TO: Texas Hazardous Waste Research Center

FROM: Gretchen Miller
Texas A&M University
(979) 862-2581
gmiller@civil.tamu.edu

SUBJECT: Annual Progress Report

PROJECT NUMBER: 513TAM0031H

PROJECT TITLE: In-situ Remediation of Hydrocarbon Contaminated Groundwater Using Polymeric Nanoparticles

PROJECT PERIOD: September 1, 2013 – August 31, 2014

DATE: September 15, 2014

Project Description/Abstract

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 in porous media, a series of column studies were conducted.

The first set of experiments was designed to determine the transport parameters of the MSCKs in porous media. The second set of experiments was conducted to determine the actual hydrocarbon loading capacity of the MSCKs over a range of retention times and influent contaminant concentrations. The breakthrough curves of these column studies will be used to calibrate a simple one-dimensional transport model to determine appropriate values for parameters such as sorption coefficients. Overall, preliminary results from this study indicate that MSCKs are a promising alternative for hydrocarbon remediation.

Objectives

The primary objective of this research project was to determine the effectiveness and viability of MSCKs for the in-situ remediation of petroleum contaminants in groundwater. 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.

Methodology

To assess the viability of MSCKs for the *in-situ* remediation of contaminants, a series of column experiments were conducted. Each aluminum column was 61 cm in height with a diameter of 15 cm and was packed with one of two types of representative porous media. The first type of packing consisted of a Texas Gold 40/70 (TG) silica sand from the Voca formation in Texas; the manufacture reports a bulk density of 1.46 g/cm^3 and a specific gravity of 2.64 g/cm^3, with a grain diameter between 0.420 and 0.210 mm. The second column media consists of a 9:1 mass ratio of TG to a Kaolin based clay. This sand and clay mixture was homogenized via rigorous mixing prior to addition to the column. The columns were configured much like a standard permeameter, with the addition of an inlet port for pulse injections of contaminants and MSCKs and a feed for a UV-Vis flow-through cell (Figure 1).

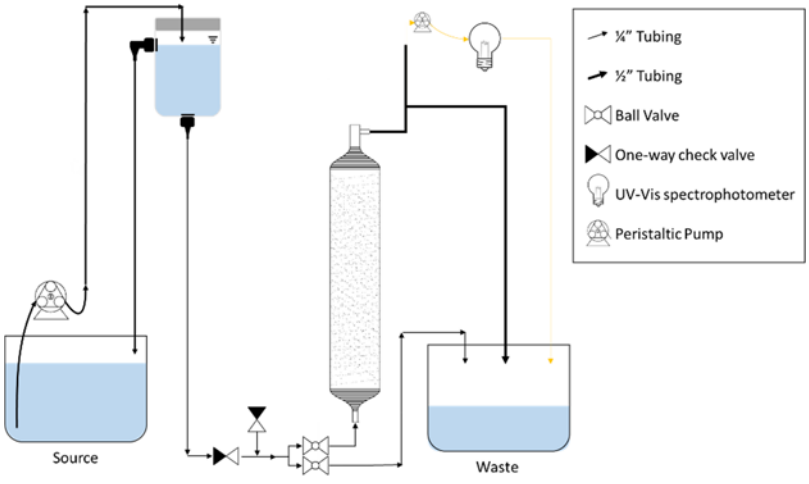

Figure 1: Experimental column setup

A single beam deuterium/tungsten lamp Helios Gamma UV-Vis Spectrophotometer was used to continuously measure absorbance of the column effluent. The Helios Gamma has an effective absorbance detection range of ±3 absorbance with a photometric accuracy of ± 0.005 at 1 absorbance. The lower and upper limits for wavelength detection are 190 nm and 1100 nm. 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, we plan to publish a journal article on it as part of our final set of deliverables.

Each of column experiments conducted, and its purpose, is summarized below:

- Four media characterization experiments
    - Sand column, constant head permeability test to determine media's hydraulic conductivity (K)
    - Sand/clay column, constant head permeability test to determine media's hydraulic conductivity (K)
    - Sand column, potassium bromide (200 mg/L) tracer test to determine intrinsic dispersivity
    - Sand/clay column, potassium bromide (200 mg/L) tracer test to determine intrinsic dispersivity
- Two MSCK transport experiments
    - Sand column, MSCK particles introduced (200 mg/L) to determine their attachment/detachment coefficients
    - Sand/clay column, MSCK particles introduced (200 mg/L) to determine their sorption coefficients
- Three contaminant sequestration experiments
    - Sand column, MSCK particles introduced (420 mg/L) with m-xylene (8 ppm), to determine sequestration of aqueous phase hydrocarbon contaminants
    - Sand column, MSCK particles introduced (420 mg/L) with mineral oil (250 mL), to determine sequestration of non-aqueous phase hydrocarbon contaminants
    - Sand/clay column, MSCK particles introduced (420 mg/L) with mineral oil (250 mL), to determine sequestration of sorbed non-aqueous phase hydrocarbon contaminants

Each experiment was repeated a minimum of five times. All experiments were conducted using micropure water. Additional details are available in the original proposal.

Accomplishments/Problems

Laboratory work was completed in August of 2014 and analysis of the results is currently underway. Preliminary results indicate that the porous media transport and sequestration properties of the MSCKs should be favorable for upscaling to a field level; recovery was nearly 100% for unloaded particles and the loading capacity for hydrocarbons was at least 2:1. Several example results are discussed and shown below (Figures 2 and 3).

Examining the breakthrough curve for MSCKs (Figure 2), we see that breakthrough first occurs at approximately 20 minutes after introduction into the column and peaks shortly thereafter. The

curve has some asymmetry, indicative of hydrodynamic dispersion and similar to that of the tracer.

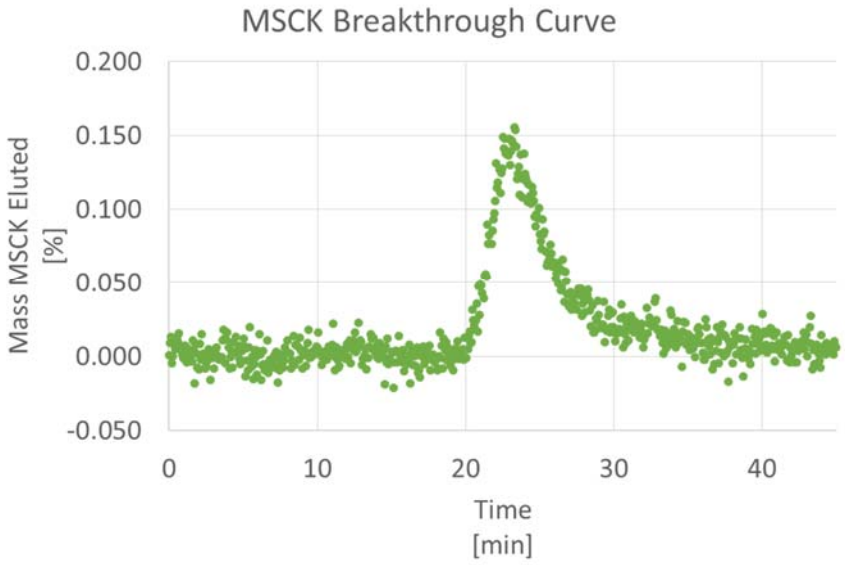

Figure 2: Breakthrough curve for MCKS in sand

Plotting the cumulative distribution function for both the tracer and the unloaded MSCKs (Figure 3), we see that MSCK recovery in sand is nearly 100%, indicating that they are readily transmitted through saturated porous media. As hypothesized, no retardation is observed. In contrast, MSCKs began eluting *before* the tracer, potentially indicating a size-exclusion effect, whereby larger particles are transported through preferential flow paths and arrive at the outlet more quickly. We are following this up with an additional column run and more extensive analysis to determine the size of MSCKs being eluted at each time step.

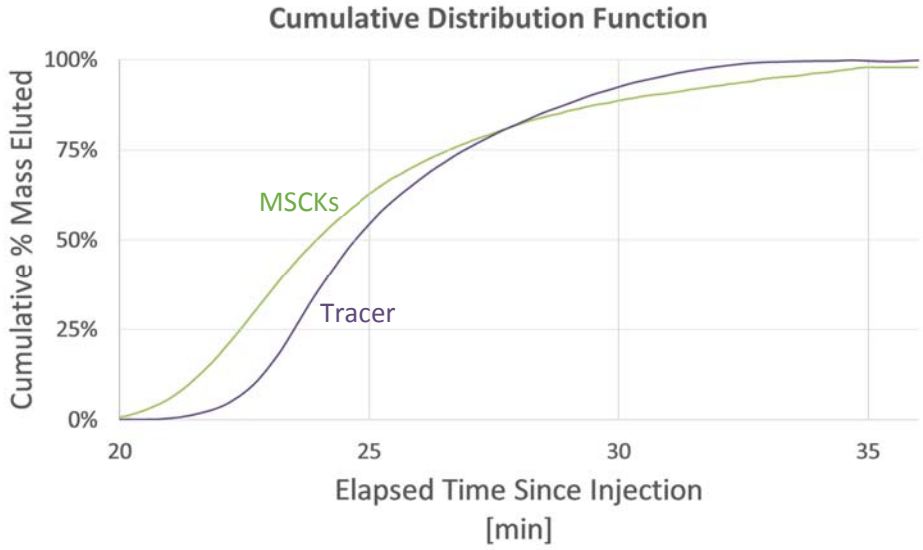

Figure 3: Cumulative effluent mass for tracer and MSCK tests in sand column

Early results of this project were presented in June at the 2014 Congress of the American Society of Civil Engineers Environmental and Water Resources Institute (ASCE-EWRI) conference in Portland, Oregon. (See list of publications for details.) Graduate Research Assistant Jonathan Sanders won an award for best student presentation in the track.

Future Work

Work Remaining on this Project:
The final analysis of the results is currently in progress; remaining tasks include fitting the 1-D model to the data to determine values for the transport and sequestration parameters. An abstract on the final project results will be submitted in late September, for presentation at the National Groundwater Association Summit in May 2015, in San Antonio, Texas. Mr. Sanders is currently writing his M.S. thesis on the project and plans to defend mid-October. From this thesis, two journal articles will be developed. The first will be a methods-style paper, submitted to the *International Journal of Environmental Analytical Chemistry*, on the methodology we have developed to use ultraviolet-visible spectrophotometry (UV/Vis) to detect and quantify MSCKs in water. The second will describe the transport and sequestration properties of the nanoparticles and will be submitted to *Environmental Science and Technology*.

Work in Addition to the Scope of this Project:
I am currently developing two proposals to continue and expand on this work. The first, entitled *Robust magnetic/polymer hybrid nanoparticles designed for remediating contaminated aquifers*, will be submitted to the National Science Foundation Sustainable Chemistry and Environmental Engineering Programs in early November 2014. The project team will include Dr. Miller, as well as two faculty from the TAMU Department of Geology: Dr. Peter Knappett and Dr. Hongbin Zhan. The second be submitted to the Department of Defense's Strategic Environmental Research and Development Program (SERDP) in early 2015. The project team will include Dr. Miller, Dr. Knappett, Dr. Zhan, and the original developer of the nanoparticles, Dr. Karen Wooley from the TAMU Department of Chemistry. The proposals will use the work presented here as preliminary data and will intend to investigate MSCK modifications to improve mobility and contaminant entrapment properties, larger-scale MSCK transport, and best-practices for modeling MSCKs.

List of Publications and Presentations

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. Won **Sustainability Track Student Paper Award**.