

Removal of hazardous oily waste from a soil matrix using surfactants and colloidal gas aphon suspensions under different flow conditions

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Abstract

In-situ surfactant flushing is an attractive alternative used for decontamination of subsurface soil. The primary objective of this research is to investigate and examine an innovative technique of in-situ flushing using colloidal gas aphon suspensions (CGA) generated from surfactant solutions. The efficiency of CGA suspensions in the removal of oily waste is compared with conventional surfactant solutions and waterfloods under different flow regimes. Results show that CGA suspensions produced using sodium dodecylsulfate had a higher recovery of waste material (56%) than conventional surfactant solutions (47%) or waterflood (43%) in the downflow (gravity-stable) mode. The efficiency of CGA suspensions was greater in the downflow mode than in upflow (gravity-unstable) or horizontal (gravity-neutral) modes, and increasing the surfactant concentration from 8 to 30 mM did not enhance the removal efficiency for either CGA suspensions or conventional surfactant solutions. CGA suspensions appeared to have better removal for the major chlorinated hydrocarbons present in the oily waste.

1. Introduction

The release of hazardous substances into the environment is becoming an increasingly widespread problem. Historically, landfills have been the most common method for disposing of hazardous waste materials, but many of the sites which were once used for landfills or surface impoundments for hazardous wastes have now become superfund sites. The comprehensive environmental response, compensation and

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liabilities act (CERCLA), known also as the superfund act of 1980, along with the resource conservation and recovery act (RCRA) are making landfill disposal very costly and limiting future land disposal [1]. Therefore, inexpensive countermeasures are needed to mitigate the effects of hazardous substances that are released into the environment. In recent years, innovative technologies such as soil washing, in-situ soil flushing, and bioremediation are gaining popularity, and it is apparent that these improved technologies can generate significant savings for taxpayers and industries.

Part of the EPA's superfund innovative technology evaluation (SITE) remediation research has been directed at in-situ flushing of contaminated soil with the aid of aqueous surfactant solutions. Unfortunately, knowledge about the application of surfactants to oil recovery has not been directly transferred to aquifer remediation because surfactants used for oil recovery are chosen on the basis of temperature and salinities that are usually much higher than those at most hazardous waste sites. Through the use of surfactants, the effectiveness of soil flushing can be increased; however, an important consideration is that large amounts of surfactants must be used, and often the porous media become clogged during flushing, making the process less efficient [2].

An innovative technology that may improve the effectiveness of soil flushing are colloidal gas aphanes (CGAs), which are generated from the surfactant solutions. CGAs consist of approximately 65% by volume gas and hence form a low-density liquid. These microbubbles have a double layer of surfactant molecules with a thin surfactant film encapsulating the air inside. CGAs offer a way of lowering the interfacial tension between organics and water while at the same time providing the viscous forces needed for efficient areal sweep.

The application of CGAs is becoming more and more widespread. They have been used in separation processes [3] and flotation processes [4]. Although they have not been used extensively in soil flushing, the application of CGAs has been tried [5-7]. The use of CGAs for in-situ remediation looks promising; however, there is little application work reported in the literature.

The main objective of this research was to investigate and compare the performance of a negatively charged surfactant (sodium dodecylsulfate, SDS) and CGA suspensions produced from this surfactant in washing oily waste from a soil matrix in unconsolidated cylindrical columns under different flow conditions. The purpose of the study was to assess the suitability of CGA suspensions in removing DNAPL from the soil matrix.

2. Background

2.1. Pump and treat processes

Conventional pump and treat technologies are among the most widely used for the remediation of aquifers. However, recent research suggests that these systems may require protracted periods of time to make significant reductions in the quantity of

contaminants associated with both the liquid and solid phases which constitute the subsurface matrix [8]. Extended periods for remediation are highly undesirable as the operation and maintenance costs associated with the remediation are usually large, and, in many cases, valuable land is used which would otherwise be available. Also, many of the organic liquids that are common ground water pollutants cannot be extracted efficiently by pump and treat methods due to their low solubilities in water and high interfacial tension with water [9]. Attention is now being focused on the feasibility of using surfactants to increase the efficiency of conventional pump and treat technology.

2.2. *Surfactants in soil flushing*

Surfactants have the ability to increase the solubility of organic liquids in water and to decrease the interfacial tension (IFT) between NAPL and water, and hence are more effective in comparison to traditional pump and treat operations [10]. Several researchers have proposed surfactant use in the remediation of NAPL contaminated sites. Also, the successful application of surfactants to enhanced oil recovery has been demonstrated [11–13]. Surfactant flushing/washing can be applied to soils containing many types of chemicals; however, the process should be targeted towards organic compounds, including hydrophobic organics, that are difficult to treat by other processes due to their low solubility in water, low volatilities, and recalcitrant properties [14].

Although researchers have established a well-developed theoretical basis for surfactant utilization and have conducted a number of promising laboratory studies, none of the field tests have been highly successful [10, 13–24]. Reasons for these difficulties include the following: (1) If the contaminant is a DNAPL, then attainment of ultralow interfacial tension may lead to its vertical mobility and possible contamination of previously clean layers; (2) there is not sufficient data available for the formulation of an optimum surfactant mixture, including data on interfacial tensions, emulsion stability, toxicity, and biodegradability; (3) An overwhelming problem in applying soil flushing is the heterogeneity of soils and the inability to locate and reach the DNAPL pools within the subsurface environment.

Large amounts of surfactants are required for soil washing, making this process uneconomical. Often the porous media become clogged during flushing, making the process less effective. CGA suspensions may reduce some of the problems associated with conventional surfactant solutions.

2.3. *Colloidal gas aphanes*

Colloidal gas aphanes were first described by Sebba [25]. They are gas bubbles encapsulated in a soapy film. Other than water, surfactant is the only chemical needed for the generation of CGAs. Two important aspects in their applications are (i) their small size, resulting in a large surface area to volume ratio, and (ii) the existence of a double film of surfactant encapsulating the gas, retarding the bubbles from coalescing.

Because of their size, CGAs can be pumped from one location to another without considerable damage to their structure. The suspensions can last for a long time before they rise upwards because of the density difference between them and the water in which they are suspended. Sufficient agitation must be provided to inhibit the separation of CGAs as foam and water. Their double layer contributes to their high stability, i.e., low coalescence, which, in turn, contributes to the appropriate conditions for them to be pumped [25].

CGAs have been used successfully in a number of applications such as flotation, in situ biodegradation, and soil flushing [26]. They have been used for the removal of contaminants from wastewater by flotation and were proven to be more efficient than conventional foam flotation because of their higher surface area per unit volume [27]. Roy et al. used CGAs to separate dyes from water by flotation [28], and Michelson et al. studied in-situ biological oxidation of hazardous organics using CGA amended with microorganisms and nutrients from a saturated unconsolidated matrix [26]. Results indicated that CGAs can be effectively applied in the separation of synthetic dyes from wastewater and in treating contaminated sites.

2.4. CGAs and soil flushing

Very little information is available in the literature regarding the use of CGAs for soil flushing [5, 7]. Based on the previous studies in which surfactants were demonstrated to be successful for soil flushing, Longe [7] conducted a study to determine the behavior and performance of CGAs for soil flushing of hydrophobic compounds. He observed removal of up to 88% for some organics, which is in contrast to only 10% removal of the same organics using a surfactant solution.

Roy et al. [5] studied the performance of CGAs and surfactants in flushing 2,4-dichlorophenoxy acetic acid (2,4-D) from soil. They observed that there is no significant difference in the performance of the two processes of soil flushing for a highly soluble compound like 2,4-D, and suggested that CGAs will be more effective for hydrophobic compounds rather than hydrophilic compounds.

CGA suspensions were also used to wash automatic transmission fluid (ATF) from a fine silty loam [6]. Results showed that CGA suspensions are more effective than conventional surfactant solutions and water. In six pore volumes, CGA suspensions removed 50%, conventional surfactant solutions 42%, and water flood removed only 20% of ATF.

In the present study, the work of Roy et al. [6] was extended using CGA suspensions to wash an actual oily waste from a soil matrix in unconsolidated soil columns under different flow regimes (downflow or gravity-stable, upflow or gravity-unstable and horizontal or gravity-neutral). CGAs were generated as in the previous work using an anionic surfactant (SDS). The efficiency of removal using CGA suspensions was compared to that of conventional surfactant solutions. This study then extends earlier work to a system of actual waste site soil and contaminants to further define the removal mechanism by CGAs. The next step in the research will be the optimization of the process for a pilot field-scale demonstration at a local superfund site.

3. Materials and methods

3.1. Materials

Soil used in this study was obtained from an uncontaminated region of a local superfund site north of Baton Rouge, Louisiana. This soil was chosen since a small pilot-scale study at this site is planned for the near future. Big lumps in the soil were crushed or pulverized and the soil was air dried before leaving it in an oven overnight at 105 °C. Dry soil sieved through a 2 mm sieve was used to pack the column. A sieve analysis of this soil sample indicated that the soil was a fine silty loam; the analysis results are presented in Table 1.

The oily waste used was from the same superfund site and was a complex mixture that consisted of a large number of toxic organic compounds of which hexachlorobenzene and hexachlorobutadiene are the major ones. Relevant properties of some of these compounds considered for this study are shown in Table 2. The waste had a density greater than water, and is therefore classified as a dense nonaqueous phase liquid (DNAPL). The viscosity of the waste was 58.8 cP; the density was 1.33, and the color was blackish brown.

The surfactant used in this study, sodium dodecyl sulfate (SDS), also known as sodium lauryl sulfate (NLS), was obtained from Life Technologies, Inc (Gaithersburg, MD). SDS is a twelve-carbon straight chain, anionic surfactant that is commercially available and relatively nontoxic. It has been demonstrated to be efficient at enhanced oil recovery [23]. It has a molecular weight of 288.38, an aqueous solution pH of 7-7.5, and is biodegradable.

3.2. Column packing

The soil was packed inside a glass column with stainless-steel top and bottom, a length of 11.5 cm, and a diameter of 5.9 cm. The procedure used for soil packing

Table 1
Physical and chemical characteristics of the soil

Property	Value
Percent sand	41
Percent silt	50
Percent clay	8.5
Percent organic matter	0.4
pH	5.7
Calcium	769 mg/kg
Magnesium	211 mg/kg
Potassium	35 mg/kg
Sodium	36 mg/kg
Phosphorous	27 mg/kg
Cation exchange capacity	5.8 meq/100 g

Table 2
Relevant physicochemical data at 298 K for the target organics in the oily waste

Compound	Aq. solubility (mg/l)	log K_{ow}	Henry's constant
1,1,2,2-Tetrachloroethane	2900	2.4	0.016
Tetrachloroethene	150	2.9	0.625
1,1,1-Trichloroethane	4400	2.5	0.625
Hexachlorobenzene	0.005	6.4	0.708
Hexachlorobutadiene	2	4.8	0.041-1.08

could be reproduced in each run without substantial variation in the characteristics of the packed soil. The column was packed in four layers by adding 115 g of soil to each layer. Each layer was compacted by giving 25 blows with a compacting rod to obtain a bulk density of about 1.5 g/cm^3 and a porosity of 0.4. At the end of the last layer, a coarse steel mesh was placed on top of the soil, and the remaining space of approximately 0.5 cm above the surface of the soil was filled with 4 mm glass beads to establish uniform flow distribution across the cross section of the column. A fine wire mesh sandwiched between two coarse meshes was placed at the influent and effluent end of the column to prevent the soil from being washed out. The pore volume for each column was calculated by multiplying the porosity of the soil column by the column volume.

3.3. Soil contamination procedure

The packed column was positioned vertically and slowly saturated with deionized water from the bottom to remove entrapped air. After the column was saturated and a stable flow was attained, its hydraulic conductivity was measured by the constant head method as recommended by Methods of Soil Analysis (ASA, 1986). Hydraulic conductivity measurements were done in triplicates for each column, and the values ranged from 1.11×10^{-4} to 2.57×10^{-4} cm/s. The water in the column was gravity drained by positioning it vertically for about 24 h.

The drained column was again kept in the vertical position and contaminated with oily waste from the bottom. The oily waste was pumped at a flow rate of approximately 0.4 ml/min into the column using a piston pump (FMI lab model QG20, Fluid Metering Inc., Oysterbay, NY). Pumping was discontinued after contaminant breakthrough in the effluent was achieved. The excess oil in the column was gravity drained for about 24 h, and the drained oily waste was collected at the effluent end in a centrifuge tube and analyzed after centrifugation. After draining the excess waste, the soil in the column was at residual saturation in relation to the oily waste.

3.4. Soil flushing experiments

Once the column was packed and sealed, a high-pressure pump with a maximum pumping pressure of 50 psi (FM, Lab pump, Model QG20) was used to deliver the

wash solutions to the column. The rate of pumping used for all experiments was about 2.6 ml/min (4.5 ft/day). A schematic representation of the setup is shown in Fig. 1. Experiments were conducted in downflow (gravity-stable), upflow (gravity-unstable), and horizontal flow (gravity-neutral) mode using water, conventional surfactant solutions, and CGA suspensions as flushing solvents. Conventional surfactant solutions and CGA suspensions were used at two different concentrations of 8 and 30 mM during the downflow mode and at 8 mM during upflow and horizontal flow modes. The pressure at the influent end was monitored using a pressure gauge.

During the downflow flushing experiments, water, conventional surfactant solutions, or CGA suspensions were pumped into the top, and the oily waste was recovered from the bottom of the soil column. For the upflow runs, the wash solvents were injected into the bottom and oily waste collected at the top. For both upflow and downflow experiments, the soil column was vertical. In the horizontal flow experiment, the column was oriented horizontally and the solvents were pumped into the inlet side while the oily waste was recovered from the other side.

The effluent was collected in 50 ml centrifuge tubes. For both water and surfactant runs, it took about an hour to collect one pore volume; for the run with CGA suspensions it took between 2 and 5 h. Since CGAs are approximately 65% air, it takes longer to collect one pore volume of liquid when compared to conventional surfactant solutions or water at the same overall pump rate.

3.5. Analysis of effluent oily waste

The oily waste used was a mixture of several toxic organic compounds that made complete analysis of all constituents difficult; thus a method based on gravimetric

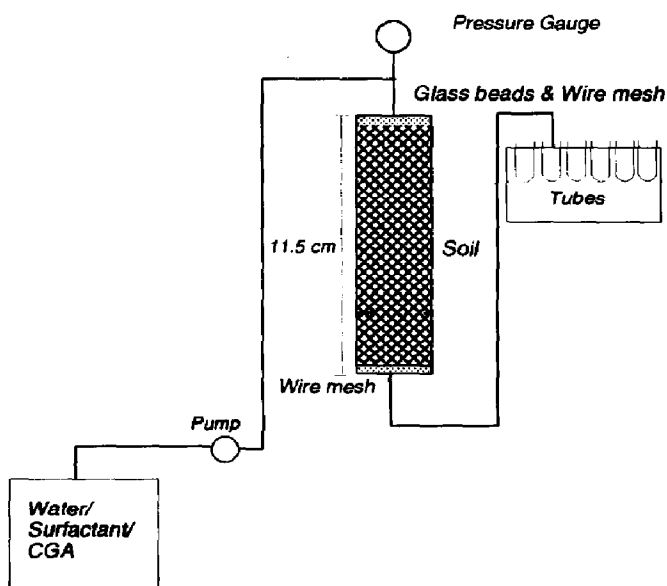


Fig. 1. Schematic of the experimental setup for soil-washing experiments.

measurements was used that simplified the analysis by treating the waste as a single component rather than as a mixture of components with varying properties. The effluent collected showed two distinct phases: a heavy oil phase and an aqueous phase. The heavy oil phase was recovered by centrifuging the effluent at 10,000 rpm for 10 min (B22 Centrifuge, 875 rotor, International Equipment Company, Needham Heights, MA) and the supernatant aqueous phase was pipetted out. The empty weight of the centrifuge tube was deducted from the weight of the centrifuge tube with the heavy oil to get the amount of the oily waste recovered. In some cases, particularly with surfactant and CGA runs, soil particles were also washed along with the oily waste. The soil and heavy oily waste mixture was separated and the weight of the tube with soil and oily waste mixture was recorded. Toluene was added to this mixture to dissolve the oily waste, which was later separated by centrifuging. This toluene washing was continued until nearly all the oily waste was removed from the soil.

The effluent samples from the soil columns were analyzed at the LSU Institute for Environmental Studies to provide a partial identification of compounds in the mixture. Standard EPA methods 8240 for volatiles and 8270 for base/neutrals were used for the analysis of the samples.

3.6. CGA generation

CGAs were generated using a unit developed in our laboratory by Chaphalkar et al. [30] based on the design recommended by Sebba [29]. It consists of a horizontal disk that rotates at a high speed and is positioned about 2 cm below the surface of the surfactant solution in a cylindrical reactor. The disk is mounted between two vertical baffles with a stainless-steel rod. A powerful stirring motor and a speed controller are connected at the top of the rod, and the disk is stirred at the critical speed (above 5000 rpm) required to make CGAs. The waves produced by the disk strike against the baffles, and when they re-enter the solution at the baffles, they entrain the air encapsulated by the soap film to make the CGA. Because high temperatures of the suspensions are probable and undesirable in this process, a stainless-steel tubing coil was constructed inside and around the reactor in order to pump cold water, thus maintaining the suspension near room temperature.

4. Results and discussion

4.1. Soil flushing experiments

The hydraulic conductivity measurements for the soil columns were done in triplicate. Hydraulic conductivity values ranged from 1.11×10^{-4} to 2.57×10^{-4} cm/s with an average of 1.66×10^{-4} cm/s and a standard deviation of 3.43×10^{-5} cm/s, indicating that the packing procedure followed in this study is reproducible.

For the overall recovery estimate, the procedure for analysis was verified to assure that in the presence of the SDS surfactant solution, the recovery was acceptable. The average recovery of oily waste was 97.5% with a standard deviation of 3.3%. The

procedure for separating the oily waste from the soil by centrifuging with toluene was also verified with known amounts of surfactant solutions, oily waste, and soil. The average recovery was 88.9% with a standard deviation of 5.4%.

Flushing experiments were performed in duplicate. The results were reproducible with only slight variations between duplicates. Figures for the percent recovery were plotted using average values; the error bars in the plots show the range of the recovery values for the duplicate runs. The percent oily waste recovered from the column after the i th pore volume was calculated as

$$R_i = \left(\frac{\sum_i W_i}{W_0} \right) \times 100 \quad (1)$$

where W_i is the mass of oil recovered in the i th pore volume and W_0 is the initial mass of waste in the soil column.

4.2. Soil flushing in the downflow mode

The downflow flushing experiments were performed with waterflood, conventional surfactant solutions, and CGA suspensions. Two concentrations of surfactant solutions and CGA suspensions were used (8 and 30 mM SDS).

The percent recovery of oily waste from the soil columns during flushing with all three solutions is shown in Fig. 2. CGA suspensions and the conventional surfactant solutions were produced from 8 mM SDS (critical micelle concentration). After six pore volumes, water removed only 43% of the waste, whereas conventional surfactant solutions and CGA suspensions removed 47% and 56%, respectively. As shown in Fig. 2, the rate of removal was maximum at the start of the flushing and decreased

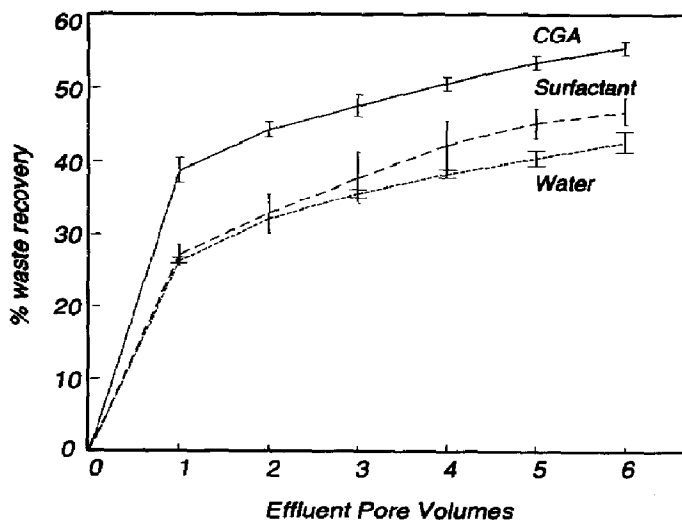


Fig. 2. Percent oil waste recovery in the downflow (gravity-stable) mode.

rapidly as the experiment progressed. The increased removal in the case of CGA suspensions and conventional surfactant solutions is presumed to result from displacement of the oily waste from the soil pore spaces, solubilization in the surfactant solution, dispersion of oil droplets in the aqueous phase resulting from electrical repulsion between the soil particles and the oil waste droplets [19, 31]. In the case of water, Abdul and Gibson [19] assumed that displacement of the waste is the main removal mechanism. They found that as the water front advances into the porous media, the trapped waste droplets become mobile, are displaced, carried by the water through the soil pores, and removed. They also noticed that as the oily waste droplets accumulate and coalesce to form longer streams of oil, they are more difficult to remove from the soil matrix.

4.3. Effect of surfactant concentration

Fig. 3(a) shows the comparison of percent recovery of oily waste with CGA suspensions at a low surfactant concentration of 8 mM and a high concentration of 30 mM. Similarly, Fig. 3(b) shows the results of conventional surfactant solutions at 8 and 30 mM. The removal of oily waste in the first pore volume was comparable for CGA suspensions generated from 8 and 30 mM surfactant concentrations. However, at the end of six pore volumes, the 8 mM suspension had better removal than the 30 mM CGA suspension. The 8 mM suspension removed 56% and 30 mM removed 51% of the oily waste after six pore volumes.

In the case of conventional surfactant solutions, Fig. 3(b) shows that 30 mM SDS had 33% removal in the first pore volume when compared to 27% removal by 8 mM SDS solution. But after six pore volumes, 8 mM SDS solution had removed 47% and 30 mM SDS solution had removed 44% of the waste. At both high and low

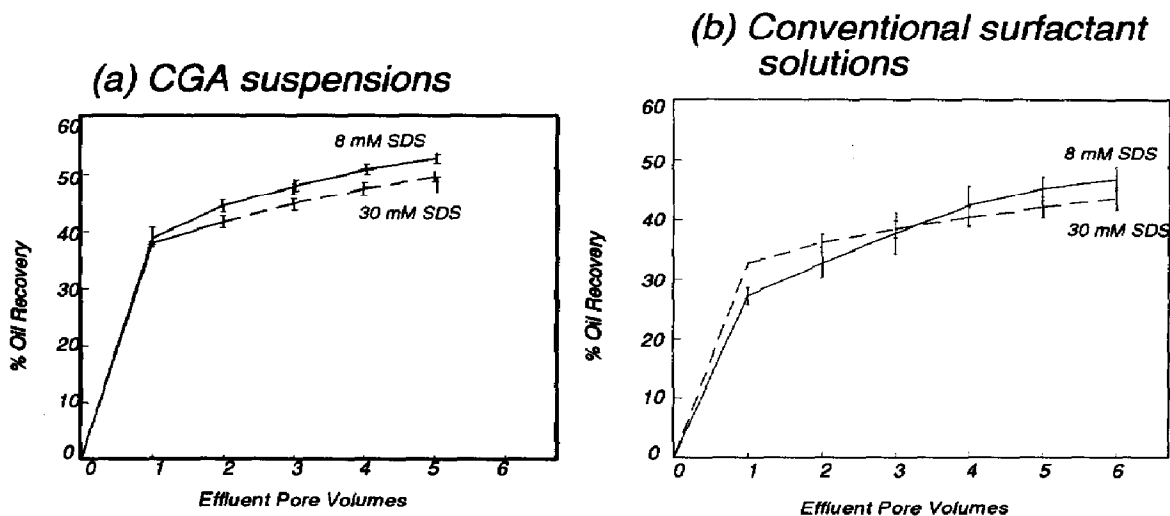


Fig. 3. Effect of surfactant concentration on oil recovery in the downflow mode.

concentrations, CGA suspensions were more effective than conventional surfactant solutions or water in removing the waste from soil. For example, at the high surfactant concentration, CGA suspensions removed 51% compared to 44% with conventional surfactant solutions and 43% with water after 6 pore volumes. At the higher surfactant concentration, solubilization should have played a major role in the removal of oily waste, but the results do not show any increase in the removal rate for either CGA suspensions or conventional surfactant solutions. These observations indicate that the removal of waste from the soil column must occur by displacement of the waste oil from soil pores rather than by dispersion or solubilization processes.

Ang and Abdul [18] reported that an increase in surfactant concentration above CMC increases the number of micelles, which in turn enhances the solubilization and dispersion of oil, but that excessive micelle formation may lead to pore clogging and restriction of flow through the soil. Recent findings in our laboratory by Liu [32] on the use of SDS in soil flushing have shown that an increase in surfactant concentration causes changes in the hydraulic properties of soil such as hydraulic conductivity and pore geometry. It was suggested that the reduction in hydraulic conductivity could be caused by the mobilization of fine grain particles and the precipitation of divalent calcium dodecyl sulfate. The soil used in that study had a high content of calcium ions (750 mg/kg of soil) which may have precipitated as calcium dodecyl sulfate and caused clogging of the water flow channels, which can decrease the removal efficiency. When combined with pore blocking due to increased soil dispersion and precipitation of calcium dodecyl sulfate, excessive micelle formation may significantly reduce the removal of oily waste at higher surfactant concentrations.

4.4. Soil flushing in the upflow mode

Fig. 4 shows the recovery of oily waste for the upflow runs using waterflood, conventional surfactant solutions, and CGA suspensions. The surfactant concentration

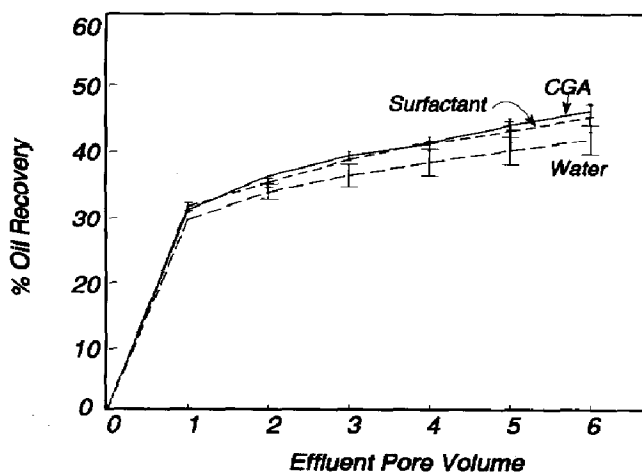


Fig. 4. Percent waste recovery in the upflow (gravity-unstable) mode.

used for both CGA suspensions and surfactant solutions was 8 mM. The waterflood, conventional surfactant solutions, and CGA suspensions all had a nearly 30% removal in the first pore volume. After six pore volumes, water removed 41% and conventional surfactant solutions and CGA suspensions both removed about 45%. CGA suspensions after seven pore volumes removed 47%. As in the downflow mode, the rate of removal was maximum at the start and decreased rapidly towards the end of the experiment. However, the removal efficiency by none of the wash solutions was as effective as in downflow mode. The main mechanisms for the removal of oily waste in the upflow mode are thought to be the same as in downflow mode. Solubilization and dispersion of oily waste cannot be expected to be significant during the CGA and surfactant runs since a low concentration of surfactant was used. Channeling was observed during the CGA runs and the effluent collected during both CGA and surfactant runs was turbid, indicating soil dispersion. We surmise that this may be one of the reasons for the low removal in case of both CGA suspensions and surfactant solutions.

4.5. Soil flushing in the horizontal flow mode

Fig. 5 shows the oily waste removal under horizontal flow using CGA suspensions, conventional surfactant solutions, and water. The concentration of surfactant used for both CGA suspensions and surfactant solutions was 8 mM. CGA suspensions removed 49% of the waste and conventional surfactant solutions removed 48% after six pore volumes. However, after six pore volumes water had removed only 42%. The removal mechanisms with different wash solutions in the horizontal flow mode are thought to be the same as in the downflow and upflow mode, and, in general, the overall behavior during CGA and surfactant runs are very similar to the ones observed during upflow and downflow runs.

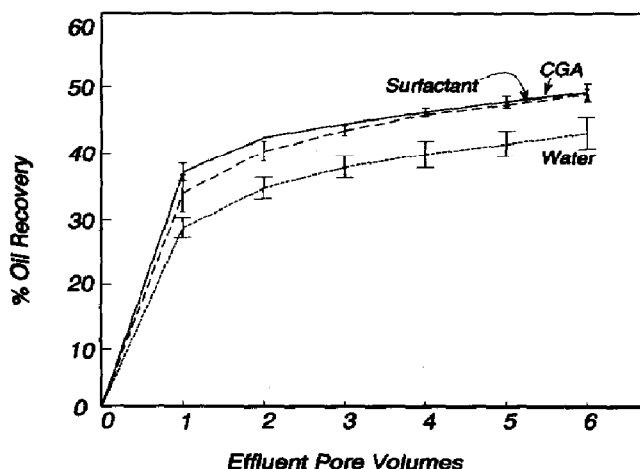


Fig. 5. Percent waste recovery in the horizontal flow (gravity-neutral) mode.

4.6. General comparison of all experiments

CGA suspensions removed 56% of the waste in downflow, 47% in upflow, and 49% in horizontal flow modes. One of the possible reasons for the higher downflow removal rate may be that in the downflow mode, the pressure difference and the density difference between the CGA suspension (which is 66% by volume air) and the oil waste both aided the displacement of the oily waste. This is not the case with the conventional surfactant solution. 8 mM SDS as conventional surfactant solution removed 47% in downflow, 45% in upflow, and 48% in horizontal flow. Water removed 43%, 41%, and 42% in downflow, upflow, and horizontal flow, respectively.

Judging from the overall performance, there is no significant reason to select one flow mode over another. The differences between the three flow modes are so small that they could be attributed to factors other than to the actual effectiveness of the flow mode itself.

4.7. Pressure buildup in soil columns during the flushing experiments

The pressure drop across the length of the soil column was monitored during the runs using a pressure gauge. Figs. 6–8 summarize these results. In the downflow runs using CGA suspensions, the pressure remained fairly low (< 14 psi). However, the pressure gradually increased to 50 psi when the flushing solution was switched to water, and returned to approximately 15 psi when switched back to CGA suspensions. CGAs may have opened the soil pores that were clogged when pumping water, as a result of which the pressure decreased substantially. When surfactants were used during downflow runs, the pressure was less than 26 psi until the fourth pore volume after which it slowly increased to values around 50 psi. This increase in pressure when using conventional surfactant solutions is probably due to clogged pores caused by the migration of clay particles to the bottom of the column as was earlier observed by Liu [32]. In some cases the pressure build-up in the soil column exceeded the limits of

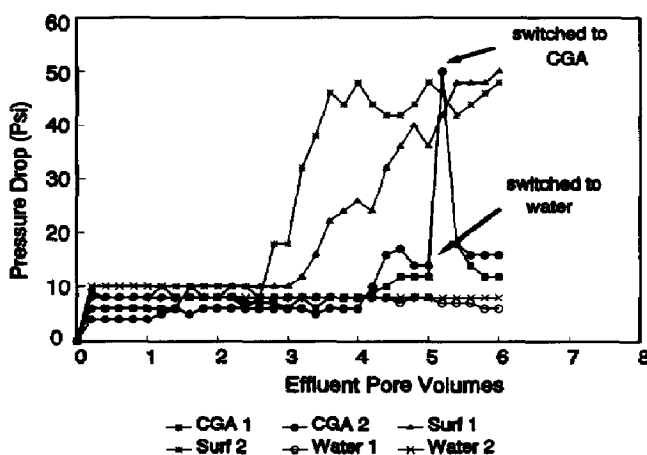


Fig. 6. Column pressure drop in the downflow mode.

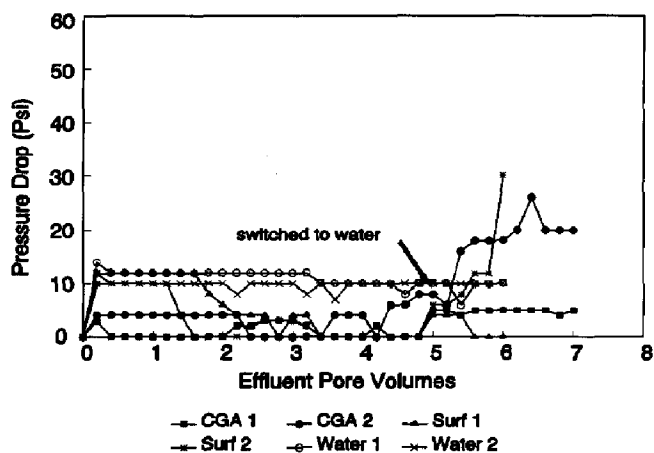


Fig. 7. Column pressure drop in the upflow mode.

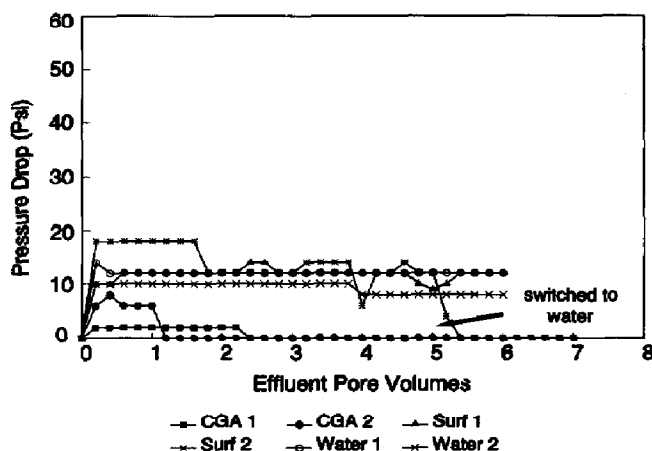


Fig. 8. Column pressure drop in the horizontal flow mode.

the pump, and the runs had to be discontinued. The pressure was fairly constant (~ 8 psi) during the water runs.

In the upflow mode, the pressure in the case of the CGA suspension was low, (< 4 psi), but when switched to water, the pressure increased to 5 psi in one case and to 20 in the other. In the case of conventional surfactant solutions, there was considerable pressure oscillation during the experiments. The pressure increased to about 10 psi by the end of the first pore volume and gradually dropped to negligible values thereafter. However, in one case, the pressure increased to 30 psi by the end of the experiment and remained negligible throughout the rest of the run. The pressure buildup for the waterflood was stable, around 10 psi throughout the run.

In horizontal flow, the pressure buildup in the case of the CGA suspensions was low (2-6 psi) in the first two pore volumes and was negligible until the end of the experiments. When surfactants were used, pressure increased (12-18 psi) during the

first pore volume, but in the subsequent volumes, the pressure stabilized around 12 psi. The pressure buildup in the case of water was somewhat low (10–12 psi).

The low pressure buildup when using CGA suspensions makes them favorable for field applications. However, we noted that the integrity of the soil was disturbed during the passage of CGA suspension through the soil column. The soil matrix developed distinct cracks that were visible near the walls of the column. These cracks persisted only during the runs with CGAs, and disappeared when the CGA suspension was replaced with either water or conventional surfactant solutions. This may in fact be a favorable situation in many cases where soil fracturing may be necessary in order to access the oil waste residing in slightly consolidated portions of the soil.

4.8. Removal of specific chemicals from the oily waste

Table 3 shows the percent recovery of volatiles (tetrachloroethene, 1,1,2,2-tetrachloroethane and 1,1,1-trichloroethane) and base/neutrals (hexachlorobenzene and hexachlorobutadiene) after flushing with CGA suspensions, conventional surfactant solutions, and water. All of these comparisons were based on the observed concentration in the original oily waste and the effluents after flushing. The removal of the volatiles (tetrachloroethene, 1,1,2,2-tetrachloroethane and 1,1,1-trichloroethane) were much larger using CGA suspensions than the conventional surfactant solution or water. The removals of the base/neutrals (hexachlorobenzene and hexachlorobutadiene) were 7–10% better for the CGA suspension than the conventional surfactant solution. The higher removal rate may be due to the phase separation which occurs with the CGA suspensions in the soil column. When the soil column is flushed with CGA suspensions, the microbubbles travel for some distance and collapse, giving rise to phase separation into a liquid and a gas front which move at different velocities through the soil. This was clearly evident in that the effluent appeared as a series of gas bubbles and liquid drops as was also noted in our earlier work [5]. The gas portion escapes into the atmosphere, possibly carrying some of the volatile compounds.

5. Conclusions

Based on the results of this study on the flushing of an oily waste from a typical soil matrix using CGA suspensions, conventional surfactant solutions, and water under different flow modes (viz. downflow, upflow and horizontal flow), CGA suspensions appear to have good potential as a fluid for remediation of contaminated soils. CGA suspensions generated from 8 mM SDS solution removed about 56% oily waste in six pore volumes compared to 47% by conventional surfactant solutions at the same concentration and 43% by waterflood in the downflow mode. They also showed higher removal than conventional surfactant solutions or water for the major chemicals in the waste (hexachlorobenzene, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane and tetrachloroethene).

CGA suspensions and surfactant solutions had almost the same removal in both upflow and horizontal flow mode. No significant difference was observed in the oily

Table 3
Cumulative percent recovery of specific chemicals from the oily waste

PV	Hexachlorobutadiene			Hexachlorobenzene			1,1,1-Trichloroethane			Tetrachloroethene			1,1,2,2-Tetrachloroethane		
	CGA	Surfactant	Water	CGA	Surfactant	Water	CGA	Surfactant	Water	CGA	Surfactant	Water	CGA	Surfactant	Water
1	29	20	1	24	17	2	46	2	0.7	25	0.1	0.6	85	0.5	6
2	31	21	3	29	18	5	47	4	2	25	0.5	2	88	10	10
3	31	22	3	29	20	5	47	5	2	25	0.5	2	88	10	11
4	31	22	3	29	20	6	47	5	2	25	0.5	2	88	10	11

waste removal with respect to different flow modes when conventional surfactant solutions or waterflood were used. Increasing the surfactant concentration did not enhance the removal efficiency of either CGA suspensions or conventional surfactant solutions. Increased soil dispersion and pore blocking may have been responsible for this decrease in the removal.

The pressure drop remained low (6–10 psi) for both CGA suspensions and water in downflow mode, whereas the pressure was as high as 50 psi in case of conventional surfactant solutions. The pressure drop in upflow and horizontal flow remained lower than that in downflow mode for all the three wash solutions.

Future experiments will focus on other experimental parameters, such as the performance of a wide range of surfactants for the recovery of the oily waste, and surfactant optimization for the on-site pilot scale demonstration to be undertaken shortly.

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