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# COMPETITIVE SORPTION AND DESORPTION OF CHLORINATED ORGANIC SOLVENTS (DNAPLs) IN ENGINEERED NATURAL ORGANIC MATTER

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Chlorinated organic solvents are among the most widespread organic contaminants present in the groundwaters and subsurface soils of many contaminated sites. The physicochemical properties of these organic chemicals, particularly when they are components of non-aqueous liquid phases (DNAPLs), make them difficult to remove once they have entered the subsurface (Pankow and Cherry 1996) and they remain among the most difficult contaminants to remediate in the environment. When released to surface or subsurface systems, DNAPLs migrate through unsaturated zones until they reach groundwater tables. They then disperse throughout the saturated soils, often forming pools on top of semi-impermeable subsurface formations or at the bottom of aquifers, creating long-term sources of contaminant plumes moving in the general direction of groundwater flow, thus potentially entering drinking-water supplies and threatening human health.

Poor performance and excessive costs have made traditional technologies and approaches less than satisfactory for remediation of DNAPL compounds at many contaminated sites. An innovative alternative approach using *in situ* irreversible immobilization and inactivation has been under development in our laboratory. The approach employs indigenous natural geosorbents, either as they exist or as appropriately modified, to bind and sequester chlorinated organic solvents irreversibly, thus eliminating or greatly reducing their associated environmental risks. Common components of DNAPLs are known to be sorbed by natural organic matter (NOM) (Allen-King *et al.* 1997). It is also known that the sorption reactions of NOM matrices for organic contaminants are directly related to specific physicochemical properties of those matrices and the degree of geochemical diagenesis

they have undergone (Binger *et al*. 1999, Weber *et al*. 1992, Young and Weber 1995, Xing and Pignatello 1997).

We have developed a superheated water technology that affects rapid diagenesis-like transformations in geologically young NOM to produce more condensed materials that are capable of effectively sorbing organic contaminants from environmental systems. A number of natural organic materials, *i.e*., a sphagnum moss peat (MI peat), oak leaves, green ash leaves, red maple leaves, pine bark, corn stalk and soybean stalk, were artificially "aged" using liquid-phase water at superheated temperatures and pressures in a batch reactor under an inert atmosphere ($N_2$). Elemental composition analyses show that carbon (C) and nitrogen (N) contents increase linearly and oxygen (O) and hydrogen (H) contents decrease linearly as treatment temperatures are increased over the range from 50$^o$C to 300$^o$C. Carbon and oxygen contents are changed much more sharply than those of hydrogen and nitrogen, thus the atomic ratios H/C, O/C and C/N ratios decrease and H/O and N/H increase with superheated water treatment, suggesting increasing degrees of geochemical maturation of geologically young organic matter with increasing treatment temperatures (Tissot and Welte 1984).

Solid state $^{13}$C NMR spectra for MI peat show that alkyl C and aromatic C significantly increased when temperature is increased from 50$^o$C to 250$^o$C, while carbohydrate C, carboxyl C and carbonyl C decreased. The results of these analyses clearly show diagenetic-like transformation of the treated materials with increasing temperatures of treatment. The hydrophobicity index (HI) and aromaticity index (ArI) calculated for MI peat samples increased respectively from 0.831 to 4.19 and from 0.71 to 1.178 with increasing treatment temperatures.

The effects of artificially accelerated geochemical condensation and maturation of natural organic matter on the sorption and desorption of trichloroethylene (TCE) and tetrachloroethylene (PCE) were investigated. The sorption and desorption of TCE and 1,2-dichlorobenzene (DCB) in the presence and absence of the competing PCE and 1,2-dichlorobenzene (DCB) were also examined. Initial batch tests to examine sorption behaviors were conducted by adding fixed amounts of treated and untreated organic materials, *i.e*., corn stalk, soybean stalks, oak leaves, red maple leaves, green ash leaves and pine bark, to aqueous solutions containing PCE. The results revealed that significantly greater amounts of PCE were sorbed by treated samples than by untreated materials. The sorption capacities of pine bark, corn stalk and soybean stalk were increased by as much as 13.5 fold after treatment with superheated water.

Complete isotherms for sorption and desorption of TCE and PCE by MI peat samples treated at temperatures ranging from 22$^o$C to 300$^o$C were determined. The sorption and desorption data were fitted well by the Freundlich isotherm model. Values of the Freundlich unit-capacity coefficient ($K_F$) can be observed (Figure 1) to increase with increasing treatment temperature for both sorption and desorption. Decreasing values of $n$, a parameter relating to both the relative magnitude and diversity of energies associated with a particular sorption process, with increasing temperatures for both the sorption and desorption steps indicates increased isotherm nonlinearity with increased temperatures of treatment. Strong correlations were observed between values of $K_F$ or $n$ and treatment

temperatures. Strong correlations were also found between values of $K_F$ or $n$ and atomic O/C ratios, with correlation coefficients ($R^2$) ranging from 0.841 to 0.983.

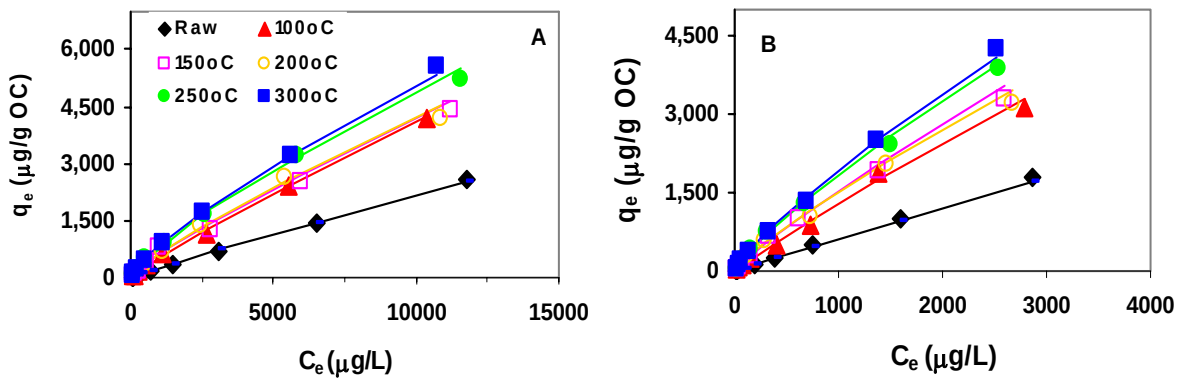


**Figure 1.** Isotherms for sorption (A) and desorption (B) of TCE by MI peat treated at different temperatures.

The sorption and desorption of TCE in the presence and absence of the competing PCE and 1,2-dichlorobenzene (DCB) were also examined for treated and untreated MI peat. The sorption and desorption data for TCE are still fitted well by the Freundlich isotherm model in the presence of the competing solutes (Figure 2). Both PCE and DCB were found to greatly depress TCE sorption, with PCE having greater effects than DCB, presumably because the molecular structure of the former is more similar to that of TCE. The nonlinearity of sorption and desorption isotherms of TCE increased in the presence of PCE and DCB.

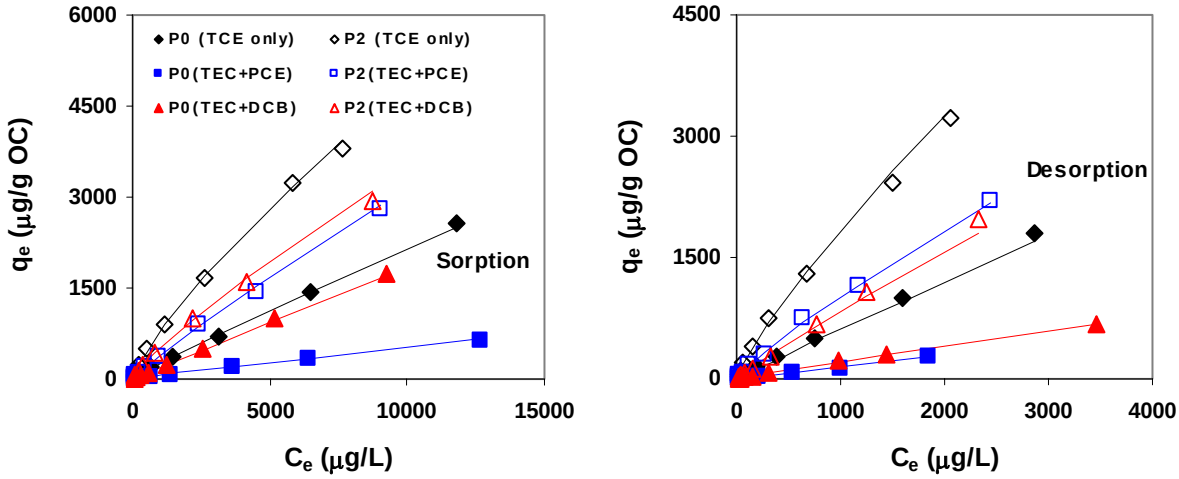


**Figure 2.** Effect of PCE and DCB on the sorption and desorption isotherms of TCE by treated (P2) and untreated MI peat (P0).

Organic contaminants are commonly present along with heavy metals at field contaminated sites. Competive sorption and desorption isotherms for DCB by treated and untreated pine needle were also determined in both the absence and presence of cadmium (100 ppm).

Pine needles were treated using superheated water at 195$^{o}$C with 50% 0.25 M $Na_4P_2O_7$ solution. The sorption and desorption isotherms of DCB were again fitted well by the Freundlich model with coefficients ($R^2$) greater than 0.988 (for sorption) and 0.967 (desorption). The treated pine needles had much higher sorption capacities for DCB than the untreated raw materials. In the presence of cadmium, DCB sorption was decreased for both treated and untreated pine needles indicating there was a competing sorption between DCB and cadmium. The results also show that the sorption capacity of treated pine needle increased for cadmium.

The results of the work reported here demonstrate that geochemical condensation and maturation of geologically young organic matter can be artificially accelerated using superheated water. The results further demonstrate that the sorption capacities and nonlinearities of artificially aged NOMs for organic chemicals, including such DNAPL components as chlorinated organic solvents, are greatly increased.

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**REFERENCES**

Allen-King, R.M., McKay, L.D. and Trudell, M.R. 1997. Organic Carbon Dominated Trichloroethene Sorption in a Clay-Rich Glacial Deposit. *Ground Water*, **35**, 124-132.

Binger, C.A., J.P. Martin, R.M. Allen-King and M. Fowler. 1999. Variability of chlorinated-solvent sorption associated with oxidative weathering of kerogen. *J. Contam. Hydrol*. **40**: 137-158.

Pankow, J.F. and J.A. Cherry. 1996. Dense chlorinated solvents and other DNAPLs in groundwater: History, behavior and remediation.

Tissot, B. P. and Welte, D. H. 1984. Petroleum Formation and Occurrence; Springer-Verlag: New York.

Weber, W. J., Jr., McGinley, P. M. and Katz, L. E. 1992. A distributed reactivity model for sorption by soils and sediments. 1. Conceptual basis and equilibrium assessments. *Environ. Sci. Technol*. **26**: 1955-1962.

Xing, B.S. and J.J. Pignatello. 1997. Dual-mode sorption of low-polarity compounds in glassy poly(vinyl chloride) and soil organic matter. *Environ. Sci. Technol*. **31**: 792-799.

Young, T.M. and W.J. Weber, Jr. 1995. A distributed reactivity model for sorption by soil and sediments. 3. Effect of diagenetic processes on sorption energetics. *Environ. Sci. Technol*. **29**: 92-97.