Report as of FY2006 for 2006NJ99B: "Enhancing the remediation of Trichloroethene (TCE) using double-walled carbon nanotubes (DWNT)"

Publications

Project 2006NJ99B has resulted in no reported publications as of FY2006.

Report Follows

Project Summary

Problem and Research Objectives

The chlorinated organic solvent trichloroethene (TCE) is one of the most commonly detected groundwater contaminants (1). Widespread application in vapor degreasing of fabricated metal parts (80% use) and in the production of organic chemicals and pharmaceuticals (5% use), resulted in increased production from 260,000 lbs in 1981 to 320 million lbs in 1991 (2). The Maximum Contaminant Level (MCL) for TCE is 0.005 mg/L. There is some evidence that TCE may cause cancer from lifetime exposure at levels above the MCL (2). The New Jersey Department of Environmental Protection (NJDEP) found that the former General Electric (GE) Company and Atlantic metal products sites in northern NJ are a source of TCE contamination in the Rahway River (3). NJDEP groundwater tests showed levels of TCE up to 20,000 µg/L at the GE site and up to 1,600 µg/L at the Atlantic metal products site. There are many other such sites in New Jersey.

The low viscosity, low interfacial tension with water, high volatility and existence as a non-aqueous-phase liquid make many physical and chemical methods of TCE remediation either ineffective or uneconomical. Furthermore, many hydro-geologic formations make remediation difficult. Reliable, cost effective methods for remediation of TCE contaminated groundwater are still needed.

The proposed research aimed to combine chemical-physical concentration and sequestration using carbon nanotubes and subsequent biodetoxification by dechlorinating bacteria to increase the efficiency of TCE removal from groundwater. The sequestration method involves the sorption of TCE onto carbon nanotubes. Carbon nanotubes are condensed carbon structures with nanoscale dimensions (1-50 nanometers) which have extraordinary mechanical, electronic, and chemical properties (5). They are produced through carbon arc discharge followed by laser removal of carbon or chemical vapor deposition on catalytic particles (6). Carbon nanotubes were superior to activated carbon for sorption and removal of dioxins from air (7). Concentration and sequestration of many environmental contaminants may be possible using carbon nanotubes. Sequestration may result in decreased environmental transport to sensitive receptors such as domestic wells or surface waters. It is currently not known if carbon nanotube-sequestered pollutants are bioavailable. If they are, sequestration followed by transformation may be possible — and necessary. Reductive dechlorination of carbon nanotube-sequestered TCE by anaerobic dehalorespiring bacteria could convert TCE to dichloroethene (DC), vinyl chloride (VC) and finally to harmless ethene.

Specific objectives and hypothesis of the study

The specific objectives of this study were two-fold: (1) What is the sorptive capacity of double walled carbon nanotubes (DWNT) for TCE? and (2) Is carbon nanotube-sequestered TCE bioavailable to dehalogenating bacteria? We hypothesized that TCE sorbed on DWNT is bioavailable to bacteria and this sorption/concentration may increase the dechlorinating efficiency of the bacteria. If feasible, a more efficient remediation technology for TCE contaminated groundwater may be developed.

Methodology

The proposed research project was carried out in two main tasks:
Task 1: Develop an isotherm for TCE sorption to DWNT.
Task 2: Determine the bioavailability of TCE sorbed on DWNT.

Experimental Methods:
Task 1. Develop an isotherm for TCE sorption to DWNT.

Task 1 used a series of three experiments. First the mass loading of DWNT to be used for sorption isotherm development was determined; the kinetics of TCE sorption to DWNT was examined; and finally a sorption isotherm for TCE to DWNT was developed.

Determination of DWNT mass loading. To carry out experiments with nanotubes and TCE, it was necessary to be able to accurately measure the amount of TCE sorbed onto the nanotubes. Since the TCE mass balance in the bottle **(Equation 1)** will depend upon headspace analysis of TCE in the gas phase, we must ensure that experiments are carried out under conditions where TCE can be detected in the gas phase. Therefore, a suitable mass loading of DWNT for the TCE concentrations to be used was found. Different loadings of DWNT (1, 5, 15, 30, and 60 mg/bottle) were placed in 60 ml bottles with two different TCE concentrations (0.0015 mM and 0.761 mM) and 40 mL of two different aqueous media: 1) microbial growth media (0.5 g/L NH_4Cl, 0.4 g/L K_2HPO_4, 0.1 g/L $MgCl_2 \cdot 6H_2O$, 0.05 g/L $CaCl_2 \cdot 2H_2O$, 0.001 g/L resazurin, and 10 mL trace metal solution per liter modified by addition of 0.01 g of $NiCl_3 \cdot 6H_2O$ per liter) (8); and 2) biologically inactivated synthetic groundwater (0.7351 g/L $CaCl_2$, 0.1 g/L NaN_3 and 0.005 g/L $NaHCO_3$) (9). Two media were examined to control for differences in DWNT sorption that may result from the presence of iron sulfide and other precipitates that may be present in living systems. The bottles were incubated in triplicate and agitated at 25°C for three days. After three days of incubation the bottles were analyzed to determine the total TCE adsorbed on to the nanotubes. The DWNT loading at which 30-70% of the TCE mass adsorption is achieved was used for further experimentation as it leaves measurable amounts of TCE in both gaseous and liquid phases to allow accurate determination of the isotherm. The total TCE adsorbed on to the nanotubes was determined from **Equation 1**.

$$\text{Total TCE} = V_{\text{head space}} C_g + V_{aq} C_e + Q_e \cdot M \qquad \textbf{(Equation 1)}$$

Where:

Total TCE = Mass of TCE added to the bottle (μmol)
$V_{\text{head space}}$ = Volume of the gaseous head space (L)
C_g = Concentration of TCE in gaseous phase (μmol/L)
V_{aq} = Volume of the aqueous phase (L)
C_e = Concentration of TCE in the aqueous phase at equilibrium (μmol/L)
Q_e = TCE sorbed per unit weight of DWNT (μmol/mg)
M = Mass of the adsorbing DWNT (mg).

C_g , the gas-phase concentration, was determined from gas chromatography analysis and comparison to known standards as described in the Analytical Methods section. The

liquid-phase equilibrium TCE concentration, C_e was determined using the relationship $C_g = H_c * C_e$, where H_c is the pseudo-dimensionless Henry's Law Constant (10). Thus, all measurements depended upon the gas-phase analysis of TCE.

Kinetics of TCE sorption to DWNT. In order to develop an isotherm for TCE sorption to DWNT, the kinetics of TCE sorption was first determined to allow selection of an adequate incubation time for the isotherm experiments. To assess kinetics of TCE sorption to DWNT, 60 mL reactors with nanotube mass loading at which 30-70% of the TCE is expected to sorb (as described in the Mass Loading section) were set up with growth media and synthetic groundwater as previously described. Samples will be collected daily and analyzed to determine the rate at which TCE is sorbed, $\frac{dQ_e}{dt}$. Consecutive days when there was no change in TCE adsorption i.e., $\frac{dQ_e}{dt} = 0$, were noted. To be conservative, the equilibrium time to be used in further experiments for isotherm development was assumed to be equal to t = time when $\frac{dQ_e}{dt} = 0$ plus one day.

Development of a sorption isotherm for TCE to DWNT. The feasibility of use of carbon nanotubes as a super sorbent for environmental pollutants will hinge, among other things, on their sorption capacity. A sorption isotherm for DWNT and TCE will be developed to determine the ultimate capacity for TCE uptake by DWNT. To obtain the isotherm, 20 reactors with the optimal experimental DWNT mass loading (as determined in the Mass Loading section) were set up. Ten different concentrations of TCE ranging from 0 to 6.08 mM were added to the reactors. A sorption isotherm was constructed by plotting the concentration of TCE in the aqueous phase at equilibrium (C_e) against TCE sorbed per unit weight of DWNT (q_e). The isotherm was fit with a sorption model (e.g., Freundlich) that will be useful for defining experimental parameters for testing and for calculations related to design aspects for the technology.

Task 2. **Determine the bioavailability of TCE sorbed on DWNT.**

The second overall objective of the study was to determine whether once sorbed to DWNT, if TCE is readily bioavailable. If nanotubes are to be used as super-sorbing sequestration agents for remediation, then the concentrated contaminants must then be non-bioavailable and difficult to desorb or they must be amenable to destructive reactions in their concentrated forms. The bioavailability of sorbed TCE to dechlorinating bacteria was examined. This will allow us to determine the extent of irreversible sequestration of the pollutants and to test our hypothesis that concentration and subsequent biotransformation could be a new effective technology for TCE remediation. Reactors filled with anaerobic growth medium and DWNT-sequestered TCE were inoculated with a dehalogenating bacterium, *Dehalococcoides ethenogenes*, known to grow on TCE and dechlorinate it to ethene (11). The bioavailability of TCE to the bacteria was determined by analyzing the end products of TCE degradation – i.e., DCE, VC and ethene over a 135 day incubation period at 25ºC. We utilized DWNT-TCE equilibrated reactors filled with anaerobic media as described in the section on Sorption Isotherm Development as the starting reactors for this experiment. An inoculum of a mixed culture containing *Dehalococcoides ethenogenes* (12) was added to achieve approximately 10^{-6} cells/mL.

Control reactors that contained no nanotubes were run to check the viability of the culture transfer and to obtain rates of dechlorination to which to compare to DWNT rates. The mass of TCE desorbed and transformed by the bacteria was determined through headspace analysis for dechlorination daughter products.

Analytical methods and chemicals:

TCE and dechlorination daughter product analysis. Gas samples were removed from bottle headspaces and analyzed for TCE, DCE, VC and ethene concentrations using a gas chromatograph (GC) coupled to flame ionization detection. A five- point standard curve was developed for each compound of interest. Double walled nanotubes were selected instead of single walled nanotubes as they have more surface area, are less expensive and commercial access to them is less problematic. The DWNT selected for this study have a wall thickness of 1-2 nm, length 0.5- 2 μm and a density of 2.1 Sigma-Aldrich, St. Louis, MO.

Principal Findings and Significance Progress Report

Our major results at this time are related to the use of an anaerobic growth medium to examine bioavailability of TCE sorbed to DWNTs and its subsequent use by dechlorinating bacteria as outlined in Task 2. We examined biotransformation of TCE in the presence of different amounts of DWNTs as outlined in the methodology section above. Table 1 shows the experimental matrix for this task. Triplicate bottles were prepared for each treatment.

Table 1. Experimental protocol for examination of TCE bioavailability when added with carbon nanotubes.

Medium	TCE Conc. (mM)	Nanotube Loading (mg/bottle)					
Anaerobic	0.0015	0	1	5	15	30	60
Anaerobic	0.761	0	1	5	15	30	60

We developed methods to distribute the DWNTs to serum bottles—a somewhat difficult task. After several attempts to do this, the bottles were ultimately loaded with DWNTs using a DWNT stock solution that was prepared by sonicating a solution of anaerobic medium (600 mL) and DWNT (900 mg) for 24 hours. The appropriate amount of the resulting suspension was transferred to the 60 mL bottles using a glass syringe purged with sterile, anoxic gas in order to accomplish the desired DWNT loading as shown in Table 1. After the medium-DWNT suspension was added, anaerobic medium without DWNT was also added to achieve a final volume of 36 mL. The bottles were then amended with TCE from a methanol-TCE stock solution. After preparation, the bottles were incubated on a shaker at 25°C and analyzed for TCE after 4 days and then again after 8 days.

On day 14, the bottles were inoculated with 4 mL of a mixed culture containing *Dehalococcoides*. The bottles were analyzed again on day 28, 45 and 135. Our findings

suggest that TCE could be dechlorinated to DCE, VC and ethene by *Dehalococcoides* in the presence of the DWNT. Further analyses of these data are on-going and will be reported at a future date.

References

(1) National Research Council. 1994. Alternatives for Groundwater Cleanup. National Academy Press, Washington, D.C.

(2) United States Environmental Protection Agency. Last update Monday, February 14th, 2005.Technical Fact sheet on Trichloroethene. http://www.epa.gov/OGWDW/dwh/t-VOC/trichlor.html

(3) New Jersey Department of Environmental Protection. Last update August 31, 2005. News releases. "DEP Directs General Electric And Atlantic Metals to Conduct Cleanup along Rahway River". http://www.state.nj.us/dep/newsrel/2005/05_0109.htm

(4) Masciangioli, M.; Zhang, W.-X. March 1, 2003. Environmental Technologies at the Nanoscale. *Environmental Science & Technology*. p. 102A-108A.

(5) Hood, E. September 2004. Nanotechnology: Looking As We Leap. *Environmental Health Perspectives*. Vol.112, Number 13. p. A741-A747.

(6) Baughman, R.H.; Zakhidov, A.A. 2002. Carbon Nanotubes- the Route Toward Applications. *Science*. 297, p. 787-792.

(7) Long, R.Q.; Yang, R.T. 2001. Carbon Nanotubes as Superior Sorbent for Dioxin Removal. *Journal of American Chemical Society*. Vol.123. p. 2058.

(8) Fennell, D.E. 1998. Composition of Alternative Hydrogen Donors For Anaerobic Reductive Dechlorination of Tetrachloroethene. Ph.D. Dissertation. Cornell University.

(9) Huang, W.; Schlautman, M.A.; Weber JR, W. 1996. A distributed Reactivity Model for Sorption by Soils and Sediments. 5. The Influence of Near-Surface Characteristics in Mineral Domains. *Environmental Science and Technology*. 30. p. 2993-3000.

(10) Gossett, J.M. 1987. Measurement of Henry's Law Constants for C_1 and C_2 Chlorinated Hydrocarbons. *Environmental Science & Technology*. 21:202-208.

(11) Maymo- Gatell, X.; Anguish, T.; Zinder, S.H. July 1999. Reductive Dechlorination of Chlorinated Ethenes and 1,2 Dichloroethane by "*Dehalococcoides ethenogenes*" 195. *Applied and Environmental Microbiology*. Vol. 65, No. 7. p. 3108-3113.

(12) Fennell DE, Nijenhuis I, Wilson SF, Zinder SH, Häggblom MM. 2004. *Dehalococcoides ethenogenes* strain 195 reductively dechlorinates diverse chlorinated aromatic pollutants. *Environmental Science & Technology*. 38:2075-2081.