FINAL REPORT
Texas Hazardous Waste Research Center Project 412TAM0012H

In-situ Remediation of Hydrocarbon Contaminated Groundwater Using Polymeric Nanoparticles

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1. OVERVIEW AND PROJECT OBJECTIVES

Groundwater contamination by hydrocarbons, particularly petroleum products, is a widespread problem in developed countries. Traditional remediation of such groundwater contaminants has involved either time intensive methods such as bio-remediation or has required the use of highly reactive, non-selective, and relatively expensive chemicals such as persulfate or hydrogen peroxide. This study investigates the potential application of magneto shell-cross-linked knedle-like (MSCK) nanoparticles as a novel remediation technology. MSCKs are spherical, amphiphillic, polymeric, nanoscale colloids which selectively sequester petroleum hydrocarbons from an aqueous environment into their interior (Figure 1).

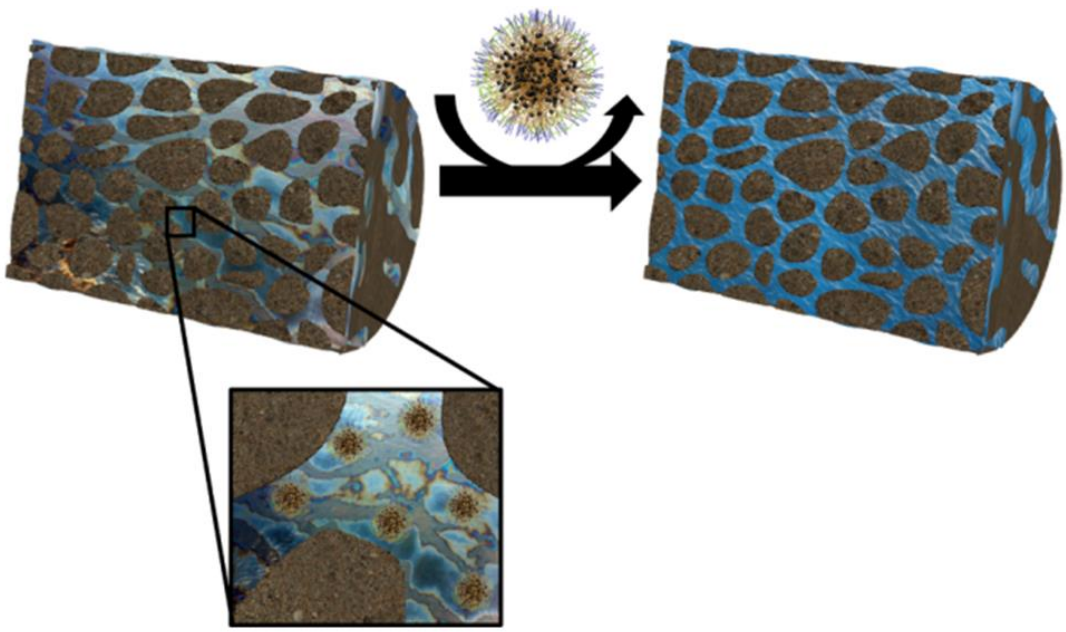


Figure 1 – Conceptual schematic of groundwater remediation using MSCKs.

The purpose of this study was to explore the transport and contaminant sequestration behavior of MSCKs in saturated porous media to determine if these engineered nanoparticles are a viable groundwater remediation technology. We tested the following three hypotheses:

1) In columns containing sand as the porous media, MSCKs will exhibit transport behaviors like that of a dissolved, ionic species of similar size, rather than a retainable suspended colloid.
2) In columns containing a sand/clay mixture as the porous media, MSCKs will not sorb to clay particles unless they have previous sequestered hydrocarbons.
3) MSCKs will have a lower hydrocarbon sequestration ratio in porous media than they do in a batch reactor (10:1); however, the ratio will be sufficient to consider their use as a remediation technology viable.

2. METHODOLOGY

To assess the viability of MSCKs for the in-situ remediation of contaminants, a series of column experiments were conducted and effluent concentrations were continuously monitored using a dual beam Shimadzu UV-2250 Spectrophotometer. Prior to conducting the column experiments, we developed a new methodology for detecting MSCKs using the instrument. Although the details are too extensive to report here, they may be found in Chapter 3 of the attached thesis.

In total, we completed 30 column representing a five replicates of a baseline characterization run plus five different experimental treatments. In the first set of experimental runs, a pulse of non-reactive tracer (bromide) was injected to determine the baseline, intrinsic transport properties of the sand or sand/clay mixtures (e.g., hydraulic conductivity, effective porosity, dispersivity). In the next set of runs, we then injected a pulse of 216 mg/L MSCK solution into the columns to determine MSCK transport properties. In the remediation experiments, we introduced *m*-xylene as an aqueous phase contaminant by replacing the influent with an 8.66 mg L^{-1} *m*-xylene solution. These tests were used to determine the effects of aqueous phase sequestration of hydrocarbons on the transport properties of MSCKs. A non-aqueous phase liquid (NAPL) sequestration experiment was conducted in the sand column; it duplicated the conditions of the tracer treatment and introduced mineral oil as a representative contaminant. This treatment was used to determine the effects of MSCK/NAPL interactions on particle transport and to determine the MSCKs efficacy of NAPL sequestration during particle transport.

3. RESULTS

Bromine injections behaved as expected (Figures 2a, 2b, and 2c), finding Darcy velocities around 35 m/d with hydraulic conductivities around 9.8 m/d. The transport experiments demonstrated that MSCKs move readily through saturated sands with virtually no particle retention (Figure 2d); however, the presence of clays retards MSCK transport via irreversible attachment and/or aggregation and straining of MSCKs (Figure 2e). Additionally, the presence of hydrocarbon contaminants, in either the aqueous phase or as NAPL, reduces the mobility of MSCKs and lowers recovery (Figures 2f, 2g, 2h). In general, mean residence times had fairly low variability across all runs, 0.95-1.05 pore volumes (Figure 3). Likewise, inter-run variability in MSCK recovery rates was low (<8%), with the exception of MSCKs in the presence of NAPL.

Based on these results, support for our initial hypotheses was mixed:

1) Hypothesis 1: Supported. MSCKs transported readily through columns containing sand as the porous media. Full recovery was achieved. The mean residence time of the particles was slightly less than anticipated, indicating some preferential flow as compared to a dissolved tracer.
2) Hypothesis 2: Not supported. MSCKs sorbed to clays under transport through sand/clay mixtures. However, recovery rates were still >60%, indicating the method still has potential for use in a wider variety of soils.
3) Hypothesis 3: Partially supported. MSCKs maintained their sequestration ratios (10:1) in porous media, but only when they were used to remediate the dissolved organic contaminant. When used with a free-phase (NAPL) contaminant, MSCKs sequestered between 3-10% of their total mass. Sequestration also significantly changed their transport properties, leading to lower recovery rates.

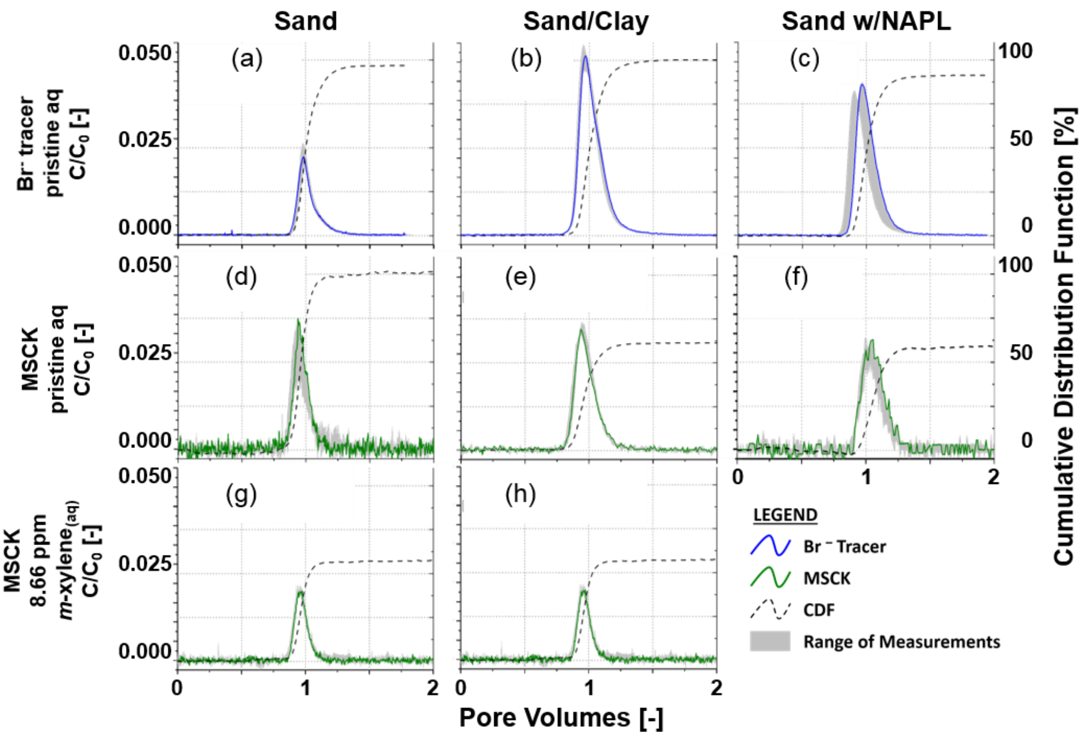


Figure 2 - Representative breakthrough (solid lines) and recovery curves (dashed lines) for each experiment. The range of all experimental values is depicted in the shaded grey area. Br^- conservative tracer tests are depicted in blue for (a) sand columns, (b) sand/clay columns, and (c) sand with NAPL pockets. MSCK transport experiments in (d) sand and (e) sand/clay as well as MSCK sequestration experiments for aqueous phase *m*-xylene in sand (g) and sand/clay (h) and free phase mineral oil in sand (f) are depicted in green.

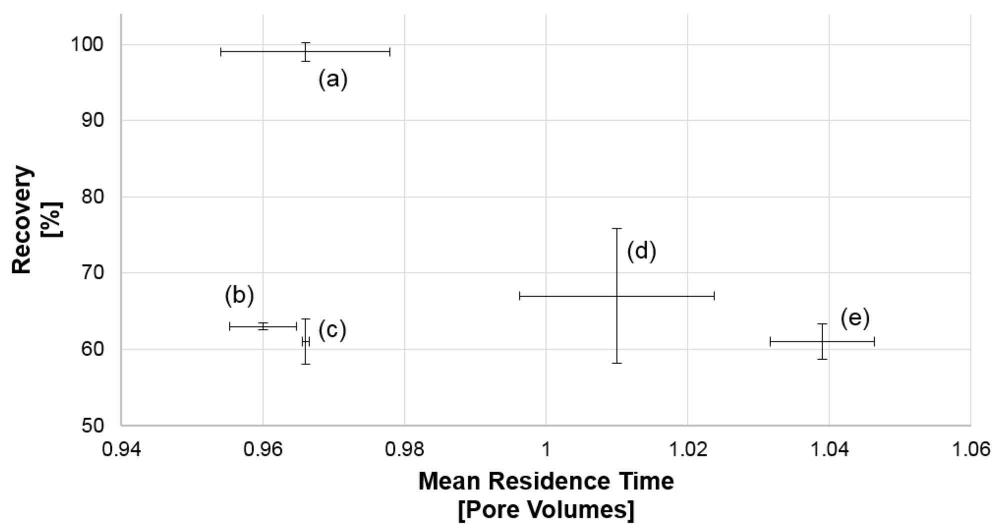


Figure 3 – Visual summary of MSCK recovery and mean residence time for (a) MSCK in pristine sand, (b) MSCK in pristine sand/clay, (c) MSCK in the presence of *m*-xylene$_{(aq)}$ in sand, (d) MSCK in the presence of NAPL (mineral oil) in sand, and (e) MSCK in the presence of *m*-xylene$_{(aq)}$ in sand/clay. Bars indicate standard deviation.

Overall, we found that MSCKs are currently a viable groundwater remediation technology for aqueous phase contaminants. However, they exhibit difficulties in the sequestration of NAPLs, the mechanisms for which we do not yet fully understand. Although this study has advanced the understanding of MSCK transport in saturated porous media, more work is needed to better understand the kinetics of their interactions NAPL contaminants. The effects of flow rate, presence of salts, changes in pH, and particle aggregation on MSCK transport and sequestration also remain to be determined.

The change in transport properties of MSCKs in the presence of aqueous phase contaminants has a number of potential applications; one possibility is the encapsulation and immobilization of existing contaminant plumes. Also, it should be noted that, in nature, NAPLs tend to diffuse into surrounding groundwater, creating local regions of high aqueous phase concentrations in the vicinity of the free phase. There is potential to make use of these properties to create treatment zones or transport barriers around pockets of free phase contaminants.

4. PROJECT MANAGEMENT AND RESEARCH PRODUCTS

4.1 Students Trained

In total, one student has been involved in conducting this research. Project funds partially supported Mr. Jonathan Sanders, an M.S. student, during Fall 2013- Spring 2015. Additional student support was provided by Dr. Karen Wooley, in the Texas A&M Chemistry Department.

4.2 Research Products

Mr. Sanders presented preliminary results from this research at the ASCE World Environmental and Water Resources Congress in May 2014 and won the "Sustainability Track Student Paper Award" for his work. We have two additional abstracts for upcoming presentations at the annual meetings of the Geological Society of America and the American Geophysical Union. All conference abstracts are provided in Appendix 2 of this document, and the citations are given below:

Sanders, J.*, A. Pavia-Sanders*, K. Wooley, and G.R. Miller, (2014), Transport Properties of Magnetic/Polymer Hybrid Nanoparticle in Saturated Porous Media, oral presentation at the ASCE World Environmental and Water Resources Congress 2014, Portland, Oregon.

Knappett, P., Sanders, J.*, A. Pavia-Sanders*, G. Miller, and K. Wooley (2015 – accepted), Remediating contaminated aquifers with magnetic engineered nanoparticles, for oral presentation at the GSA Annual Meeting, Baltimore, Maryland.

Sanders, J.*, A. Pavia-Sanders*, G.R. Miller, P. Knappett, and K. Wooley (2015 – in review), Characterizing the Transport of a Novel, Engineered Nanoparticle for Use in Remediation of Hydrophobic Contaminants, for presentation at the AGU Fall Meeting, San Francisco, California.

Mr. Sanders successfully defended his thesis in June 2015. A pdf copy is being transmitted to the THWRC with this document.

Finally, we are writing two journal articles on this work and anticipate that they will be submitted for review this fall. Draft manuscripts are available upon request, and the articles will be submitted to the THWRC upon final publication:

Sanders, J.*, A. Pavia-Sanders*, K. Wooley, P. S. K. Knappett, and G.R. Miller (In prep.), Transport, Characterization, and Modeling of Polymeric Nanoparticles Engineered for the Selective Entrapment and Recovery of Contaminants in Saturated Porous Media, for submission to *Environmental Science and Technology*.

Sanders, J.*, A. Pavia-Sanders*, K. Wooley, P. S. K. Knappett, and G.R. Miller (In prep.), Method for the determination of engineered nanoparticle transport parameters and remedial capabilities in saturated porous media, for submission to *Environmental Science and Technology Letters*.

4.3 Research Proposals

We have submitted one proposal for federal research funding to continue this work:

"SusCHEM: Robust Magnetic/Polymer Hybrid Nanoparticles Designed for Remediating Contaminated Aquifers," NSF Environmental Engineering Program, PI: Peter Knappett, Co-PIs: Gretchen Miller, Karen Wooley, Hongbin Zhan; May 2015 – April 2018, $469,012 total.

Although it was not funded, it received favorable reviews, and we plan to submit it to the same program in October 2015. I plan to be lead PI on this year's proposal. The proposal will address the issues noted above, and includes support for redesign of certain particle features to promote transport and sequestration.

4.4 Project Budget

The project was at its budget of $30,000. Personnel and travel expenses were slightly over the projected figures, while equipment and supply costs were lower than anticipated.

	Budgeted Expenses	**Actual Expenses**
A. Salaries		
I. Principal Investigators		
Gretchen Miller	$ 5,519	$ 0
II. Graduate Assistant		
GSR – Year 1	$ 14,285	$ 22,049
GSR – Year 2		
B. Travel and Conference Registration	$ 3,740	$ 3,428
C. Equipment	$ 4,248	$ 4,523
D. Supplies	$ 2,208	$ 0
E. Other Expenses	$ 0	$ 0
TOTAL PROJECT COSTS	**$ 30,000**	**$ 30,000**

APPENDIX: SUPPLEMENTAL INFORMATION

Transport Properties of Magnetic/Polymer Hybrid Nanoparticle in Saturated Porous Media

Jonathan Sanders[1], Adriana Pavia-Sanders[1], Karen Wooley[1], Gretchen Miller[1]
[1]Texas A&M University

Groundwater contamination by hydrocarbons, particularly petroleum products, is a widespread problem in developed countries. Traditional remediation of such groundwater contaminants has involved either time intensive methods such as bio-remediation or has required the use of highly reactive, non-selective, and relatively expensive chemicals such as persulfate or hydrogen peroxide. This study investigates the potential application of magneto shell-cross-linked knedle-like (MSCK) nanoparticles as a novel remediation technology. MSCKs are spherical amphiphillic polymeric nanoscale colloids which selectively sequester petroleum hydrocarbons from an aqueous environment into their interior. To determine the transport, retention, and contaminant removal properties of these nanoparticles, a series of column studies were conducted. Column conditions were saturated with low Reynolds numbers. The first set of experiments was designed to determine the transport parameters of the MSCKs in porous media. Dependent variables included: electrical conductivity of the simulated groundwater, grain size distribution of the media, and presence or absence of non-expansive clay (to test for sorption of MSCKs to exchange sites). The second set of experiments was conducted to determine the hydrocarbon loading capacity of the MSCKs over a range of retention times and influent contaminant concentrations. The breakthrough curves of these column studies were used to calibrate a simple three dimensional reactive transport model to simulate the in-situ remediation of a benzene plume at a theoretical site. Overall, this study indicates that MSCKs are a promising alternative for hydrocarbon remediation.

Abstract #82311

Characterizing the Transport of a Novel, Engineered Nanoparticle for Use in Remediation of Hydrophobic Contaminants

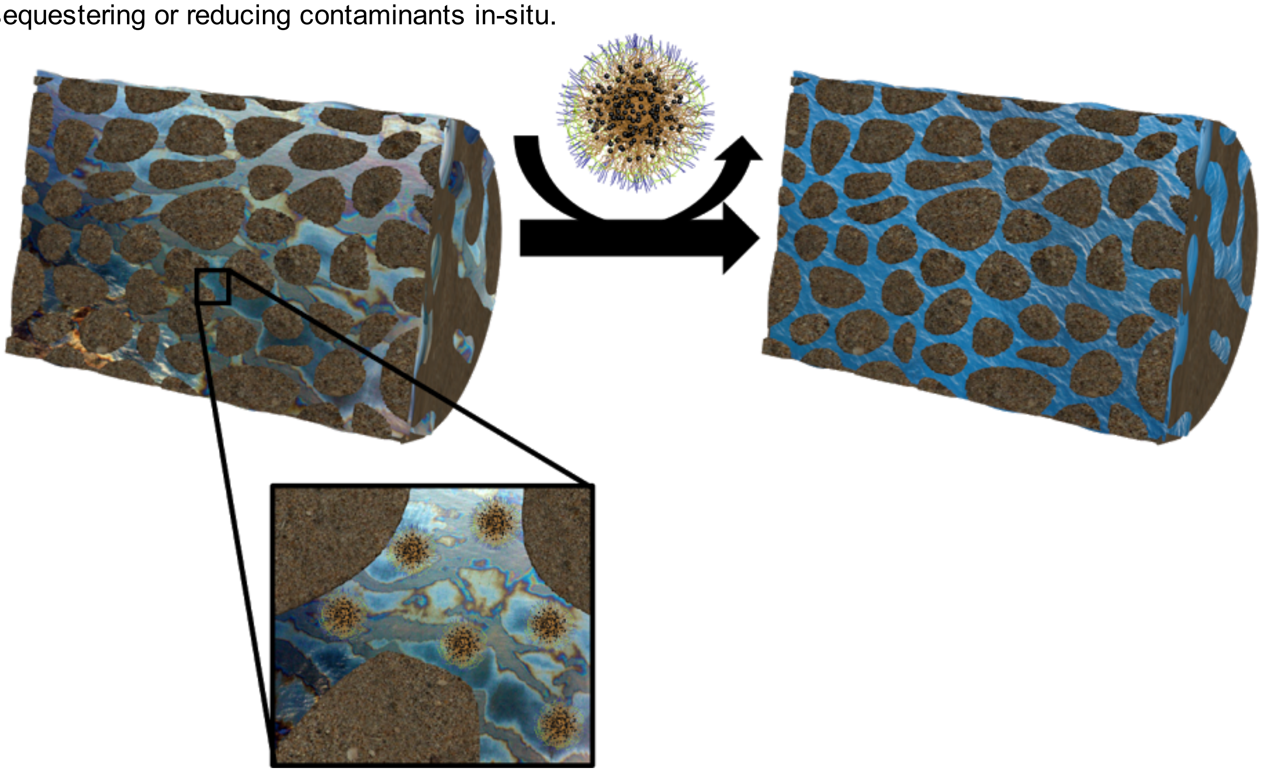
Jonathan Edward Sanders, Texas A & M University College Station, College Station, TX, United States

Abstract Text:

Magnetic shell crosslinked knedel-like nanoparticles (MSCKs) were originally engineered to aid in the cleanup of oil spills. These polymeric particles are spherical and approximately 70 nm in diameter. MSCKs have a hydrophobic shell and hydrophilic core which encapsulates suspended iron oxide nanoparticles, rendering them magnetic. MSCKs operate like discrete surfactant packets: increasing the mobility and apparent solubility of hydrophobic species, but do so within the confines of discrete particles which can then be recovered by filtration or magnetic removal. MSCKs accomplish this via sequestration of hydrophobic species from through the hydrophilic shell and into the hydrophobic core where hydrocarbon contaminants are entropically stabilized. In batch reactor testing, MSCKs have been shown to sequester crude oil up to ten times their mass (1000 mg of oil per 100 mg of MSCKs). This study examines the transport characteristics and contaminant sequestration capabilities of MSCKs in saturated porous media, in order to establish their potential for use in groundwater remediation.

Baseline MSCK transport parameters were determined via one dimensional impulse column experiments. MSCKs were readily transported in saturated sand, with an average recovery rate of 99%. In the presence of 10% clay particles, recovery was reduced to 68%. MSCKs were able to completely sequester an aqueous phase pollutant (8.7 mg/L m-xylene), although it further reduced their recovery rate to 61% in sand and 53% in clay. The presence of a free phase contaminant (5% of pore space occupied by mineral oil) reduced MSCKs recovery in sand to 53%. The MSCKs recovered in the effluent had sequestered the mineral at ratios far below their capability (3-10 mg of oil per 100 mg of MSCKs).

Overall, this study indicated that MSCKs show a number of promising attributes for use in remediation. However, further manipulation of their chemical and morphological properties is needed, with the objective of making “loaded” MSCKs either more amenable to transport and recovery or capable of permanently sequestering or reducing contaminants in-situ.



Topic Selection: Microorganisms, Colloids, Engineered Nanoparticles, and Emerging Contaminants in the Environment

Title: Characterizing the Transport of a Novel, Engineered Nanoparticle for Use in Remediation of Hydrophobic Contaminants
Submitter's E-mail Address: jonathan.sanders.8613@gmail.com
Preferred Presentation Format: Assigned by Program Committee (Oral or Poster)

First Presenting Author

Presenting Author

Jonathan Edward Sanders

Primary Email: jonathan.sanders.8613@gmail.com

Affiliation(s):

Texas A & M University College Station
College Station TX 77840 (United States)

Student: Yes

1-4 NOVEMBER
GSA 2015
Baltimore, Maryland, USA

The deadline for abstract submissions and modifications has been reached however the following actions are still available to you:

View Submission (no changes allowed)

Printable Receipt (Abstract Submission)

Abstract #267767

REMEDIATING CONTAMINATED AQUIFERS WITH MAGNETIC ENGINEERED NANOPARTICLES

KNAPPETT, Peter S. K.[1], **SANDERS, Jonathan**[2], MILLER, Gretchen[2], PAVIA-SANDERS, Adriana[3] and WOOLEY, Karen[3], (1)Geology and Geophysics, Texas A&M University, College Station, TX 77843, (2)Civil Engineering, Texas A&M University, College Station, TX 77843, (3)Chemistry, College Station, TX 77843, jonsanders2004@email.tamu.edu

Magnetic shell crosslinked knedel-like nanoparticles (MSCKs) were engineered to aid in the cleanup of oil spills. These engineered nanoparticles (ENP's) are approximately 70 nm in diameter. MSCKs have a hydrophilic shell and hydrophobic core which encapsulates suspended iron oxide nanoparticles, rendering them magnetic. MSCKs operate like discrete surfactant packets: increasing the mobility and apparent solubility of hydrophobic species, but do so within the confines of discrete particles which can then be recovered by filtration or magnetic removal. MSCKs accomplish this via sequestration of hydrophobic species from through the hydrophilic shell and into the hydrophobic core where hydrocarbon contaminants are stabilized. In batch tests MSCKs sequestered crude oil ten times their mass (1000 mg of oil per 100 mg of MSCKs). The objective of this study is to quantify their transport and contaminant sequestration capabilities in saturated porous media as a first step towards their potential use in aquifers plagued with hydrophobic contaminants.

MSCK transport and reaction efficacy was determined with one dimensional impulse column experiments. MSCKs were readily transported in saturated sand, with an average recovery rate of 99%. In the presence of 10% clay particles, recovery was reduced to 68%. In the presence of xylene, MSCKs completely sequestered the aqueous phase pollutant (8.7 mg/L), although recovery of the MSCKs fell to 61% in sand and 53% in clay. The presence of a non-aqueous phase liquid (NAPL) (5% mineral oil by volume) further reduced MSCKs recovery in sand to 53%. The MSCKs recovered in the effluent had sequestered the mineral at ratios far below their capability demonstrated in batch experiments (3-10 mg of oil per 100 mg of MSCKs).

This study demonstrates that MSCKs show promising attributes for use in remediation. However, further manipulation of their chemical and morphological properties, and further testing of optimal groundwater flow rates and injected concentrations of the MSCK's is needed to optimize their performance in situ.

Abstract ID#: 267767
Password: 598463
Meeting: 2015 GSA Annual Meeting in Baltimore, Maryland, USA (1-4 November 2015)
Session Type: Topical Session
Primary Selection: T108. Nanomaterials in Hydrogeology
Abstract Title: REMEDIATING CONTAMINATED AQUIFERS WITH MAGNETIC ENGINEERED NANOPARTICLES
Preferred Presentation Format: Poster
Discipline Categories: Hydrogeology Environmental Geoscience