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Delivery of vegetable oil suspensions in a shear thinning fluid for enhanced bioremediation

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ABSTRACT

In situ anaerobic biological processes are widely applied for dechlorination of chlorinated solvents in groundwater. A wide range of organic substrates have been tested and applied to support the dechlorination processes. Vegetable oils are a promising type of substrate and have been shown to induce effective dechlorination, have limited geochemical impacts, and maintain good longevity. Because they are non-aqueous phase liquids, distribution of vegetable oils in the subsurface has typically been approached by creating emulsified oil solutions for injection into the aquifer. In this study, inexpensive waste vegetable oils were suspended in a shear-thinning xanthan gum solution as an alternative approach for delivery of vegetable oil to the subsurface. The stability, oil droplet size distribution, and rheological behavior of the oil suspensions that are created in the xanthan solutions were studied in batch experiments. The injectability of the suspensions and the oil distribution in a porous medium were evaluated in column tests. Numerical modeling of oil droplet transport and distribution in porous media was conducted to help interpret the column-test data. Batch studies showed that simple mixing of vegetable oil with xanthan solution produced stable suspensions of the oil as micron-size droplets. The mixture rheology retains shear-thinning properties that facilitate improved uniformity of substrate distribution in heterogeneous aquifers. Column tests demonstrated successful injection of the vegetable oil suspension into a porous medium. This study provides evidence that vegetable oil suspensions in xanthan gum solutions have favorable injection properties and are a potential substrate for in situ anaerobic bioremediation.

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1. Introduction

Several kinds of organic substrates can be used to stimulate microbial activity for enhanced anaerobic bioremediation of contaminants in the subsurface. These substrates can be categorized by their viscosity/flow characteristics as: soluble (dissolved aqueous) substrates, low-viscosity fluids, viscous fluids, and solid substrates (AFCEE and NFESC, 2004). Vegetable oils are viscous non-aqueous phase liquids (NAPLs) that are promising substrates for bioremediation of chlorinated solvents and PAHs in groundwater (AFCEE and NFESC, 2004; Boulicault et al., 2000; Scherr et al., 2009). Vegetable oils have been shown to induce effective dechlorination, to have limited geochemical impacts, and to exhibit good longevity (AFCEE, 2007; Hunter et al., 1997).

Because vegetable oils are NAPLs, distribution in the subsurface can be difficult (e.g. Lee et al., 2001; Zenker et al., 2000). Laboratory tests of pure oil injection resulted in significant residual oil in porous media and a correspondingly large decrease in permeability (Coulibaly and Borden, 2004; ESTCP, 2006). The vegetable oils may tend to stay at the top of the aquifer after injection because they are much less dense than water (ESTCP, 2006). Emulsification of vegetable oils has been

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applied for improved delivery of the substrates (Borden, 2007a; Borden and Rodriguez, 2006; Hunter, 2005). Emulsified oil substrates have been tested in the laboratories and applied in the field for the remediation of dense NAPL (DNAPL) contaminants (Harkness and Fisher, 2013; Lee et al., 2007), dissolved chlorinated contaminants (Borden, 2007b; Hunter, 2002; Long and Borden, 2006), and heavy metals or radionuclides (Gihring et al., 2011; Lindow, 2004; Lookman et al., 2013; Tang et al., 2013). Emulsified oil has also been used for reactive particle delivery for subsurface remediation (Berge and Ramsburg, 2009; Huff, 2011; Quinn et al., 2005).

Injection of emulsified oil has achieved improved substrate distribution and demonstrated improved remediation performance compared to pure oil injection (AFCEE and NFESC, 2004; Borden, 2007a). However, in heterogeneous porous media systems, uniformly distributing emulsified oil is a challenge (Clayton and Borden, 2009; ESTCP, 2006). Emulsified oil can readily be injected into high-permeability zones, but concurrently achieving effective distribution of the oil into low-permeability zones is difficult. Remediation of low-permeability zones, which are bypassed during the substrate delivery, will be controlled by mass transfer of dissolved contaminants and substrates between the oil-contacted and the bypassed zones. These mass transfer processes can significantly prolong the remediation process.

Shear thinning fluids (STFs) can potentially be used as a strategy to overcome this challenge, delivering oil droplets more uniformly in heterogeneous porous media. Owing to their shear thinning characteristics, these fluids can enhance the distribution of entrained amendments into lower permeability zones, thereby enhancing the remediation processes (Chokejaroenrat et al., 2013; Kananizadeh et al., 2015; Silva et al., 2013; Zhong et al., 2008, 2011). STFs have been tested and applied as a means to deliver dissolved remedial amendments (Chokejaroenrat et al., 2013, 2014; Kananizadeh et al., 2015; Smith et al., 2008; Truex et al., 2015; Zhong et al., 2008, 2011, 2013) or reactive particles (Comba and Sethi, 2009; Dalla Vecchia et al., 2009; Oostrom et al., 2007; Tiraferri et al., 2008; Truex et al., 2011a,b) to the subsurface for the purpose of enhancing remediation effectiveness.

Use of waste vegetable oil in lieu of virgin vegetable oil reduces the expense of the remedial substrate. Waste oils often contain other organics produced in the cooking processes, which typically complicates the emulsification processes. Thus, the practice of emulsifying waste oil for use as a remedial substrate has not been implemented (ESTCP, 2006). Fresh, food-grade vegetable oil and waste cooking vegetable oil has been compared as substrate in PAH biodegradation in contaminated soil (Scherr et al., 2012). The waste oil had higher viscosity and density than the fresh oil, but the difference in PAH removal efficacy between these oils was small.

In this study, the ability to form micron-size waste vegetable oil droplet suspensions in shear thinning xanthan gum solutions was investigated as an alternative approach to effectively deliver vegetable oil to the subsurface for enhancing bioremediation of heterogeneous contaminated materials. Xanthan gum is a biopolymer commonly used to form shear-thinning fluids. It is an extracellular polysaccharide produced by the bacterium *Xanthomonas campestris* and it has both a high molecular weight ($>2 \times 10^6$ g/mol) and high water solubility (Garcia-Ochoa et al., 2000). Aqueous Xanthan gum solutions have relatively high static viscosity, even at low concentrations, and they exhibit significant shear thinning (Zhong et al., 2013).

A series of laboratory batch tests were conducted to characterize the properties of vegetable oil suspensions in a xanthan gum solution with respect to oil droplet stability, oil droplet size distribution, and rheological behavior. Column tests were conducted to evaluate injection of the oil suspension into porous media. A numerical model was developed to use simulations to help interpret the experimental results.

2. Materials and methods

2.1. Laboratory tests

2.1.1. Materials and procedures

Xanthan gum (Kelzan XC) polymer powder (Kelco Oil Field Group, Houston, TX) was used to form shear thinning fluids. The powder was used as-received without further purification. Tap water was used to prepare polymer solutions. Waste vegetable oil (WVO), consisting of used cooking oil (General BioDiesel, Seattle, WA), was used as the substrate in characterization batch tests and in delivery experiments. Fresh vegetable oil (VO) was also used in batch tests to study the stability of oil droplets when mixed in xanthan solution. Accusand (grade 20/30) (Unimin Corporation, Le Sueur, MN) was the porous medium for the delivery experiments. Methylene chloride (CH_2Cl_2) (99.9%, Sigma-Aldrich Inc. Milwaukee, WI) was used to extract the oil from the column effluent samples and from sand samples for subsequent determination of oil concentrations.

WVO or VO at concentrations of 1.0, 1.5, 2.0, 3.0, and 6.0 wt.% were mixed into a 2500 mg/L xanthan gum solution to form oil-in-xanthan solution suspensions. Preliminary tests showed that when xanthan gum concentration was less than 2500 mg/L, oil suspensions were not stable. The 1.5 wt.% concentration WVO suspension was used in the column tests and the other suspensions were used in characterization and stability studies. A calibrated optical microscope system equipped for oil particle number counting and oil droplet size determination was used to determine the oil droplet size distribution in the suspensions. The rheological properties of the oil–xanthan mixtures were characterized using a Physica 101 rheometer (Anton Parr Inc. Ashland, VA) with a CC27-SS measuring unit. The stability studies and the oil droplet size measurements were conducted at room temperature.

Oil delivery experiments were conducted in a PVC column ($L = 143.5$ cm and $ID = 2.54$ cm). Pressure ports P1, P2, and P3 were used for transducers and were located at 0, 52.7, and 103.5 cm from the inlet end, respectively. The column was packed with 20/30 Accusand and saturated with deionized water before the injection of oil–xanthan mixture. A HPLC pump was used to provide a 1 mL/min (1.67×10^{-8} m^3/s) constant flow rate. A fraction collector was used to collect column effluent samples. After fluid injection, the column was disassembled and the sand, with retained oil, was sampled for determination of oil concentration. Two column tests were conducted; parameters for these tests are listed in Table 1.

2.1.2. Oil concentration determination

For effluent samples, 7 mL of oil–xanthan mixture was extracted 3 times, each with 5 mL of new CH_2Cl_2. In each extraction, the interaction time was 1 h when the extraction vial