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EVALUATION OF NON-IONIC SURFACTANTS WITH AND WITHOUT HYDROGEN
PEROXIDE FOR THE IN-SITU REMEDIATION OF NAPL CONTAMINANTS

by

Charles E. Holada

A Thesis submitted to the Graduate College
in partial fulfillment of the requirements
for the degree of Master of Science
Geosciences
Western Michigan University
April 2017

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Charles E. Holada, M.S.

Western Michigan University, 2017

Laboratory studies were conducted on Quillaja saponins and nine other surfactants commonly used to remove non-aqueous phase liquids (NAPLs) from soils and aquifers. The NAPL contaminant tested was diesel fuel. Static batch reactors containing an aged diesel-contaminated soil was treated with saponins and nine other commercially available surfactants to determine how much diesel fuel could be removed with the pore fluids after 1 day and 10 days of contact time. Of all the surfactants tested, saponins achieved the greatest removal of diesel fuel after 1 day and 10 days. There was large disparity in the diesel fuel removed by the other nine surfactants tested, which suggests a high degree of specificity controlled by the soil, rather than the NAPL itself. The amount of diesel fuel removed was much greater after 10 days than after 1 day, which demonstrates the importance of allowing contact time after introducing surfactants into a NAPL contaminated system, especially one with little or no mixing.

Column studies were then conducted with saponins as the only surfactants, with and without co-injection with hydrogen peroxide (H_2O_2). Because mixing has been shown to enhance contact between NAPL and surfactants, and therefore NAPL removal, H_2O_2 was tested as a co-injectate that could provide mixing in the pores of the columns because of its tendency to auto-decomposition to O_2 gas on soils. Columns were used to simulate a Push-Pull application of surfactants, which is increasingly being used for small NAPL contaminated sites (e.g., gasoline stations). The columns were charged with Ottawa sand (20-30 mesh) that had been artificially contaminated with diesel fuel and mixed every month over a year-long period. Two doses of saponins were injected (500 times and 1000 times the critical micelle concentration) alone and with a 5% H_2O_2 solution. When injected alone, the higher dose of saponins achieved greater NAPL removal than the lower dose. For both saponin doses tested, NAPL removal was significantly enhanced when co-injected with H_2O_2 . The greatest removal achieved was when a solution of saponins 1000 times the CMC was injected in a 5% hydrogen peroxide solution. The results suggest that injecting saponins with low concentrations of H_2O_2 has the potential to enhance surfactant-enhanced NAPL recovery in Push-Pull applications in the field.

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ACKNOWLEDGEMENTS

I would like to begin by thanking my advisor, Dr. Dan Cassidy for all the time he spent supporting, assisting and teaching me so much these past two years. Not only has he taught me so much, he has helped make me a better scientist, writer and person. I would not be here today if it not been for all his help.

I would also like to thank all of my family and friends, who were there for me whenever I needed them and kept me going through all of the hardships and difficulties of graduate school.

Charles E. Holada

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1.0 INTRODUCTION

1.1 Properties of Surfactants

Surfactants are ubiquitous in nature, are widely used in industry, and have applications and in many aspects of our daily lives. Surfactants lower the surface tension of water and can emulsify organic compounds that are normally quite insoluble in water. For this reason, surfactants are widely used as detergents, emulsifiers and foaming agents, and have applications in the cosmetics, pharmaceutical, and medical industries. Surfactants have also been used for decades in the petroleum industry for a variety of applications, including enhanced oil recovery and washing petroleum hydrocarbons from drilling cuttings.

Surfactants are comprised of two parts, or moieties; (1) a hydrophobic moiety that is soluble in non-aqueous phase liquids (NAPLs) but not in water, and (2) a hydrophilic moiety that is soluble in water but not in NAPLs. This molecular structure makes surfactants amphipathic. This dual nature of surfactants, having a part which is soluble in water and another part which is not, enables surfactants to behave in special ways at interfaces such as the liquid-air interface; the liquid-solid interface and the oil-water (liquid-liquid) interface. When added in sufficient quantities to a system with water and NAPLs, surfactants aggregate and configure their molecular structure to form a micelle (Figure 1). Normally spherical in shape, micelles are an ordered aggregation of surfactants with the hydrophobic moieties on the exterior and the hydrophobic moieties on the interior.

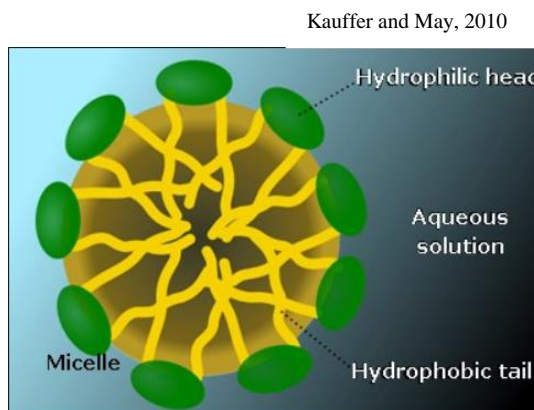


Figure 1 Diagram of a micelle

The hydrophobic interior of the micelle can dissolve NAPLs, and the hydrophilic exterior makes the entire structure soluble in water. This allows the micelle to act as a vehicle to make abundant in water of organic compounds that would otherwise be only sparingly soluble in the aqueous phase. The hydrophobic nature of a NAPL greatly reduces its aqueous solubility, which limits its

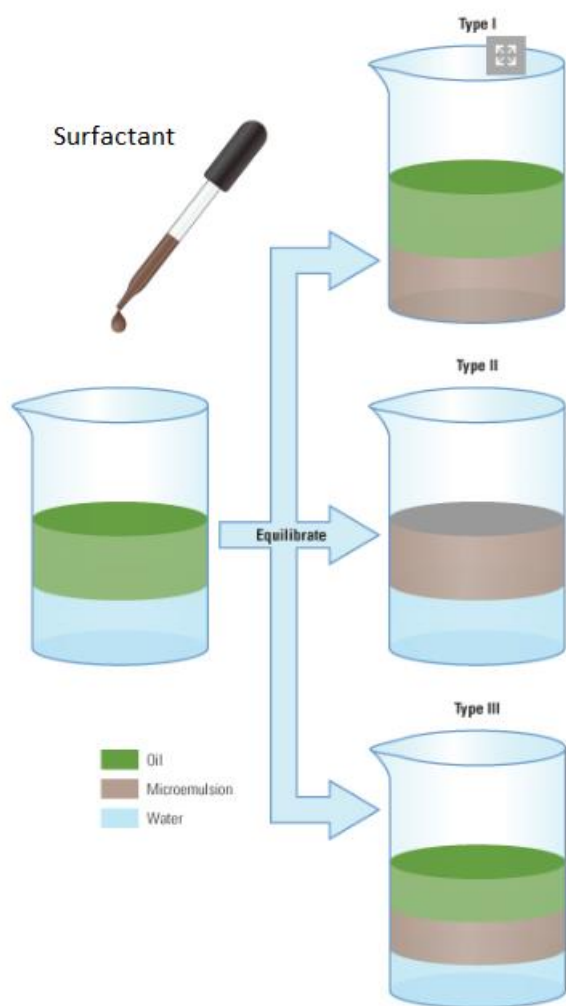


Figure 2 Winsor type Emulsion

Schlumberger

mobility in water. This in turn makes it very difficult to remove NAPLs using conventional pump and treat remediation systems (Fountain et al., 1996). However, adding surfactants emulsifies NAPL so it can be removed by pumping groundwater.

The addition of surfactant in a NAPL contaminated media enhances the apparent solubility of individual organic compounds. Once injected into the subsurface, in the presence of NAPL and water, the surfactants begin to form micelles, emulsifying the NAPL. Nanometer-sized micelles form at the interface between the immiscible liquid, the aqueous phase and the surfactant itself creating a microemulsion, which

can be divided into three different categories, or types. Figure 2 depicts the different categories of microemulsions which are found to be thermodynamically stable, depending on the relative amount of oil and water, and the degree to which the surfactant is hydrophobic vs. hydrophilic in nature (Castro Dantas et al., 2003). In a Winsor Type I microemulsion the surfactant is

preferentially soluble in water and oil-in-water (o/w) microemulsions form. The surfactant-rich water phase coexists with the oil phase where surfactant is only present as monomers at small concentration. In a Winsor Type II microemulsion the surfactant is mainly in the oil phase and water-in-oil (w/o) microemulsions form. In Winsor II systems, the surfactant-rich oil phase coexists with the surfactant-poor aqueous phase (Winsor II). A Winsor Type III, or middle-phase microemulsion is a three-phase system where a surfactant-rich middle-phase coexists with both excess water and oil surfactant-poor phases (Winsor III). Winsor Type III is the best model for the microemulsions generated when doing surfactant-enhanced aquifer remediation.

The effectiveness of a surfactant is evaluated based on its ability to lower the surface tension while using the minimum amount of surfactant to cause micelle formation (Mulligan, 2005). The point at which the concentration of a surfactant enables the formation of micelles is termed the critical micelle concentration (CMC) and this property is influenced by several factors including pH, temperature, ionic strength and salinity (Bera et al., 2013; Mulligan, 2005; and Zhou et al., 2011). Manipulating surfactants and exploiting their surface active behavioral properties has led to a multitude of possible applications that have relatively recently been shown to be promising alternatives in the environmental remediation industry.

Some of the earlier applications of surfactants in the environmental industry were at contaminated sites undergoing surfactant enhanced aquifer remediation (SEAR). The technical basis to support these applications was to increase the effectiveness of simple groundwater pump and treat systems and enhance the mobilization and recovery of residual NAPL. The addition of relatively inexpensive surfactants in SEAR would reduce the operating time of pump and treat systems and achieve regulatory cleanup goals. A main challenge faced with SEAR is meeting regulatory requirements to recover the volume of material injected into the subsurface, and

developing a complete conceptual site model that fully defines the hydrogeological system that controls the movement and chemical interactions of injected material in the subsurface.

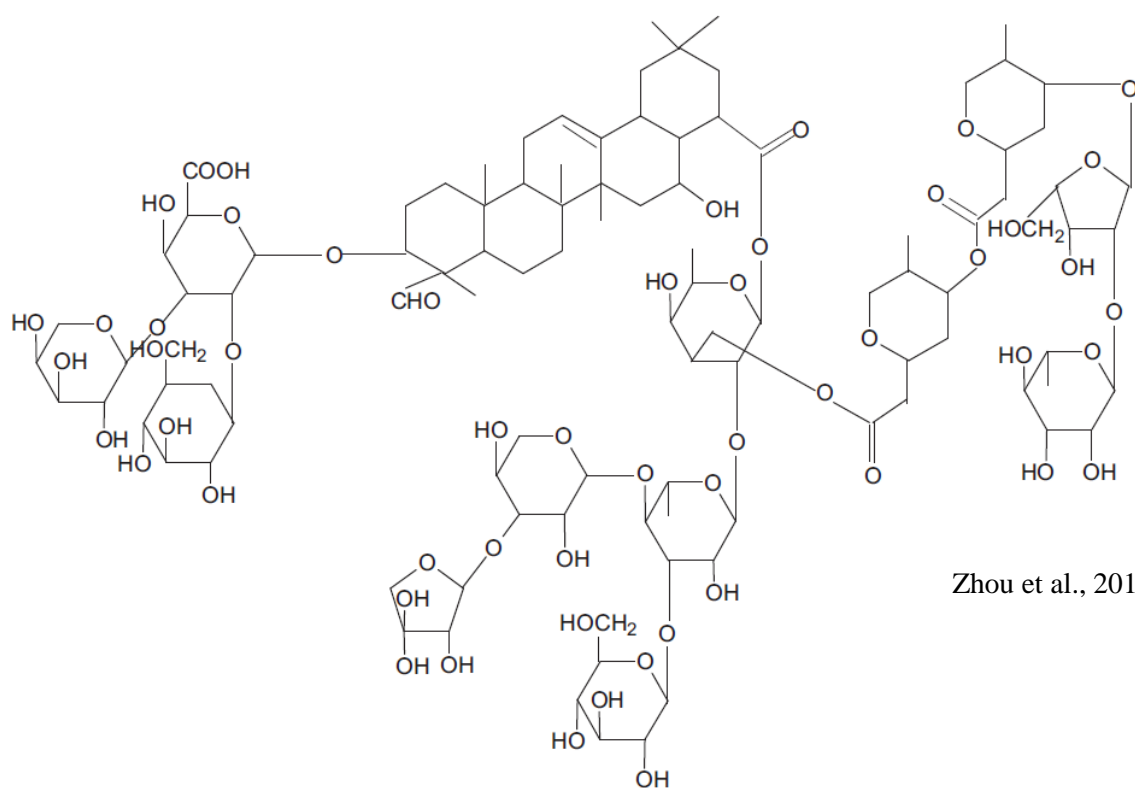
Surfactants can be synthesized from petroleum hydrocarbons, but also occur naturally in high concentrations in many plants, including alfalfa, soy beans and soapwort. Both petroleum-based and plant-based surfactant perform comparably, but plant-based surfactants are typically less toxic and more biodegradable. Petroleum-based surfactants can be engineered to mimic the properties of natural surfactants, but this approach is less sustainable than using plants, which are renewable resources. For these reasons, plant-based surfactants more desirable to practitioners.

Ahmadi et al. (2014) investigated the use of a natural surfactant derived from micro particles of the mulberry leaf on lowering the interfacial tension (IFT) in a mixture of distilled water and kerosene. Their research was able to determine that a mixture of just 1 wt% of the mulberry leaf derived surfactant could effectively lower the IFT of kerosene by 60%. Furthermore, they applied their findings to design an experiment using a core displacement apparatus to show that the naturally derived surfactant could increase the sweep efficiency of brine flooding in enhanced oil recovery (EOR) from 49% to 66.8% of the original oil in place. This research concluded that there may be more economical, naturally occurring surfactants available that could achieve the objectives of EOR while eliminating the use of industrial surfactants that may be less biodegradable and more toxic to the environment.

1.2 Saponins

A comparison of the effectiveness of plant-based surfactants versus synthetic surfactants on the removal of crude oil contamination from soils was conducted by Urum et al. (2005). In their research, they used rhamnolipid and saponins as their source for natural surfactants and SDS as the synthesized surfactant. Their research was accomplished by using GC/MS to measure the concentrations of hydrocarbons on soil washed with each surfactant compared to a control. The results of their research indicated that, although SDS showed a greater overall effectiveness at removing crude oil contamination from soil, comparatively, each surfactant performed differently at removing specific constituents found within the composition of crude oil. Urum et al. (2005) showed that SDS was best at removing the aliphatic constituents and that rhamnolipids and saponins were better at removing the aromatic hydrocarbons.

Saponins are a family of surfactants that, along with natural occurrence as plant-derived surfactants, have a unique molecular structure with the potential for remediating mixed contaminated sites. In general, co-contaminated sites pose more difficult challenges to environmental remediation practitioners. The base structure of saponins is categorized as a triterpene sapogenin, which is hydrophobe. Attached to this are various hydrophilic functional groups including acids, carbohydrates and other glycosides (Zhou et al., 2011). The molecular weight of saponin was determined by Mitra and Dungen (1997) to be approximately 1,650 g/mol. The configuration of the saponin molecule is unique because it doesn't take on the elongated chain-like configuration that is common in other surfactant compounds which has attributed to saponin's ability to act as an effective chelator for various heavy metals including



Zhou et al., 2011

Figure 3 Molecular Structure of Quillaja Saponin

cadmium, zinc, copper, lead and nickel (Hong et al. 2002, Song et al., 2008, Chen et al., 2008, Castro Dantas et al., 2003 and Lu et al., 2014).

Utilizing saponins from the Quillaja soapbark tree to wash soil contaminated with polycyclic aromatic hydrocarbons (PAHs) was evaluated by Zhou et al. (2011). Their findings showed that the effective properties of saponins (10% purity) are not immune to changes in environmental conditions, and that the CMC of saponins varied with changing pH as well as with increasing concentrations of electrolytes (Table 1). Overall, there was a decrease in the CMC of saponins as pH decreased and as the concentration of the NaCl electrolyte solution increased (Zhou et al., 2011). As with the CMC, changes in pH were also shown to affect the saponin's ability to enhance the solubilization of PAHs, specifically phenanthrene (Figure 4). Saponins were shown to be most effective at enhancing the solubilization of phenanthrene when its CMC was lowest, which occurs in conditions of low pH or in the presence of elevated concentrations of electrolytes (Zhou et al., 2011). Ultimately, Zhou et al. were able to show that saponins have a greater capacity at enhancing PAH solubility than other tested synthetic surfactants and biosurfactants. Their evaluations included calculating the molar solubility ratio (MSR), weight solubility ratio (WSR) and the micelle-water partition coefficient (K_m) of phenanthrene. Table 2 below presents the quantitative results of their evaluations in comparison with other synthetic surfactants and biosurfactants.

Table 1 Effect of pH and Electrolyte Concentrations on the CMC Values of Quillaja Saponin

Conditions		CMC ($\mu\text{mol/L}$)
pH	4.0	16.5
	5.0	28.1
	6.0	58.6
	7.0	85.3
	8.0	92.5
NaCl concentrations (M)	0.01	30.9
	0.05	24.2
	0.10	22.0
	0.50	10.1
	1.00	5.2

Zhou et al., 2011

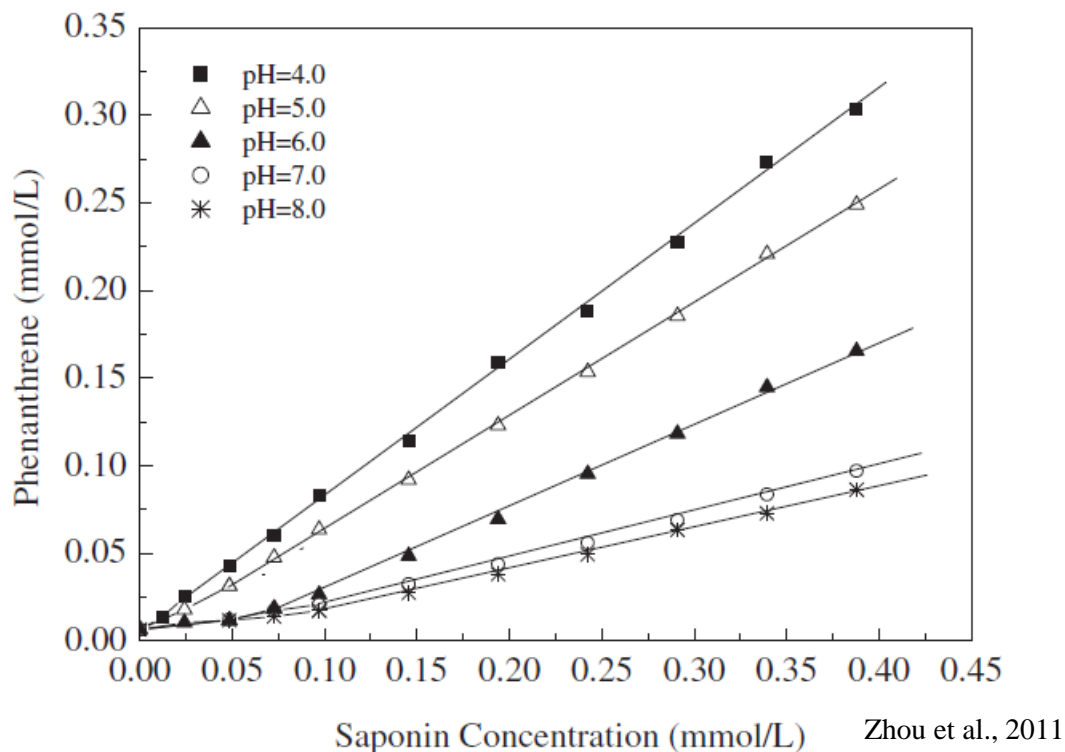


Figure 4 Changes in Phenanthrene Solubilization at Different pH

Table 2 Comparison of Saponin Solubilization for Phenanthrene With Other Surfactants

Surfactants	MW	MSR	WSR	LgK _m	Ref.
Saponin	1650	0.606	0.0655	6.50	This study
Rhamnolipid	—	0.0425	—	—	Shin et al., 2004
Monorhamnolipid	504	0.057	0.02	—	Zhang et al., 1997
Dirhamnolipid	650	0.021	0.006	—	Zhang et al., 1997
Brij-58	1124	0.199	0.0316	6.12	This study
		0.18	0.0285	6.2	Prak and Pritchard, 2002
Brij-35	1198	0.13	0.0193	6.1	Prak and Pritchard, 2002
Tween-80	1310	0.265	0.0361	6.22	This study
		0.19	0.0258	6.2	Prak and Pritchard, 2002
Tween-20	1228	0.14	0.0203	6.1	Prak and Pritchard, 2002
TX-100	625	0.141	0.0402	5.99	This study
		0.111	0.0316	5.70	Edwards et al., 1991
Igepal CA-720	735	0.104	0.0252	5.68	Edwards et al., 1991
Tergitol NP-10	683	0.160	0.0417	5.72	Edwards et al., 1991

Zhou et al., 2011

Similarly, PAH impacted soil washed with Quillaja saponins was also evaluated by Kobayashi et al., 2012. While they obtained similar results as Zhou et al. (2011) with respect to solubilization enhancement of certain PAHs, their research evaluated the tendency for saponins to adsorb onto soil particles of artificially spiked soils having different organic content profiles. Two different soils were tested and the influence of organic content was represented on a sorption isotherm plot showing the sorbed amount of saponins at increasing concentrations in each respective soil (Figure 5). They concluded that, although saponins were effective at enhancing the solubilization of PAHs, their effectiveness can be limited by a high content of native organic material (NOM). However, this is true for any and all surfactants.

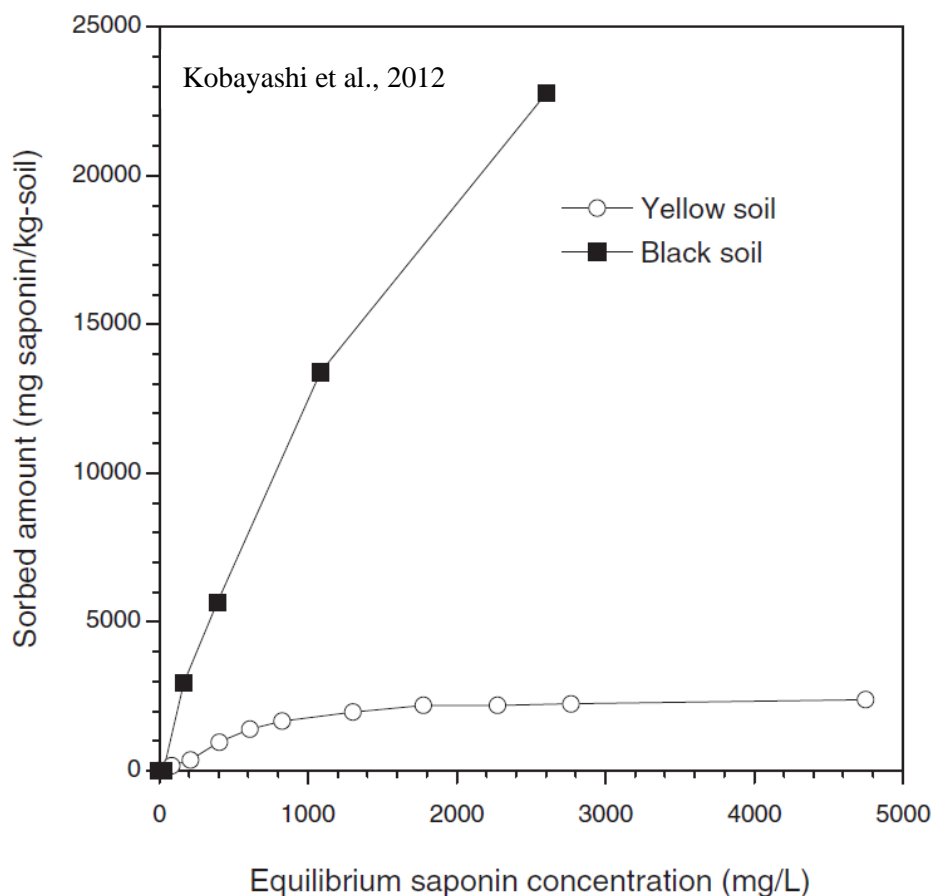
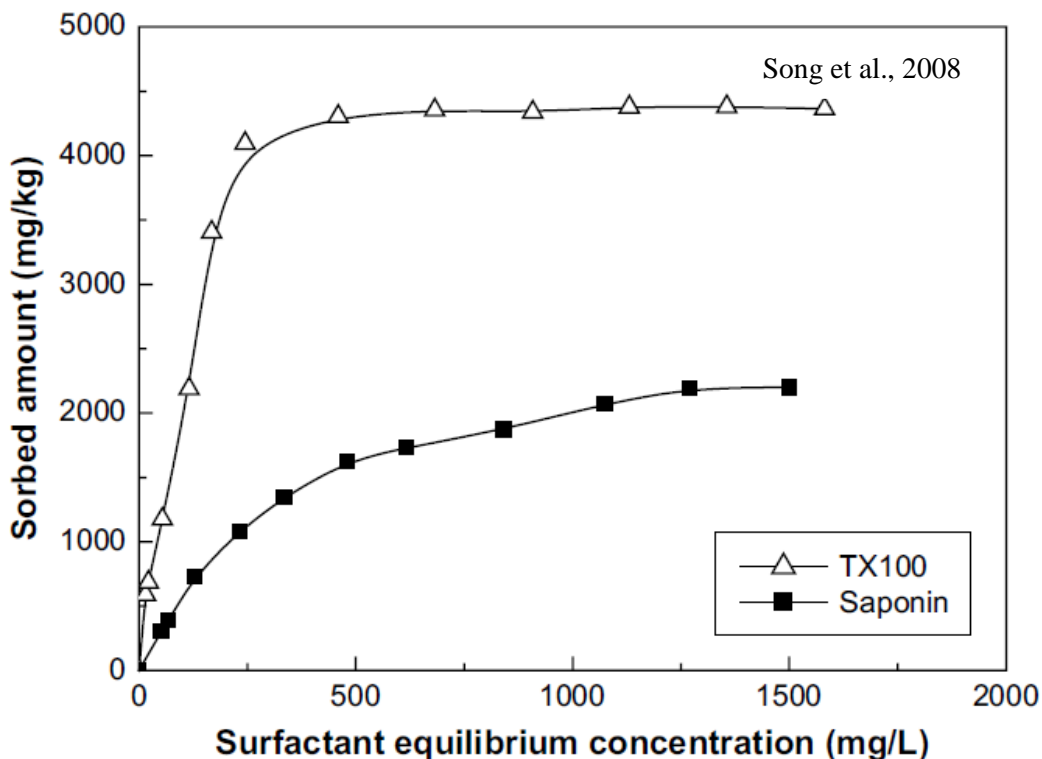


Figure 5 Sorption Isotherms for Saponin on Soil with Different Organic Content

Song et al. (2008) further demonstrated the soil washing capabilities of saponins in a mixed contaminant scenario. Their research showed that saponins effectively increased the desorption of phenanthrene from soil, which was also shown to perform better than a comparable synthetic surfactant, Triton X100 (Figure 6). Although Triton X100 showed success at partitioning phenanthrene into its micelle, there was an increase in the potential for the surfactant to adsorb onto solid soil particles as the concentration of the surfactant increased. This, in turn, caused the phenanthrene to persist in the soil as well. In contrast, saponins were shown to have an increase in phenanthrene partitioning with increasing surfactant concentration without the increase in adsorption onto the soil particles. The structure of the saponin enriched micelle further allowed cadmium present in the soil to chelate with the polar carboxyl group located on the exterior of the micelle. Essentially, Song et al. (2008) were able to show that saponins may be

Figure 6 Sorption Isotherms of Saponin and TX 100 on a Soil



effective for the remediation of mixed contaminant sites. Mixed contaminant sites pose their own challenges because while one remedial technique might work to clean up one contaminant at a site, the technique may not have an impact on other contaminants present at the site which may exacerbate the impacts of other contaminants present on the site.

Lu et al. (2014) demonstrated the effectiveness of soil washing methods using natural saponins derived from tea seed (tea saponin). Their research showed that tea saponin was effective at removing cadmium from artificially contaminated soil samples spiked with cadmium nitrate, at an efficiency ranging from 64.6% to 74.5%. Higher desorption rates were achieved nearly two-fold by adding NaNO_3 as a background electrolyte (Figure 7). This was attributed to the cation exchange taking place between the Na^+ and Cd^{2+} ions whereby the Na^+ showed greater affinity to replace the Cd^{2+} ions on the particle surfaces. Desorption of cadmium was shown to occur relatively quickly, reaching equilibrium within 20 minutes of reaction time.

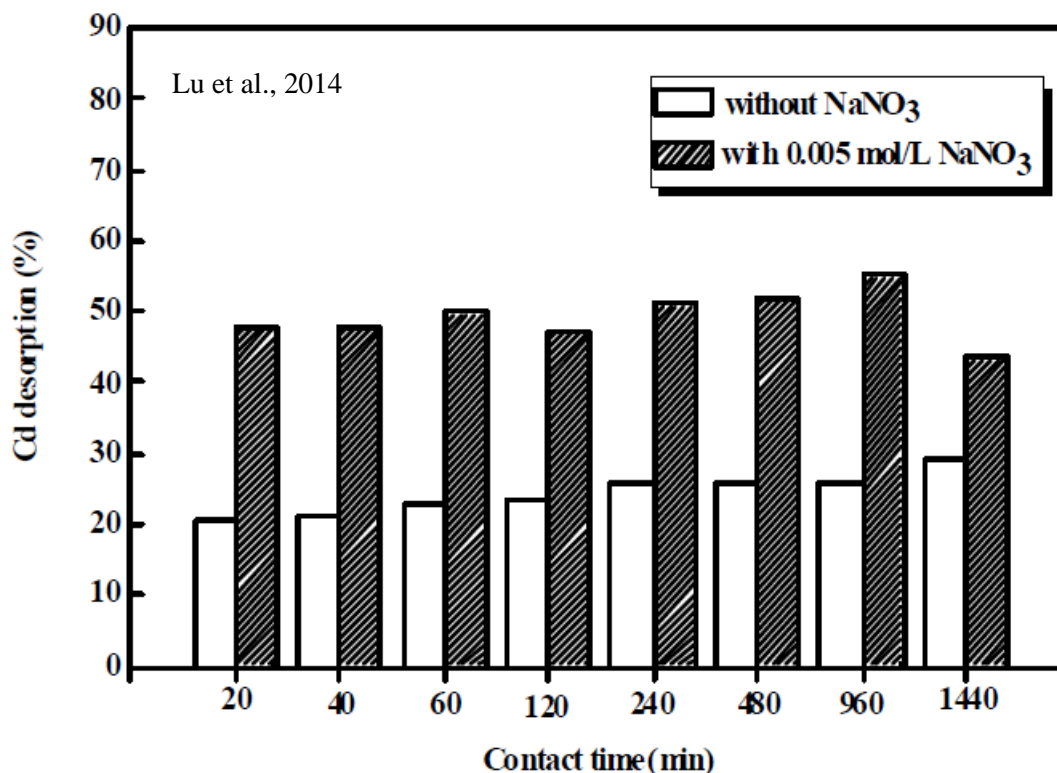


Figure 7 Effects of Electrolytes on the Desorption of Cadmium with Saponin

This reaction time was quicker than desorption studies performed by Chen et al. (2008). In their research, they used saponin derived from the bark of the quillaja tree to treat kaolin clay soils artificially contaminated with cadmium, copper and lead. Chen et al. (2008) presented a comparison of metal desorption efficiencies using quillaja bark saponin and SDS with an ethylenediaminetetraacetic acid (EDTA) chelate. Their research showed that saponin effectively competes with the kaolin clay for metal complexation based on Lewis Acid-Base interaction induced by pH, structure size or charge of surfactant solution. Several important characteristics of saponins were determined by Chen et al. (2008) including the effects of pH on the CMC of aqueous saponin alone and with saponin complexed with copper and nickel. They found that the CMC of saponin at a near-neutral pH of 6.5 s.u. remained unchanged when chelated with heavy metals and that micelles were more difficult to generate at a higher alkaline pH of 10 s.u. The effectiveness of removing heavy metals from a kaolin soil system using saponins was shown to

be a viable alternative when compared to EDTA or SDS. Although greater removal was observed using EDTA, the results using saponins were comparable and performed much better than SDS.

Through the development of surfactant technology, researchers have found that the applications for surfactants in site remediation can vary depending on what type of surfactant is used as well as in the methods of implementation. The typical application of surfactants in environmental remediation has been to inject the aqueous surfactant into the subsurface. Promising alternative applications of surfactants that have been successful in remediating contaminated sites include soil washing, enhanced bioremediation, enhanced *in situ* chemical oxidation, enhanced pump and treat and activation of *in situ* chemical oxidants. Moreover, surfactants such as saponins have been shown to be successful at remediating sites with mixed contaminants (i.e., metals and organics).

Laboratory studies were recently done in the Department of Geosciences at Western Michigan University on the potential for saponins to be used in soil washing applications (Beach, 2016). These studies focused on PAH-contaminated soils from manufactured gas plants, and demonstrated that saponins were quite effective at washing soils in mixed and static reactors to remove PAH-NAPL. The work described in this thesis builds on the findings of Beach (2016), but focuses on soils contaminated with diesel fuel. Specifically, this study compared the soil-washing ability of saponins with nine other surfactants in static batch reactors, and conducted column studies on diesel-contaminated soil to investigate the ability of saponins to be used in push-pull applications in the field.

1.3 Push-Pull Technology

“Push-Pull” refers to the use of the same well(s) for injection and extraction of groundwater, in contrast to the traditional application of using dedicated injection wells and extraction wells to create a “sweeping zone”. Push-Pull applications can be used for pump tests, tracer studies, and for injecting amendments to promote remediation (Istok et al. 1997). A U.S. Department of Energy study conducted research to develop a modified push-pull and demonstrate its utility for performing site characterization and surfactant enhanced recovery. In their investigation, intermediate-scale laboratory experiments were conducted using the push-pull remediation technique and TCE contaminated soils from an existing site. Along with the lab studies, pilot-scale field experiments were conducted at non-contaminated portions of the field sites solely for the purpose of demonstrating the utility of these push-pull tests at the field scale. The surfactant used in their experiments was hexadecyl diphenyl oxide disulfonate (DOWFAX).

After 9 liters of the surfactant solution were injected, 30 minutes passed and then the system was pumped for 24 hours at a rate of 15 ml/min. The results of the DOWFAX in the push-pull remediation shows an increase in TCE solubilization from 0.6 g/L to 3.2 g/L and three times greater TCE recovery while using DOWFAX compared to experiments in which DOWFAX was not used. The Department of Energy determined, after their experiments, that single-well push-pull tests are a useful method for both obtaining site-specific information on the behavior of injected surfactants as well as pilot-scale field experiments. The DOE recommends more information be conducted before push-pull surfactant enhanced aquifer remediation is taken to full scale, entire site cleanup

Fountain et al. (1996) demonstrated the practice of creating microemulsions in a field scale study to enhance the effectiveness of a pump and treat system designed for the remediation of a dense non-aqueous phase liquid (DNAPL) plume at a Canadian military base. Their research modified a pump and treat system with the addition of ethoxylated surfactants to increase the solubility and mobilization of the DNAPL constituents, specifically tetrachloroethylene (PCE). They designed column experiments using soil from the site to evaluate the effectiveness of lowering the interfacial tension (IFT) of PCE using nonylphenol ethoxylate and a phosphate nonylphenol ethoxylate. One interesting discovery made from the column experiments was that the mixture of the two surfactants was more efficient at emulsifying the DNAPL than using nonylphenol ethoxylate alone. This was attributed to the formation of more viscous emulsions by nonylphenol ethoxylate.

Pennell et al. (1993) assesses the potential utility of *in-situ* surfactant enhanced flushing as an aquifer remediation strategy. To test their experiments, soil columns were set up using Ottawa sand artificially contaminated with dodecane. Polyoxyethylene (20) sorbitan monooleate (POE) was the surfactant used in a concentration of 43.2

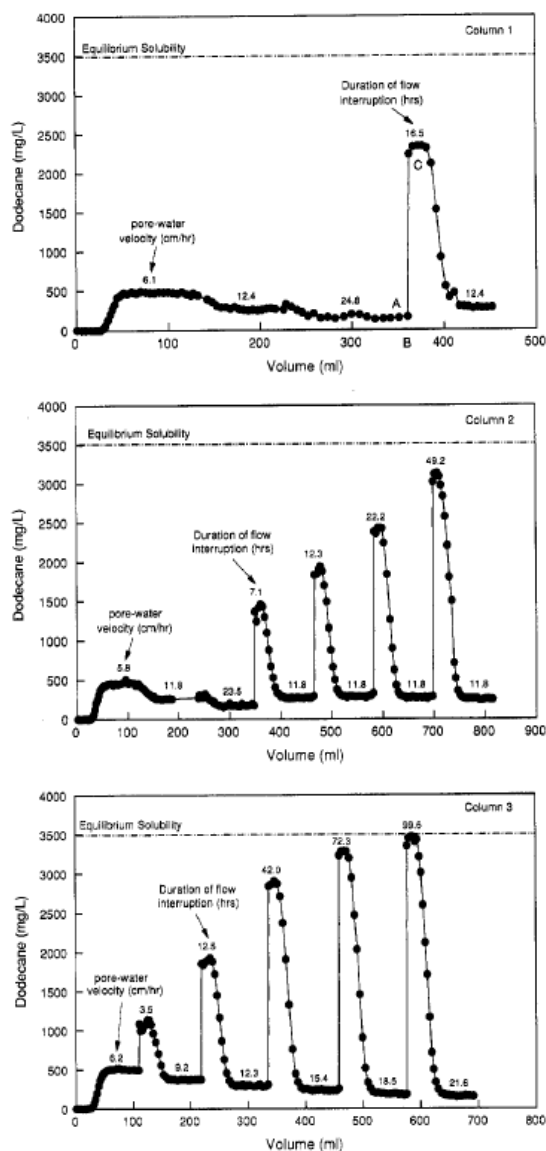


Figure 8 Measured Effluent Concentrations of Dodecane after Flushing

Pennell et al., 1993

g/L (approximately 3300X CMC). Their designed soil columns housed the contaminated Ottawa sand. Then the POE solution was pumped up through the column and the concentration of dodecane in the effluent was measured. The pore water velocities ranged from 6 to 25 cm/hr, and resting periods between injecting POE and measuring the effluent ranged from 3.5-100 hours.

The results of their column experiments are seen in Figure 8, above. The solubilization of dodecane in the column experiments was rate-limited. As we can see in the figure above, the dodecane concentrations in the effluent increased following periods of flow interruptions (resting periods). A reduction in steady state effluent concentrations of dodecane was also observed as the pore water velocity was increased.

1.4 Research Objectives

This research continues and builds on previous research on saponins for NAPL removal from soils done by Beach (2016). In this study, saponins were tested for their ability to remove aged diesel fuel from a contaminated soil in Georgia in static batch reactors, like those used by Beach (2016). In addition to saponins, nine other commercially available surfactants were also tested. Because Beach (2016) showed that emulsion and removal of PAHs increased dramatically over the first 10 days of contact with saponins, these static batch reactors were sampled on day 1 and day 10 to determine what effect this contact or “resting” period would have on diesel fuel removal with the ten surfactants tested. The primary goal of this research was to develop and inform the *in situ* surfactant-enhanced NAPL removal using the Push-Pull application, which uses the same well(s) for injection of surfactants into the subsurface (Push) and extraction of emulsified and otherwise mobilized NAPL with groundwater (Pull). Laboratory column reactors packed with Ottawa sand artificially contaminated for one year with diesel fuel were used to simulate in the laboratory a Push-Pull application in the field. In addition to injecting two different doses of saponins into the column reactors, co-injection of saponins with hydrogen peroxide was also investigated. Hydrogen peroxide auto-decomposes to form molecular oxygen, and the resulting bubbles have the potential to enhance mixing in the pores. The recovery of diesel fuel after injecting a solution of saponins alone, and after injecting a solution of saponins with 5% hydrogen peroxide was compared, to evaluate the potential of this approach to improve surfactant-enhanced NAPL recovery.

2.0 MATERIALS AND METHODS

2.1 Batch Studies

These studies were done to determine the effectiveness of ten different surfactants for potential soil washing applications. The surfactants were tested for their ability to remove total petroleum hydrocarbons (TPH) from a soil contaminated primarily with Diesel fuel from Georgia in both emulsified form and in non-aqueous phase liquid (NAPL) form.

2.1.1 Test Soil

The test soil (Figure 9) was from Diesel fuel depot in Macon, Georgia, and was contaminated mostly with Diesel fuel. The depot was closed and all the tanks removed in 1995, which means that the hydrocarbons spilled into the soil had at least two decades of aging in place.

The contaminated soil was first homogenized thoroughly by hand in the lab. Table 3 lists selected properties measured in the homogenized Diesel-contaminated soil. Characterization of the homogenized soil was done according to methods of soil analysis (Klute, 1994). A sample of uncontaminated soil from the same site was used to measure the native organic material (NOM) content. The course-grained and fine-grained fractions



Figure 9 Diesel Contaminated Soil used in Batch Studies

were separated using an ASTM standard 230 sieve, having apertures 0.065 mm in diameter, which is the cutoff particle diameter between silt and sand. The homogenized soil had an

average TPH concentration of 47,100 mg/kg (47.1 g/kg), which is considered the “baseline” or untreated TPH concentration, and is used to calculate percent TPH removal in the results. TPH concentrations were measured using EPA Method 8015.

Table 3 Properties of the diesel fuel-contaminated soil used in the batch studies

Analyte	Result with units
Course-Grained Fraction	74%
Fine-Grained Fraction	26%
Native Organic Material (NOM)	0.1%
Total Carbonates	0.4%
pH	6.9
TPH Concentration	47.1 g/kg

2.1.2 Static Batch Reactors

Static reaction vessels (600 mL beakers) were set up with 500 mL of contaminated soil, and the pores were filled with water (Control) or a surfactant solution. There was little or no standing water in the vessels. The total pore volume in each vessel was estimated to be approximately 0.2 L, based on a total volume of 0.5 L and assuming a porosity of 0.4. Based on the soil having a gravimetric water content of 10% (Table 3), each vessel contained approximately 50 mL of retained water, and received 150 mL of water or surfactant solution. The pore spaces were filled by pouring 150 mL of a solution of the respective surfactant at a concentration of 20 g surfactant/L solution into the vessels containing the contaminated soil. Tap water was used because groundwater from the site was not available. Control vessels were also set up with tap water only, and no added surfactant. Duplicate vessels were set up for each

reaction/surfactant scenario; one was sampled after 1 day and the second was sampled after 10 days. When the reaction vessels were sampled, the pore waters and any NAPL that had been mobilized/washed were separated from the soil by pouring the liquid from the vessels. The soil, with any retained pore fluid not removed via pouring was sampled and analyzed for TPH concentrations. The bulk liquid removed from each vessel was analyzed for TPH to quantify the total amount of Diesel fuel removed in both emulsified form, NAPL form, and dissolved (aqueous) form. The bulk liquid removed from the vessels was first extracted using methylene chloride, and the extract was then injected into the GC/MS to quantify TPH according to EPA method 8015. Before the bulk liquid was extracted to quantify TPH, the interfacial or surface tension was measured using the surface tensiometer (Figure 10).

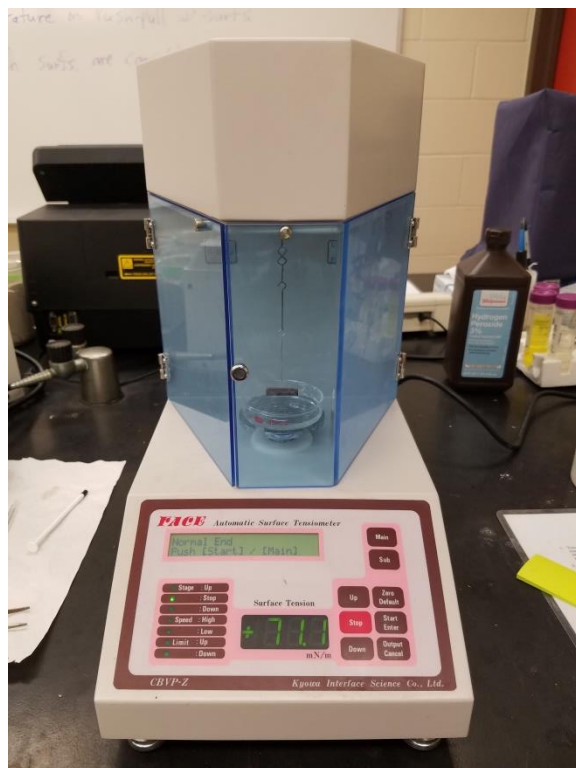


Figure 10 Surface Tensiometer

The ten surfactants tested are listed in Table 4, including trade names (if applicable) and chemical names. The surfactants were obtained directly from the manufacturer or vendor, or were purchased from Sigma Aldrich. Duplicate reaction vessels were set up for 11 different reaction scenarios, one Control (with nothing added) and ten surfactants added at a 2% concentration. A picture of one set of the 11 reactors is shown in Figure 11.

Table 4 List of the ten surfactants tested in batch studies

Surfactant Name	Description
TOXIMUL 8320	Butyl Polyalkylene Oxide block copolymer (100%).
AMMONYX LO	Lauramine Oxide (30%)
NACCONOL 90G	Sodium Dodecylbenzene Sulfonate (91.6%)
BIO-TERGE PAS-8S	Sodium Octane Sulfonate (37.8%)
STEPANATE SXS	Sodium Xylene Sulfonate (40%)
BIOSOLVE	Water Based, Biodegradable, Wetting Agents & Surfactants
PETROSOLVE	Isotridecanol, ethoxylated (20-50%), Fatty Acid Methyl Ester Ethoxylate (20-50%), Rhamnolipids (20-50%)
Rhamnolipids	A blend of $C_{26}H_{48}O_9$ and $C_{32}H_{58}O_{13}$, supplied by Jeneil Biosurfactants Company, USA
Saponin	Triterpene glycoside obtained from Quillaja bark and b-D-glucuronic acid with carboxyl group of sugar moiety
Polysorbate 80	Polyoxyethylene (20) sorbitan monooleate

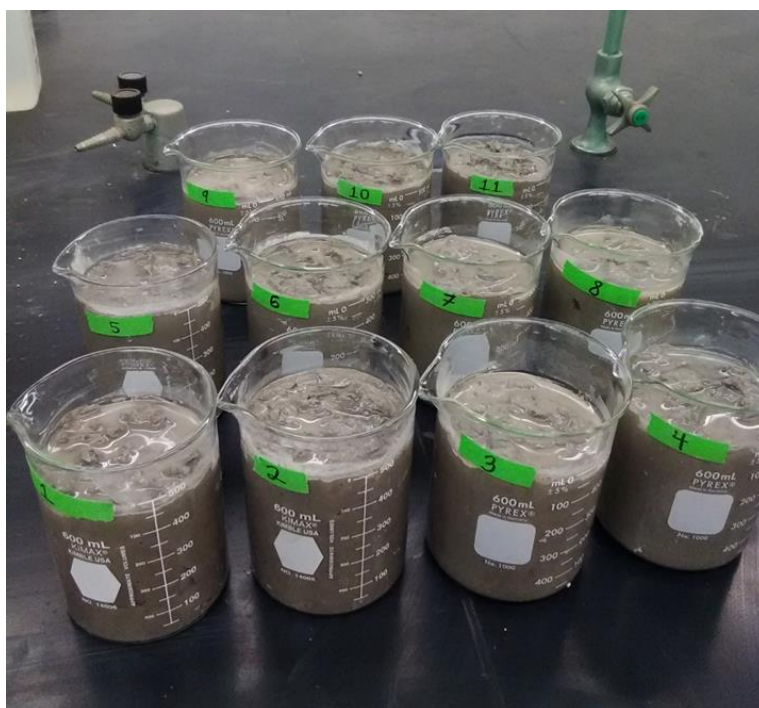


Figure 11 Eleven Batch Reactors - Ten Surfactants and One Control

2.2 Column Studies

These studies were done to determine the effectiveness of co-injecting low concentration (5%) hydrogen peroxide with lab grade saponins. The saponins and hydrogen peroxide were tested for their ability to remove total petroleum hydrocarbons (TPH) from Ottawa sand artificially contaminated with diesel fuel.

2.2.1 Soil Columns

The columns were PVC, 2-inches inner diameter x 2-feet length (Figure 12). The total volume of a cylinder with these dimensions is approximately 1.25 L. The caps on the top and bottom extended the volume to approximately 1.33 L, which was confirmed by repeatedly filling the all the columns with water and transferring to graduated cylinders to measure the exact volume.

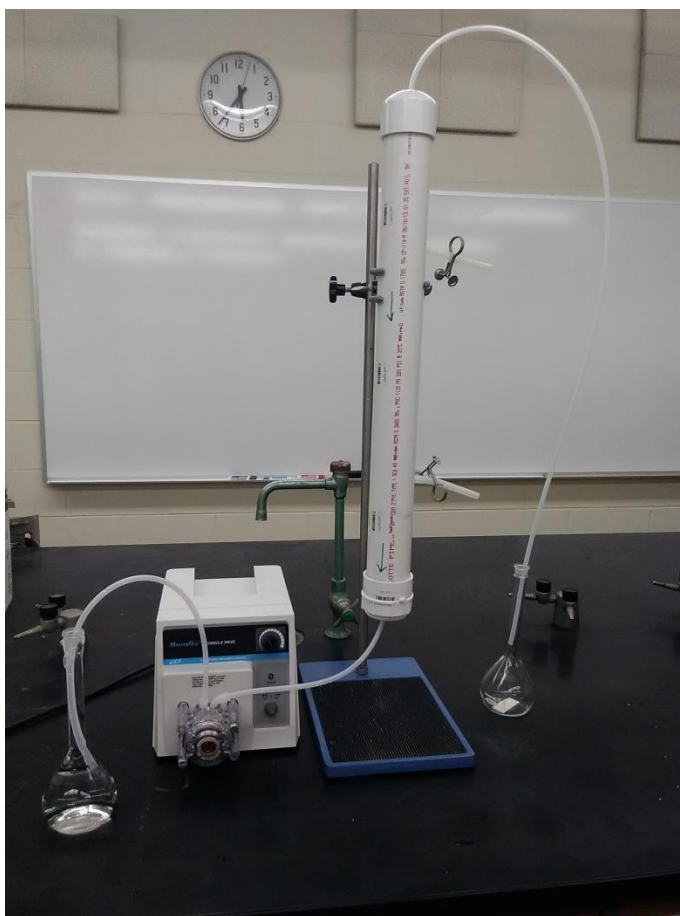


Figure 12 Soil Column Reactor Setup

2.2.2 Test Soil

Ottawa sand (20-30 mesh coarse sand) was artificially contaminated with diesel fuel purchased from the Shell gas station on the corner of Westnedge and Michigan avenues in Kalamazoo, MI. Aliquots of 2 kg of Ottawa sand were contaminated with 100 g of diesel fuel, and then allowed to cure for one year in closed, glass jars kept in a refrigerator (3°C) to prevent any biodegradation of the diesel fuel. The jars were shaken for 5 minutes every month, to provide mixing.

The volume of a 2-kg aliquot of Ottawa sand is 1.21 L, based on the well-established bulk dry density of Ottawa sand of 1.65 kg/L (Ojuri and Fijabia, 2012). The density of diesel fuel is 0.83 kg/L, which means that the 100-g aliquot of diesel fuel in each soil column occupied a volume of 0.12 L, taking up the entire volume of each soil column of 1.33 L. Using the porosity of well packed Ottawa sand of 0.38 (Ojuri and Fijabia, 2012), the total initial pore volume in each column packed with the diesel-contaminated Ottawa Sand was approximately 0.5 L.

2.2.3 Column Study Reactors

Each aliquot of diesel-contaminated Ottawa sand was then packed into one of the PVC columns described above, ensuring that each column received the same amount of both diesel Fuel and Sand. Nylon mesh was obtained from Industrial Netting with a 60-mesh size, having apertures 0.250 mm in diameter which is smaller than the smallest grain size in the 20-30 mesh Ottawa Sand (0.595mm). Three layers of Nylon mesh were placed at the bottom of the columns

in order to ensure that no sand particles entered the opening used to pump water with surfactants through the columns.

Before starting the column experiments, peristaltic pumps were calibrated to pump 1.0 L of fluid/day, to achieve one pore volume (PV) replacement every 12 hours (0.5 days), or two PV replacements per day. Tap water was used in the Control column, and to prepared the solutions of saponins and/or hydrogen peroxide. The only concentration of hydrogen peroxide used was 5%. Two concentrations of saponins were used; 500 times the CMC and 1000 times the CMC. The solutions were pumped into the columns from bottom to top (Figure 13). The columns were saturated from bottom to top to force out any air present in the pores, thus ensuring that all the pores in each column were saturated. The bottom-to-top saturation step was intended to be analogous to the “push” or injection phase of a push-pull application in the field. While the columns was being charged with fluid to saturate the pores, no fluids were



Figure 13 Soil Column Reactors

removed from the top of the columns. After the columns received 0.5 L of the respective fluid, the pumps were turned off and the columns sat for 7-days. A resting time of 7 days was used to ensure that sufficient time was allowed for emulsion to take place. The batch studies described in this thesis, and similar results obtained by Beach (2016) indicate that the rate of NAPL emulsion in poorly mixed systems increases linearly for approximately 5 to 10 days before the rates decreases. This was the reason for choosing a 7-day resting period in the column studies.

After this 7-day resting period, the pumps were turned on at a flow rate of 1.0 L/day, with flow from top to bottom. The flow was reversed to simulate the “pull” or extraction phase of a push-pull application in the field. During the pull phase, only tap water was passed through the columns. A reservoir (volumetric flask) of tap water was pumped from the top of each column downward through the soil at a rate of 1.0 L/day, and was collected at the bottom. Again, this operation was done to mimic the push-pull approach, with a reversal in the direction of flow (i.e., a “push” from the bottom of one pore volume, followed by a “pull” from the top, after the resting period). Two pore volumes were passed through the columns during the extraction phase, because most push-pull applications in the field extract 1.5 times to 3 times the volume that was injected (Laughlin, 2015., Pennell et al, 1993.) Each 100 mL aliquot of the effluent, which represents 0.2 of the entire PV in the columns, was collected separately. The temperature and pH of each 100 mL aliquot were measured, and then the sample was extracted with methylene chloride and the TPH was measured using EPA Method 8015.

3.0 RESULTS AND DISCUSSION

3.1 Batch Studies

The results after a 1-day contact period are listed in Table 5, and the results after 10 days of contact are listed in Table 6. Listed in these tables are the following: the final, treated, TPH concentrations measured in the soil for each reaction scenario, the percent removal of TPH, the TPH concentrations in the bulk liquid removed from the reaction vessels, a mass balance on the TPH removed, and the interfacial tension measured in the bulk liquid.

Table 5 Results from the Batch Studies after one day of contact with the surfactants

Reaction Scenario	TPH Conc. (g/kg)	% TPH Removed*	TPH in Liquid (g)	Mass Balance** (g)	Interfacial Tension (mN/m)
Control (no surfactant)	48.2	-2.3%	0.073	0.60	69.3
TOXIMUL 8320	46.3	1.7%	0.074	-0.31	27.0
AMMONYX LO	50.4	-6.8%	0.061	1.60	34.2
NACCONOL 90G	49.1	-4.5%	0.215	1.22	49.7
BIO-TERGE PAS-8S	48.7	-3.4%	0.184	0.95	43.3
STEPANATE SXS	46.9	0.4%	0.194	0.10	46.9
BIOSOLVE	50.8	-7.9%	0.092	1.87	41.3
PETROSOLVE	46.4	1.5%	0.036	-0.30	37.5
Rhamnolipids	49.9	-5.9%	0.112	1.46	39.3
Saponin	48.4	-2.8%	0.463	1.09	46.8
Polysorbate 80	50.7	-7.6%	0.478	2.21	42.2

*Calculated based on baseline TPH concentration of 47.1 g/kg.

**The difference in the calculated mass of TPH removed from soil and the mass of TPH measured in the bulk liquid

Table 6 Results from the Batch Studies after ten days of contact with the surfactants

Reaction Scenario	TPH Conc. (g/kg)	% TPH Removed*	TPH in Liquid (g)	Mass Balance** (g)	Interfacial Tension (mN/m)
Control (no surfactant)	46.9	0.4%	0.064	-0.03	69.7
TOXIMUL 8320	26.6	43.5%	9.492	-0.35	7.0
AMMONYX LO	22.9	51.4%	12.717	1.10	6.7
NACCONOL 90G	25.5	45.9%	11.271	0.90	6.5
BIO-TERGE PAS-8S	28.4	39.7%	9.447	0.47	6.9
STEPANATE SXS	32.7	30.6%	7.633	0.72	7.4
BIOSOLVE	41.4	12.1%	3.211	0.47	7.2
PETROSOLVE	37.9	19.5%	5.736	1.32	7.5
Rhamnolipids	25.3	46.3%	9.486	-0.98	4.3
Saponin	21.3	54.8%	13.471	1.09	6.2
Polysorbate 80	26.8	43.1%	10.232	0.49	7.1

*Calculated based on baseline TPH concentration of 47.1 g/kg.

**The difference in the calculated mass of TPH removed from soil and the mass of TPH measured in the bulk liquid

The Control reactor sampled on Day 1 and Day 10 showed no significant TPH removal, interfacial tension measurements were near 70mN/m. The surface tension of tap water was measured in the lab to be 70 ± 2 mN/m. These data indicate that no measurable natural surfactants were present in the Control reaction vessels. Although native organic material (NOM) can serve as a natural surfactant, the NOM content in the Diesel-contaminated soil was low (Table 3), which is consistent with the lack of any indication of surfactants in the 1-Day and 10-Day Controls.

The results in table 6 show that of all the surfactant solutions tested, at 20 g/L, saponins performed the best by removing 54.8% of TPH from the soil. BIOSOLVE on the other hand removed only 12.1% of the TPH from the soil, making BIOSOLVE the worst performer of all the surfactants tested. All surfactants increased the TPH concentration in the bulk liquid between day 1 and day 10, and decreased the residual TPH concentration in the soil. The values

of interfacial tension on Day 10 are also significantly less than on Day 1 for all reaction scenarios besides the Control. The values of interfacial tension on measured on Day 1 are well below the Control, which is consistent with the surfactant present in the pore water. However, 1 day of contact time was not sufficient to allow any significant removal of the NAPL via emulsion, or via displacement of un-emulsified NAPL by changing surface and capillary forces. In contrast, on day 10 the values of interfacial tension are much lower for all reaction scenarios other than the Control. All 10 of the surfactants reduced the IFT significantly after 10 days. Urum et al. (2004) measured interfacial tension values to be 4.5 mN/m for rhamnolipid and 6.0 mN/m for saponin, and these values are consistent with the 10-Day IFT measurements in this study. The interfacial tension value for rhamnolipid was measured to be 4.3 mN/m and the interfacial tension value for saponin was measured to be 6.2 mN/m (Table 6). The ability of surfactants to reduce IFT allows them to “loosen” occluded NAPL in soils so they can be removed via pumping groundwater. tendency to remove oil from soil. As IFT values decrease, capillary forces holding the NAPL and soil together are reduced. The values of IFT in Table 6 for surfactants other than rhamnolipids and saponins are within the IFT values observed in soil washing and other surfactant enhanced remediation applications that remove significant amounts of NAPL (Urum et al., 2003).

3.2 Column Studies

Figure 14 below shows the cumulative mass of diesel fuel removed over 2 pore volumes (1 day). Table 5 lists the total mass of TPH removed and collected from each column reactor after 2 pore volumes were passed through the soils exposed for 7 days to each reaction scenario.

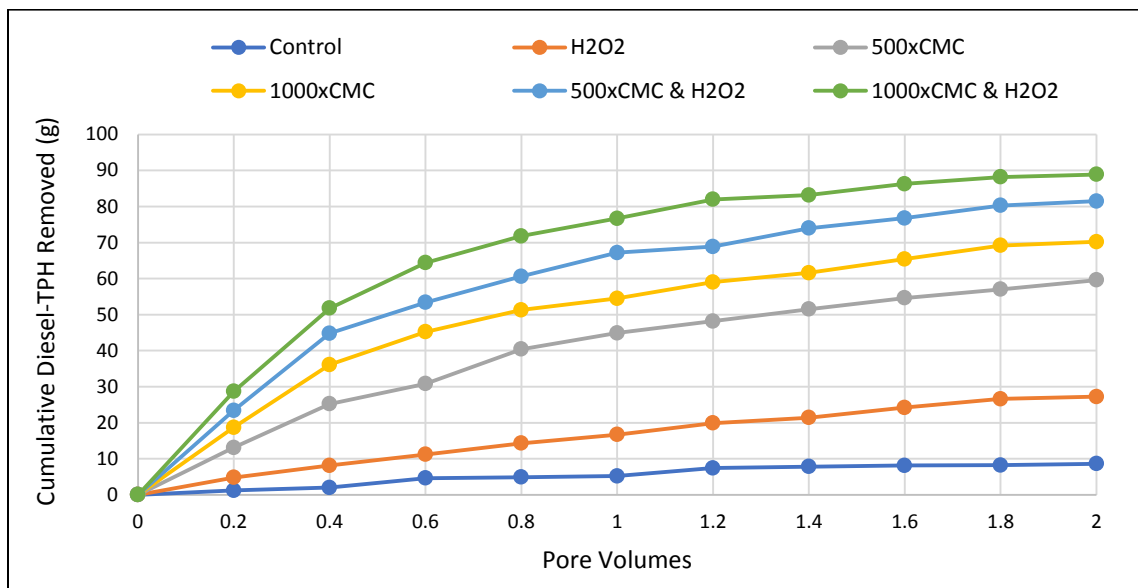


Figure 14 Cumulative TPH-NAPL Removal

Table 7 Total mass of TPH removed in each column and the average temperature and pH in the effluent

Reaction Scenario	Total Mass of TPH Removed (g)	Average temperature (C°)	Average pH
Control	8.6	21.9	6.5
H2O2	27.2	22.0	6.6
500xCMC	59.6	21.8	6.4
1000xCMC	70.2	22.2	6.6
500xCMC & H2O2	81.5	22.1	6.5
1000xCMC & H2O2	88.9	21.9	6.7

The data presented above in Figure 14 and Table 7 clearly demonstrate that the presence of a 5% hydrogen peroxide (H_2O_2) concentration enhanced the removal of diesel fuel from the artificially contaminated Ottawa sands in the column reactors. A concentration of H_2O_2 of 5% was selected for these column experiments because H_2O_2 is such a strong oxidant and higher concentrations raise concerns about safety and require a greater injection pressure because of off-gassing of O_2 . However, higher concentrations should be tested in future studies.

The column with 5% hydrogen peroxide removed over three times more TPH than did the Control with no hydrogen peroxide. Likewise, both concentrations of saponins tested (500 times the CMC and 1000 times the CMC) removed significantly more TPH when they were present with 5% hydrogen peroxide than without hydrogen peroxide. Specifically, soils treated with a concentration of saponins 500 times the CMC removed 37% more TPH with hydrogen peroxide than without hydrogen peroxide. Likewise, soils treated with a saponins at a concentration 1000 times the CMC removed 27% more TPH with hydrogen peroxide than without hydrogen peroxide.

Not surprisingly, these results also clearly show that the amount of TPH removed from the columns increased as the concentrations of saponins increased, with and without hydrogen peroxide. For example, the soil treated with saponins at 1000 times the CMC removed 18% more TPH than saponins present 500 times the CMC, and the soil exposed to saponins at 500 times the CMC removed nearly 6 times more TPH than the Control, with no saponins. This is consistent with previous studies not NAPL removal with saponins and other surfactants (Beach, 2016.; Urum, 2003., Fountain et al, 1996).

The results from the column studies demonstrate that hydrogen peroxide markedly enhanced the removal of diesel fuel from the artificially contaminated Ottawa sands. This conclusion is the most important finding of this study, and merits some discussion. First, the TPH was removed from the columns, collected, and measured. More TPH was collected from every reaction scenario with hydrogen peroxide than without, regardless of whether saponin were also present to emulsify the NAPL. The exact mechanism by which hydrogen peroxide enhanced NAPL removal in these studies was not identified. However, the most likely reason was the mixing in the pores of the soil created by the auto-decomposition of hydrogen peroxide to water and molecular oxygen, as described in Reaction 1.



The release of O_2 gas creates bubbles, which provides mixing as the bubbles move upwards in the soil. Mixing increases contact between surfactants and NAPL in pores, which enhances emulsion. This mixing and the upward moving bubbles can also dislodge un-emulsified NAPL in the soil, and move it upwards. The results show that this process happened to some extent in the column studies, because the column with hydrogen peroxide and no saponins showed more NAPL removal than the Control. As indicated in Reaction 1, the decomposition of hydrogen peroxide also releases some heat ($\Delta\text{H}^\circ = -98.2 \text{ kJ/mol}$) (Easton et al., 1952), which would also increase rates of mass transfer and would tend to enhance NAPL emulsion. However, temperatures were monitored in the reactor effluent, and no increase in temperature above background was detected.

4.0 CONCLUSIONS

Of the ten surfactants tested in static batch reactors, saponins achieved the greatest removal of diesel fuel from a soil with aged diesel fuel contamination. There was large disparity in the diesel fuel removed by the different commercially available surfactants tested, which indicates that there is high degree of sensitivity in the effectiveness of surfactants that may depend on the soil itself, and not only on the NAPL. The amount of diesel fuel removed was much greater after 10 days than after 1 day, which demonstrates the importance of allowing contact time after introducing surfactants into a NAPL contaminated system when little mixing is provided.

In column studies designed to simulate a Push-Pull application of surfactants for the *in situ* remediation of NAPL-contaminated aquifers, the amount of diesel fuel removed from artificially-contaminated Ottawa sands increased as the concentration of saponins injected increased. The injection of 5% hydrogen peroxide-enhanced NAPL removal whether saponins were injected or not. It is likely that the enhanced NAPL removal achieved with hydrogen peroxide is due to the mixing provided by the release of gas accompanying its auto-decomposition. However, the best removal achieved was when a solution of saponins 1000 times the CMC was injected in a 5% hydrogen peroxide solution. The enhancement of diesel fuel removal achieved with hydrogen peroxide was greatest when it was co-injected with saponins. The saponins tested were stable in a 5% hydrogen peroxide solution. The results suggest that co-injection of saponins with low concentrations of hydrogen peroxide has the potential to enhance surfactant-enhanced NAPL recovery in Push-Pull applications in the field.

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