3-D Microemulsion (3DMe)™

TECHNICAL BULLETIN 3.0

Micelle Distribution Column Experiment

Background

3-D Microemulsion (3DMe)™, a form of HRC Advanced®, is a state-of-the-art specialty chemical substrate developed to provide a low-cost, slow-release electron donor to stimulate the in-situ anaerobic degradation of contaminants in soil and groundwater. Unlike emulsified-oil-type substrates, 3DMe was designed to provide superior distribution in the subsurface, thereby reducing the cost of product application. 3DMe was also designed to avoid the significant reduction in subsurface hydraulic conductivity often associated with emulsified-oil-type substrates. 3DMe is a slightly viscous liquid that incorporates a molecular structure composed of tetramers of lactic acid (polylactate) and fatty acids esterified to a carbon backbone molecule of glycerin.

Subsurface Transport

3DMe achieves superior subsurface distribution through surface-active properties that promote the spontaneous formation of micellar structures (Shah, et al., 1972; Lindman, et al., 1982). This unique characteristic allows for moderate aqueous transport of the substrate prior to its adsorption onto the aquifer matrix where it both partitions organic contaminants from solution and promotes rapid biodegradation through efficient hydrogen generation. (The surface-active properties of 3DMe, formation of micelles, and recommended 3DMe application details are described in Regenesis 3-D Microemulsion Technical Bulletin 2.0.)

Demonstration of 3DMe Movement

It is well known that slow-release electron donors, such as emulsified-oil-type substrates, do not distribute well in soil and groundwater. In fact, extensive experiments using emulsified-oil-type substrates in sand test cells demonstrated that the emulsified-oil substrate moved less than 2 meters, even after 10 days of continuous emulsion feed. Furthermore, no emulsified-oil substrate moved more than 8 meters, regardless of injection volumes, and no additional water volume moving through the sorbed emulsion could facilitate further distribution (Borden, et al., 2005).

Experimental Design

In an effort to analyze the subsurface transport properties of 3DMe relative to the known shortcomings of emulsified-oil-type products, a controlled laboratory experiment was conducted using a dedicated aquifer simulation column (column) that was packed with

REGENESIS

Advanced Technologies for Groundwater Resources

1011 Calle Sombra, San Clemente, CA 92673 / www.regenesis.com

sand. The 6-inch-diameter, 20-foot-long column was constructed of transparent polycarbonate. The column was filled with fine-grained sand and packed to prevent channeling. The pore space was determined to be 30.5 percent (approximately 9 gallons). The column was filled with water by peristaltic pumps at a rate of 2.5 gallons per hour (see Figure 1).

A microemulsion of 3DMe was created by preparing a 1:3 3DMe-to-water mixture using a common high-shear pump, and was further diluted with water to generate a final 1:50 microemulsion. To visually track movement of the microemulsion in the sand column, it was dyed with methylene blue, which is absorbed by the hydrophobic portions of the 3DMe microemulsion. The dye does not partition into water.

After the column was first saturated with water, the 3DMe microemulsion was fed into the column at a rate of 2.5 gallons per hour. After 20 hours, the microemulsion feed was stopped and water was injected into the column at the same rate (2.5gallons/hour). This water feed continued for 12 hours (about 3.3 pore volumes).

Movement of the dyed microemulsion and resulting dyed micelle suspension were observed visually throughout the study. In addition, water effluent from the column was analyzed for the methylene blue by UV-Visible Spectroscopy. Components of 3DMe in the effluent were also confirmed by direct measurement with both liquid chromatography and infrared analysis.

Results and Discussion

After 13 hours, an estimated 3.6 pore volumes of the 3DMe microemulsion (1:50 product-to-water mixture) had been fed into the column. As expected, due to the unique hydrophile/lipophile balance of the 3DMe material, the bulk of the microemulsion appeared to adhere to the sand surfaces within the first 1 meter of the column, as evidenced by the dark blue color (see Figure 2). However, it was at this time that the first "break through" (material exiting the column) was detected by spectroscopy. Further analysis clearly indicated that the material in the effluent was, in fact, colloidal 3DMe (Micellar suspension), as evidenced by the presence of the intact esters, carboxyl, and carbonyl peaks apparent under infrared spectrum analysis (see Figure 3). While the bulk of the injected 3DMe remained stationary, micelles were forming and carrying the material more than 20 feet, with only 3.6 pore volumes, in less than 13 hours.

Approximately 20 hours after 3DMe injection, the bulk of the microemulsion continued to sorb onto soil near to the injection point (within the first 2 meters of the column), as evidenced by a dark blue color. At that time, the column was switched to a water feed, without any 3DMe, to emulate continued groundwater flow following 3DMe application. A striking pattern began to emerge as a light-blue-colored "front" began to move down the column.

It is apparent that water continuing to flow past the 3DMe was redistributing the product through the column as suspended micelles, which, in turn, were resorbing onto the column in a forward-moving "front." As more water was fed through the column, the 3DMe continued to redistribute, forming a light-blue-colored pattern (see Figure 4). Throughout the 12-hour period of the water feed, a 3DMe micelle suspension of low concentration was documented exiting the 20-foot-long column, as evidenced by microscopy and validated by liquid chromatography as well as infrared analysis.

Summary

3DMe was designed to achieve superior distribution in the subsurface and the advanced performance capability of the material was clearly demonstrated in a controlled laboratory column study. During the study, it was shown that 3DMe, when injected into the subsurface, initially sorbed onto the sand matrix. However, once in place, the material redistributed gradually through micelle formation and sorption in a distribution "front." 3DMe micelles were documented to move 20 feet through the sand column in 13 hours (3.6 pore volumes). The ability of 3DMe to remain relatively stationary, yet form micelles that continually redistribute, clearly demonstrates the product's superior subsurface distribution capability. This is significant when compared to other electron-donor substrates. Highly soluble substrates such as lactate and sugar solutions rapidly ferment and "wash out," requiring the expense of multiple injections. Emulsified-oiltype products have been clearly documented to sorb within the first 2 meters of the injection and then remain immobile, significantly limiting the effective radius of any injection point. In addition, emulsified oils often coalesce in the subsurface, reducing hydraulic conductivity.

The scientific evidence clearly demonstrates that the unique transport properties of 3DMe make this product an advantageous choice for stimulating effective in-situ anaerobic biodegradation.

REGENESIS

Advanced Technologies for Groundwater Resources

1011 Calle Sombra, San Clemente, CA 92673 / www.regenesis.com

Figure 1
Experimental Packed Column (20-foot-long, 6-inch diameter)

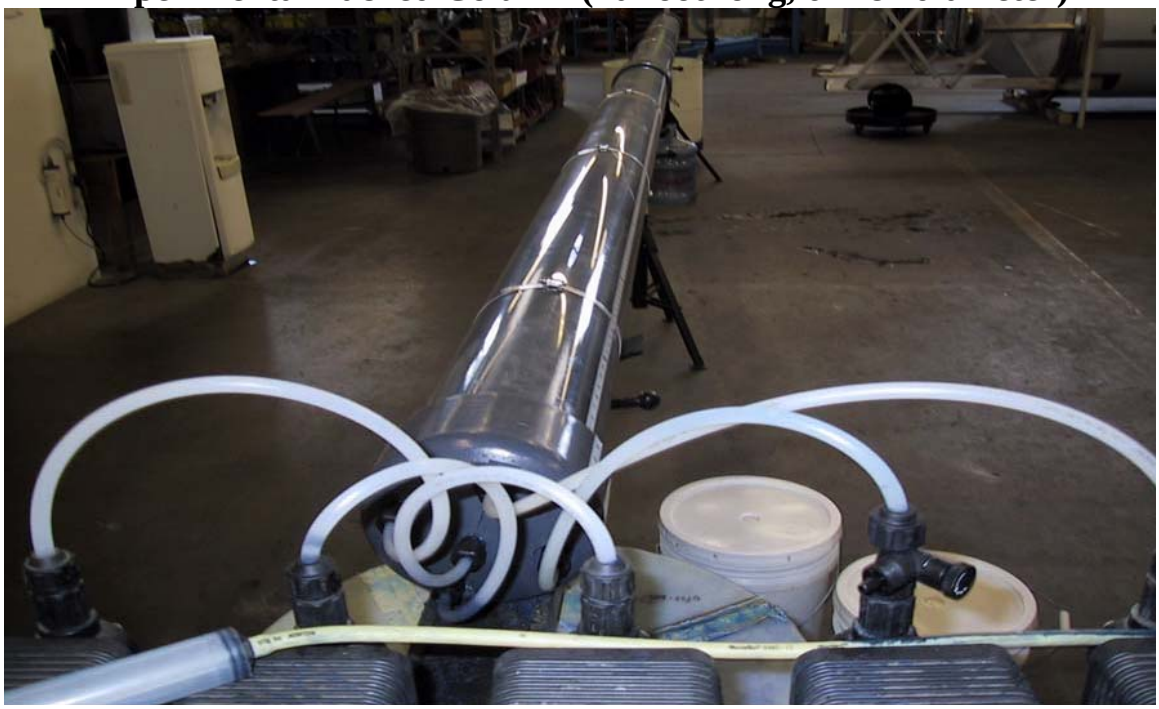

Figure 2
3DMe Movement at 13 hours (3.5 pore volumes)

REGENESIS
Advanced Technologies for Groundwater Resources

1011 Calle Sombra, San Clemente, CA 92673 / www.regenesis.com

Figure 3
Infrared Spectrum of Organic Material Exiting ASV at 13 Hours

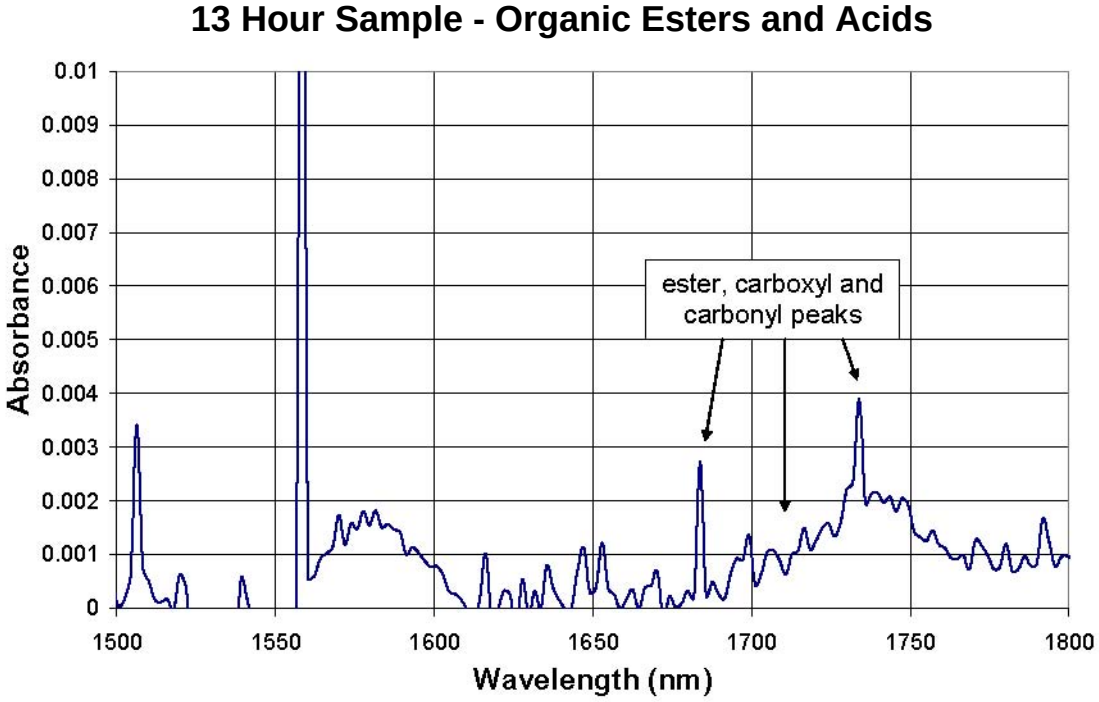

Figure 4
Micelle Formation and 3DMe Redistribution with Water Feed

REGENESIS
Advanced Technologies for Groundwater Resources

1011 Calle Sombra, San Clemente, CA 92673 / www.regenesis.com

References

Shah, D.O., Tamjeedi, A., Falco, J. W., and Walker, R. D., 1972, Interfacial Instability and Spontaneous Formation of Microemulsions, Am. Inst. Chem. Eng. J., 18:111-1120.

Lindman, B., Kamenka, N., Brun, B., and Nilsson, P.G., 1982, On the Structure and Dynamics of Microemulsions Self-Diffusion Studies, (ed.) Robb, I.D., Microemulsions, Plenum Press, NY.

Bordon, R.C., Lieberman, M.T., and Zawtocki, C.E., 2005, Enhanced Anaerobic Bioremediation Using Emulsified Edible Oil, Workshop, Eighth International In-Situ and On-Site Bioremediation Symposium, Baltimore, Md.

REGENESIS

Advanced Technologies for Groundwater Resources

1011 Calle Sombra, San Clemente, CA 92673 / www.regenesis.com