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.

Key Words: subsurface delivery; vegetable oil; shear thinning fluid; bioremediation; amendment.

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 (Boulicault et al., 2000; AFCEE and NFESC, 2004; Scherr et al., 2009). Vegetable oils have been shown to induce effective dechlorination, to have limited geochemical impacts, and to exhibit good longevity (Hunter et al., 1997; AFCEE, 2007).

Because vegetable oils are NAPLs, distribution in the subsurface can be difficult (e.g. Zenker et al., 2000; Lee et al., 2001). 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 applied for improved delivery of the substrates (Hunter, 2005; Borden and Rodriguez, 2006; Borden, 2007a). Emulsified oil substrates have been tested in the laboratories and applied in the field for the remediation of dense NAPL (DNAPL) contaminants (Lee et al., 2007; Harkness and Fisher, 2013), dissolved chlorinated contaminants (Hunter, 2002; Borden, 2007b; Long and Borden, 2006), and heavy metals or radionuclides (Lindow, 2004; Gihring et al., 2011; Lookman et al., 2013; Tang et al., 2013). Emulsified oil has also been used for reactive particle delivery for subsurface remediation (Quinn et al., 2005; Berge and Ramsburg, 2009; Huff, 2011).

Injection of emulsified oil has achieved improved substrate distribution and demonstrated improved remediation performance compared to pure oil injection (Borden, 2007a; AFCEE and NFESC, 2004). However, in heterogeneous porous media systems, uniformly distributing emulsified oil is a challenge (ESTCP, 2006; Clayton and Borden, 2009). 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 and 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 (Zhong et al., 2008, 2011; Silva et al., 2013, Chokejaroenrat et al., 2013, Kananizadeh et al. 2015). STFs have been tested and applied as a means to deliver dissolved remedial amendments (Zhong et al., 2008, 2011, 2013; Smith et al., 2008; Chokejaroenrat et al., 2013, 2014, Truex et al., 2014; Kananizadeh et al. 2015) or reactive particles (Oostrom et al., 2007; Tiraferri, et al., 2008; Comba and Sethi, 2009; Dalla Vecchia et al., 2009; Truex et al., 2011a, 2011b) 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 for use as substrate 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, but 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 ($1.67 \times 10^{-8} \text{ m}^3/\text{s}$) 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.

Table 1: Summary of Column Tests

	Test-1	Test-2
Mass of Accusand packed	1352.6 g	1356.6 g
Pore volume (PV) of the Column	226.6 mL	222.5 mL
Porosity	0.31	0.31
Injection Volume	11.5 PV	21.1 PV

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 hour when the extraction vial was placed on a rotational mixer. The oil suspension- CH_2Cl_2 mixture was then centrifuged to separate the CH_2Cl_2 phase from the xanthan solution. The solvent was withdrawn using a syringe after each extraction. CH_2Cl_2 from the 3 extractions was combined and then vaporized completely inside a fume hood and the mass of oil in the vial was measured. The oil mass was used to calculate the oil concentration in the effluent.

For the sand samples, about 50 g of sand was extracted 3 times with 20 mL of CH_2Cl_2 . When separated from sand, the extractant was filtered through a $0.25 \mu\text{m}$ PTFE filter to remove fine sand particles. After the extraction, sand was dried in an oven to obtain the dry weight for

each sample. The saturation, the percentage of oil volume in total pore volume of porous medium, of retained oil in the column was calculated based on the oil mass and sand weight.

2.2. Numerical Modeling Approach

2.2.1 Flow Model

The flow of xanthan gum solution, a shear-thinning, non-Newtonian fluid, was simulated by coupling the Brinkman equation (Brinkman, 1949) (equation 1) with the continuity equation (equation 2):

$$\frac{\rho}{n} \frac{d\vec{u}}{dt} = \nabla \cdot \left[-P + \frac{\mu}{n} (\nabla \vec{u} + (\nabla \vec{u})^T) - \frac{2\mu}{3n} (\nabla \cdot \vec{u}) \right] - \frac{\mu}{k} \vec{u} \quad (1)$$

$$\nabla \cdot (\rho \vec{u}) = 0 \quad (2)$$

Where μ is the viscosity of the fluid [Pa.s], $\vec{u}$ is the velocity vector [m/s], P is the pressure [Pa], k is the permeability of the porous media [m²], and n is the porosity. The Brinkman model is a generalization of Darcy's law, accounting for the influence of an effective viscosity. This equation has previously been used to simulate non-Newtonian flow in porous media (Uscilowska, 2008; Chokejaroenrat et al., 2013, Kananizadeh et al. 2015).

Fluid viscosity was considered as a function of shear rate and xanthan gum concentration following a power law equation (Zhong et al., 2008):

$$\mu = \max \left\{ \mu_{\infty}, \min \left[a \left(\frac{c}{c_0} \right) \gamma^b, \mu_0 \right] \right\} \quad (3)$$

where μ_{∞} and μ_0 correspond to the viscosity at high and low shear rates respectively, a and b are power law constants, and γ is the shear rate. The shear rate was defined as (Zhong et al., 2008; Martel et al., 1998, Kananizadeh et al. 2014):

$$\gamma = \frac{2.37 u}{\sqrt{k n}} \quad (4)$$

Where u is the magnitude of velocity [m/s]. Previous work (Soo and Rake, 1984, 1986a, b; Coulibaly, 2003) has reported the porous medium permeability and porosity reduction due to oil emulsion attachment to soil particles. Following Soo et al. (1986a, b), permeability reduction was accounted as:

$$k_f = k_i - k_i * \beta * \frac{C_s}{n_0} \quad (5)$$

where k_f is the effective permeability, k_i is the initial soil permeability, C_s is the wt% of oil attached to dry sand, n_0 is the initial porosity, and β is the flow restriction parameter, which is the fitting parameter in this simulation. At each time step, the porosity was updated using k_f and the Kozeny-Carman equation (Zhang et al., 2009).

2.2.2 Transport Model

Transport of xanthan gum and vegetable oil droplets were simulated based on an advection-dispersion-reaction (ADR) equation:

$$\frac{\partial C_i}{\partial t} - R = -\frac{\vec{u}}{n} \cdot \nabla C_i + \nabla \cdot (D \nabla C_i) \quad (6)$$

where, D is dispersion coefficient [m^2/s], C is the concentration of the species [kg/m^3], i represents the simulated species (including vegetable oil droplets and xanthan gum) and R is the reaction rate [$\text{kg}/(\text{m}^3 \cdot \text{s})$]. Xanthan gum was treated as a non-reactive species. Deposition of oil droplets in the packed column was simulated by considering droplet attachment/detachment as well as straining processes (Bradford et al., 2002, 2003):

$$R = \frac{\rho_b}{n} \frac{\partial C_s}{\partial t} = k C_{oil} \Psi_{str} - k_d \frac{\rho_b}{n} C_s \quad (7)$$

Here, C_{oil} is the concentration of oil [kg/m^3], k is a rate reflecting combined attachment and straining processes [s^{-1}], Ψ_{str} is a dimensionless colloid straining function, and k_d is the detachment rate [s^{-1}]. The colloid straining function, Ψ_{str} , is described by equation 8, as a power law function of distance. In equation 8, α is a fitting parameter which controls the colloid spatial distribution shape, d_{50} is the mean diameter of the soil particle, and z is the distance from the inlet (Bradford et al., 2003).

$$\Psi_{str} = \left(\frac{d_{50} + z}{d_{50}} \right)^{-\alpha} \quad (8)$$

2.2.3 Model Implementation

The column was simulated in a cylindrical coordinate system using the finite element COMSOL Multiphysics software (version 4.3a, COMSOL Inc.). The Computational Fluid Dynamic (CFD) Module of COMSOL Multiphysics was used to solve the flow model, and the Subsurface Flow Module was applied to solve the transport model. For the flow model, a constant velocity boundary condition was applied at the column inlet, and an atmospheric pressure boundary was set at the outlet. For the transport model, a constant concentration condition was imposed at the column inlet, and the outlet boundary was considered as an outflow where advection is the most influential mechanism and all species were transported out of the domain. A structured mesh with 22,500 elements for the domain representing half of the column was defined to ensure the stability of the numerical model. The fully coupled numerical solver, which updates the Jacobian matrix at each iteration, was used to solve the numerical model.

Simulations were conducted to fit the experimental data, including pressure changes over time, oil droplet breakthrough curves, and retention profiles. The k_i and β variables were treated as fitting parameters for flow model, and k , k_d , and α were fitting parameters for the transport model. By adjusting k and k_d , Hydrus 1D (Simunek et al., 2008) was first used to fit oil droplet breakthrough curve and retention profile under a Newtonian flow condition. The results were used as an initial value to fit the coupled non-Newtonian flow and transport problem. Table 2 provides the parameters used in the COMSOL simulation.

Table 2. Parameters used in the simulation

Parameter /Property	Units	Value
Fluid Properties		
Flow rate	$\text{m}^3 \text{s}^{-1}$	1.67×10^{-8}
Density	kg m^{-3}	995
Polymer initial concentration	kg m^{-3}	2.5
Oil initial concentration (C_{oil})	kg m^{-3}	14.9
Soil properties		
Permeability* (k_i)	m^2	6×10^{-11}
Bulk density (ρ_b)	kg m^{-3}	1866
Flow restriction parameter* (β)	—	5
Porosity (n_0)	—	0.31
Dispersivity (α)	m	0.02
Mean diameter of the soil particle (d_{50})	mm	0.713
Oil droplet deposition constant		
Deposition rate* (k)	h^{-1}	4.675
Detachment rate* (k_d)	h^{-1}	0.0237
Straining parameter * (α)	—	0.3
Viscosity parameters		
<i>Xanthan (2.5 kg/m^3) + VO (14.9 kg/m^3)</i>		
A	cP	1050
B	—	-0.742
μ_o	cP	5770
μ_∞	cP	1.002

* denotes fitting parameters

3. Results and Discussion

3.1. Oil-in-Xanthan Suspension Characterization

3.1.1. Oil-Xanthan Mixture Stability and Oil Droplet Size

The stability of the oil-xanthan suspension is important with respect to the preparation and storage of injection solutions prior to injection. Rapid separation of oil and aqueous phases hinders delivery of the oil as colloidal droplets, thereby limiting distribution in the subsurface (Lee et al., 2001). The oil-in-xanthan mixtures were monitored for 100 hours, during which time no phase separation was observed (Figure 1). Stability of these suspensions over a 100 h timeframe is expected to provide sufficient time for mixture preparation and injection during field operations.

Figure 1. Phase behavior of 6 wt% VO and 6 wt% WVO mixed into a 2500 mg/L xanthan/water solution. No phase separation was observed over a 100-h observation period.

Figure 1 also showed that the constituents in the waste vegetable oil produced in the cooking processes did not affect the stability of the STF-stabilized oil suspension. Since the use of waste vegetable oil in lieu of virgin vegetable oil reduces the expense of the remedial

substrate, WVO was used in the oil droplet study, oil suspension rheological tests, and delivery column experiments.

Oil droplet size was measured as a function of time for the mixture of 6 wt% WVO in a 2500 mg/L xanthan solution (Figure 1) over a period of 168 h (Table 3). Oil droplet size was observed to remain reasonably stable over a 168 h period. The slight size increase between 72 h and 168 h is statistically insignificant. These data also suggest that the oil suspension is relatively stable over a time period sufficient for field operations of mixing and injecting the oil suspension into the subsurface.

Table 3: Droplet size as a function of aging time for 6 wt% WVO in a 2500 mg/L xanthan solution

Time of aging	Mean droplet size (μm)	Standard deviation (μm)
fresh suspension	4.69	5.29
72 hours	4.63	4.04
168 hours	5.30	4.68

The oil droplet size distribution was measured for 1, 2, and 3 wt% of WVO suspensions. The number of oil droplets peaked at a droplet size around 1.5 μm (Figure 2) for all three mixtures. It is feasible for droplets at this size to be able to flow through the pores of many types of porous media. The oil droplet size distribution in xanthan solution varies with oil concentration, with higher oil concentrations having a larger number of large droplets (Figure 2 inserted plot). Similar observations were reported by Lee et al. (2007) when corn oil was used to prepare micro-emulsions. The increase in oil phase content from 1 wt% to 3 wt% enhances the collision frequency between the oil droplets and therefore increases the rate of coalescence,

resulting in larger droplet sizes (Sun and Gunasekaran, 2009). Based on the oil droplet size distribution results, 1.5 wt% oil concentration was selected for column experiments.

Figure 2. WVO droplet size distribution in a 2500 mg/L xanthan solution for oil concentrations of 1.0 wt%, 2.0 wt%, and 3.0 wt%. The inserted plot is a close-up of the number of oil droplets with a size of 4 μm and larger.

3.1.2. Rheological Properties of Oil-in-Xanthan Suspensions

The shear thinning properties of the injection solution promote a more uniform distribution of the delivered amendment in heterogeneous subsurface environments (Martel et al. 1998; Zhong et al, 2008, 2011). The addition of 1.5 wt% WVO to a 2500 mg/L xanthan solution did not alter the viscosity or shear thinning behavior of the solution (Figure 3). Therefore this oil-in-xanthan suspension possesses characteristics to provide a more uniform distribution of the oil droplets in the subsurface, which is an obvious advantage over the delivery using surfactant-based oil emulsions.

The shear rate $\dot{\gamma}$ in of 1.5 wt% WVO in a 2500 mg/L xanthan solution during injection into a medium can be determined using equation 4 (Martel et al. 1998; Zhong et al, 2008). For

the 20/30 Accusand, $\alpha = 2.37$ (Zhong et al., 2008), $u = 3.29 \times 10^{-5}$ m/s, $k = 2.55 \times 10^{-10}$ m² (Schroth et al., 1996), and $n = 0.3$, and the calculated γ is 8.92 s^{-1} . From Figure 3, the viscosity at this shear rate is about 200 cP, which is higher than the viscosity of the pure WVO (Figure 3). However, for injection of this oil-xanthan mixture through a 10.2-cm (4-inch) diameter well having a 1.83-m (6-ft) screened interval, a typical injection rate of between 1.26-1.89 L/s (20-30 gal./min) results in a calculated shear rate (at the well screen) of between 311.5 and 467.2 s^{-1} . At this shear rate, the viscosity of the oil-xanthan solution would be less than 10 cP (extrapolating Figure 3 based on the fitted equation). This viscosity is less than most of the oil emulsions designed for substrate delivery in subsurface remediation activities (AFCEE, 2007). According to Darcy's Law, the injection pressure (at a fixed injection rate) is lower when the injected solution has a lower viscosity. Thus, the oil-in-xanthan mixture should facilitate substrate injection. Furthermore, the shear thinning property of the oil suspension should enable a more uniform distribution of the injection oil droplets in heterogeneous subsurface systems, based on observations from laboratory tests (Zhong et al., 2008, 2011) and field demonstrations (Truex et al., 2014).

Figure 3. Rheology analysis of 2500 mg/L xanthan solution both without oil and with a suspension of 1.5 wt% WVO. A power-law fit of the data (Equation 3) and the WVO rheology are also shown.

3.2. Oil Suspension Delivery in Porous Media Columns

3.2.1. Injection Pressure

Pressure data measured at the 3 ports in soil column Tests 1 and 2 (Table 1) are presented in Figure 4. The pressure plots for the two tests nearly overlap over the shorter duration of Test 1. The injection pressure rapidly increased to about 93.1 kPa, 65.5 kPa, and 44.8 kPa (13.5 psi, 9.5 psi, and 6.5 psi) for P1, P2, and P3, respectively, after injection of about 1.3 pore volumes (PV). After that, the pressures kept increasing but at much slower rates. From 1.3 PV to 11.5 PV injection (Test-1), the injection pressures increased by 24.1 kPa, 13.8 kPa, and 10.3 kPa (3.5 psi, 2.0 psi, and 1.5 psi) for P1, P2, and P3, respectively. From 1.3 PV to 21 PV (Test-2), the injection pressures increased by 41.4 kPa, 24.1 kPa, and 13.8 kPa (6.0 psi, 3.5 psi, and 2.0 psi)

for P1, P2, and P3, respectively. The initial rapid pressure increase is attributed to the viscosity of WVO-xanthan mixture under the injection shear conditions in the column. The subsequent moderate pressure increases are interpreted as being due to the increasing WVO saturation in the column over time as the WVO becomes entrained in the porous media. The difference in the slopes in P1, P2, and P3 would then be related to variation in the WVO distribution with distance from the column inlet.

Figure 4. Experimental and numerical simulated pressure in ports P1, P2, P3 versus injected PV for Test-1 and Test-2 column fluid delivery experiments. Pressure ports P1, P2, and P3 are located at 0, 52.7, and 103.5 cm from the column inlet end, respectively.

3.2.2. Oil Concentration in Column Effluent

Oil was initially observed in the column effluent from Test-2 at 0.7 PV injection (Figure 5) indicating some dispersion of oil in the column, similar to what would be expected for a

solute. The effluent oil concentration increased slowly over time and did not reach the full injected concentrations, indicating that a portion of the oil was retained in the porous media. At 11.5 PV of injection, the effluent oil concentration was 0.43 and 0.68 wt% in Test-1 and Test-2, respectively. In Test-2, the effluent WVO concentration continued to increase, reaching about 1 wt% (~66% of the injected concentration) at 21 PV of injection, with an increasing trend through the end of the test.

Figure 5. Effluent WVO concentrations in Test-1 and Test-2, with Test-2 simulation results. The injected suspension had 1.5 wt% oil content.

3.2.3. Oil Concentration in Sand

In Test-1 (11.5 PV injection), the WVO retained in the column was the highest at the injection end and decreased linearly to a distance of about 80 cm from the inlet, with insignificant amounts of retained WVO past that point (Figure 6). In Test-2 (21 PV injection), the WVO retained in the column was also highest at the injection end, but not higher than that in Test-1, despite a larger total quantity of oil having been injected into the column. In Test-2,

additional WVO accumulation occurred toward the effluent end of the column as compared to Test-1, implying that injection of a greater quantity of oil-xanthan mixture results in a more uniform distribution of retained oil in the porous medium.

The oil saturation in the pore space for both tests was calculated using the bulk density and porosity of the packed sand and is plotted in Figure 7. For Test-1, the oil saturation was 34.7% and 2.3% of the pore space at the inflow end and the effluent end, respectively. For Test-2, the oil saturation was 32.6% and 13.1% of the pore space at the inflow end and the effluent end, respectively. These results suggest that the oil retention occurred until reaching a maximum saturation (about 35%). With further oil injection, delivered oil is not accumulated at the inlet but is instead retained farther into the column. Thus, the oil saturation progressively increases towards a maximum saturation with distance from the inlet, as is illustrated in Figure 7. This behavior is consistent with the moderate pressure increases observed over the duration of the experiments and the profile of generally increasing oil concentration in the effluent during the test. Maximum oil saturation is likely a function of the porous media properties and injection conditions. If the retention behavior of micron-scale droplets observed in the column is up scaled to field-scale delivery, then (i) plugging of the pore space and large pressure increases during injection over time are less likely; and (ii) the oil retention and related mass of substrate available to induce and sustain biological reactions would be predictable for field applications based on tests to determine the oil saturation for the site-specific porous media.

The hypoexponential oil retention profile in the column of Test-1 (Figure 6) is a clear indication that the droplets are retained by straining. The modeling results (Section 3.3.2) also demonstrated that straining was the retention mechanism. However, the staining of oil droplets did not result in the plugging of the pore space, which would be the case if the colloids were

solid particles. The oil phase passed through the porous media when a maximum oil saturation was reached, as was observed in Test-2 (Figure 6). We speculate that when the retained oil reached the maximum saturation, the soft oil droplets arriving at the pore throats might be squeezed and pushed through the throats.

Figure 6. Oil concentration distribution in sand from Test-1 and Test-2 column experiments and corresponding simulations.

Figure 7. Oil saturation in sand pack pore space across the column. Delivery of more oil-xanthan solution in Test-2 resulted in a considerable increase in oil saturation for sediment closer to the effluent end, while remaining relatively stable near the influent end.

3.2.4. Mass Balance of Oil

The injected oil was trapped in the porous medium, carried out by the effluent, or stayed in the oil-xanthan mixture retained in the column pore spaces (Table 4). Total mass recovery was 98.5% and 96.8% for Test-1 and Test-2, respectively. With more oil-xanthan mixture injected, the percentage of injected oil retained in the porous medium was reduced (from 62.4% to 52.7%, i.e. more oil droplets were received in the effluent), suggesting a maximum oil saturation is reached in the porous medium. This oil retention behavior was also illustrated by the shape of the oil saturation curves in Figure 7, i.e. the saturation was increased in Test-2 in the column section towards the effluent end.

Table 4: Oil Recovery Results from Column Tests and Simulation

Properties	Test-1				Test-2			
	Mass (g)		% of injected		Mass (g)		% of injected	
	Experiment	Simulation	Experiment	Simulation	Experiment	Simulation	Experiment	Simulation
Total Injected	38.82	38.89	100	100	70.48	71.2	100	100
Adhered to Sand	24.22	25.55	62.4	65.69	37.14	38.14	52.7	53.56
In pore water at end of tests	3.40	1.54	8.8	3.95	3.34	1.76	4.7	2.47
In effluent	10.58	11.8	27.3	30.34	27.78	31.3	39.4	43.96
Total mass recovery	38.21	38.89	98.5	100	68.26	71.2	96.8	100

3.3. Numerical Simulation of Oil Delivery

3.3.1 Flow Model

The mathematical modeling results were compared with the experimental data. First, the power law equation (Equation 3) was able to reasonably fit the shear rate curve, as illustrated in Figure 3. The μ_{∞} parameter value was chosen as the viscosity of water. The values of μ_0 , a , and b are provided in Table 2. This equation was incorporated to simulate the non-Newtonian flow of vegetable oil and xanthan gum mixture.

Figure 4 provides a comparison of simulated and experimentally measured pressure change over time. The numerical model was able to capture a sharp increase of pressure from the beginning of the experiments to about 1.3 PV. The simulated and observed pressure values at the end of this sharp increase stage were consistent with each other at the port P1. In addition, the model was able to simulate the subsequent moderate pressure increase for port P1. Based on

our sensitivity analysis, the continuous although moderate increase in pressure over time can be attributed to the permeability and porosity reduction due to additional oil attachment. At the end of Test-1 and Test-2, the simulated effective permeability of the column (k_f) was about 0.3% of the original permeability at the location of port P1. According to equation 5, with more vegetable oil retained in the column (i.e. higher C_s), the effective permeability reduced, leading to an increase of pressure. Qualitatively and consistent with the observations, the slope of pressure increase was higher at locations closer to the column inlet (e.g., port P1), because more vegetable oil droplets were entrapped to the sand closer to the column inlet. However, the simulation underestimates the rate of pressure increase for ports P2 and P3. While the reasons for this discrepancy are not completely clear, we suspect that the spatially non-uniform distribution of oil may be a contributing factor. Corresponding to equation 5, the fitting parameter β is a function of the average pore size of the sediment, median pore diameter, median droplet diameter, standard deviation of the pore size distribution, and surface coverage parameter (Coulibaly, 2003). The fitting parameter β was set to a uniform value for the entire column, but it may be more appropriate to use spatially variable values to represent the variation of oil droplet deposition and the porosity along the column. Another contributing factor might be the solid particles that potentially existed in the waste oil, while they not considered in the modeling. These particles would be retained in the porous media, reduce the permeability, and increase the injection pressure.

3.3.2 Vegetable Oil Droplet Transport and Retention

Figures 5 and 6 illustrate the experimental and simulated results for oil breakthrough curves and retention profiles, respectively. The simulated breakthrough curves (Figure 5) for Tests 1 and 2 were identical during the first 12 PVs, because the only difference between the two

experiments was duration of the vegetable oil and xanthan gum mixture injection. The mathematical model was able to capture the initial sharp increase (occurring within the first 1 PV) and later moderate increase of oil droplet concentration in the effluent. For retention profiles (Figure 6), the mathematical model predicts a higher retention in Test-2 than in Test-1 along the column, which is consistent with the longer injection duration of Test-2. The model was able to capture the high attached concentration at the column inlet, which was followed by an initial sharp drop and then a slower decrease of the concentration in the later part of column. Our analysis suggested that the high attached phase concentration at the inlet was due to straining processes, which were considered to be dependent on the distance from the inlet. The average ratio of droplet diameter and the grain diameter in this study is in the range of 0.006-0.007, which is within the reported threshold (0.002-0.008) (Bradford et al., 2005; Xu et al., 2006) of straining for colloids with diameters of 0.5-5.1 μm . Finally, the simulated mass balance results matched very well with the experiment (Table 4), which further confirms the validity of model.

The fitted values for deposition rate k , detachment rate k_d , and straining parameter α were 4.675 h^{-1} , 0.0237 h^{-1} , and 0.3, respectively. Here, the small k_d value indicates that only a small amount of deposited oil droplets will detach from the sand, as demonstrated by a moderate increase of oil droplet concentration in the effluent (Figure 5). The fitted value of α is comparable but slightly smaller than the previously reported value for colloids (i.e., 0.43) (Bradford et al., 2003). Typically, the higher the straining parameter α , the sharper the decrease in the concentration of attached oil droplets (due to straining) at the inlet. The deposition rate k combined the effects of both droplet attachment and straining processes, which are very difficult to differentiate from each other.

To evaluate the relative contribution of attachment and straining, classical filtration theory (CFT) without considering straining (Nathalie Tufenkji, 2004) was applied to analyze the attachment of vegetable oil droplets in the column. According to the CFT, the rate of droplet attachment k_{att} can be expressed as (Harvey and Garabekian, 1991; Ryan and Elimelech, 1996):

$$k_{att} = \frac{3(1-n)u\alpha\eta_0}{2dn} \quad (9)$$

Here d [m] is diameter of the collector, which in this case is the mean diameter of the sand grain (d_{50}); α is the collision efficiency factor, representing the fraction of vegetable oil droplets that remain attached after collision; and η_0 is the single collector efficiency, representing the frequency of vegetable oil droplet collisions with the porous medium grain surfaces, which can be calculated using the correlation (Nathalie Tufenkji, 2004):

$$\eta_0 = 2.4A_s^{1/3}N_R^{-0.081}N_{Pe}^{-0.715}N_{vdw}^{0.052} + 0.55A_sN_R^{1.675}N_A^{0.125} + 0.22N_R^{-0.24}N_G^{1.11}N_{vdw}^{0.053} \quad (10)$$

where A_s is the Happel correction factor, N_R is the interception number, N_{Pe} is the Peclet number, N_{vdw} is the London-van der Waals attractive forces number, N_A is the attraction number, and N_G is the gravitational number. With a Hamaker number for oil droplets being 10^{-20} J (Coubibaly et al., 2006) and an average oil droplet diameter of $4.69 \mu\text{m}$ for fresh solution (Table 3), a η_0 was estimated as 0.005, with 25.64%, 74.35%, and 0% of the contribution being from diffusion, interception, and sedimentation processes, respectively. Because it is not clear what value is appropriate for α with this system, an α value of 1 was assumed, which gives the conservatively highest possible k_{att} of 2.81 h^{-1} . According to this estimation, the fitted k is 1.66 times greater than the highest possible k_{att} , further indicating the function of straining in addition to the filtration. Because CFT was derived under different systems as in this study (e.g. Newtonian

flow, rigid particles), quantitative CFT analysis should not be directly applied. However, this analysis qualitatively supports our previously stated hypothesis (and is consistent with the experimental observations) that oil droplets will accumulate in the porous space during the transport, which will lead to a reduction of permeability and porosity, and will therefore result in an increase in pressure.

To better understand and have a better control during application of this oil delivery approach, several aspects of the technology merit future study, including the mechanism of oil droplets stabilization by STF, temperature influence on oil suspension stability, and the impact of shearing on the size and stability of oil droplets.

4. Conclusions

Effective delivery of vegetable oil to the subsurface can facilitate bioremediation processes. The use of shear-thinning fluid is a potential approach for oil delivery. Batch tests were used to study the oil droplet size distribution, droplet stability, and rheological properties of waste vegetable oil (WVO) or fresh vegetable oil (VO) in shear-thinning xanthan solution mixtures. Column experiments were conducted to study the delivery of WVO droplets into porous media. Suspensions of micron-sized oil droplets with a mean oil droplet size of 1.5 μm were readily obtained with 1 to 3 wt% oil mixed into a 2500 mg/L xanthan solution. No phase separation was observed in these suspensions within 168 h and the oil droplet sizes remained relatively stable in this time period. This stability of the suspensions is expected to provide sufficient time for mixture preparation and injection in field applications. The oil suspensions demonstrated significant shear-thinning properties, facilitating injection and promoting a uniform distribution of the oil droplets in heterogeneous porous media. During delivery, the oil retention did not

exceed 35% saturation of the pore space at the column inlet and oil accumulation occurred further into the porous media in column tests with continued injection up to 21 pore volumes. Although the injection pressure increased moderately, the effluent oil concentration continued to rise with longer solution injection, reaching to about 66% of the injected concentration without raising a concern about porous media plugging. The oil-in-xanthan suspension properties and observed distribution of delivered oil in the soil column showed that delivery of oil using STFs is a promising approach for distributing WVO in aquifers as a long-duration bioremediation substrate. Potentially, the solution characteristics would lead to a relatively uniform oil distribution from the injection well and minimize issues associated with oil clogging of pore space near the well and associated high injection pressures.

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