfactant solutions. Similar observations were made by Mandava (1994) for desorption of

naphthalene from soil using natural surfactant solutions. A mass balance on HCB in the aqueous phase and on soil accounted for more than 90% of the total HCB. Closure of HCB obtained in the present study provided confidence in the analytical techniques and experimental procedures.

Desorption isotherms were constructed from the experimental data for natural surfactant solutions and are shown in non-linear form in Fig. 5. It is evident from the figure that the isotherms for all the concentrations are concave upwards throughout, which is an unfavorable condition for adsorption (Wark and Warner, 1981) but positive for desorption. The presence of surfactant solutions reduces the adsorption of the hydrophobic organic compounds onto the soil (Edwards *et al.*, 1994). The soil used in this study has very low organic matter content (0.2%) and thus offers little or no resistance for the desorption of HCB. Natural surfactant solutions desorb HCB from soil and solubilize it into their micelles. This is indicated by the fact that at low solid phase concentration the aqueous phase concentrations are low and at higher solid phase HCB concentrations the aqueous phase concentrations are limited by the solubility of HCB in the respective solutions. It should also be noted that at very high contamination levels, such as 90 mg HCB per kg soil, some of the HCB may be in the form of crystals precipitated on the soil surface rather than sorbed on the soil. The desorption noticed at high contamination levels could be due to the solubilization of the HCB crystals rather than the desorption from soil. Regression analysis performed on these isotherms indicates that the isotherms can best be described by either a power law or an exponential fit. The exponent of the aqueous phase concentration in the power law is in the range of 1.3–1.6 and the coefficient of determination (r^2) for the regression is in the range of 0.87–0.96. The exponential curve fit yielded an r^2 value in the range of 0.81–0.96.

Figures 6(a) and (b) show the Freundlich and Langmuir isotherms, respectively, for the three

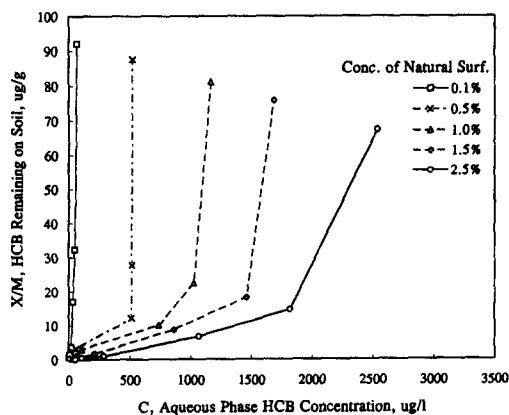


Fig. 5. Desorption isotherms for hexachlorobenzene in natural surfactant solutions in non-linear form.

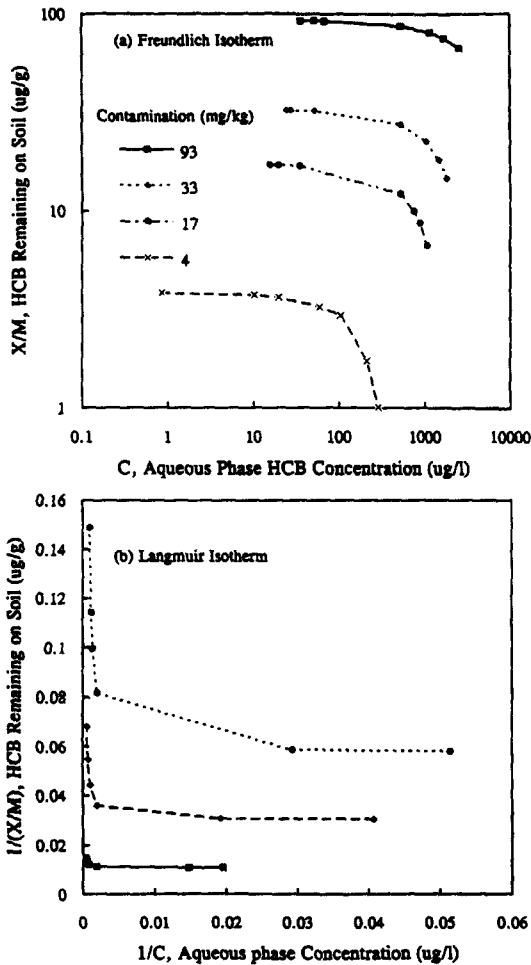


Fig. 6. Desorption isotherms for hexachlorobenzene: (a) Freundlich and (b) Langmuir.

contamination levels. Data is plotted as a Freundlich isotherm with HCB remaining on the soil per gram soil (X/M) versus the aqueous phase HCB concentration. There seems to be a linear relationship between the HCB remaining on the soil and the aqueous phase HCB concentration for high soil contamination levels (93 mg per kg soil). When the contamination is reduced, the linear correlation seems to fail. The linearity seems to fail particularly at high surfactant concentrations. At low contamination levels (4 and 17 mg/kg) and for high surfactant concentrations very little HCB is available for desorption. This is indicated by the decrease in the value of X/M or HCB remaining on soil for a relatively narrow range of aqueous phase HCB concentrations (Fig. 6a). A Langmuir isotherm for the desorption data is plotted in Fig. 6(b). It is clear from this figure that the isotherm is not linear at lower contamination levels as was noted for Freundlich isotherms. The same argument used for Freundlich isotherms seems to be valid for Langmuir isotherms also. The data fit the Langmuir isotherm at higher contamination levels (93 mg/kg).

SDS solutions. Figure 7(a) shows the plot between aqueous phase HCB concentration that is desorbed from soil and concentration of SDS for different levels of soil contamination. For SDS solutions, the same trend as followed for natural surfactant solutions was observed. For low contamination levels, aqueous phase HCB was significantly less than the HCB solubility in the respective solutions. For the higher contamination level there was a sharp increase in the aqueous phase concentration of HCB from 8 mM (0.23%) to 15 mM (0.43% w/w) SDS concentration. This sharp increase was also noticed in solubility studies. It should be noted that the CMC of aqueous SDS solutions is 8 mM; however, the presence of soil significantly alters the CMC of surfactants (Liu *et al.*, 1992). The CMC of SDS in soil–water systems will be higher than 8 mM, and thus there should be a significant increase in HCB recovery from soil when SDS concentration was increased from 8 to 15 mM. The aqueous-phase HCB concentrations were within 10–15% of the HCB solubility of respective solutions at higher contamination levels.

Figure 7(b) shows the variation of percent of HCB desorbed from the soil with natural surfactant

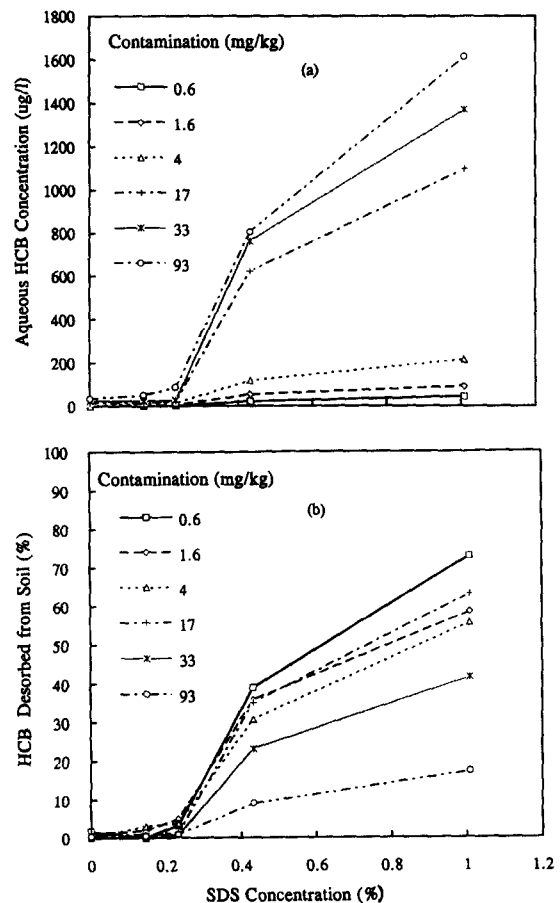


Fig. 7. Desorption of hexachlorobenzene from soil with SDS solutions: variation of (a) aqueous-phase hexachlorobenzene and (b) percent desorbed.

concentration. For a lower contamination level, a maximum of about 75% of HCB was recovered when 35 mM SDS was employed as compared to 90% by 2.5% natural surfactant solutions. Irreversible adsorption of HCB with soil is thought to be responsible for the unavailability of the remaining adsorbed HCB. For other contamination levels (1.6, 3.9 and 17 mg/kg) about 60–70% HCB was recovered, and for the higher contamination levels (33 and 93 mg/kg) about 40 and 15% HCB was recovered. It is believed that by repeating the washing process one would be able to recover significant amounts of HCB from soil and lower the residual saturation of HCB.

Comparison between natural surfactant and SDS solutions. As discussed in the last two sections of the desorption studies, natural surfactant solutions and SDS solutions have shown similar behavior in desorbing HCB with soil. The isotherms for natural surfactant solutions exhibit concavity upwards, which indicates that the systems are favorable for desorption (Fig. 5). SDS solutions also exhibited similar upward concavity when non-linear isotherms were plotted (not shown). Both natural surfactant and SDS solutions at the maximum concentrations employed (2.5% and 35 mM or 1%, respectively) were able to desorb as much as 90 and 75% of the total HCB on the soil, respectively, for low contamination levels. The aqueous HCB concentrations approached 80–90% of the surfactant enhanced solubility of HCB in the respective solutions for highly contaminated soils. In both cases, solubility was the limiting factor. Water could desorb only a small fraction of that recovered by surfactant solutions. This study clearly indicates that natural surfactant solutions are comparable in performance to commercial surfactants in solubilizing and desorbing hydrophobic compounds and should be further investigated.

Application of natural surfactant solutions to soil flushing. The results of solubility and desorption studies established that natural surfactant solutions are comparable to other commercial surfactants. The results of preliminary flushing experiments with one-dimensional columns are presented in this section.

Results of the column flushing experiments are presented in Fig. 8 for 0.5 and 1% natural surfactant solutions. The columns were packed with soil contaminated to a level of 70–80 mg HCB per kg soil. The concentration of HCB in the effluent reached as much as 80% of HCB solubility in the respective solutions by four pore volumes, and HCB recovery per pore volume remained fairly constant.

The removal of HCB during the first pore volume after saturation of the column was practically negligible. HCB recovery started increasing as the pore volumes of surfactant pumped through the column increased. This is because during the first few pore volumes the saturation water was replaced with

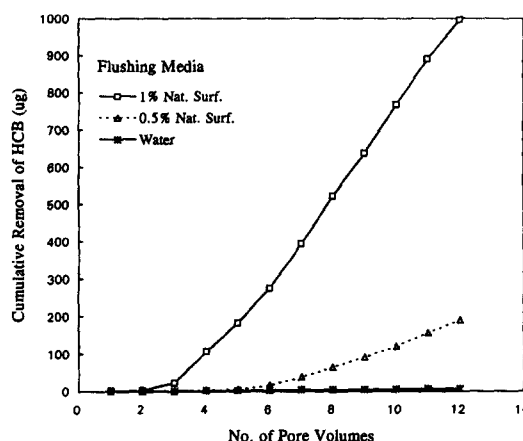


Fig. 8. Recovery of hexachlorobenzene from one-dimensional soil columns flushed with natural surfactant solutions and water flood.

surfactant solution and the surfactant was undergoing adsorption with soil. Surfactants are known to undergo adsorption onto soil, and natural surfactant, being a mixture of organics, may adsorb to soil significantly (Vigon and Rubin, 1989; Liu *et al.*, 1991). About 3–4 pore volumes of surfactant were pumped before achieving a surfactant breakthrough. The surfactant concentration in the column effluent was measured using a UV/Vis spectrophotometer and the correlations developed by the present author and co-workers (Roy *et al.*, 1997). HCB concentrations increased steadily after the first pore volume and approached the maximum HCB concentration by the fifth pore volume. This maximum concentration was about 80% of the surfactant enhanced solubility of HCB in the natural surfactant solution of the corresponding concentration. The removals were fairly constant beyond the fifth pore volume. The experiments were terminated after 12 pore volumes. Natural surfactant recovered about 20 and 100 times more HCB in 12 pore volumes than a water flood. The cumulative HCB removed from the soil column after 12 pore volumes as a percent of initial HCB in the column was about 0.02, 0.4 and 4% for water flood 0.5 and 1% for natural surfactant, respectively. It should be noted that experiments were terminated after 12 pore volumes and higher removal could be achieved by continuing the flushing operations. However, the difference between the water flood and surfactant runs is very clear from these results, showing enhanced recovery of HCB with natural surfactants in soil washing.

CONCLUSIONS

Natural surfactant solutions were employed in this study to enhance aqueous solubility of HCB and to desorb HCB from contaminated soils. The following conclusions can be made from the study.

- Solubility of HCB increases linearly with surfactant concentration beyond CMC. However, the solubility beyond 10% natural surfactant concentration is not linear and follows a saturation-type curve. The inefficient extraction of Ritha into water and saturation of the surfactant micelles with HCB are thought to be responsible.
- Solubility of HCB in SDS solutions increase linearly with SDS concentration beyond CMC for concentrations up to 100 mM (2.9% w/w).
- Natural surfactant solutions are comparable to SDS solutions in solubilizing HCB. About 10.5 g of fruit pericarp powder and about 5.5 g of SDS are required in 1 liter of water to solubilize 1 mg HCB.
- Batch desorption studies show that the natural surfactant solutions are favorable for desorbing HCB from soil-like SDS solutions.
- HCB concentration in the natural surfactant solution approached up to 90% of the HCB solubility in the respective solutions in batch desorption studies for soils contaminated to high levels, and the HCB recoveries were up to 90% of the total HCB for soils contaminated to lower levels.
- Desorption behavior observed for natural surfactant was very similar to SDS solutions.
- The desorption isotherms follow both Freundlich and Langmuir isotherms at higher soil contamination levels.
- Natural surfactant solutions performed much more efficiently than a simple water flood in recovering HCB from one-dimensional soil columns.

Acknowledgements—This research was partially supported by a grant from the United States District Court, Middle District of Louisiana through Louisiana State University.

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