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Comparison of Soil Washing Using Conventional Surfactant Solutions and Colloidal Gas Aphron Suspensions

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Abstract

Surfactants have proven to be an effective way of augmenting the removal and mobilization of organics from contaminated soil. A more recent and innovative technology to aid the removal of contaminants from soil is the use of colloidal gas aphron (CGA) suspensions. The performance of CGAs and surfactant solutions in washing soils contaminated with 2,4-dichlorophenoxy acetic acid (2,4-D) was investigated and compared with the process of washing soils with aqueous solutions of surfactants as in conventional surfactant flushing. In general it was observed that there was no significant difference in the performance of the two processes of soil washing for a highly soluble compound like 2,4-D. However, the surfactant consumption per gram of 2,4-D recovered from the soil was higher for conventional washing than for CGA solutions. CGAs also had a significant advantage over surfactant solutions in that at low flow rates, the pumping of CGAs showed lower pressure drops across the soil column.

INTRODUCTION

Surfactant solutions have been reported to be successful in removing various organics from sand and soil (*1–8*). There are two principal limitations in using surfactant solutions for *in-situ* soil washing. The first of these is the large pressure drop associated with the injection of the sur-

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factant solution into the soil. This presents an obstacle for the actual field application of the process because of high energy consumption and possible perturbation of the soil integrity. The second limitation is the extent of surfactant recovery both for economic reasons and the need to reduce further contamination of the soil with a surfactant. Thus there are incentives to study ways of minimizing surfactant consumption. Colloidal gas aphrons (CGAs) may provide a solution not only to the recovery problem but also to high pressure buildup. Colloidal gas aphrons are gas bubbles encapsulated in a soap film. Surfactant, water, and air are the only elements that are needed for CGA generation. The colloidal properties of the system are due to the small size of the bubbles (25–125 μm). A CGA is different from a conventional air or soap bubble in its structure. A CGA has a double layer of surfactant molecules forming a thin film encapsulating the air, as opposed to conventional soap bubbles which have only one layer around them. The double layer that CGAs possess contributes to their high stability, which in addition to the small size of the bubbles and its low viscosity (close to that of water), present ideal conditions for the suspensions to be pumped without significant degeneration of CGAs (*9*). CGAs have been used successfully in a number of flotation applications (*10–12*). CGAs have proved to be promising in facilitating decontamination by improving the containment of subsoil hydrocarbon spills (*13*). It has also been demonstrated that CGAs have potential as a means of providing oxygen and nutrients to microorganisms used for soil bioremediation (*13*). Longe (*14*) carried out a lab-scale study to determine the behavior and performance of CGAs for washing sand contaminated with hydrophobic compounds and showed that surfactants in the form of CGAs have some advantages.

In this paper we compare the performance of both conventional surfactant solutions and CGAs produced using sodium dodecylbenzenesulfonate (DDBS) surfactant for washing soil columns contaminated with a water-soluble herbicide, viz, 2,4-D.

EXPERIMENTAL

2,4-D and DDBS were supplied by Sigma Chemical Company. Their properties are summarized in Table 1. A soil sample was dried, ground, and mixed with fine sand to obtain a typical soil containing 69.3% sand, 12.3% silt, 18.3% clay, and 0.1% organic matter. It was then contaminated by dissolving 2,4-D in methanol and mixing the solution with the soil followed by methanol evaporation. Two different levels of soil contamination were studied: one contained 5 g of 2,4-D per kg of soil and another contained 1.7 g of 2,4-D per kg of soil.

TABLE 1
Properties of DDBS and 2,4-D

Properties	DDBS	2,4-D
Structure	CH_3—$(CH_2)_{10}$—CH_2—CH_6H_4—$SO_3^{2-}H^-Na^+$	(2,4-Cl_2—C_6H_3O)CH_2CO_2H
Molecular weight	348.5	221.0
CMC (*19*)	1.5 m*M*	—
Nature	Anionic	—

The soil was packed in steel columns 30.5 cm long and 6.4 cm in diameter (Fig. 1) using a tamping rod. Six batches of 251 g soil were compacted exactly the same way to obtain a packed density of 1.74 g/cm^3 and a resulting hydraulic conductivity of 2.26 × 10^{-4} cm/s. The remaining space at the top of the column, approximately 3.2 cm, was filled with coarse sand to prevent any channeling, and the effluent end of the column contained a porous stone that served as a filter. A piston pump was used to provide

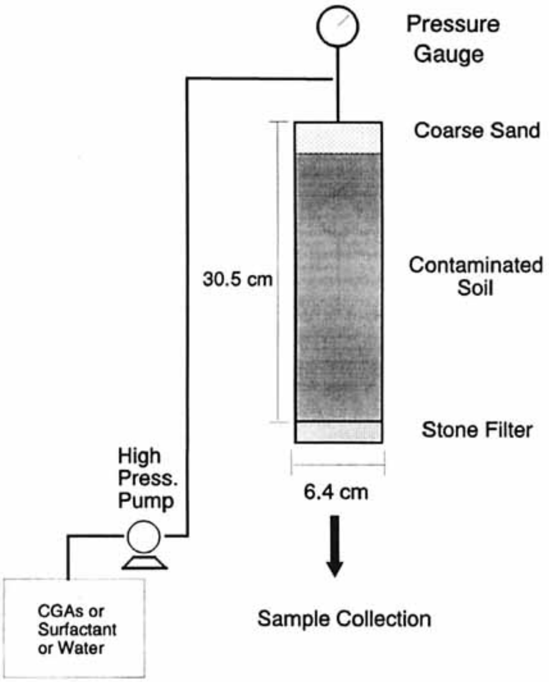

FIG. 1. Schematic of the soil column used in the experiments.

a downflow wash, thus preventing any fluidizing. The pump was set at 5.4 mL/min and was used to inject the different washing solutions into the soil columns.

CGAs were produced using DDBS at its critical micellar concentration (CMC) using the same procedure described in our earlier work (*15*, *16*). A particle size analysis of CGAs was performed, the results of which are shown in Fig. 2 (*22*).

The soil washing runs were performed by injecting the wash solutions after saturation of the column with water. The effluent samples were collected after 1 h, which was the approximate time for column saturation (one pore volume). The pH of each sample was measured, and the sample was filtered through a 0.45-μm syringe filter before analysis for 2,4-D and surfactant concentration.

The soil with 5 g of 2,4-D per kg of soil was washed using four different methods. The first method consisted of alternating flushes with conventional surfactant solution and water. The second method involved alternating flushes with CGA suspension and water. The third and fourth methods were continuous injections of surfactant solution and CGA suspension, respectively.

For the soil with 1.7 g of 2,4-D per kg of soil, two different methods were employed. The first consisted of alternating flushes with surfactant solution and water, and the second one involved alternating flushes with CGA suspension and water.

The method used for 2,4-D analysis was based on an application note developed by Schuster et al. for Hewlett-Packard (*17*). Solution A consisted of 0.005 *M* KH_2PO_4 with 0.001% CH_3COOH, and B of acetonitrile and methanol in 1:1 ratio, also with 0.001% CH_3COOH. We used an isocratic run using 65% A and 35% B. The column used was an ODS Hypersil with 5 μm particles, 200 mm long, and 4 mm i.d. The flow rate was 1.0 mL/min. The detector used was a UV multiple wavelength detector set at a wavelength of 230 nm (a bandwidth of 12 nm), with a reference wavelength and bandwidth of 450 and 30 nm respectively.

The adsorption of 2,4-D on the soil and the solubility of 2,4-D at different pH values was also studied. For the adsorption experiment, eight flasks were filled with 200 mL of a solution of 2,4-D and water, each with different concentrations ranging from 1 to 255 mg/L. Five grams of soil were added to each flask and shaken on a shaker table for 48 h. The initial and equilibrium concentrations in each flask were monitored using HPLC. For the 2,4-D solubility experiment, four different flasks were filled with 100 mL of buffered solutions at pH 2.1, 4.1, 7.0, and 9.7, respectively. Four grams of 2,4-D were added to each flask to guarantee saturation of the solution. Each flask was stirred using a magnetic stirrer for 24 h, and the 2,4-D

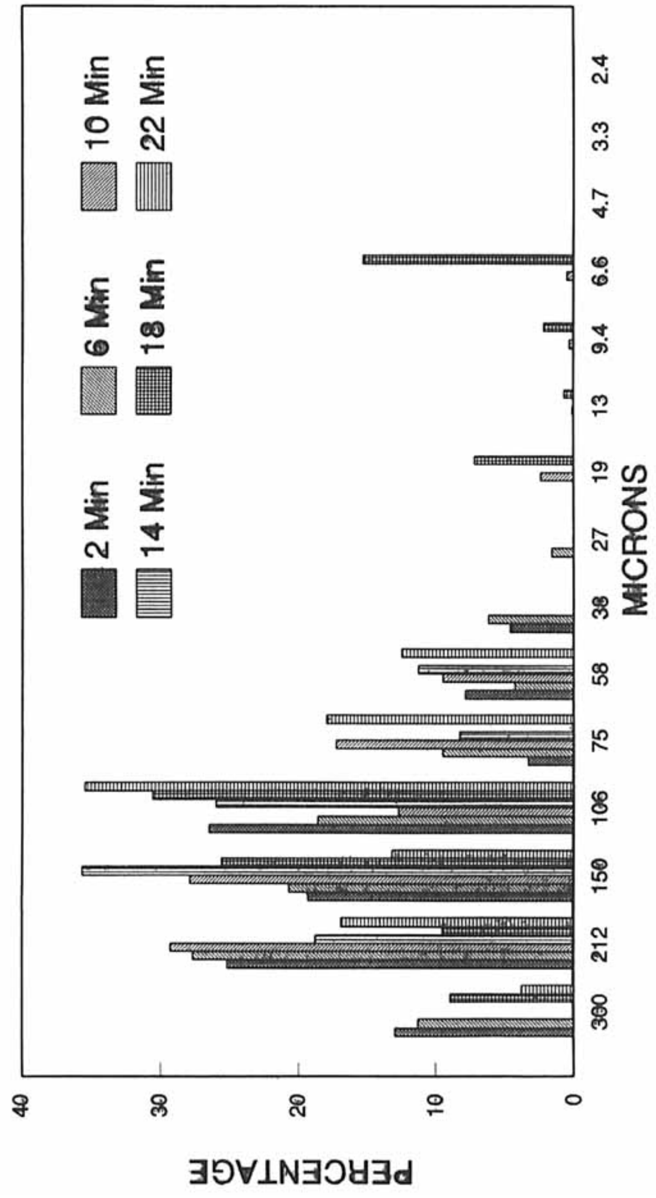

FIG. 2. CGA particle size analysis.

concentrations and the final pH values were measured to obtain values of the solubility of 2,4-D at different pH values.

Surfactant analysis was done using the standard methylene blue assay procedure (*20*).

RESULTS AND DISCUSSION

2,4-D Adsorption and Solubility

The adsorption isotherm for 2,4-D on the soil is presented in Fig. 3. We observed that the absorbed concentrations are very small, varying from 1 to 7%. This indicates that there is very little adsorption of 2,4-D on the soil. The value of the adsorption coefficient (K_d) was calculated using a linear regression resulting in 2.15 (mL/g) with a $R^2 = 0.88$. The adsorption of many compounds of soil is influenced by the organic content of the soil and its composition. Orgam et al. (*18*) reported that soils with low or no organic content have very low or zero adsorption coefficients for 2,4-D. The value obtained for K_d in this experiment is somewhat similar to that obtained by Ogram for Webster Soil. This soil used by Ogram et al. (*18*) had an organic content of 3.59% as opposed to the soil used in this experiment, which had only 0.1% organic content. The low R^2 obtained from the regression for K_d suggests that the absorbed 2,4-D concentration on soil is so small that variation in reproducibility of HPLC determinations of 2,4-D in the supernatant may have to be taken into account.

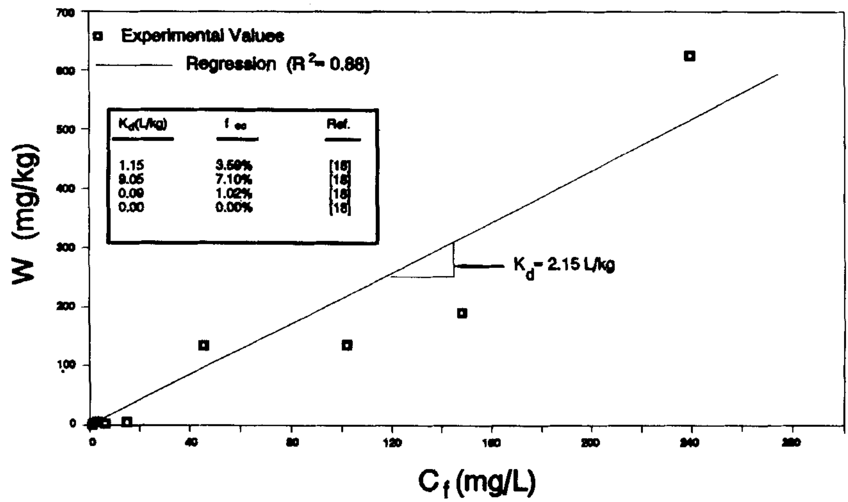

FIG. 3. Adsorption isotherm for 2,4-D on the soil.

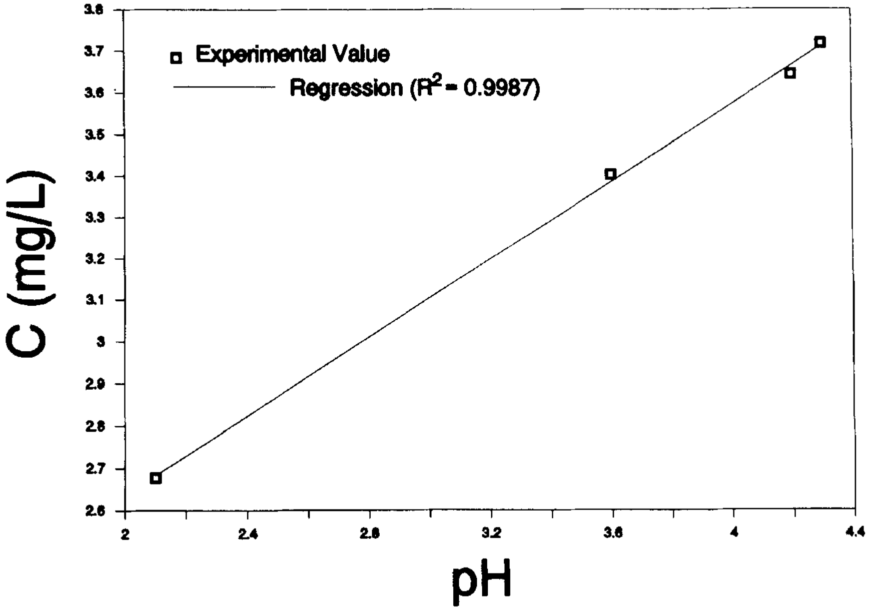

FIG. 4. Variation in 2,4-D solubility in water as a function of pH.

The solubility of 2,4-D as a function of pH does not exist in the current literature. Figure 4 shows the solubility of 2,4-D at various pH values. A linear regression of log 2,4-D concentration versus pH was done. The regression obtained was the following:

$$\log [2,4\text{-D}] = 1.69 + 0.47\,\text{pH} \quad \text{with} \quad R^2 = 0.98 \qquad (1)$$

where [2,4-D] is the concentration in mg/L. 2,4-D is an ionic compound and its aqueous solubility increased from 476 to 5218 mg/L over a pH range of 2.1 to 4.3

Soil Washing Using Surfactant Solution

Soil washing runs were performed either with alternate flushes of surfactant and water or continuous flushes with surfactant. In both cases, prior saturation of the soil column with water was done.

The removal of 2,4-D in the first flush was high in all cases. For the soil with 5 g of 2,4-D per kg of soil (high contamination), the concentration in the effluent in the first flush was as high as 7.1 g/L for the alternate flushes and 6.3 g/L for the continuous flush. This is logical given the fact that the liquid injected in the first flush (distilled water for the alternate run and surfactant solution for the continuous run) had a pH around 7.0, thus providing an adequate pH for 2,4-D solubilization. Further, we observed a gradual decrease in effluent 2,4-D concentration in subsequent flushes for the soil with high 2,4-D contamination, and a drastic decrease after the first flush in the soil with 1.7 g of 2,4-D per kg of soil (low contamination).

Figure 5 shows plots of the percentage of the mass of 2,4-D remaining in the soil versus the volume pumped (in this case the volume collected in the effluent). The two runs with high contamination on the soil share a similar trend as far as the shapes of the curves are concerned. After the first flush with approximately the same volume (one pore volume), a removal of about 25% of 2,4-D was achieved, followed by a linear decrease in the percentage of 2,4-D remaining on the soil. Both runs in this region showed very similar rates of removal. Following the fourth flush, the removal rate (slope) decreased gradually with each flush.

The run performed on low contamination soil showed a different trend from the previous ones, since there was a substantial decrease in the percentage of 2,4-D remaining in the soil after only one flush, followed by a lower rate in the second flush and a very insignificant removal after that. It can therefore be concluded that the removal of 2,4-D is controlled by its aqueous solubility. Based on the results, it appears that a comparable

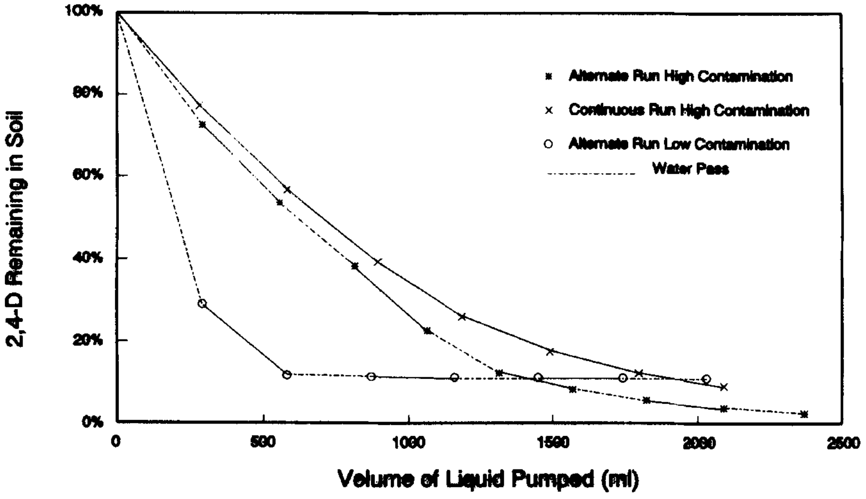

FIG. 5. Comparison of soil washing of 2,4-D using conventional surfactant solutions in continuous flush and alternate flushes with water.

rate of removal can be achieved by using either distilled water or an aqueous surfactant solution.

The difference between the percentages of 2,4-D remaining in the soil at the end of each run, although small, could be attributed to the possible variation in the distribution of 2,4-D in soil. In other words, more 2,4-D could have been in contact with the fluid pumped in the case of the highly contaminated soil washed with alternate runs than in the others. This could have been the result of small variations in the soil packing process, thus creating some clogged pores into which the solution did not migrate. It is also possible that the clay particles dislodged during the pressurized run could have clogged some of the larger pores inhibiting 2,4-D removal. Although there are small differences in the final amount of 2,4-D left on the soil after each run, there appeared to be not enough information to assert whether surfactant solution was more efficient than distilled water in removing 2,4-D from this kind of soil.

Soil Washing Using CGA Suspension

Soil washing runs were performed with CGA suspensions, either with alternate flushes with water and CGA suspensions or in a continuous mode with only the CGA suspension. In both cases, prior saturation of the soil column with water was achieved before the experiments.

The concentration of 2,4-D in the effluent of the first flush was similar for the three runs and it varied from 6.2 to 6.7 g/L. The concentrations for the observed pH of the effluent were slightly higher than what they should have been according to the solubility experiments. For example, at pH = 4.4 the concentration should be 5.85 g/L while the experimental value was 6.18 g/L. It is not clear if this may be due to the fact that the constant injection of fluid (either water or CGAs) at pH values close to neutral proably produced an effluent oversaturated in 2,4-D.

For both the alternate and continuous runs in the case of highly contaminated soil, the initial removal was constant. Figure 6 shows very similar linear trends (constant removal rates) up until 80% was removed in the alternate run and up until 55% for the continuous one, both for highly contaminated soil. The difference was probably as a result of the fact that the continuous run was performed for the same amount of time as the alternate one, and since CGAs are approximately 60% air, the volume of liquid collected for a certain period of time is considerably less for CGAs than for water. For the soil with low contamination we observed a different trend, although very similar to the one shown by soil washing using surfactant solutions as described previously. A fast removal of 2,4-D during the first flush was followed by a decrease in the removal rate during the next two flushes and insignificant removal after that.

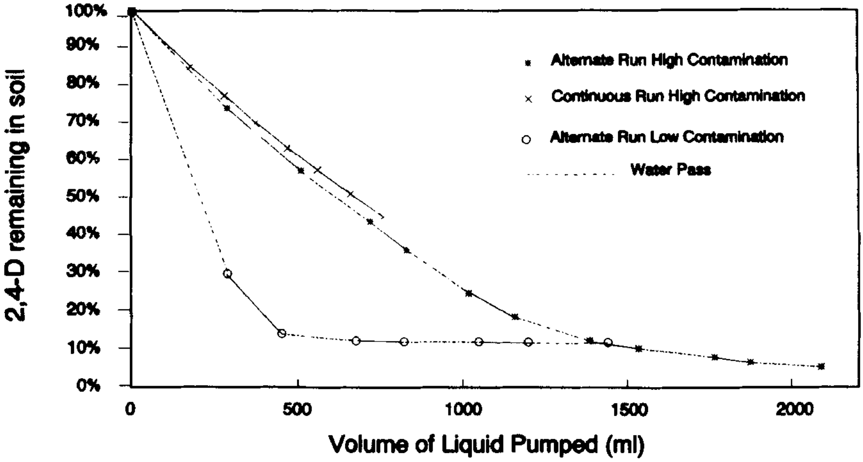

FIG. 6. Comparison of soil washing of 2,4-D using CGA suspensions in continuous flush and alternate flushes with water.

The overall behavior and removal rates were, in general, similar to the one observed in the surfactant runs, and as explained in the last section, 2,4-D removal seemed to be controlled by its high aqueous solubility.

The small differences in the overall removal, as explained in the last section, can be attributed to minor variations in the packing of the column and to the possible clogging of some pores. In general there were no significant differences in the overall removal of 2,4-D which would allow us to decide whether CGA suspensions are more efficient than distilled water or aqueous surfactant solutions in removing 2,4-D from contaminated soil.

As far as the overall removal was concerned, the performances of the six different experiments on soil washing showed no significant differences. The only apparent benefit is that alternating passes with water and surfactant or water and CGAs removed somewhat more 2,4-D than the continuous runs done with water, surfactant, or CGAs alone. But as stated before, these differences are so small that they could be attributed to factors other than the actual effectiveness of the method itself. The observation, however, cannot be overlooked because other researchers, such as Abdul et al. (7), reported that alternate washes involving surfactant and water improved the removal of contaminants from the soil. Compounds that are more hydrophobic than 2,4-D will have a singificant adsorption capacity on soils and should be considered to validate these observations.

Both surfactant solutions and CGA suspensions were equally efficient in removing 2,4-D from soil columns. However, the efficiency in terms of

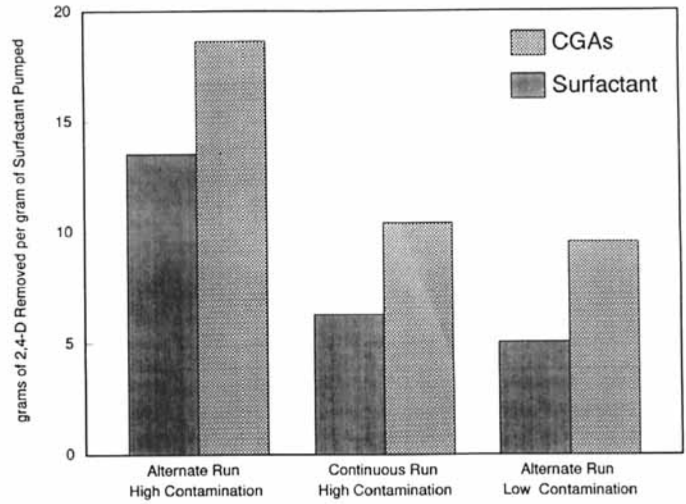

FIG. 7. Comparison of mass of 2,4-D removed per gram of surfactant used in the form of conventional surfactant solutions in the form of CGAs.

removal per gram of surfactant used was striking. Figure 7 shows a comparison of the two methods in terms of the grams of 2,4-D removed per gram of surfactant used. CGAs showed significantly more removal of 2,4-D for the same amount of surfactant in all the runs, which led to the conclusion that when used for removing more hydrophobic contaminants, where water is not an efficient solvent, the use of CGAs will be more promising economically compared to conventional surfactant solutions.

Pressure Build-up in Soil Columns

The pressure difference was monitored using a pressure gauge connected to the influent end of the column. Figure 8 shows the values of the pressure differential between the influent and effluent ends of the column. We observed a constant increase in pressure difference in experiments with both continuous surfactant flush and alternating surfactant and water flush. During the experiment involving alternating CGA suspension and water flushes, there was a sudden and repetitive decrease in pressure when pumping CGAs. Continuous CGA injection showed an initial oscillation in pressure followed by a constant low pressure compared to any of the other fluids used. In other words, conventional liquids (both surfactant solutions and distilled water) registered pressures as high as 26 psi at the end of the runs, without showing any evidence of stabilization, as opposed to CGAs which registered a constant 2 psi after stabilization. The reason for this

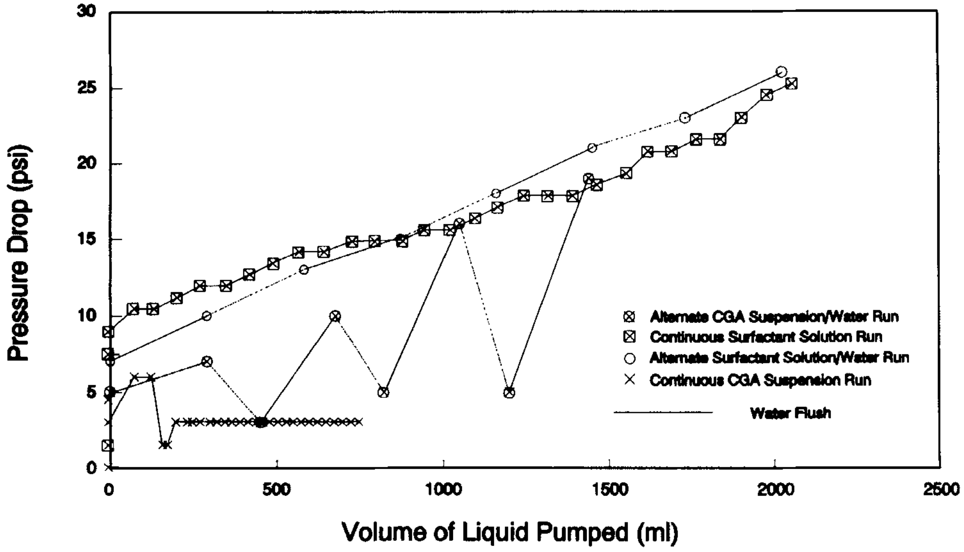

FIG. 8. Pressure drops in the soil columns when water, surfactant solution, and CGAs are pumped through.

increase in pressure when using conventional fluids is probably due to the migration of clay particles to the bottom of the column, thus clogging the pores and reducing the hydraulic conductivity. When CGAs are used it is possible that air entrained in the microbubbles entered the column and exited successfully without disturbing the soil integrity, thus maintaining a constant hydraulic conductivity. The initial oscillation in the pressure when CGAs are used is probably caused by the saturation water in the column which displaces some particles and slightly alters the initial hydraulic conductivity.

The low pressure buildup using CGAs is promising, since the removal of contaminants can be carried out with less perturbation of the soil structure in addition to less surfactant consumption compared to the use of conventional surfactant solutions. Furthermore, it would be correct to assume that if CGAs had been pumped continuously until the same volume of liquid had passed through (compared to the surfactant solution run), higher overall removals could be expected. CGA suspensions showed considerably lower pressure buildups and possibly maintained the integrity of the soil. This may permit access of CGA suspension to all soil pore spaces, thus improving the removal of 2,4-D, as opposed to surfactant solutions and water which, by displacing clay particles, may isolate regions in the soil and possibly inhibit 2,4-D removal from those areas. This observation is similar to that of Peter et al. (*21*).

In general, it was observed that 2,4-D was removed effectively from soil columns using either surfactant solutions or CGA suspensions. As far as the overall removal was concerned, there was no significant difference in the performance of these solvents in washing 2,4-D from soil columns. In addition, no significant difference was observed in the overall removal of 2,4-D when using different initial soil contamination. Surfactant consumption was observed to be less using CGAs than using surfactant solutions, i.e., CGAs removed more 2,4-D per gram of surfactant pumped. CGAs had a significant advantage over surfactant solutions in that when pumped at slow rates, the pressure buildup in the soil was significantly smaller than when surfactant solutions or water were pumped through.

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REFERENCES

1. W. D. Ellis, J. R. Payne, and G. D. McNabb, *Treatment of Contaminated Soils with Aqueous Surfactants*, U.S. EPA Report EPA/600/2-85/129, 1985.
2. M. P. Esposito, B. B. Locke, and J. Greber, *Superfund Standard Analytical Reference Matrix Preparation and Results of Physical Soil Washing Experiments*, U.S. EPA Report EPA/600/9-88/021, 1988.
3. D. J. Wilson, *Sep. Sci. Technol.*, *24*, 717 (1989).
4. O. K. Gannon, P. Bibring, K. Raney, J. A. Ward, D. J. Wilson, J. L. Underwood, and K. A. Debelak, *Ibid.*, *24*, 1073 (1989).
5. C. Porzucec, *Surfactant Flooding Technology for in situ Clean up of Contaminated Soils and Aquifers. A Feasibility Study*, Los Alamos National Laboratory, Los Alamos, New Mexico, 1990.
6. C. Ang and S. A. Abdul, *Ground Water Monit. Rev.*, *11*, 121 (1991).
7. S. A. Abdul and T. L. Gibson, *Environ. Sci. Technol.*, *25*, 665 (1991).
8. A. N. Clarke, P. D. Plumb, and T. K. Subramanyam, *Sep. Sci. Technol*, *26*, 301 (1991).
9. F. Sebba and S. M. Barnett, *Proc. Second Int. Cong. Chem. Eng.*, *IV*, 27 (1981).
10. F. Sebba, *Chem. Ind. (London)*, p. 91 (4 February 1985).
11. P. T. Shea and S. M. Barnett, *Sep. Sci. Technol.*, *14*, 757 (1979).
12. B. Ferguson, C. Hinkle, and D. J. Wilson, *Sep. Sci.*, *9*, 125 (1974).
13. E. J. Fugate, "The Use of Colloidal Gas Aphrons to Facilitate Decontamination of Subsoil Hydrocarbon Spills," M.S. Thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, 1984.
14. T.A. Longe, "Colloidal Gas Aphrons: Generation, Flow Characterization and Application in Soil and Groundwater Decontamination," Ph.D. Dissertation, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, 1989.
15. D. Roy, K. T. Valsaraj, and V. J. Amedee, *Fluid/Part. Sep. J.*, In Press.
16. D. Roy, K. T. Valsaraj, and S. A. Kottai, *Sep. Sci. Technol.*, *27*, 573 (1992).

17. R. Schuster and A. Gratzfeld-Hüsgen, *Analysis of Phenoxy-acidic Herbicides and Bentazone by HPLC with Diode-array Detection,* Application Note 12-5091-0302, Hewlett-Packard, Waldbron, Germany, 1990.

18. A. V. Ogram, R. E. Jessup, L. T. Ou, and P. S. C. Rao, *Appl. Environ. Microbiol., 49,* 582 (1984).

19. K. T. Valsaraj, A. Gupta, L. J. Thibodeaux, and D. P. Harrison, *Water Res., 22,* 1173 (1988).

20. *Standard Methods for the Examination of Water and Wastewater,* 16th ed., APHA/AWWA/WPCF, Washington, D.C., 1985, Method 512.

21. R. W. Peters, C. D. Montgomery, L. Shem, and B. G. Lewis, *Surfactant Flooding of Diesel-Fuel-Contaminated Soil,* Paper presented at the ACS National Meeting, Atlanta, Georgia, April 14–19, 1991.

22. P. Chaphalkar, Department of Civil Engineering, Louisiana State University, Baton Rouge, Louisiana 70803, Unpublished Data.

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