Final Report
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Engineered Natural Geosorbents for *In Situ* Immobilization of DNAPLs and Heavy Metals

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A. Introduction

Extensive subsurface contamination by dense non-aqueous phase liquid (DNAPL) organic solvents and heavy metals is common place at many DOE facilities. Poor performances and excessive costs have made traditional technologies and approaches less than satisfactory for remediation of such sites. It is increasingly apparent that marginal improvements in conventional methods and approaches will not suffice for clean up of many contaminated DOE sites. Innovative approaches using new and/or existing technologies in more efficient and cost-effective ways are thus urgently required.

The irreversible in-situ immobilization and inactivation concept proposed in this study is an innovative and promising approach. The concept is predicated on the hypothesis that natural geosorbents, either as they exist or as appropriately modified, can be employed to bind and sequester chlorinated organic solvents, other hydrophobic organic compounds and heavy metals irreversibly, and thereby eliminate or greatly reduce their associated environmental risks. The technologies that can be brought to bear on the implementation of this concept are for the most part readily available, but in neither organized form nor optimized state. The research described here effectively addresses both deficiencies.

Common components of dense non-aqueous-phase liquid (DNAPL) contaminants, including chlorinated organic solvents and polycyclic aromatic hydrocarbons (PAHs), and most heavy metals are known to be sorbed by various types of natural organic matter (NOM), mineral, and/or clay components of typical soils and sediments. It is also known that the specific physicochemical properties of these geosorbents significantly effect the relative strength and extent of their respective sorption reactions with different organic and inorganic contaminants. The more aromatic and chemically condensed (i.e. “hard carbon”) forms of soil/sediment NOM have much higher and less reversible sorption capacities for organic chemicals and heavy metals than do the more aliphatic and highly amorphous (i.e., “soft carbon”) forms (Weber et.al,1992). The sorption properties of soil NOM matrices are thus directly related to the degree of geochemical diagenesis they have undergone in the terrestrial and aquatic environment. It has recently demonstrated in our laboratories that the sorption energies and capacities of soil sediment NOM matrices for organic chemicals can be greatly increased by treatment with superheated water at accelerated temperatures and pressures to simulate and accelerate geochemical diagenesis of SOM. The sorption capacities of many other naturally occurring materials (e.g., bark, peanut husks, peat, bentonite, zeolites, etc.) for heavy metals also have been shown to be improved by thermal treatment.

There is mounting evidence that many sorbed hydrophobic organic contaminants and heavy metals become more strongly sequestrated and thus less mobile and bioavailable to environmental receptors after prolonged periods of contact with soils, i.e., the so-called “aging effect”. Enhancement in the sorption and sequestration properties of natural soils and sediments can also be achieved by adding relatively low cost sorbent materials. In addition to the possibility of enhancing sequestration capacities of indigenous soils by modification of their SOM, it is also likely that amendments of such soils with other inexpensive and readily available natural materials can also be used to produce inexpensive “smart” geosorbents. It can logically be hypothesized that the environmental risks posed by chlorinated organic solvents, PAHs and heavy metals can be substantially reduced if these contaminants are bound so strongly by the soils and sediments of a given system that they are rendered essentially immobile, and thus also biologically unavailable for potential food-chain magnification.

Project Objectives

The overarching goal of this study has been development of a comprehensive data and knowledge base with respect to the mechanisms of binding and sequestration of DNAPL components, hydrophobic organic contaminants and heavy metals by different types of soil matrices. Our ultimate objective was the application of this knowledge and information base as a platform for designing specifically engineered geosorbents capable of in-situ long-term immobilization and inactivation of non-aqueous phase organic liquids and heavy metals at contaminated DOE sites and facilities. The engineered geosorbents were developed using readily available organic and inorganic materials, modified as necessary to impart a prescribed set of sequestration properties. Such modifications were in some cases involve treatments to change the inherent properties of the native soil matrices, and in some cases the addition of other low-cost and readily available natural materials. The end products of the research efforts will be a suite of cost-effective media that can be prepared and applied on-site to immobilize and inactivate DNAPL, other organic chemical and heavy metal contaminants.

Specific research design criteria for accomplishing the overarching goal and end objective defined above included: 1) design of engineered modifications for selected indigenous geosorbents to further enhance their sorption and sequestration capacities with respect to the target contaminants; 2) monitoring and evaluation of the sorption/sequestration performance of the indigenous and modified natural geosorbents using the technology referenced in objective 1 above; and 3) parallel tests of the bioavailability of sequestered contaminants to appropriate indicator organisms (e.g., earthworms and plants) with respect to their toxicities and potential bioaccumulation.

B. Results and Accomplishments

1. Production of engineered natural geosorbents.

An innovative technology for effecting rapid diagenesis-like transformations in geologically young natural organic matter (NOM) to produce chemically more condensed materials capable of effectively sorbing organic contaminants from environmental systems has been developed in our laboratories. At the outset of each treatment, an organic raw material was placed (with minimum headspace) in a bench scale LC series reactor, and N_2-purged Mili-Q water was added to the reactor in an amount required to provide a predetermined water content. The reactor was then purged with nitrogen gas for at least 30 minutes to eliminate residual oxygen, after which the gas inlet and outlet valves were closed and heating of the reactor to a preset desired temperature was initiated. The organic materials were treated at various temperature and pressure conditions.

A number of natural organic materials comprising various forms of cellulose, hemicellulose, lignin and humics (i.e., a relatively old sorghum moss peat, a young peat, oak leaves, green ash leaves, red maple leaves, pine bark, corn stalk and soybean stalk) have been used as raw source materials. All of them are readily available, inexpensive, and eventually incorporated into environmental systems by natural processes. The selected organic materials were treated using liquid-phase water at superheated temperatures and pressures under an inert atmosphere (N_2) to produce condensed organic solids we refer to here as engineered natural organic sorbents (ENOS). Treatment conditions were optimized in terms of temperature, time, moisture content, and catalyst addition. Upon completion of a production run the treated materials were removed from the reactor, transferred to a fume hood, dried, ground, passed through a 1-mm sieve. The changes in their physicochemical properties were characterized and their effects on immobilization of organic contaminants and heavy metals in soils were determined.

2. Characterization of the physicochemical properties of ENOS materials produced.

Significant changes in the physicochemical properties of the treated peat were observed in terms of elemental composition, functional groups and molecular structure, pH, density, surface area and surface morphology.

2.1. Elemental Compositions. A calibrated LECO CHN-1000 Analyzer employing a high-temperature combustion technique was used to perform elemental analyses of carbon (C), hydrogen (H), nitrogen (N) on the organic materials before and after superheated water treatment. Oxygen (O) contents were determined by mass balance and ash content

The initial mass- percent compositions of elemental C, H, N and O contents of the raw organic materials varied somewhat (Table 1). After superheated water treatment, C and N contents were increased by factors ranging respectively from 1.23 to 1.46 and 1.41 to 2.01. Conversely, H and O contents were decreased by as much as 21.1% and 57.2% respectively.

Table 1. Elemental Compositions [a] of ENOS Source Materials Prior to and After Processing

	C [b]		H		N		O	
	Before	After	Before	After	Before	After	Before	After
CA peat [c]	52.2	64.1	5.96	4.70	0.73	1.13	38.4	21.3
MI peat [c]	45.2	63.3	6.03	5.32	2.51	3.70	41.8	19.2
Almond husks [c]	49.2	70.8	6.40	5.25	0.48	0.75	41.7	18.7
Ash leaves [c]	49.8	69.1	6.61	6.31	0.81	1.42	41.3	19.2
Oak leaves [c]	48.0	63.2	6.66	5.78	0.80	1.29	42.7	23.3
Pine needles [c] [d]	50.6	71.1	6.93	6.36	0.33	0.66	39.4	17.6
Corn stalks [c]	46.1	67.3	6.31	5.55	0.84	1.69	45.3	21.0
Peanut husks [c]	50.8	70.0	6.36	5.52	0.85	1.24	39.5	17.7
Soybean stalks [c]	44.6	62.6	6.28	5.89	0.79	1.31	46.9	24.0
Wheat straw [c]	46.4	67.1	6.33	5.56	0.39	0.77	45.4	22.1

[a] Mass Percent, [b] Average of two replicates, [c] CA, MI peat and almond husks were treated at 250 °C, and other natural organic materials were treated at 200 °C, [d] Pine bark and cones had elemental compositions similar to those of pine needles.

To gain better insight to specific relationships between treatment temperatures and changes in elemental composition, the effects of processing the MI peat, ash leaves, maple leaves, oak leaves, corn stalks and soybean stalks were determined over greater ranges of temperature. \
The data shown in Figure 1 reveal that C and N contents increased linearly and H and O contents decreased linearly with increasing treatment temperature. Correlation coefficient (R^2) values for the linear relationships shown in Figures 1 range from 0.849 to 0.996. As treatment temperatures increase the C and O contents change much more sharply than do the H and N contents. Increasing C and decreasing H and O mass percent compositions can be attributed to deoxygenation and dehydrogenation reactions, with oxygen-associated functional groups such as carbonyl, carboxyl, and methoxyl groups, being reduced, and oxygenated aliphatic group carbons becoming more aromatic and condensed (Ioselis, Rubinsztain et al. 1985; Lu, Vassallo et al. 1997).

Indices of atomic ratios are useful for identification of humic substances from different sources, the monitoring and elucidation of structural changes that occur as a result of specific geochemical reactions, and the degrees of humification, maturation and oxidation of NOMs in specific environmental systems and situations (Steelink 1985; Belzile, Joly et al. 1997). As illustrated in Figure 2, a strong linear relationship between atomic ratio H/C vs. O/C atomic ratios was observed for various degrees of processing of ash leaves, corn stalks, maple leaves, MI peat, oak leaves, and soybean stalks, with correlation coefficients ranging from 0.989 to 0.999. Not surprisingly, these atomic ratios changed similarly with increased temperature for most of the raw organic materials tested, with correlation coefficients ranging from 0.806 to 0.998. The single exception was the N/H atomic ratio for MI peat, an exception that can be attributed to the relatively high initial nitrogen content of this raw source material.

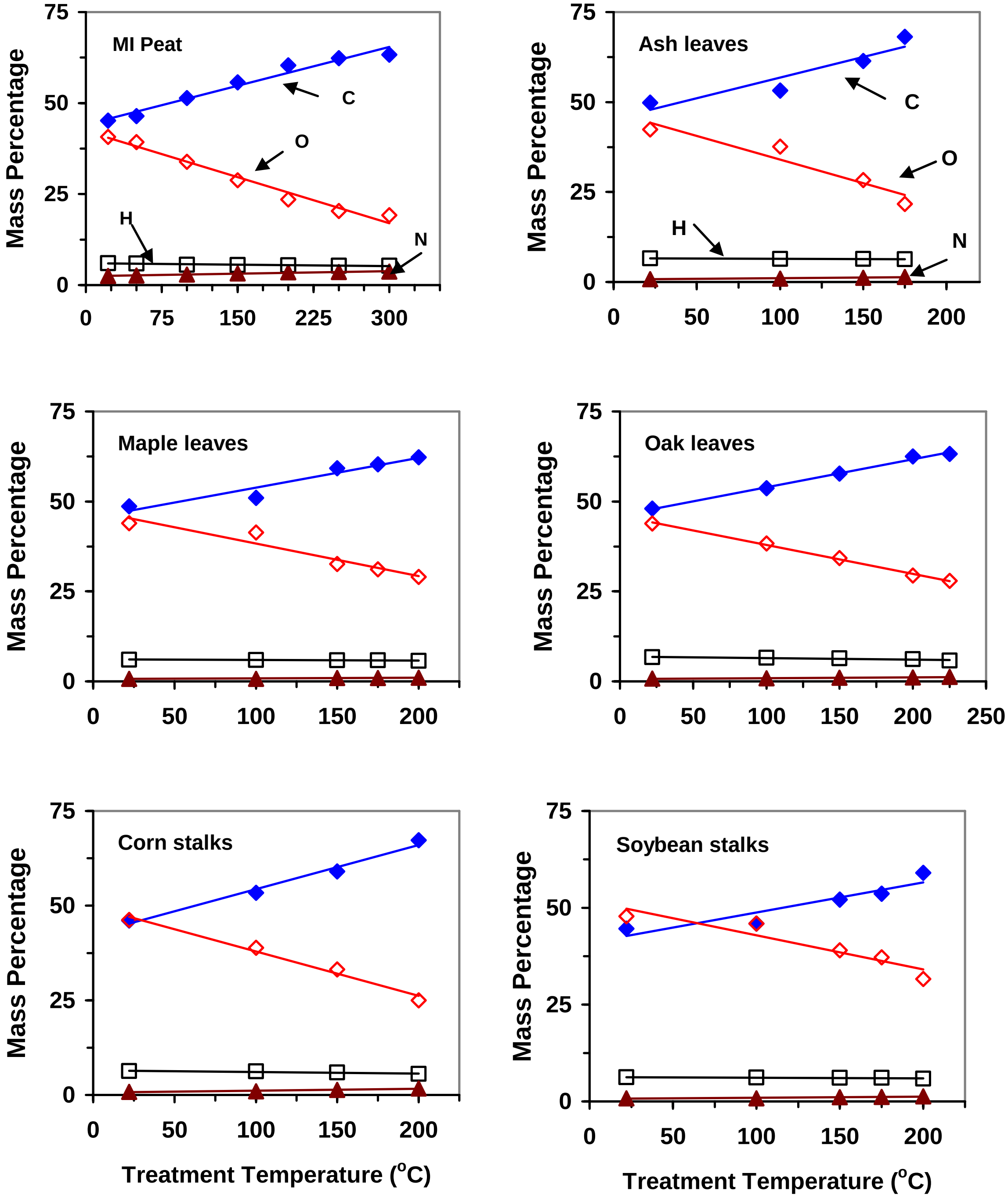

Figure 1. Effects of treatment temperature on elemental compositions of selected natural organic materials tested

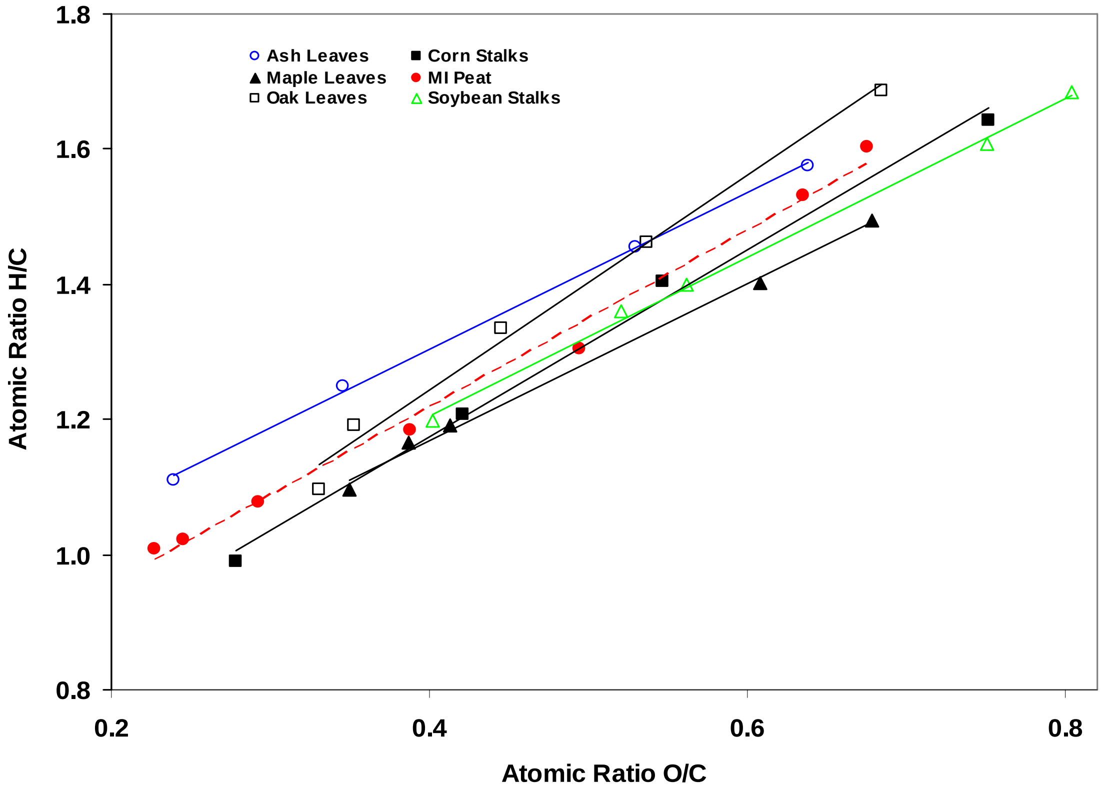

Figure 2. Relationships between oxygen/carbon and hydrogen/carbon atomic ratios for organic materials treated by superheated water at different temperatures

2.2. Surface Areas and Morphologies. The BET surface areas of MI peat can be observed in Figure 3A to have remained essentially unchanged by treatment at 50°C and 100°C for two hours, but then to have increased sharply by an order of magnitude when treatment temperature was increased to 150°C. Surface areas subsequently decreased with further increases in treatment temperatures from 150°C to 300°C however, although still remaining 4-7 times greater than that of the untreated sample. Similar results were obtained for soybean stalks (Figure 3B), CA peat, and pine needles (data not shown), the other three raw materials analyzed for surface areas and morphologies. These findings suggest that changes in the surface areas of such natural organic materials can be initiated only under conditions of superheating (> 100 °C) liquid water, a condition in which the chemistry (e.g., dielectric constant, ionic dissociation constant and density) of this medium changes dramatically (Uematsu and Franck 1980; Marshall and Franck

1981; 1988). While the available data does not allow rigorous interpretation of this significant surface area behavior, it appears an interesting and important related area for further study.

Scanning electronic microscopy (SEM) images reveal that the surface morphology of MI peat is also changed significantly with increased treatment temperature (Figure A-1 in the Appendix). While untreated MI peat surfaces are observed to be highly furrowed, processing at increased temperatures appears to render surface morphology smoother and more "condensed" in appearance.

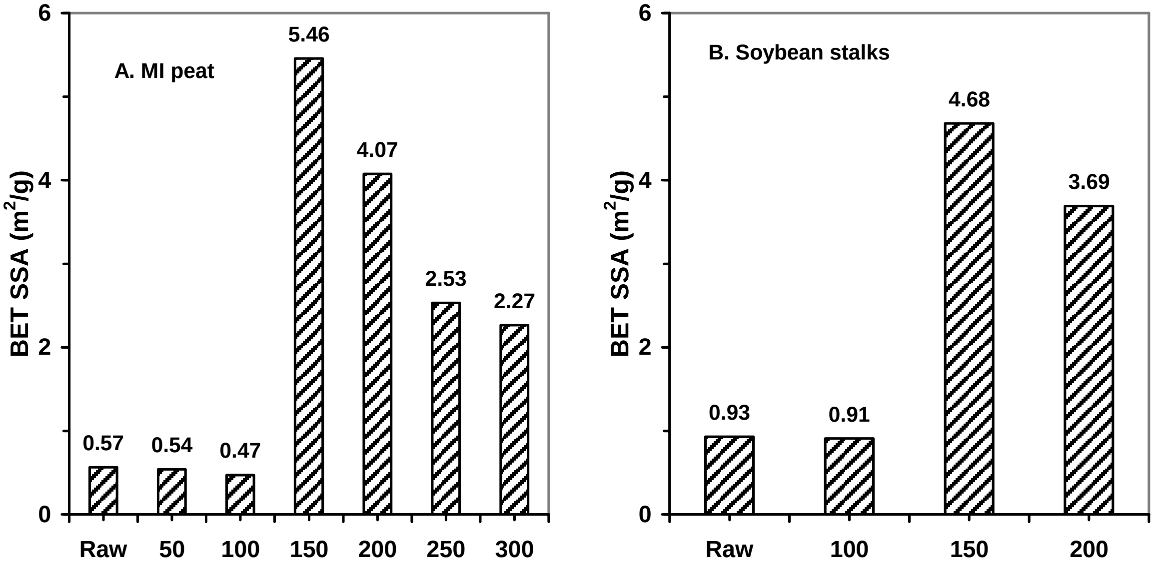

Figure 3. Effects of thermal treatment on specific surface areas of MI peat (A) and soybean stalks (B)

2.3. FTIR Analyses. Typical infrared radiation frequency ranges in which specific functional groups and structures observed for organic matter are listed in Table A-1 of the Appendix to this Report, which begins on page 73. FTIR analysis of treated and untreated organic materials were performed using a Nexus 870 FT-IR Spectrometer.

The FTIR spectra of Michigan peat shown in Figure 4 reveal the presence of aliphatic, aromatic, carboxylic, and carbohydrate forms of organic carbon. Distinct changes are observed after treatment of this material at different superheated water temperatures. While the aliphatic C of the material did not change significantly as treatment temperature was increased from 50 ^{o}C to 100 ^{o}C, its aliphatic C increased remarkably from 150 ^{o}C to 300 ^{o}C and formed two distinct and sharp peaks at wave number of 2927 cm^{-1} and 2850cm^{-1}. Its aromatic C with C=C stretching at 1630 cm^{-1} and 1242 cm^{-1} greatly increased as treatment temperature was increased from 50°C to 300°C. As noted in Figure 4, there was initially an increase in the bonded OH group for carboxylic C at a temperature of 50 °C, followed by a substantial decrease as temperatures increased from 100°C to 300°C.

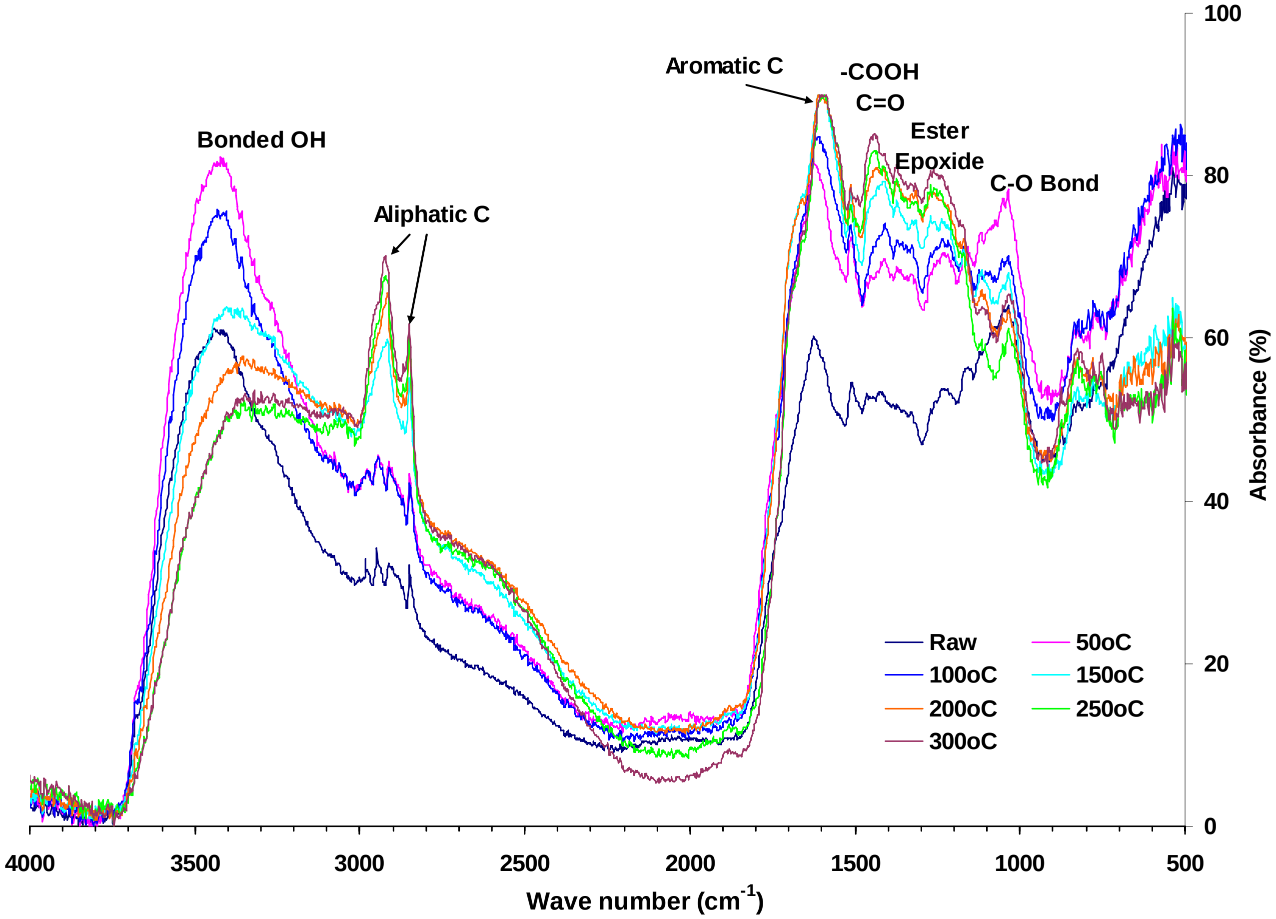

Figure 4. FTIR spectra for MI peat treated at different superheated water temperatures

The carboxylic C, aliphatic C, aromatic C, and carbohydrate C structures observed in raw corn and soybean stalks were remarkably changed after superheated water treatment at 100°C, 150°C and 200°C (Figure A-2 in the Appendix). For corn stalk samples, hydroxyl groups associated with O-H stretching at 3440 cm^{-1} slightly increased at 100°C, then decreased from

150^{o}C and 200^{o}C. Aromatic C at 1604cm^{-1}, carboxylic C at 1704 cm^{-1}, and aliphatic C at wave numbers of 2931 cm^{-1}, 1340 cm^{-1}, 1191 cm^{-1}, and 1120cm^{-1} increased as temperature increased from 100^{o}C to 200^{o}C. Similar changes in carbon structures and functional groups for soybean stalks occurred when temperatures were increased from 100 ^{o}C to 200 ^{o}C. Significant changes were also observed in the FTIR spectra of other natural organic materials tested (i.e., almond husks, pine bark, pine cones, pine needles, ash leaves, oak leaves, peanut husks, and wheat straw) after treatment (Figures A-3 and A-4 in the Appendix).

2.4. Solid-State ^{13}C NMR Analyses. Changes in the molecular structures and functional groups of MI peat samples were further characterized using solid-state ^{13}C-NMR analysis before and after superheated water treatment. Integrations were performed over the 0-210 ppm range of chemical shift in NMR spectral regions. The NMR results are consistent with the FTIR results discussed above, confirming the changes in alkyl, methoxyl, O-alkyl, aromatic, phenolic, and carboxyl carbons as functions of treatment temperatures. As shown in Figure 5 and in Table A-2 of the Appendix, alkyl C and aromatic C were increased significantly as a result of processing. Conversely, oxygenated aliphatic C, carbohydrate C, and carboxyl C gradually decreased as treatment temperatures were increased from 50 ^{o}C to 250 ^{o}C. At 250 ^{o}C the functional carbon forms are dominated by aliphatic and aromatic carbons, and methoxyl, o-alkyl, carbohydrate and carboxyl carbons are significantly reduced. The relative percentages of aliphatic and aromatic carbons increased respectively from 23.1 and 37.2% for the untreated peat to 36.6 and 56.7% for the peat treated at 250^{o}C. Percentages of carbohydrate, carboxyl and carbonyl carbons decreased respectively from 29.1, 6.9 and 2.9% to 2.72, 2.8, and 1.2%. Comparing the five functional forms of organic carbon for untreated peat and peat treated at 250^{o}C, the total percentage increase in aliphatic and aromatic carbon is approximately equal to the total percentage decrease of oxygenated aliphatic, carboxyl and carbonyl carbon, indicating that increases in aromatic and aliphatic carbons came at the expense of oxygen-containing carbons.

The aromaticity (I_{Ar}) and hydrophobicity indices (I_H) are often used respectively to quantify degrees of organic carbon aromaticity and hydrophobicity in natural organic matter. These indices were calculated for MI peat from the ^{13}C-NMR spectra. I_{Ar} and I_H values were calculated for both treated and untreated MI peat samples. The results show that I_{Ar} values gradually increase as treatment temperatures increase. For the MI peat they increase by a factor of 1.8 from 0.65 for the untreated control to 1.18 for the peat treated at 250^{o}C. The corresponding I_H

values increase even more significantly; i.e., by a factor of 5.0 from 0.81 for the untreated control to 4.15 for peat treated at 250 °C. The plots of I_{Ar} and I_H values as functions of treatment temperatures and O/C atomic ratios given in parts A and B of Figure A-5 show strong linear correlations between both indices and treatment temperature, with correlation coefficients of 0.976 and 0.938, respectively.

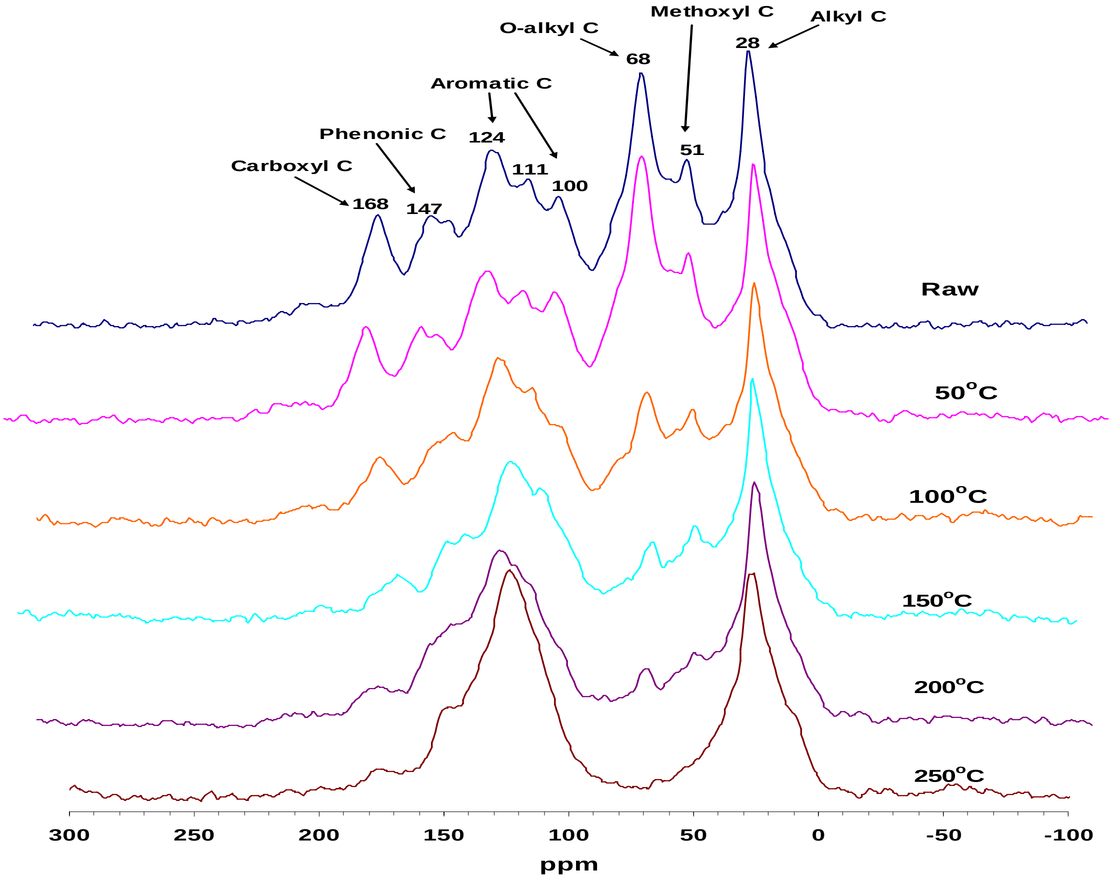

Figure 5. Solid state 13C-nuclear magnetic resonance (NMR) spectra of MI peat treated at different superheated water temperatures (with water/solid: 1/2)

Not surprisingly, strong relationships are also observed in parts C and D between the aromaticity and hydrophobicity indices and the corresponding elemental atomic ratios of O/C and H/O. As O/C ratios increase I_{Ar} and I_H values decrease. As H/O values increase both I_{Ar} and I_H increase.

3. Characterization of the sorption and desorption properties of ENOS materials

The sorption/desorption properties of the modified natural organic materials were examined with respect to three dense non-aqueous phase liquid (DNAPL) compounds, e.g., trichloroethylene (TCE), tetrachloroethylene (PCE), and 1,2-dichlorobenzene , one polycyclic aromatic hydrocarbons (PAHs), i.e., phenanthrene, and two heavy metals, i.e., cadmium and Zn.

3.1. Chlorinated compounds.

Initial tests to examine the sorption and desorption behaviors of DNAPL compounds 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 (5000 ppb) at room temperatures for 2-3 days. After completion of the sorption steps, the organic material samples were placed in fresh water solution to examine the extent to which the sorbed PCE was then desorbed. As illustrated in Figure 6, significantly greater amount of the PCE was sorbed by treated samples than by untreated materials. Sorption capacities of pine bark, corn stalk and soybean stalk were increased up to 13.5 times after they were treated with superheated water at 200°C. Desorption was greatly decreased for the treated materials.

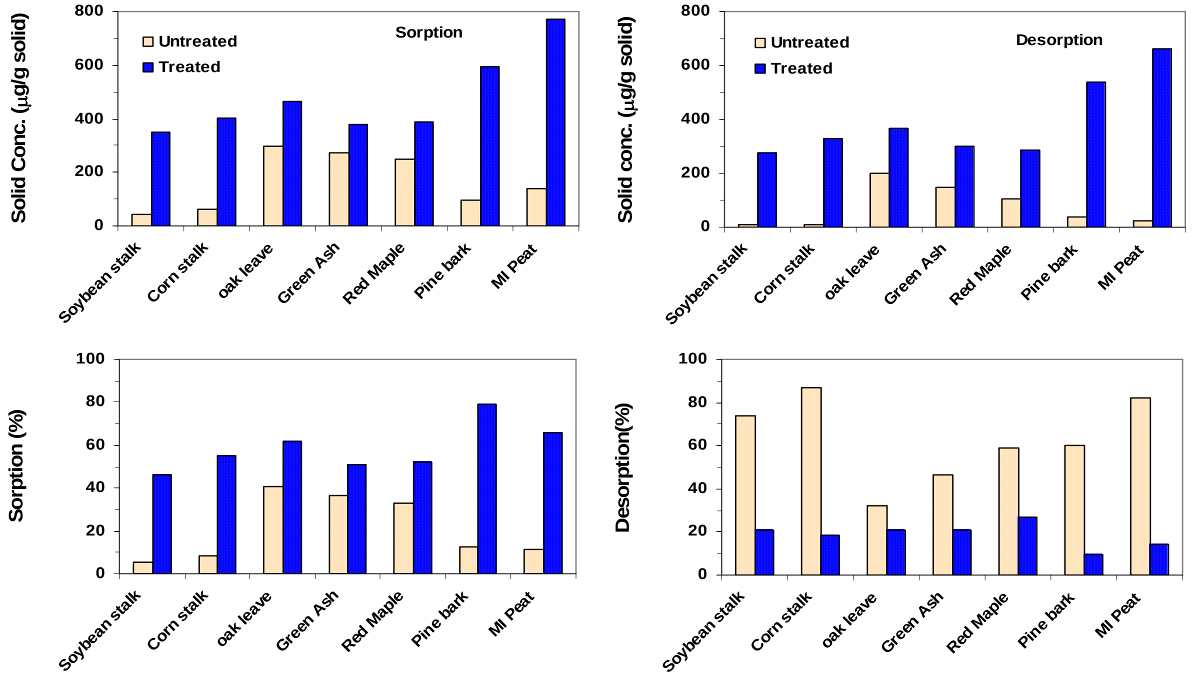

Figure 6. Sorption and desorption of PCE by different natural organic materials before and after superheated water treatment

Complete isotherms for sorption and desorption were determined for TCE by MI old peat samples treated at temperatures ranging from 50°C to 300°C for five hrs with 50% water content at N_2 atmosphere and untreated pine needle (PN), pine bark (PB), peanut husk (PH), almond shell (AS), and MI young peat (MP) were determined. The Freundlich model was used for analyzing the equilibrium sorption and desorption data. This model has the form

$$q_e = K_F C_e^n \qquad (1)$$

where q_e and C_e are solid phase and residual solution phase equilibrium concentrations, respectively, K_F is the Freundlich unit-capacity coefficient, and n is a parameter relating to both the relative magnitude and diversity of energies associated with a particular sorption process.

The result of model fits to the sorption and desorption data of MI old peat for TCE are shown in Figure 7 and for PCE in Figure A-5(Appendix). Related TCE sorption and desorption model parameters are summarized in Table 2. Values of K_F can be observed to increase with increasing treatment temperature for both sorption and desorption. The decreasing n values with increasing temperatures for both the sorption and desorption indicate increased isotherm nonlinearity with increased temperatures of treatment. There are strong correlations between values of K_F and n and treatment temperatures and atomic ratios of O/C with correlation coefficients (R^2) ranging from 0.841 to 0.983.

The sorption and desorption of TCE in the presence and absence of the competing PCE and 1,2-dichlorbenzene (DCB) were also examined for treated and untreated MI peat. 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 A-7 in the Appendix).

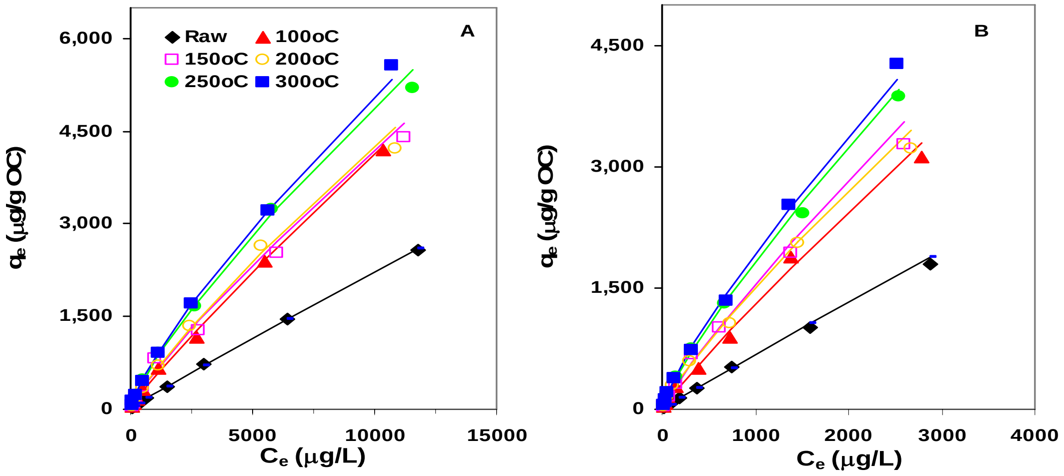

Figure 7. Isotherms for TCE sorption (A) and desorption (B) by MI peat treated at different temperatures for 5 hrs at 50% water content.

Table 2. TCE Freundlich model parameters for MI peat treated at different temperatures

	Sorption			Desorption		
Peat	K_F [a]	n	R^2	K_F	n	R^2
Raw	0.378	0.943	0.998	0.743	0.984	0.998
100°C	1.106	0.893	0.996	2.264	0.918	0.994
150°C	1.814	0.841	0.996	3.552	0.879	0.996
200°C	1.940	0.835	0.992	4.486	0.848	0.994
250°C	3.295	0.793	0.998	6.140	0.825	0.997
300°C	3.731	0.783	0.998	7.132	0.811	0.998

a: Units in (μg/g)/(μg/L) ^{n}

3.2. PAH compounds.

PAH compounds are often found to co-exist with chlorinated organic contaminants as DNAPL components in many contaminated sites. The sorption capacities and behaviors of produced ENOS for phenanthrene, a representative PAHs, were also determined. The effects of treatment temperatures, processing time, and moisture contents on the enhancement of sorption capacities of organic materials for phenanthrene were evaluated.

3.2.1. Effects of Temperature. MI peat and soybean stalk samples treated for five hrs at 50% (v/w) moisture content at temperatures ranging from 100 °C to 300 °C under a nitrogen atmosphere were exposed to the essentially saturated phenanthrene aqueous solution for 21 days. As illustrated in part A of Figure 8, the percentages of initial phenanthrene sorbed by MI peat samples from aqueous solution greatly increased greatly as a function of increased processing temperature, ranging from 58% for the unprocessed (22 °C room temperature) peat to 97% for that processed at 300°C. Moreover, the percentages of initial phenanthrene sorbed by the peat that were released in the subsequent desorption step of the experiment decreased by factors of up to nearly 30, ranging from 43% to 1%. Part B of Figure 8 shows the same results expressed in terms of solid-phase equilibrium phenanthrene concentrations. It can be noted also that the sorption capacity of MI peat for phenanthrene reached its maximum at 250°C.

Parts C and D of Figure 8 show comparable data regarding the effects of processing temperature on soybean stalk sorption/desorption behavior, and similar results were observed for corn stalks, oak leaves, almond shells, ash leaves, maple leaves, peanut husk, pink bark, pine cones, pine needles, and wheat straw (Figures A-8 and A-9 in the Appendix).

<u>3.2.2. Effects of Processing Time.</u> The effects of the duration of processing on the capacities of MI peat for sorption of phenanthrene were determined on samples processed at a temperature of 250^{o}C and 50% moisture content for from 1 to 24 hours. The results (Figure A-10 of Appendix) revealed that the percentages of phenanthrene sorbed were almost doubled from 45% for raw MI peat to 86% for peat samples processed for only one hr. As processing time was increased from 3 to 5 hrs, these percentages increased marginally to 92% and 96%, after which longer processing times of 10 and 24 hrs resulted in essentially no further increases in sorption capacity. The subsequent desorption of the phenanthrene was also reduced significantly by superheated water processing. More than half (58 %) of the phenanthrene sorbed by the raw peat samples was released during the desorption step of the experiment , whereas only 11%, 4%, and 3% of the phenanthrene sorbed on the processed peat samples treated respectively for 1, 5 and 24 hrs, desorbed. respectively.

<u>3.2.3. Effects of Moisture Content.</u> MI peat samples were treated at 250^{o}C for 5 hrs with moisture contents of 0, 25, 50, 75 and 100% water (v/w). Sorption of phenanthrene from the near saturated aqueous solution was observed to increase as water content during processing was increased from 0 to 50%, and then to decrease slightly as water content was further increased to 75% and 100%. More specifically, 72% of the initial solute was sorbed by peat processed without water, the sorption percentages increased to 85%and 92% for peat processed respectively with 25% and 50% moisture, and then decreased to 88% and 85% for peat processed respectively with 75% and 100% of moisture (Figure A-10 in Appendix). Desorption of the sorbed phenanthrene initially decreased as a function of increased moisture content during processing from 21% for the peat treated without water to 7 % for that processed at 50 % moisture level and then increase modestly to 11% for the peat processed at 100% moisture.

From the above data, the degrees of enhancement of sorption capacities of MI peat samples for phenanthrene were dependent on a number of treatment conditions. It is clearly showed that treatment temperature is the most important factor for improving their physicochemical properties and sorption properties. Optimal treatment conditions were 200^{o}C to 250^{o}C at 50%

moisture content for five hours in batch reactors under inert atmosphere. These treatment conditions were used for further experiment for treating peat and other organic materials.

The effects of temperatures ranging from 50^{o}C to 300^{o}C during processing at 50% moisture levels on the sorption capacities of MI peat were further evaluated by measurement of isotherms for sorption and desorption of phenanthrene. Equilibrium sorption and desorption data and best-fit Fruendlich model are shown in Figure 9, and related Freundlich model parameters are summarized in Table 3. As processing temperatures increased, the Freundlich unit-capacity coefficients (K_F) increased dramatically, while the best-fit model n values decreased for both sorption and desorption. Increased values of K_F indicate increased sorption capacities while decreasing n values indicate increasing isotherm nonlinearity. The n values for sorption and desorption decreased from 0.974 for raw peat to 0.665 for peat treated at 300^{o}C. This is not unexpected because the peat samples became more condensed, and aromatized as processing temperatures increased, a factor previously demonstrated as impacting the sorption behaviors of organic sorbents(Johnson et al. 1999; Johnson et al. 2001)

Sorption and desorption isotherms for phenanthrene were also determined for other treated and untreated natural organic materials, i.e., MI young peat, pine cones, pine needles, pine bark, peanut husks, and almond shells. The results showed their isotherms are fitted well with the Freundlich model, with coefficient (R^2) values greater than 0.957 (Figure 10 and Table 4). The K_F values were increased by a factor of 13.4 to 30.3 for sorption isotherms, ranging from 6.5 to 18.9 for untreated materials and from 123.7 to 502.1 for treated materials, and by a factor of 4.36 to 12.8 for desorption isotherms, ranging from 29.8 to 56.9 for untreated materials and from 145.3 to 524.4 for treated materials. Their n values decreased for both sorption data, ranging from 0.801 to 1.010 for untreated materials and from 0.608 to 0.756 for treated materials, and desorption data, ranging from 0.702 to 0.991 for untreated materials and from 0.693 to 0.789 for treated materials. The results suggested that the sorption of phenanthrene by the natural organic materials tested increased and the subsequent desorption of the sorbed phenanthrene decreased as a result of superheated water treatment.

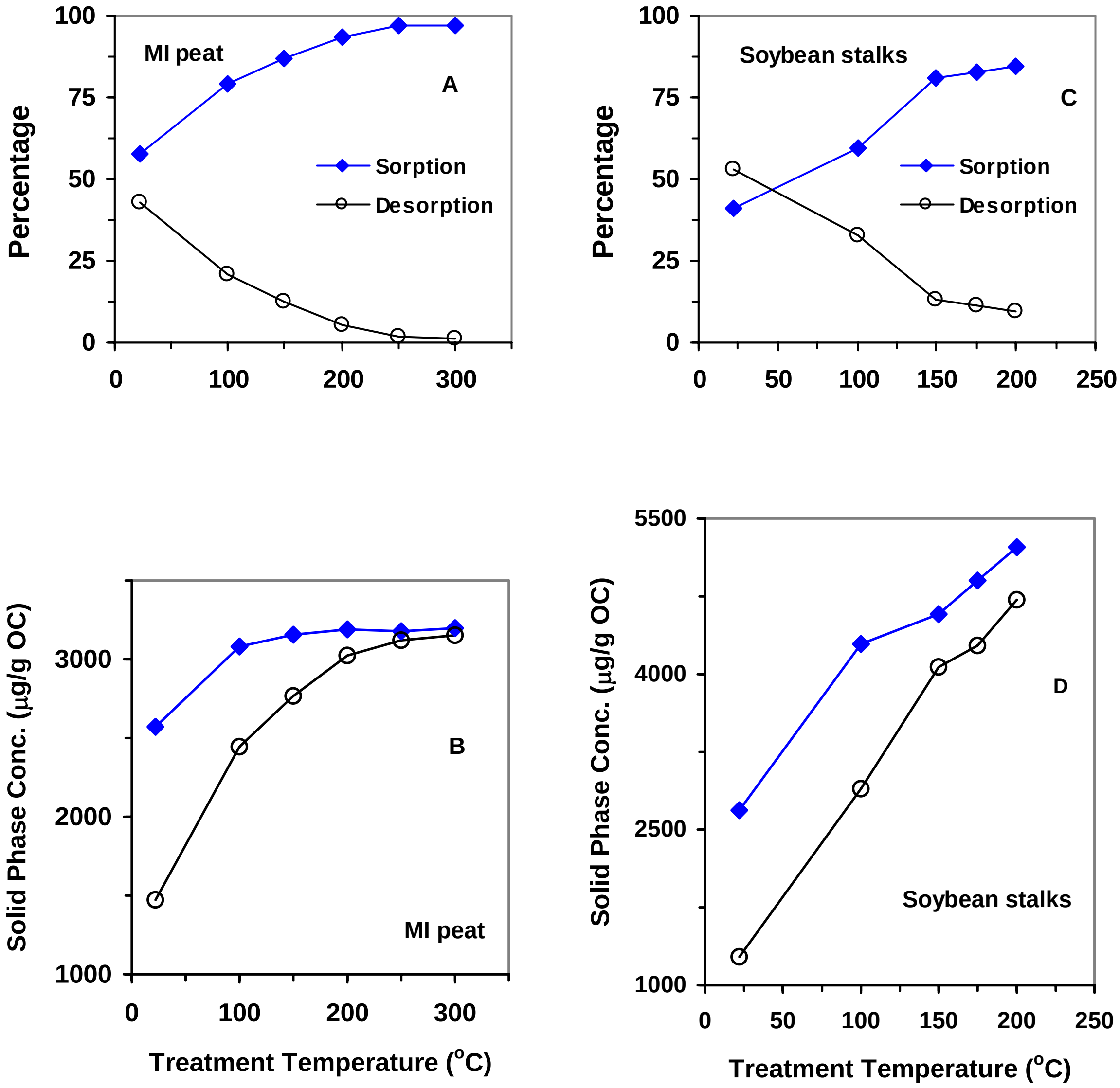

Figure 8. Effects of treatment temperature on the sorption and desorption of phenanthrene

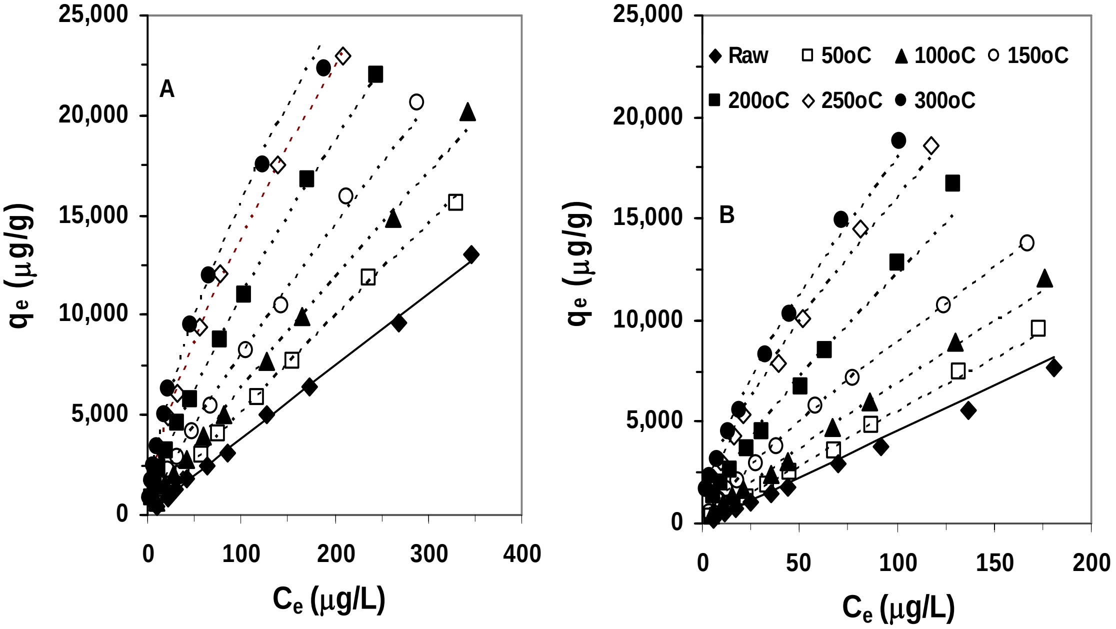

Figure 9. Phenanthrene sorption (A) and desorption (B) isotherms for MI peat treated in superheated water for 5 hrs at different temperatures.

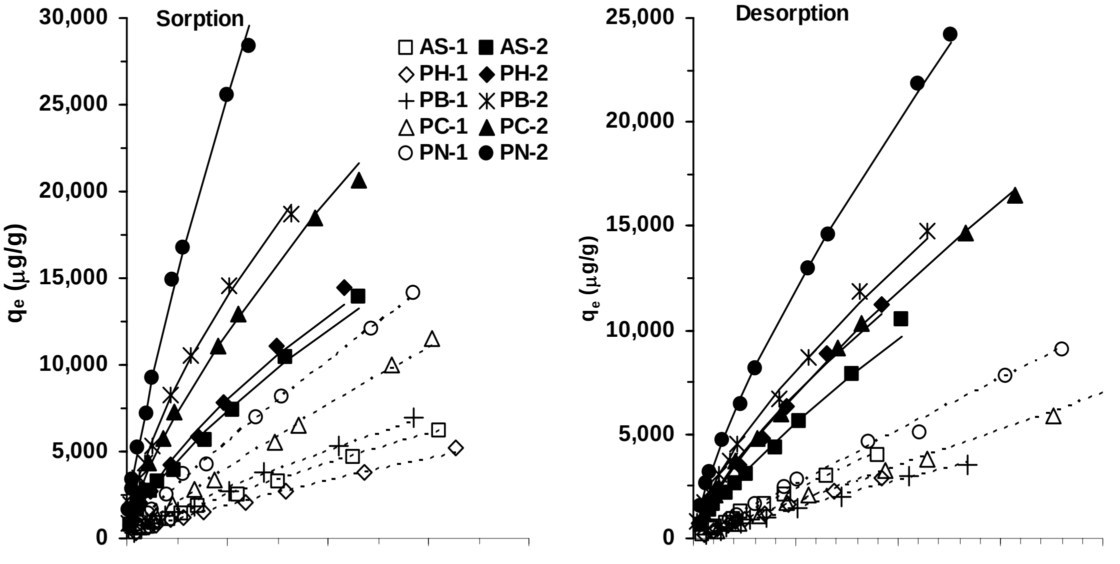

Figure 10. Phenanthrene sorption (A) and desorption (B) isotherms by natural organic materials before and after superheated water treatment for 5 hrs (AS: almond shell, PH: peanut husk, PC: pine cone, PN: pine needle, PB: pine bark, 1: untreated, 2: treated)

Table 3. Phenanthrene Sorption and Desorption Isotherm Freundlich Parameters of MI Peat Treated with Superheated Water at Different Temperature

Treatment Temperature (°C)	Sorption			Desorption		
	K_F [a]	n	R^2	K_F	n	R^2
22 (Raw)	45.01	0.965	0.999	46.52	0.974	0.995
50	63.62	0.953	0.998	64.47	0.958	0.998
100	98.45	0.904	0.997	105.9	0.906	0.989
150	159.5	0.851	0.999	176.0	0.853	0.994
200	306.2	0.776	0.991	336.1	0.782	0.996
250	611.8	0.679	0.998	665.7	0.691	0.999
300	744.6	0.662	0.997	836.2	0.665	0.993

a: Units in (μg/g)/(μg/L) ^{n}

Table 4. Freundlich parameters of different natural organic materials treated by superheated water at 250°C

Material	Sorption			Desorption		
	K_F [a]	n	R^2	K_F	n	R^2
MP-1[a]	15.8	0.943	0.977	33.2	0.961	0.982
MP-2	502.1	0.634	0.990	524.4	0.701	0.993
PC-1	10.1	1.010	0.994	29.8	0.991	0.980
PC-2	212.1	0.689	0.993	216.9	0.789	0.994
PN-1	18.9	0.937	0.991	56.9	0.830	0.986
PN-2	318.4	0.756	0.964	343.5	0.789	0.989
PB-1	18.2	0.801	0.997	35.6	0.702	0.957
PB-2	265.5	0.655	0.999	265.0	0.699	0.976
PH-1	9.2	0.834	0.985	33.2	0.710	0.973
PH-2	123.7	0.669	0.990	229.7	0.693	0.976
AS-1	6.5	0.916	0.991	33.3	0.793	0.963
AS-2	144.2	0.608	0.984	145.3	0.754	0.973

a: Units in (μg/g)/(μg/L) ^{n}

b: MP: Michigan peat, AS: almond shells, PH: peanut husks, PC: pine cones, PN: pine needles, PB: pine bark, 1: untreated, 2: treated

3.3. Heavy metals.

3.3.1. *Selections of raw organic materials*. A number of organic materials, i.e., MI old peat, MI young peat, WA peat, corn stalk, soybean stalk, oak leaves, green ash leaves, and pine needle, were selected to measure their sorption capacity for heavy metals. Cadmium ($Cd(NO_3)_2$) was chosen as a representative of heavy metals. Ground organic materials (75 mg) were mixed with 50 ml $Cd(NO_3)_2$ (100 pm) solution with 0.01 M $NaNO_3$ as ion background for 2 days. The results showed that all the selected organic materials had very strong sorption for Cd^{2+}, although their sorption capacities varied greatly (Table 5). MI old peat had highest sorption capacity with a Cd^{2+} concentration of 57207.2 μg/g solid and corn stalk had lowest sorption capacity with a Cd^{2+} concentration of 23421.7μg/g among the test materials. Their distribution coefficients ($K_{oc}= q_{e/}C_e$, the ratio of solid and aqueous phase Cd^{2+} concentrations at equilibrium) varied greatly among the tested organic materials, ranging from 347.8 to 2783.4. The sorbed Cd^{2+} was strongly attached to the sorbent materials with only 3.03 to 28.72% of Cd^{2+} desorbed. Desorption K_{oc} values were 5.6 – 8.5 times higher than those for sorption.

Table 5. Sorption and desorption of cadmium from solution by raw organic materials

	Sorption			Desorption		
	Sorption (μg/g)	Sorption (%)	K_{oc} (L/Kg)	Remaining (μg/g)	Desorption (%)	K_{oc} (L/Kg)
MI old peat	57207.2	79.45	2783.4	55608.2	3.03	23339.4
MI young peat	52604.8	72.94	1943.8	50107.3	5.12	13798.5
WA peat	32460.4	45.50	595.6	28717.0	12.68	5079.4
Corn stalk	23421.7	32.66	347.8	17130.7	28.72	1843.2
Soybean stalks	48868.9	67.35	1496.8	43190.2	12.07	5345.0
Oak leaves	33061.6	45.83	610.4	27405.4	18.17	3210.8
Green ash	42575.1	59.20	1043.5	37265.8	13.12	4760.8
Pine needles	28138.0	38.35	418.8	21565.0	26.44	2252.2

3.3.2. Effects of engineering treatments. It is evident that the raw organic materials had reasonably high sorption capacities for heavy metals, but these capacities were found to decrease after superheated water treatment, as shown for example in Figure 11 for sorption of Cd^{2+} by MI old peat. The major sorption mechanism of natural organic materials for heavy metals is most likely ion-exchange by carboxyl and phenolic functional groups. These functional groups are reduced or eliminated an high temperatures, and exchange sorption capacities for metals thus decline. Because the application potential of ENOS materials would be enhanced if they had strong sorption capacities for both organic contaminants and heavy metals, a number of oxidants and other materials were added to reactors containing MI old peat, MI young peat, pine needles, and soybean stalks in superheated water treatment at both 200°C and 250°C. The sorption capacities of the treated materials for cadmium were determined in batch studies. The results, given in Table 6, show that MI old peat for example still had very strong sorption capacity for cadmium when treated at 250°C in the presence of $Na_4P_2O_7$, while its sorption capacities were significantly reduced when treated by superheated water alone or in the presence of either $ZnCl_2$ or Fe_2O_3. For MI young peat treated by superheated water with $KMnO_4$ or $Na_4P_2O_7$, pine needles treated with $Na_4P_2O_7$, soybean stalks treated with $(NH_4)_2S_2O_8$, sorption capacities for cadmium either increased or remained essentially unchanged.

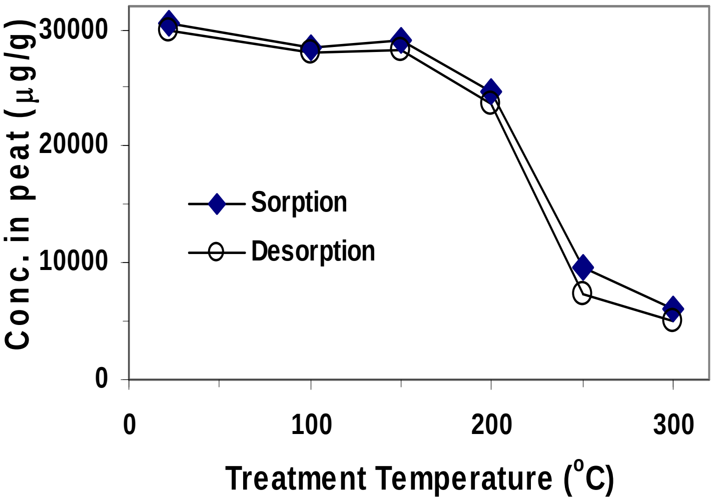

Figure 11. Treatment temperature effects on sorption and desorption of Cd^{2+} by MI old peat

Isotherms for sorption and desorption of cadmium by these materials were determined. and the Langmuir isotherm model (Equation 3) used for analysis of the equilibrium data.

$$q_e = \frac{q_m . bC_e}{1 + bC_e} \tag{3}$$

where q_e and C_e are as previously defined, q_m is the maximum (plateau) sorption capacity, and b is a constant. The results of the model fits to the sorption and desorption data of MI young peat, pine needle and soybean stalk treated at different conditions for cadmium are shown in Figure 12, and related model parameters sorption are summarized in Table 7. The results suggest that the sorption and desorption data are fit well by the Langmuir model with values of q_m ranging from 18181.82 µg/g to 58823.53 µg/g for sorption and from 150820.96 µg/g to 71123.76 µg/g.

Table 6. Sorption and desorption of cadmium from aqueous solution by natural organic materials treated using superheated water at different conditions

	Sorption			Desorption		
	Sorbed (µg/g)	Sorbed (%)	K_{oc} (L/Kg)	Residual (µg/g)	Desorbed (%)	K_{oc} (L/Kg)
MI old peat						
P0: Raw	57207.2	79.4	2783.4	54795.6	4.5	15684.0
P1: P0+ $ZnCl_2$	12122.7	16.8	145.7	10945.1	14.5	4552.4
P2: P0+$Na_4P_2O_7$	53300.7	74.3	2073.2	47407.4	11.4	5633.9
P3: P0+ Fe_2O_3	10098.4	14.1	117.5	8932.5	17.3	3633.7
P4: P0+ Water only	9715.6	29.4	137.6	7326.5	24.5	1076.6
MI young peat						
MP0: Raw	40426.1	55.4	805.1	35583.3	13.51	5069.0
MP1: MP0+ $KMnO_4$	47491.0	66.2	1211.3	41941.4	9.15	7646.9
MP2: MP0+$Na_4P_2O_7$	45685.9	62.8	1066.7	40378.1	12.94	5298.9
MP3: MP0+$(NH_4)_2S_2O_8$	9908.0	13.4	107.4	9079.7	15.42	4648.8
MP4: MP0+ Water only	14540.3	19.9	169.8	13978.2	8.32	5482.6
Pine needles						
PN0: Raw	28137.9	38.4	418.9	21564.9	26.4	2252.2
PN1: PN0+$(NH_4)_2S_2O_8$	9622.6	13.3	104.3	9521.9	7.9	9821.3
PN2: PN0+$KMnO_4$	19167.6	26.5	242.3	17290.6	13.3	5214.2
PN3: PN0+ $Na_4P_2O_7$	42089.6	57.7	882.9	29479.6	32.5	1657.5
PN4: PN0+ Water only	11725.4	16.1	131.4	10883.3	13.1	5531.1
Soybean stalks						
SS0: Raw	37097.9	32.2	1680.2	ND	ND	ND
SS1: SS0+ $(NH_4)_2S_2O_8$	40051.8	33.9	1861.4	ND	ND	ND
SS2: SS0+ $Na_4P_2O_7$	3821.0	3.3	121.4	ND	ND	ND
SS3: SS0+ $KMnO_4$	26063.3	22.4	1032.3	ND	ND	ND

Table 7. Langmuir model parameters of sorption and desorption of treated and untreated organic materials for cadmium from aqueous solutions.

	Sorption			Desorption		
	q_m	b	R^2	q_m	b	R^2
MI young peat						
MP0: Raw	41666.67	0.0749	0.994	48780.49	2.1134	0.914
MP1: MP0+ $KMnO_4$	42122.99	0.0955	0.996	48285.85	0.845	0.951
MP2: MP0+$Na_4P_2O_7$	34399.73	0.0696	0.989	38343.56	1.1601	0.997
Pine needles						
PN0: Raw	26357.41	0.0209	0.988	42680.32	0.2115	0.963
PN1: PN0+ $(NH_4)_2S_2O_8$	18181.82	0.006	0.993	15082.96	0.813	0.925
PN3: PN0+ $Na_4P_2O_7$	39231.07	0.0624	0.999	30193.24	0.2941	0.979
Soybean stalks						
SS0: Raw	43122.04	0.0434	0.995	71123.76	0.1195	0.925
SS1: SS0+$(NH_4)_2S_2O_8$	58823.53	0.0165	0.976	37735.85	0.5532	0.974

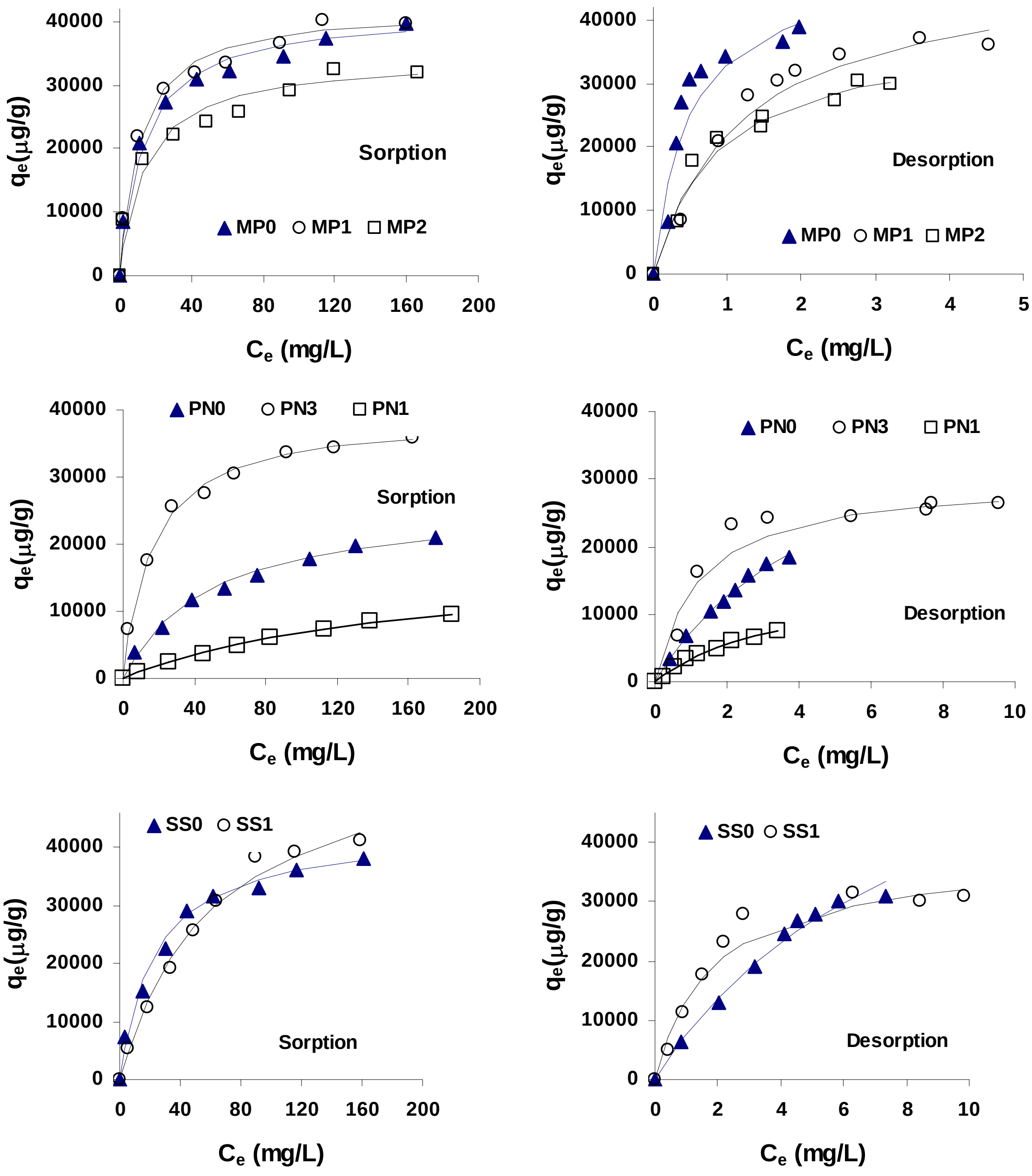

Figure 12 Cadmium sorption and desorption isotherms for treated and untreated organic materials (MP: MI young peat, PN: pine needles, SS: soybean stalks)

***3.3.3. Sorption rates*.** Sorption rates for uptake of cadmium by treated and untreated MI young peat, pine needle and soybean stalk samples were also determined. The quantity of cadmium sorbed at time *t*, q_t (μg/g), was determined from a mass balance between the concentrations in solution initially and at time *t*. To analyze the sorption rates of compounds onto the peat samples, a pseudo-second-order rate model given in Equation 4 was selected for analysis of the rates of sorption of cadmium by the sorbent samples.

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \qquad (4)$$

$$v_0 = kq_e^2 \qquad (5)$$

The parameter *k* in Equation 4 is the sorption rate constant (g/μg min) and q_e is the concentration of compound sorbed at equilibrium (μg/g), and v_0 is initial sorption rate (μg/min). Their sorption rat data were fitted well by the second-order model yielding R^2 values greater than 0.993 (Figure 13 and Table 8). Sorption for cadmium by the tested organic samples was found to be very rapidly and they reached their equilibria around 2 hours. The rate constant values of *k* were generally increased for treated samples with oxidants.

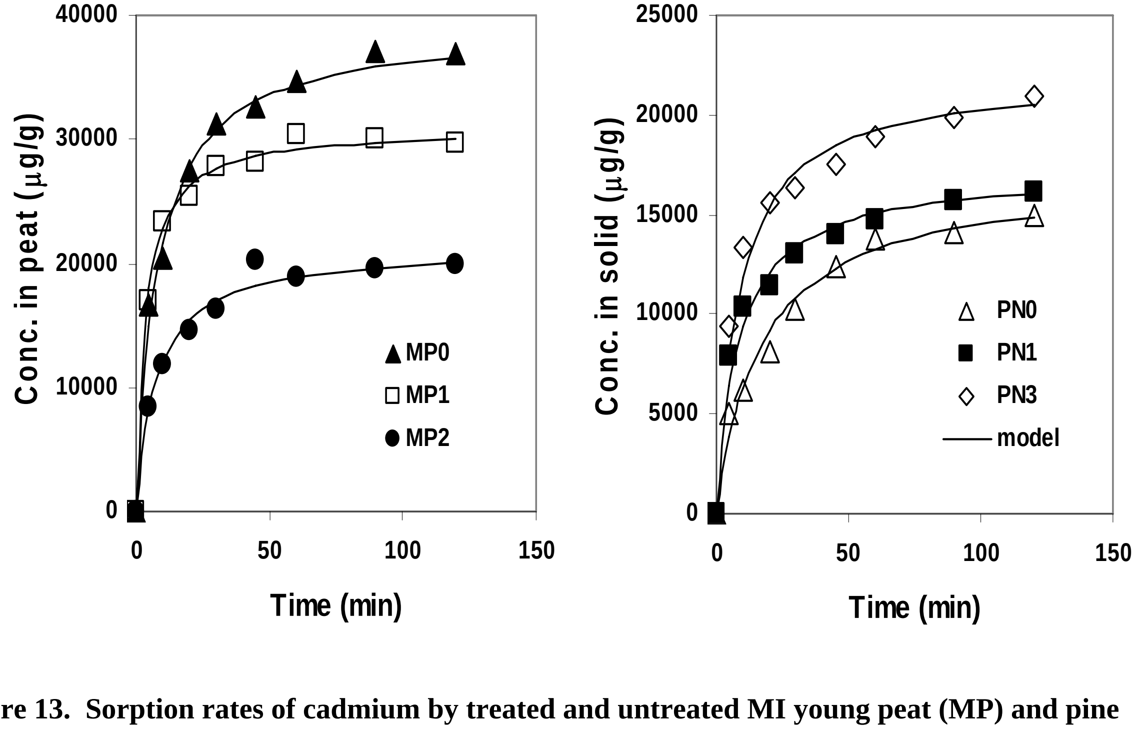

Figure 13. Sorption rates of cadmium by treated and untreated MI young peat (MP) and pine needles (PN) from aqueous solution.

Table 8. Model parameters for Cadmium sorption rates

	q_e	k x 10^{-5}	v_0	R^2
MI young peat				
MP0: Raw	39062.5	0.316	4819.3	0.999
MP1: MP0+ $KMnO_4$	30959.8	0.897	8598.5	0.999
MP2: MP0+$Na_4P_2O_7$	21276.6	0.620	2806.6	0.997
Pine needles				
PN0: Raw	17006.8	0.344	995.3	0.994
PN1: PN0+$(NH4)_2S_2O_8$	17094.0	0.708	2067.4	0.999
PN3: PN0+ $Na_4P_2O_7$	21978.1	0.529	2556.2	0.999
Soybean stalks				
SS0: Raw	28818.4	0.245	2038.3	0.993
SS1: SS0+$(NH_4)_2S_2O_8$	31847.1	0.238	2412.6	0.994

3.3.4. Effects of pH, ionic strength, and sorbent mass. The effects of pH, ion strength and mass amount on the sorption and desorption of cadmium by treated and untreated organic materials were also determined. MI young peat and pine needle were exposed to $Cd(NO_3)_2$ solution with 0.01 M $NaNO_3$ as background and their pHs were adjusted using 1 N HNO_3 or NaOH. The results showed that uptake of cadmium by both treated and untreated MI young peat and pine needle increased when pH of solution increased from 2.0 to 7.0. At pH 2.0, less than 3% or 1% of cadmium was sorbed by MI young peat or pine needle and their sorption reached their maximum at pH 7.0 for both materials, then decreased when pH increased to 8.0. However, the desorption from both treated and untreated MI young peat and pine needle was decreased when pH increased from 2.0 to 8.0. At pH 2.0, 71.8% and 85.6% of the sorbed cadmium was desorbed from raw and MI young peat, while 93% and 90.7% of sorbed cadmium was desorbed from raw and treated pine needles. Desorption changes over a pH range from 5.5 to 8.0 ranged from 10% to 25% (Figure 14).

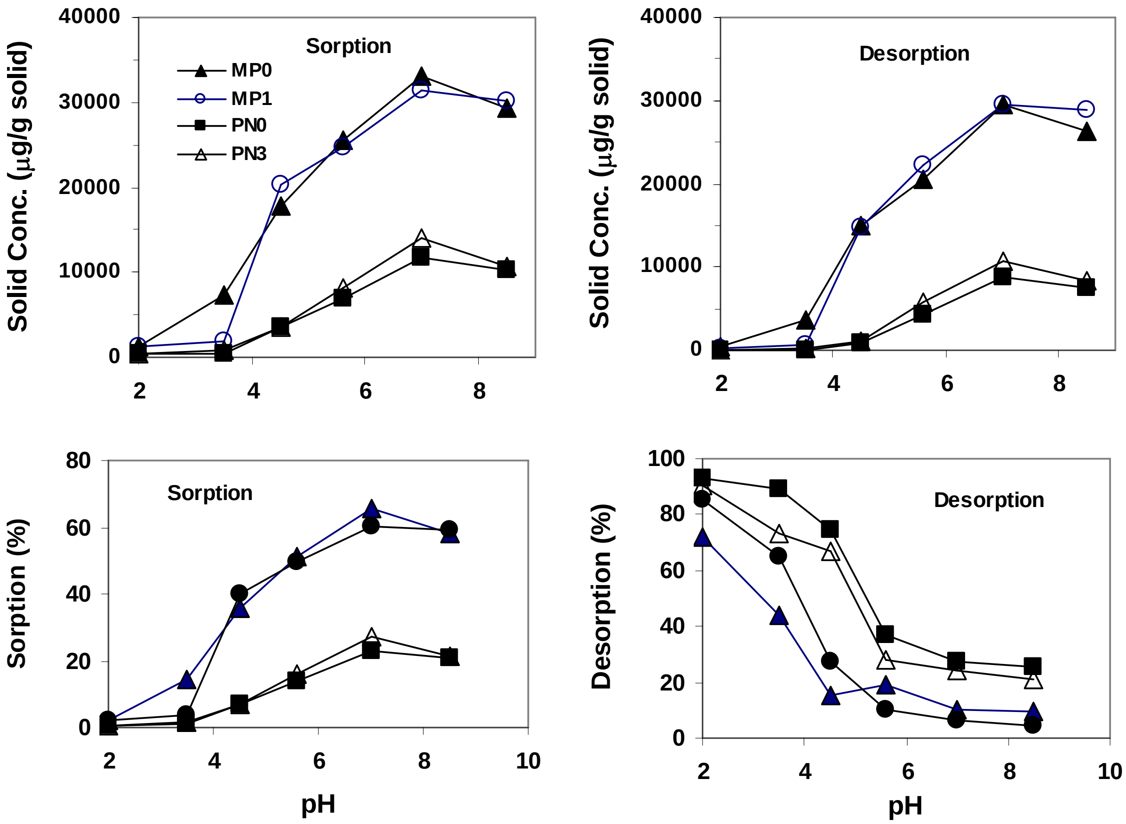

Figure 14. Effect of pH on the sorption and desorption of cadmium by treated and untreated organic materials (MP: MI young peat, PN: pine needle)

The effects of ionic strength of solution on the sorption and desorption of cadmium by treated and untreated MI young peat and pine needle were also determined (Figure 15). Ground organic materials were mixed with $Cd(NO_3)_2$ solution with $NaNO_3$ concentrations ranging from 0, 0.005, 0.01, 0.1 and 0.5 M for 2 days to determine sorption and desorption of cadmium. The results showed that both materials had high sorption and lowest desorption for cadmium in Mili-Q water. When ion strength increased, cadmium sorption decreased and desorption increased and they were more evident when $NaNO_3$ concentrations increased to 0.1 M. In 0.1 M $NaNO_3$ solution, treated MI young peat sorbed much more cadmium than raw peat, i.e., 47.9% vs. 6.7%. Treated pine needles (28.2%) also sorbed much more cadmium than raw pine needles (3.9%) from 0.1 M $NaNO_3$ solution. For desorption, almost 100% of sorbed cadmium were desorbed from raw MI young peat in 0.1 M and 0.5 M $NaNO_3$ solution, while only 42.1% and 59.7% of sorbed cadmium were desorbed from treated peat. Similar results were found for pine needle (Figure 15).

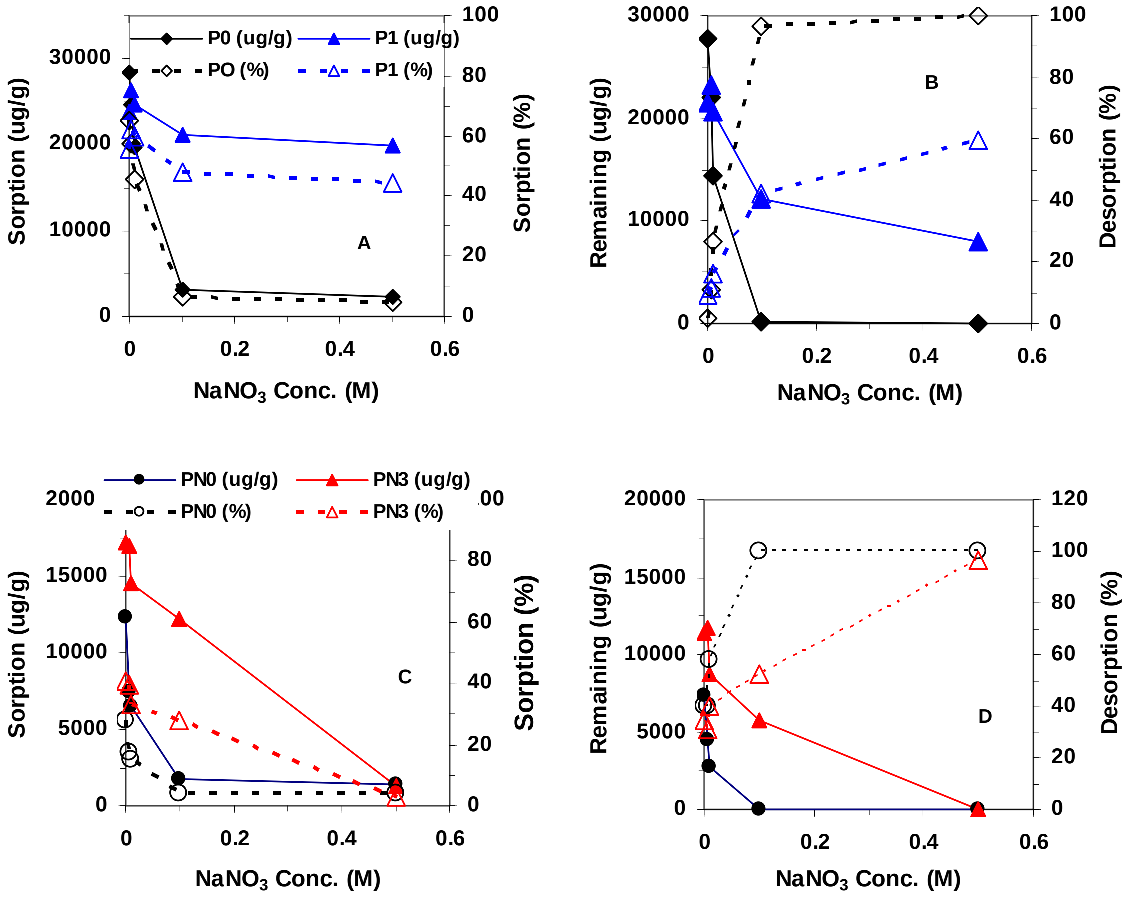

Figure 15. Effects of ionic strength on the sorption (A, C) and desorption (B, D) of cadmium by treated and untreated MI young peat and pine needles.

The effects of sorbent mass on the sorption and desorption of cadmium by treated and untreated pine needle and soybean stalk from aqueous solution were also investigated (Figure 16). Different amounts of the organic materials, i.e., 0, 25, 75, 125, 150 and 175 mg, were added to test tubes containing $Cd(NO_3)_2$ (100 ppm) in 0.01-$NaNO_3$ solution for 2 days to measure sorption and desorption of cadmium by treated and untreated soybean stalk and pine needle. Cadmium concentrations in the sorbents were much higher at the lower sorbent amount, i.e., 25 and 75 mg, for both soybean stalk and pine needle, then decreased when sorbent amount increased till 150 mg of sorbents, and level off at 175 mg. Treated soybean stalks and pine needles both took up more cadmium than their respective raw materials. It is not surprising that total sorption percentage increased and desorption of cadmium from both soybean stalk and pine needle decreased with increasing sorbent amount. More sorbed cadmium was desorbed from untreated soybean stalk (6.6 – 32.7%) and pine needle (33.5 – 75.5%) than from treated soybean stalk (2.7 – 27.2%) and pine needle (26.5 - 33.0%) (Figure 16).

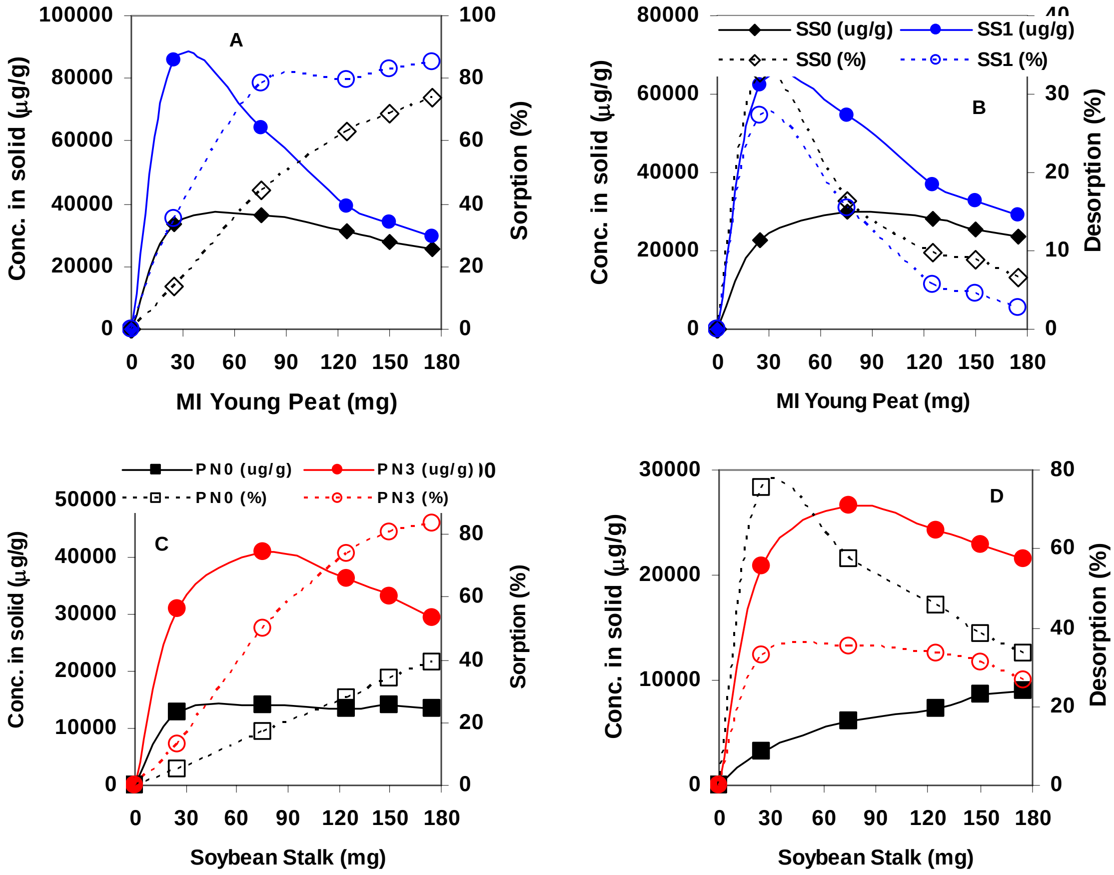

Figure 16. Effects of sorbent mass on the sorption (A, C) and desorption (B, D) of cadmium by treated and untreated MI young peat and soybean stalks

3.4. Mixtures of organic compounds and heavy metals.

Organic contaminants are commonly present along with heavy metals in contaminated sediments. Combined sorptions and desorptions of organic compounds and heavy metals by treated and untreated organic sorbents were therefore investigated. Sorption and desorption Isotherms for sorption and desorption of 1,2-dichlorobenzene (1,2-DCB) by treated and untreated pine needles were determined with presence (100 ppm) and absence of cadmium. The results, shown in Figure 17 and Table 9, indicate that sorption and desorption isotherms of

1,2-DCB are still fitted well by the Freundlich model, with R^2 values greater than 0.988 for sorption and 0.967 for desorption. In the presence of cadmium, 1,2-DCB sorption was decreased for both treated and untreated pine needles, indicating competitive interactions between 1,2-DCB and cadmium.

Cadmium sorption and desorption isotherms for treated and untreated pine needles were also determined in the presence and absence of 1,2-DCB (5000 ppb). Sorption and desorption data for cadmium were fitted well by the Langmuir model, with R^2 values greater than 0.978 for sorption and 0.950 for desorption (Figure 18 and Table 10). In the presence of 1,2-DCB, sorption of cadmium was reduced more for treated pine needles than for raw pine needles. This may be because treated pine needles had greater capacities for 1,2-DCB than did raw pine needles. When cadmium concentrations were increased in solution, the sorption of 1,2-DCB was decreased (Figure 19).

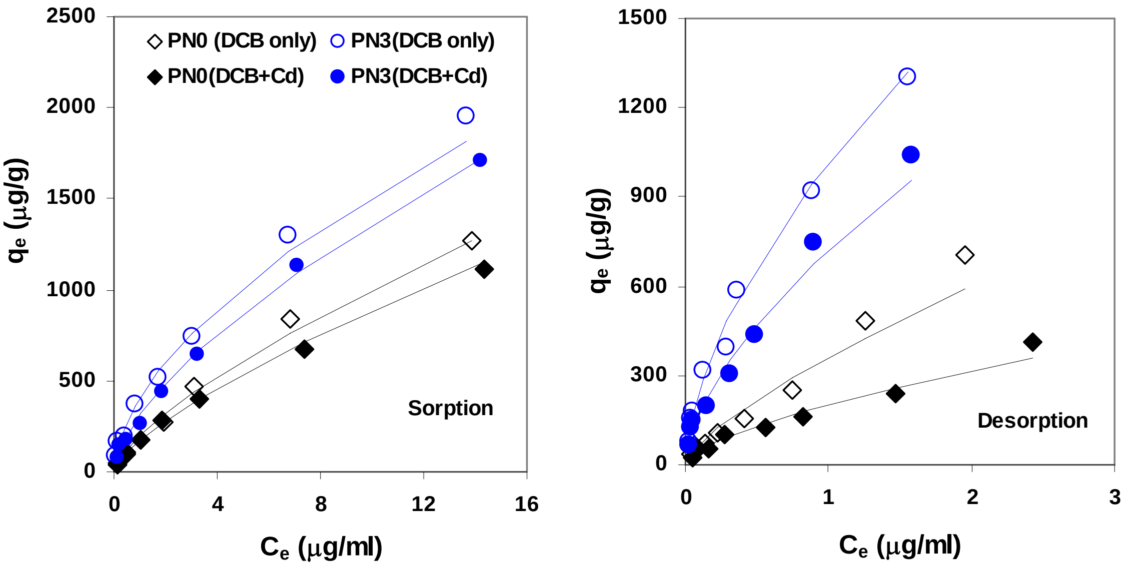

Figure 17. 1,2-dichlorobenzene orption and desorption isotherms for treated and untreated pine needles with and without the presence of cadmium.

Table 9. Freundlich model parameters of sorption and desorption of treated and untreated pine needles for 1,2-DCB with and without cadmium

	Sorption			Desorption		
	K_F	n	R^2	K_F	n	R^2
Pine needle						
PN0: 1,2-DCB only, no Cd^{2+}	194.3	0.713	0.993	362.1	0.728	0.968
PN0: 1,2-DCB + Cd^{2+}	166.8	0.725	0.995	202.5	0.643	0.973
PN3: 1,2-DCB only, no Cd^{2+}	400.5	0.578	0.990	1011.8	0.596	0.967
PN3: 1,2-DCB + Cd^{2+}	308.3	0.646	0.988	720.6	0.628	0.977

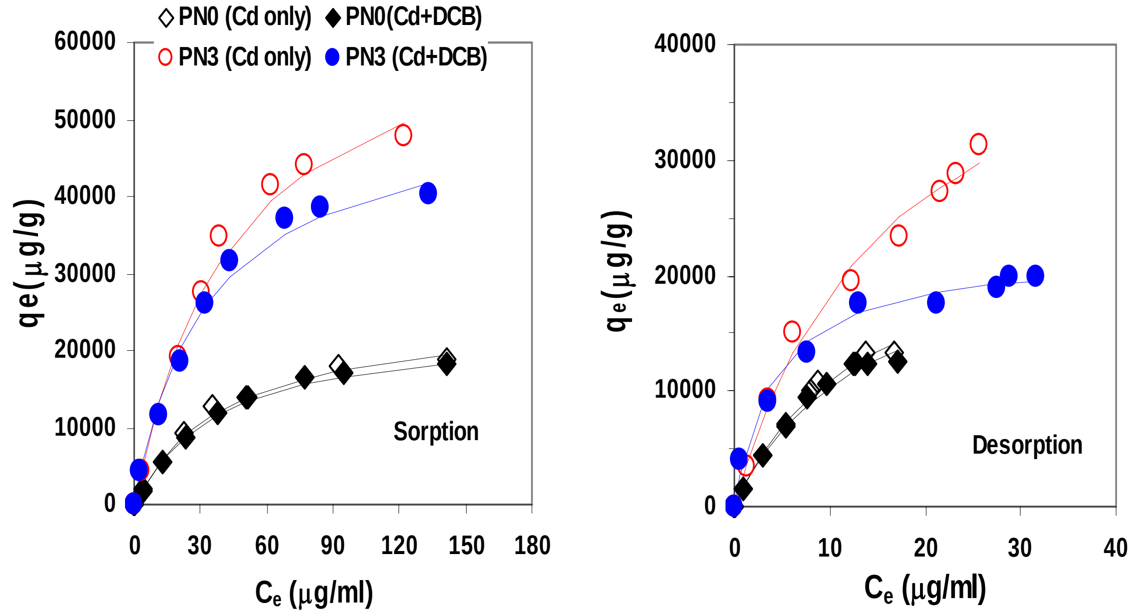

Figure 18. Cadmium sorption and desorption isotherms for treated and untreated pine needles with and without presence of 1,2-dichlorobenzene.

Table 10. Langmuir model parameters for sorption and desorption of cadmium by treated and untreated pine needles with and without the presence of 1,2-DCB

	Sorption			Desorption		
	q_m	b	R^2	q_m	b	R^2
Pine needles						
PN0: Cd^{2+} only, no 1,2-DCB	24813.9	0.025	0.990	25839.8	0.073	0.95
PN0: Cd^{2+} +1,2-DCB	23419.2	0.026	0.991	23640.7	0.078	0.963
PN3: Cd^{2+} only, no 1,2-DCB	67567.6	0.023	0.978	48543.7	0.061	0.953
PN3: Cd^{2+} +1,2-DCB	51813.5	0.031	0.987	22271.7	0.231	0.993

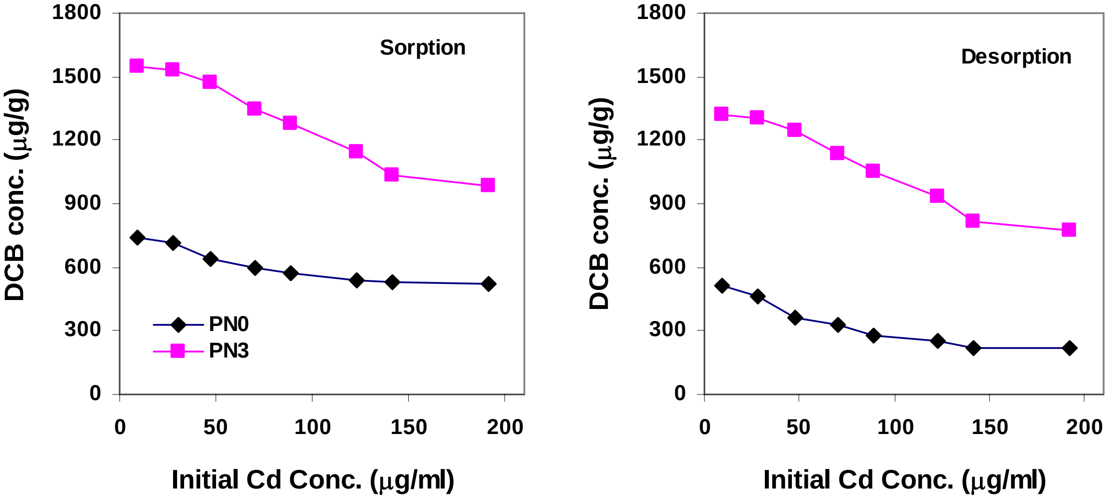

Figure 19. Effects of initial cadmium concentration on the sorption and desorption of 1,2-dichlorobenzene by treated and untreated pine needles.

4. Effects of ENOS materials on the bioavailability, environmental mobility and environmental fate of DNAPLs, PAHs and heavy metals in sediments.

Natural organic matter (NOM) has been recognized as a dominant environmental domain for collection and concentration of many persistent and toxic organic contaminants, and thus to have profound impacts on the transport and fate of such contaminants in environmental systems. The specific chemical properties and macromolecular structures of NOM have been shown to significantly affect its capacities for sorption and sequestration of different types of contaminants. A number of inexpensive and readily available natural materials such as modified groundnut husks, sphagnum moss peat, and brown seaweed biomass have been found to adsorb metals from water. Various soil amendments including organic matter and minerals have been applied to contaminated soils for reducing the environmental mobility and bioavailability of organic compounds and heavy metal contaminants. Peat for example has a high cation exchange capacity, and is an effective sorbent for removal of both heavy metals and organic compounds.

The results presented earlier in this Report show that the sorption capacities of a number of readily available organic materials are greatly increased for DNAPL components and PAH compounds as a result of processing by superheated water treatment. It can be hypothesized that the environmental risks posed by persistent organic compounds and heavy metals will be substantially reduced if these contaminants are bound so strongly by the natural geosorbents present in a given system that they are rendered irreversibly immobile, and thus also biologically less available for potential food-chain magnification. To verify this hypothesis and explore the potential application of treated organic materials, a number of organic materials were treated with superheated water and employed as ENOS additives or amendments to different soil samples contaminated with representative DNAPL compounds (e.g., TCE and PCE), PAH compounds (e.g., pyrene), and heavy metals (e.g., cadmium). The effects of these ENOS materials on the environmental mobility and bioavailability of these aged contaminants were then evaluated by measuring contaminant uptake by earthworms, degradation by inoculated microorganisms, aqueous desorption and sequential extraction.

4.1. DNAPL compounds - TCE and PCE.

MI peat, pine needles, and maple leaves were treated with superheated water at 200^{o}C for 5 hrs. Treated and untreated organic materials were added to North Campus (NC) soil as amendments. TCE or PCE was spiked to NC soil amended with treated and untreated organic materials at predetermined concentrations and 26-27% water content levels and aged for 75 days at ~ 10°C. Contaminant recoveries, bioavailabilities, and environmental nobilities were then determined. The three following types of experiments were conducted:

1) TCE was aged at 488 μg/g in NC soil amended with 10% treated and untreated MI peat, pine needles and maple leaves, respectively;
2) PCE was aged at 541 μg/g in NC soil amended with 0, 5, 10, 15, and 20% of treated MI peat; and
3) TCE was aged at 48.8, 97.6, 244.0, 488.0, 976.0 and 1464.0 μg/g in NC soil amended with 10% treated MI peat;

After aging, concentrations of TCE or PCE remaining in the soil samples were determined using methanol extraction in a sonicator for 3 hrs. The recoveries of both TCE and PCE, as shown in Table 11, varied among amended and unamended soil samples. For NC soil without amending any organic sorbent, only about 3% of initially applied TCE remained in the soil samples. The recovery of TCE remarkably increased in the soil samples amended with 10% of organic materials, ranging from 20.3 to 36.3% for untreated organic materials, and from 54.5 to 79.3% for treated ENOS. TCE was spiked at different initial concentrations and aged in the soil amended with 10% of treated MI peat samples, its recovery from soil samples decreased with increased initial concentrations. PCE was spiked and aged in NC soil amended with different amounts of treated MI peat (0 to 20% of NC soil) at the same initial concentration, after aging for 75days, its recovery from soil samples increased from 15.6 to 78.9%. The data showed that organic materials, especially ENOS, significantly increased retention of volatile TCE and PCE in soil samples.

Bioavailability was determined by exposing TCE or PCE aged soil samples to earthworms (*Eisenia foetida*) for 10 days, and concentrations in worm tissue were determined. As shown in Table 12, TCE concentrations in worm tissues varied among the soil samples amended with different materials. Worm uptake from NC soil without amendments was logically smaller than that for amended soil samples because of the much higher TCE concentrations in the amended soils. However, based on percentages of TCE uptake by worms, the availability of TCE from untreated soil samples is a factor of 1.7 to 9.3 higher than that from soil samples amended with untreated organic materials and a factor of 6.3 to 15.2 higher than that from samples amended with treated organic materials. For soils amended with 10% treated MI peat and aged with different initial TCE amounts, concentrations in worm tissues increased and uptake percentages decreased as TCE concentrations increased in soil samples. For soil samples amended with different quantities of this ENOS, concentrations in worm tissues and percentages of PCE decreased as the amount of treated MI peat increased.

The environmental mobility of aged TCE and PCE was determined by measuring aqueous desorption using a multiple decant-refill technique. Soil samples were weighed in 35-ml centrifuge tubes and fully filled with background solution and the tubes were shaken in an end-over-end shaker for pre-determined time intervals. At each sample time, the tubes were centrifuged to separate aqueous solution from soil solids. To reduce the chemical loss from evaporation, the tubes were cooled to about 10°C in a refrigerator before sampling. The desorption rates of TCE and PCE from aged soil samples as revealed in Figure 19 are characterized well by a three-parameter, two-component, first-order rate model

$$\frac{C_t}{C_0} = \phi_r \exp(-k_r t) + (1-\phi_r)\exp(-k_s t) \qquad (6)$$

in which C_0 is the initial concentration of chemical in sediment, C_t is the concentration of chemical in sediment at time *t*, ϕ_r is the fraction of chemical which is rapidly released, 1-ϕ_r is the fraction of chemical which is slowly released from a sediment, k_s is a first-order rate constant for the slowly released fraction, k_r is a first-order rate constant for the rapidly released fraction. The model parameters were presented in Table 12.

Table 11. Effects of Amendments on Retention and Recovery of TCE and PCE from North Campus Soil

	Different Types of ENOS[a]						
	NONE	**10% MI Peat**		**10%Pine Needles**		**10%Maple Leaves**	
	NC only	Untreated	Treated	Untreated	Treated	Untreated	Treated
Spiked Conc.(µg/g)	488.0	488.0	488.0	488.0	488.0	488.0	488.0
Recovered Conc.(µg/g)	14.37	99.19	361.3	177.3	387.1	141.4	265.9
Recovery %	2.95	20.3	74.0	36.3	79.3	27.6	54.5

Different Spiking Concentrations[a]

Spiked Conc.(µg/g)	10% MP1[b]	48.8	97.6	244.0	488.0	976.0	1464.0
Recovered Conc.(µg/g)		32.7	73.3	157	361.3	451.4	629.4
Recovery %		67.0	75.1	74.0	64.4	46.3	42.9

Different ENOS Amounts[c]

Added MP1%	None	5%	10%	15%	20%
Spiked Conc.(µg/g)	541.0	541.0	541.0	541.0	541.0
Recovered Conc.(µg/g)	84.23	152.8	266.3	314.4	427.0
Recovery %	15.6	28.3	49.2	58.1	78.9

a. Spiked with TCE b. Treated MI peat c. Spiked with PCE

Table 12. Effects of ENOS Amendments on the Bioavailability and Environmental Mobility of TCE and PCE Sorbed by North Campus Soil

	A: Different Types of ENOS[a]						
	NONE	**10% MI Peat**		**10%Pine Needles**		**10%Maple Leaves**	
Treatment	NC only	Untreated	Treated	Untreated	Treated	Untreated	Treated
				Bioavailability			
Uptake (μg/g)	2.15	1.11	3.25	2.95	4.97	11.72	6.86
Uptake (%)	0.0364	0.0039	0.0024	0.0048	0.0034	0.0213	0.0058
				Desorption Model Parameters			
ϕ_r	0.796	0.748	0.689	0.782	0.654	0.777	0.697
K_r	0.589	0.568	0.529	0.764	0.357	0.898	0.411
			B: Different Spiking Concentrations				
Spiked Conc.(μg/g)	10% MP1[b]	48.8	97.6	244.0	488.0	976.0	1464.0
				Bioavailability			
Uptake (μg/g)		0.72	2.86	3.03	3.25	3.63	4.24
Uptake (%)		0.0072	0.0116	0.0055	0.0024	0.0025	0.0018
				Desorption Model Parameters			
ϕ_r		ND	0.468	0.688	0.689	0.765	0.816
K_r			0.382	0.363	0.529	0.495	0.449
				C: Different ENOS Amounts			
MP1 %		Non	5%	10%	15%	20%	
				Bioavailability			
Uptake (μg/g)		4.15	4.62	4.36	3.51	3.70	
Uptake (%)		0.0114	0.0081	0.0052	0.0040	0.0032	

a. Spiked with TCE b. Treated MI peat c. Spiked with PCE

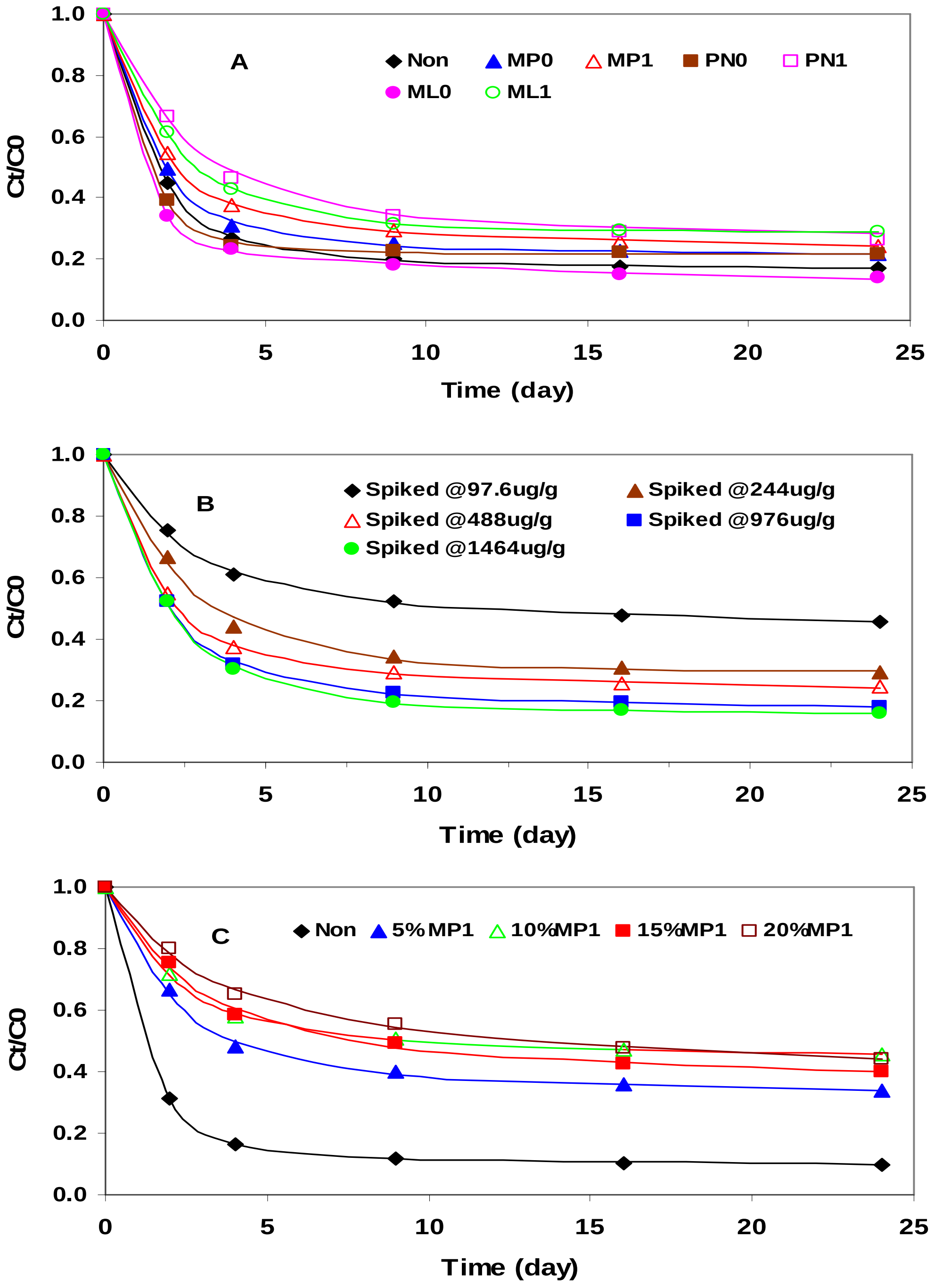

Figure 19. Aqueous desorption rates of TCE (A, B) and PCE (C) from North Campus soil amended with different types and amounts of ENOS

4.2. PAH compounds.

MI peat and soybean stalks were treated with superheated water at 200oC for 5 hrs, dried and sieved with 1-mm sieve. Treated and untreated MI peat and soybean stalks were applied to radiation-sterilized North Campus soil and Chelsea soil at 0 to 20% of soil samples and these soils were contaminated with ^{14}C-labled pyrene at a concentration of 100 μg/g. After the soil samples were aged at room temperatures under dark for 105 days, the remained pyrene, its distribution in soil, its bioavailability and microbial degradation were determined. For comparison, soils that were spiked with 14C-pyrene for 1 day without ENOS amendments were used as fresh soil samples. Two batches of experiments were conducted:

1) Different types of ENOS. Pyrene was aged at 100 μg/g in NC soil and Chelsea soil amended with 10% treated and untreated MI peat and soybean stalks, respectively;
2) Different ENOS amounts. Pyrene was aged at 100 μg/g in NC soil amended with 0, 5, 10, and 20% of treated and untreated MI peat and soybean stalks, respectively.

4.2.1. Recovery and distribution of pyrene. Pyrene remained in soil samples were extracted using methanol in sonicator and the fractionations remained in soil were combusted using a biological oxidizer, and its total 14C radioactivity were determined using a liquid scintillation counter. More than 84% of initially applied pyrene remained in soil samples. The distribution of remained pyrene in soil samples was determined by sequential extraction. Freeze-dried soil samples were extracted with 0.01 M $CaCl_2$ aqueous solution for 48 hrs, then with mixture of methanol and water (1:1, v/v) for 24 hrs in an end-over-end shaker. The soil samples were extracted with methanol solution in a sonicator for 5 hrs. The soil samples with non-extractable pyrene and its metabolites were freeze-dried again and spilt into two parts, one part was combusted with the biological oxidizer for determining total amount of non-extractable pyrene remained in soil samples, and another part was subjected to saponification using 0.1 M sodium pyrophosphate ($Na_4P_2O_7$) and 0.1 M sodium hydroxide (NaOH) solution to separate humic and fulvic acids from humin of organic matter in soil samples. All 14C radioactivities were measured using the liquid scintillation counter (LSC). The sequential extraction of pyrene aged in soil samples was based on the protocol revealed in Table 13 to separate different fractions of organic matter in soil with corresponding PAH components. These PAH fractions in soil samples will have different availability for environmental transport, fate and ecological receptors. The data, as shown in Table 14, show that the pyrene fractions that may be readily available as the fractions extracted in both water and mixture of methanol and water decreased by factor of up to 10, and the fractions that were non-extractable and will be not available to the environment increased up to 3.3 times as a result of aging and amendments of MI peat and soybean stalks, especially for soil amended with treated MI peat and soybean stalks in both NC soil and Chelsea soil. The data also show that most of non-extractable pyrene was immobilized in humin fractions of organic matter. As the amounts of treated MI peat and soybean stalks increased, the readily available fractions of pyrene in NC soil decreased from 18.51% for aged soil samples without ENOS amendments to 1.17% for the soil samples amended with 20% of treated MI peat and to 1.58% for soil samples amended with 20% of treated soybean stalks, conversely, the not available fractions of pyrene increased from 8.44% to 35.36% and 28.50 for respective soil samples (Table 15).

Table 13: Protocol for Sequential Extraction of Aged Pyrene from Soil Samples

A: Sequential Soil Extraction				
Water extraction (shaking)	MeOH:H_2O (1:1, v/v) (shaking)	MeOH only (sonication)	$Na_4P_2O_7$ & NaOH (saponification)	Combustion
B: Relevant Organic Matter (OM) Fractions				
Dissolved OM	Labile OM	Sorbed OM	Humic & Fulvic acids	Humin (hard carbon)
C: Corresponding PAH Fractions				
Dissolved PAHs, polar metabolites	Loosely sorbed PAHs	Sorbed PAHs	Bound PAH	Bound PAHs
D: Availability of Relevant PAH Fractions				
Readily available	Available	Potentially available	Not available	Not available

Table 14. Effects of ENOS on the Distribution of Aged Pyrene in NC and Chelsea Soils – by Sequential Extraction

Soil Treatment	Water %	MeOH & Water %	MeOH %	Non-Extractable[c] %	Humic & Fulvic Acids %	Humin %
			NC Soil			
Fresh Soil (No aging or ENOS)	0.95	18.86	72.66	7.53	4.45	3.08
Aged Soil[a] **No ENOS**	0.68	17.83	73.05	8.44	4.92	3.52
Aged Soil **+10% MP0[b]**	0.34	7.93	81.29	10.44	4.86	5.58
Aged Soil **+10% MP1[b]**	0.26	1.60	69.93	28.21	4.59	23.62
Aged Soil **+ 10% SS0[b]**	0.69	9.54	75.37	14.40	7.27	7.13
Aged Soil **+ 10% SS1[b]**	0.44	2.95	73.18	23.43	5.50	17.93
			Chelsea Soil			
Fresh Soil (No aging or ENOS)	0.70	9.71	74.05	17.41	7.54	9.87
Aged Soil[a] **+No ENOS**	0.58	8.78	68.11	22.90	8.16	14.74
Aged Soil **+ 10% MP0[b]**	0.33	5.70	71.00	23.41	6.77	16.64
Aged Soil **+ 10% MP1[b]**	0.12	1.31	63.26	35.35	7.14	28.21

a. Soils were aged for 105 days

b. MP: MI peat, SS: soybean stalks. 0: untreated, 1: treated

c. Non-extractable fraction included both humic and fulvic acids and humin

Table 15. Effects of Different Amounts of ENOS on the Distribution of Aged Pyrene in NC Soil – by Sequential Extraction

ENOS Amounts	Water %	MeOH & Water %	MeOH %	Non-Extractable[c] %	Humic & Fulvic Acids %	Humin %
Untreated MI Peat –MP0						
Aged Soil[a] No ENOS	0.68	17.83	73.05	8.44	4.92	3.52
Aged Soil[a] +5% MP0[b]	0.48	14.09	75.61	9.32	5.95	3.38
Aged Soil + 10% MP0	0.34	7.93	81.29	10.44	4.86	5.58
Aged Soil + 20% MP0	0.17	5.05	81.50	13.67	4.76	8.91
Treated MI Peat –MP1						
Aged Soil[a] +5% MP1[b]	0.41	3.38	80.47	15.87	4.85	11.02
Aged Soil + 10% MP1	0.26	1.60	69.93	28.21	4.59	23.62
Aged Soil + 20% MP1	0.27	0.90	63.45	35.36	6.89	28.47
Untreated Soybean Stalks – SS0						
Aged Soil[a] +5% SS0[b]	0.55	19.80	70.49	11.15	5.99	5.16
Aged Soil + 10% SS0	0.69	9.54	75.37	14.40	7.27	7.13
Aged Soil + 20% SS0	0.71	10.92	90.87	14.33	4.58	9.75
Treated Soybean Stalks – SS1						
Aged Soil[a] +5% SS1[b]	0.49	8.00	75.45	14.87	7.34	7.52
Aged Soil + 10% SS1	0.44	2.95	73.18	23.43	5.50	17.93
Aged Soil + 20% SS1	0.27	1.31	69.84	28.50	7.47	21.03

a. Soils were aged for 105 days

b. MP: MI peat, SS: soybean stalks. 0: untreated, 1: treated

c. Non-extractable fraction included both humic and fulvic acids and humin

4.2.2. Bioavailability of aged pyrene. The bioavailability of aged and unaged pyrene in both NC and Chelsea soils were first determined by exposing contaminated soil samples to earthworms ((*E. foetida*) for 14 days. After uptake experiments, the worms were transferred to Petri dishes with wet filter papers to purge their gut contents and freeze dried to determine dry worm weight. The pyrene concentrations in worm tissues were determined by combustion using the biological oxidizer and LSC to measure 14C activities. The pyrene remained in soil samples after worm uptake were also determined by combustion and LSC. The biota-soil accumulation factors (BSAF) were calculated by dividing pyrene concentrations in worm tissues with its concentrations remained in soil samples after uptake test, and the percentages taken up by worms were also calculated based the pyrene amounts presented in soil samples at the beginning of uptake experiments. As shown in Table 16, the availability of pyrene to earthworms was remarkably decreased in both aged and ENOS amended NC and Chelsea soils and pyrene concentrations in worm tissue decreased by factor of up to 25 and their BSAF values were reduced by factor of up to 22.0 from fresh soil samples to soil sample amended with treated MI peat or soybean stalks. As the amounts of ENOS increased in soil samples, pyrene concentrations in worm tissues and its uptake percentages and BSAF values were steadily decreased (Table 17). The reduction in pyrene availability to earthworms were much more significant in soil samples amended with treated MI peat or soybean stalks than that of soils amended with the untreated organic materials.

The contaminants in soil may be available to human by ingestion through intentionally consumption of fruit or vegetables that are grown in contaminated soils or through hand or mouth of children playing in polluted soils. *In vivo* gastrointestinal extraction procedures have been used to assess the bioavailability of metals in soil. The oral bioavailability of the soil contaminants primarily depends upon the ability of the stomach and small intestine to dissolve the contaminant and adsorption of the contaminant through the intestinal membrane. Absorption requires that the contaminants be dissolved in a carrier e.g. bile. It is generally accepted that most of the uptake takes place in the small intestine (Dressman, Amidon et al.). In the stomach, the acid dissolves adsorbed contaminants while in the intestine the soil organic matter is dissolved and the more sequestered contaminants are released. This fraction is then available for internal exposure, i.e. entering the blood stream (Scott and Dean 2005). The bioavailability of aged and unaged pyrene to human was evaluated by measuring its desorption into an artificial stomach solution using the so-called physiologically based extraction test (PBET). Gastric juices were synthesized through first mixing 15 g of glycine and 1 L of deionized water with its pH adjusted to 1.5 using HCl, then adding pepsin (1 g), bovine serum albumin (BSA) (5 g), and type III porcine mucine (2.5 g). As shown in Figure 20, the fraction of pyrene in NC soil extracted by the stomach solution were reduced by aging process, especially for the soil sample amended with treated MI peat. However, its physiological availability increased by addition of untreated MI peat, this might be due to more dissolved organic carbons from untreated MI peat.

Table 16. Effects of Different ENOS on the Uptake of Pyrene by Earthworms from Soil

Soil Treatment	**NC Soil**			**Chelsea Soil**		
	Uptake (µg/g worm)	**Uptake** (%)	**BSAF**[c]	**Uptake** (µg/g worm)	**Uptake** (%)	**BSAF**
Fresh Soil (No aging or ENOS)	1156.89	2.97	10.49	498.59	1.41	4.74
Aged Soil[a] **No ENOS**	602.21	2.43	8.25	425.49	1.47	4.18
Aged Soil + 10% MP0[b]	502.96	1.77	5.61	214.59	0.81	2.18
Aged Soil + 10% MP1[b]	45.60	0.15	0.48	39.59	0.13	0.43
Aged Soil + 10% SS0[b]	403.54	1.98	4.56	Not determined		
Aged Soil +10% SS1[b]	46.92	0.15	0.58	Not determined		

a. Soils were aged for 105 days
b. MP: MI peat, SS: soybean stalks. 0: untreated, 1: treated
c. Biota-soil accumulation factor

Table 17. Effects of ENOS Amounts on the Uptake of Pyrene by Earthworms from Soil

ENOS Amount	**Untreated MP**	**Treated MP**

	Uptake (µg/g worm)	Uptake (%)	BSAF	Uptake (µg/g worm)	Uptake (%)	BSAF
Aged Soil[a] No ENOS	602.21	2.43	8.25			
Aged Soil[a] +5% MP[b]	630.41	1.70	6.20	76.90	0.32	0.86
Aged Soil + 10% MP	502.96	1.77	5.61	45.60	0.15	0.48
Aged Soil + 20% MP	250.65	1.02	2.54	22.33	0.06	0.22
	Untreated SS			**Treated SS**		
Aged Soil + 5%SS	654.03	2.79	7.35	62.30	0.19	0.63
Aged Soil + 10%SS[b]	403.54	1.98	4.56	46.92	0.15	0.58
Aged Soil + 20%SS	Worm died			Worm died		

a. Soils were aged for 105 days

b. MP: MI peat, SS: soybean stalks.

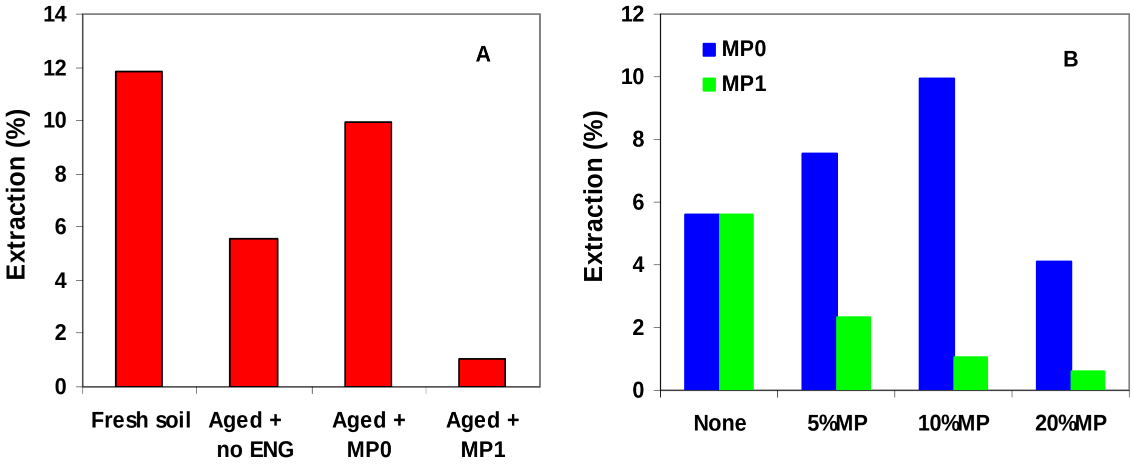

Figure 20. Effects of treated (MP1) and untreated (MP0) MI peat at 10% (A) and different peat amounts (B) on the physiological extraction of pyrene from aged NC soil

4.2.3. Microbial degradation. Once organic contaminants enter into soils, besides their sorption by soil particles, some of them will be degraded by indigenous or inoculated microorganisms. The environmental fate of target organic contaminants will be controlled by their sorption by soil and degradation by microorganisms. The biodegradability of aged and unaged pyrene from both NC and Chelsea soils amended with treated and untreated MI peat or soybean stalks at different ratios were determined for evaluating the effects of ENOS materials on the environmental fate of pyrene. The contaminated soil samples were transferred into 150-ml flasks fitted with a Teflon tape-wrapped silicon stopper with an 18-gauge needle inserted through each stopper. A 2.0-mL glass vial has been attached to the end of the stopper inside of the flask, and 1.5 ml of 0.5 N NaOH was injected using a 3.0-mL syringe through the needle into the vial. A specially isolated microbial consortium was inoculated to the flasks contained with soil samples and mineral medium to mineralize pyrene from soil samples. The alkali was removed periodically and mixed with 5.0 mL of scintillation cocktail for measuring the 14C radioactivity of the collected CO_2 in NaOH solution.

The mineralization rates of pyrene in both NC and Chelsea soils were presented in Figure 21 and the data showed that its mineralization rates varied greatly among soil samples amended with different ENOS materials. In the NC soil, pyrene was rapidly mineralized into CO2 in fresh soil samples, aged samples without ENOS amendments and aged samples amended with untreated MI peat, and reached its plateau at about 40 days. Its mineralization was reduced in the aged soil without addition of ENOS and increased in aged soil samples amended with untreated MI peat, compared to that of fresh soil samples. The results suggested that MI peat might enhance microbial growth in the reactors which led to increased pyrene mineralization and it also suggested that pyrene sorbed by geologically young MI peat was still readily available for microbial degradation. However, the mineralization of aged pyrene was greatly reduced in soil samples amended with treated MI peat, treated and untreated soybean stalks with only 28.6%, 20.4% and 27.7% of pyrene transformed into CO_2, respectively. As indicated above, the sorption capacities of treated MI peat and soybean stalks for hydrophobic compounds were greatly increased, which might lead to lower mineralization of pyrene. For soil samples amended with untreated soybean stalks, it was observed that microbes did not grow well as the reactors with other soil samples, which suggested that soybean stalks might be toxic to the microbial consortium. For Chelsea soil samples, pyrene was also rapidly mineralized in fresh soil samples, aged soils without ENOS amendments and with addition of untreated MI peat. The mineralization of pyrene was also increased with addition of untreated MI peat, but with less pyrene converted into CO_2 than that of fresh soil samples. This phenomenon may due to higher organic matter content (6.5%) in Chelsea soil. Not surprisingly, the mineralization of pyrene was remarkably reduced in the soil samples amended with treated MI peat with only 29.2% of pyrene transformed into CO_2 comparing to 59.3 to 67.8% of pyrene mineralized in other soil samples.

The environmental fate of aged and unaged pyrene in the soil samples was also evaluated. Besides the measurement of accumulated CO_2 released from pyrene mineralization, the 14C radioactivity of pyrene residues in the both aqueous medium and remained soil samples were also measured after biodegradation. The pyrene residues in aqueous medium are supposed to be water soluble metabolites of pyrene resulting from its microbial degradation because of the low water solubility (0.13 μg/mL) of pyrene. The pyrene residues in both CO_2 and aqueous medium are considered to its degradation products and they may not pose environmental risks. As shown in Table 18, more than 63% of pyrene was degraded in fresh NC soil. Comparing to about 50% of pyrene degraded in aged NC soil without ENOS amendments, untreated MI peat increased pyrene degradation with 66.3% of pyrene degraded, however, only 40.6% of pyrene was degraded in aged soil samples amended with untreated soybean stalks. The degradation of pyrene was greatly reduced in the soil samples amended with treated MI peat and soybean stalks with 32.5% and 25.3% of pyrene degraded, respectively. The reduction in pyrene degradation might be attributed to the high sorption capacities of treated MI peat and soybean stalks a result of superheated water treatment with more than 70% of pyrene remained in soil particles after biodegradation. As shown in Table 19, the degradation of pyrene increased as the amount of untreated MI peat increased and decreased with increase of treated MI peat, untreated and treated soybean stalks in NC soil. Similar results were found for pyrene biodegradation in Chelsea soil samples with 76.2%, 66.6%, 70.8%, and 34.8% of pyrene degraded in fresh soil, aged soil without ENOS amendments, aged soil amended with untreated and treated MI peat.

The residues of pyrene remained in soil particles after microbial degradation might include its original compound and metabolites and their distribution in soil samples was further evaluated by the above sequential extraction procedure. The data, as shown in Table A-3 of the Appendix, indicated that after its biodegradation, very high percentages of pyrene were extracted from soil samples by water, ranging from 1.00 to 4.64% in NC soil samples and from 1.48 to 5.09% in Chelsea soil and large fractions were remained in soils as non-extractable pyrene residues, ranging from 27.2 to 52.9% of pyrene residue remained in NC soil and 46.0 to 60.3% of pyrene residue remained in Chelsea. These values were much higher than that of pyrene residues from the soil samples before microbial degradation, in which only 0.12 to 0.95% of aged pyrene were extracted by water and 7.35 to 35.4% of pyrene remained in soil samples as non-extractable fractions. Most of non-extractable pyrene residues (62.0 to 95.3%) were immobilized in the humin fractions of the organic matter in soil samples. The data also show that treated MI peat and soybean stalks greatly reduced the fractions of pyrene residues extracted by water and the mixture of water and MeOH and increased the non-extractable fractions of pyrene residues in both NC and Chelsea soils (Table A-3 of Appendix). Both water-extractable fractions and the non-extractable fractions of pyrene residues in biodegraded soils increased as the amounts of treated MI peat and soybean stalks increased (Table A-4 of Appendix).

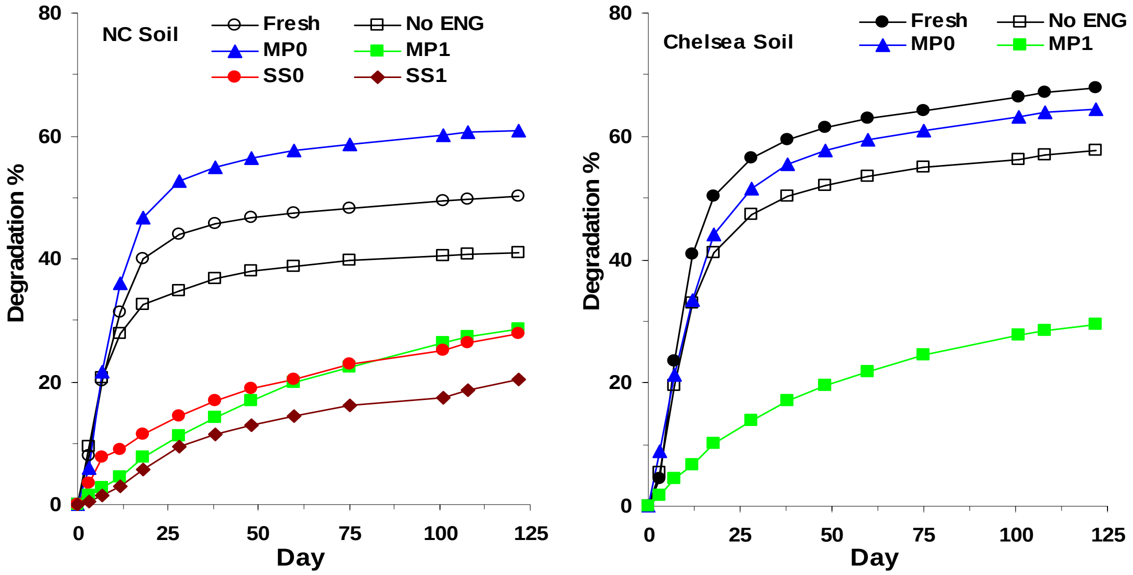

Figure 21. Effect of treated and untreated MI peat (MP0 and MP1) and soybean stalks (SS0 and SS1) on the degradation of pyrene aged in North Campus (NC) and Chelsea soils

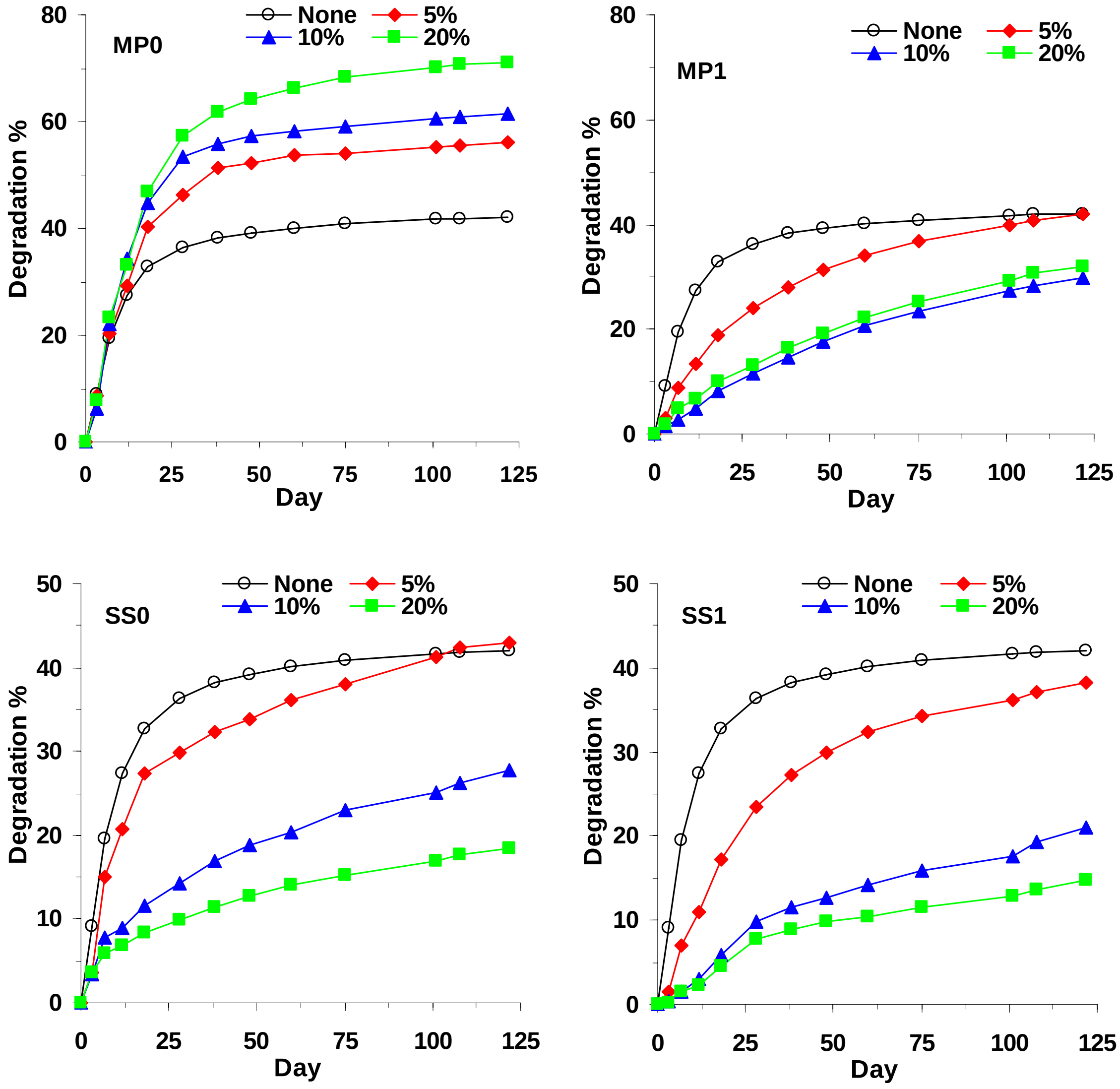

Figure 22. Effects of different amounts of treated and untreated MI peat (MP0 and MP1) and soybean stalks (SS0 and SS1) on the degradation of pyrene aged in NC soil

Table 18. Effects of Different ENOS on the Environmental Fate of Pyrene in Soil – After Microbial Degradation

Soil Treatment	NC Soil			Chelsea Soil		
	Mineralization - CO_2[c] (%)	Residue in H_2O[c] (%)	Residue in Soil[c] (%)	Mineralization - O_2[c] (%)	Residue in H_2O[c] (%)	Residue in Soil[c] (%)
Fresh Soil (No aging or ENOS)	50.30	12.84	35.63	68.22	7.99	28.13
Aged Soil[a] No ENOS	41.22	8.65	46.61	59.70	6.91	33.23
Aged Soil +10% MP0[b]	60.50	5.79	37.78	63.82	6.98	31.29
Aged Soil +10% MP1[b]	28.98	3.51	70.97	29.82	5.03	70.79
Aged Soil +10% SS0[b]	28.08	12.57	64.89	Not determined		
Aged Soil + 10% SS1[b]	21.38	3.93	73.60	Not determined		

a. Soils were aged for 105 days and biodegraded for 122 days

b. MP: MI peat, SS: soybean stalks. 0: untreated, 1: treated

c. After biodegradation, fractions of initially applied pyrene in gas (CO_2), liquid (water-soluble metabolites), and solid phase (fractions remained in soil).

Table 19. Effects of ENOS Amounts on the Environmental Fate of Pyrene in Soil – After Microbial Degradation

ENG Amount	Untreated MP			Treated MP		
	Mineralization - CO_2[c] (%)	Residue in H_2O[c] (%)	Residue in Soil[c] (%)	Mineralization - O_2[c] (%)	Residue in H_2O[c] (%)	Residue in Soil[c] (%)
Aged Soil[a] No ENOS	41.22	8.65	46.61			
Aged Soil[a] +5% MP[b]	58.64	7.54	36.52	42.69	7.56	53.69
Aged Soil + 10% MP	60.50	5.79	37.78	28.98	3.51	70.97
Aged Soil + 20% MP	71.50	8.38	26.29	30.65	4.09	71.25
	Untreated SS			**Treated SS**		
Aged Soil + 5%SS	44.52	11.67	50.44	33.26	5.04	66.45
Aged Soil + 10%SS[b]	28.08	12.57	64.89	21.38	3.93	73.60
Aged Soil + 20%SS	18.98	10.84	64.96	15.07	3.22	82.06

a. Soils were aged for 105 days and biodegraded for 122 days.

b. MP: MI peat, SS: soybean stalks.

c. After biodegradation, fractions of initially applied pyrene in gas (CO_2), liquid (water-soluble metabolites), and solid phase (fractions remained in soil).

The effects of treated MI peat on the sequestration of a mixture of four PAH compounds in sediment were also determined. Clean Huron River sediments were spiked with four PAH compounds, i.e., phenanthrene (Phen), anthracene (Anth), pyrene (Pyre), and chrysene (Chry), and aged for 56 days. The contaminated sediment samples were divided into three fractions and each fraction was mixed with 5% raw MI peat (A), 5% MI peat treated at 250oC for 5 hrs (B), respectively. The sediment samples without adding peat were used as control (C). Sediment A, B, and C were further aged to sequester these compounds in the sediment.

After the sediments were aged with and without peat sample for another 62 days, the bioavailability of PAH compounds in those sediment samples was determined by exposing them to earthworms (*E. foetida*) and aquatic worms (*Lumbriculus variegates*) for 14 days. The amount of PAH compounds taken up by the organisms was determined (Figure 23). The results show that uptake of PAH compounds by both earthworms and aquatic worms was remarkably reduced in the sediment samples amended with treated and untreated MI old peat. The concentrations of total PAHs in earthworms were 325.8 μg/g worm tissue from unamended sediment and their concentrations were reduced to 124.0 and 103.1 μg/g worm tissue for sediments amended with untreated and treated peat samples. For aquatic worms, these values were 374.9, 246.2 and 197.6 μg/g worm tissue, respectively.

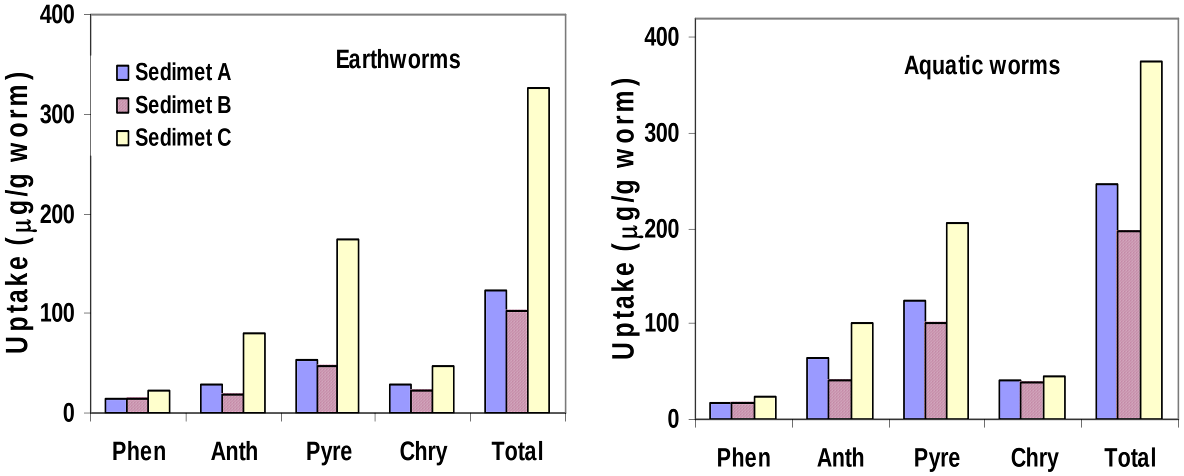

Figure 23. Effects of amendments of treated MI old peat on the uptake of PAH compounds by earthworms (Eisenia foetida) and aquatic worms (Lumbriculus variegates) from Huron River sediment (A: 5% raw peat, B: 5% 250oC treated peat, and C: no peat)

The environmental mobility of PAH compounds was determined by measuring their leachability from those sediment samples with water. Sediment samples were packed in glass columns and leached using a 0.01-M $CaCl_2$ solution containing 200 mg/L NaN_3 to prevent microbiological degradation. The leached water solutions were collected to determine PAH concentrations. The total amounts and percentages leached were calculated for each compound. The results showed that the leachability of PAH compounds were reduced for 5 – 10 times for sediment samples amended with peat (Figure 24).

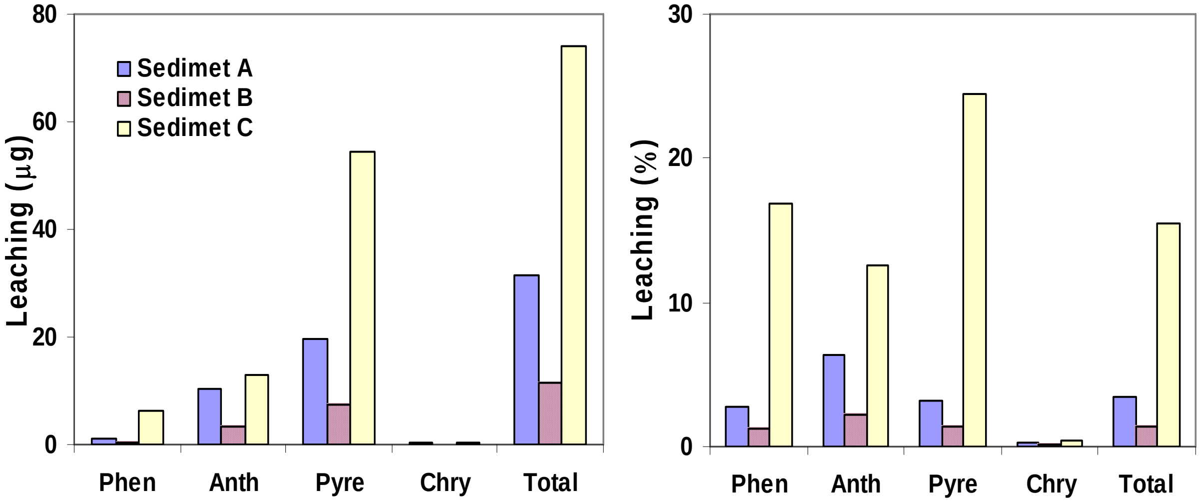

Figure 24. Effect of amendment of treated MI old peat on the leaching of PAH compounds from Huron River sediment (A: 5% raw peat, B: 5% 250°C treated peat, and C: no peat)

4.3. Heavy metals

The effects of ENOS materials on the environmental mobility and bioavailability of heavy metals were also determined. Pine needles and MI peat were treated with saturated $Na_4P_2O_7$ aqueous solutions at 200°C for 3 hrs. A representative heavy metal cadmium (($CdNO_3)_2$) was spiked to North Campus (NC) soils amended with treated and untreated pine needles and MI peat. Zeolite and montmorillonite, which were dried at 100oC for 24 hr before their using, were also respectively added to NC soil to test their sorption capacities for Cd^{2+}. The three types of experiments listed below were conducted.

1). Cd^{2+} was aged at 100 μg/g in NC soils amended with 10% of different types of ENOS, i.e., untreated pine needles (PN0), treated pine needles (PN1), untreated MI peat (MP0), treated MI peat (MP1), Zeolite (ZE), montmorillonite (MT), mixture of CP0 and ZE (1:1, w/w), and mixture of CP1 and ZE (1:1, w/w);
2). Cd^{2+} was aged at 100 μg/g in NC soils amended with 0, 2.5, 5.0, 10.0 and 15.0% MP1 to evaluate the effects of the ENOS amounts; and
3). Cd^{2+} was aged at 0, 40, 72. 111.7, and 195.9 μg/g in NC amended with 10% of MP.

After aging, total Cd^{2+} concentrations in the soil samples were extracted using Aqua regia digestion procedures (concentrated HNO_3 and 3 M-HCl) and determined by atomic absorption spectroscopy (AAS). Most of the applied Cd^{2+} was recovered from the soil samples (100.3 to 117%) because of its low volatility and non-degradability. NC soil samples spiked with Cd^{2+} at the same concentration as the aged soil samples were used as fresh soil sample for comparison. Its extractability was first determined by measuring extractable metal fractions using 1-M NH_4OAc solution, and then determined by an EPA Toxicity Characteristic Leaching Procedure (TCLP) using 0.1-M glacial acetic acid and 0.0643-M NaOH. These two fractions of metal are supposed to be readily available to plants and to leaching. As shown in Table 20, more than 50% of the Cd^{2+} was extractable from the fresh soil sample, and 42.5% from aged soil, which indicated that aging reduced the extractability of Cd^{2+} from soil. For the aged soil amended with 10% untreated pine needles (PN0) and montmorillonite (MT), the extractabilities of Cd^{2+} were greater than that from the aged soil without amendments. However, the extractable Cd^{2+} was remarkably reduced in the soil samples aged with 10% treated pine needles (PN1), untreated (MP0) and treated (MP1) MI peat, and zeolite (ZE), suggesting that these materials can greatly decrease the availability of heavy metals in soil. Similar results were found for the available fractions extracted using TCLP methods, although the values were much smaller than that of the extractable Cd^{2+} from both unamended aged and fresh soil samples.

The availability of Cd^{2+} in the soil separated into four fractions, i.e., the soluble and exchangeable fraction (F1) extracted by 0.1-M KNO_3, the organically bound fraction (F2) extracted by 0.5 M-NaOH, the inorganically bound fraction (F3) extracted by 0.05-M NaEDTA, and the residual fraction (F4) determined by the Aqua regia digestion procedure. The data show that soluble and exchangeable fraction (F1) of Cd^{2+} was reduced in the aged soil sample compared to that of fresh soil samples. In the soil samples aged with sorbent materials: untreated pine needles slightly increased and untreated MI peat and montmorillonite greatly increased the F1 fractions in their respective soil samples; and, treated pine needles, treated MI peat and zeolites reduced soluble and exchangeable Cd^{2+} by 32 to 54% compared to that of soil samples aged without amendments. Not surprisingly, the organically bound fractions (F2) of Cd^{2+} were increased in the soil added with organic sorbents, especially treated pine needles and MI peat. The F2 fractions did not change too much in the zeolite- and montmorillonite-amended soil samples. The effects of different amounts of ENOS was determined by aging with 0 to 15% treated MI peat in NC soil. The extractable and soluble cadmium increased and the organically bound fractions increased as the MI peat increased. The effects of ENOS on the extractability and fractionation of cadmium at different initial concentrations were also determined. The extractable, soluble and exchangeable, and organic bound Cd^{2+} decreased as initial Cd^{2+} concentrations increased.

The bioavailability of Cd^{2+} from the above soil samples was determined by its uptake by earthworms, corn and soybean plants. Earthworms were exposed to the Cd^{2+} contaminated soil samples under dark at room temperatures for 14 days. After uptake experiments, the worms were purged for their gut contents and dried in the freeze drier to get dry worm weight, Cd^{2+} in worm tissues were extracted by digestions with concentrated HNO_3 and 33% H_2O_2 in 90^oC water bath for 2 hrs. Germinated corn or soybean seeds were planted in the Cd^{2+} contaminated soil samples in small pots. The pots were placed and watered periodically in a growth chamber at 25 ± 2^oC with a 16/8-hr light-dark cycle for 21 days. Corn or soybean plants were harvested and dried in a 70^oC oven, cut into small pieces and extracted with concentrated HNO_3 and 3-M HCl in a 90^oC water bath for 2-3 hrs. Cd^{2+} concentrations in all extraction solutions were measured using AAS. Concentrations of Cd^{2+} remaining in the soil samples were also determined. Cd^{2+} concentrations in worm and plant tissues and biota-soil accumulation factors (BSAF = Cd^{2+} concentration in biological tissue/ Cd^{2+} concentration in the soil) were calculated as measures of its availability to worms and plants in soil. The data, as shown in Table 21, show that aging without amendments reduced Cd^{2+} uptake by worms and corn compared to fresh soil samples. All amendments other than untreated pine needles reduced Cd^{2+} uptake by worms or corn from soils, and treated pine needles and MI peat had more significant impacts than other amendments. Soils amended with zeolite killed all worms and the corn because of its high alkalinity. The uptake of Cd^{2+} by worms and soybean decreased as the amounts of treated MI peat increased and its uptake increased as the initial Cd^{2+} concentrations in soil increased.

Table 20. Effects of ENOS on the Extractability and Fractionation of Cadmium in North Campus Soil

	Extractability		**Fractionation**			
Soil Treatment	**Extractable (%)**	**TLCP (%)**	**F1 (%)**	**F2 (%)**	**F3 (%)**	**F4 (%)**
	A. Different Types of ENGs					
Fresh Soil (No aging or ENOS)	52.4	1.73	21.5	12.2	63.0	7.61
Aged Soil [a] (No ENOS)	42.5	1.40	15.5	13.0	59.5	10.1
Aged Soil +10% PN0	50.0	1.54	16.8	17.9	60.0	10.0
Aged Soil +10% PN1	16.5	1.05	7.08	29.6	58.9	14.0
Aged Soil +10% MP0	38.0	1.01	30.0	18.4	50.1	15.1
Aged Soil +10% MP1	29.1	1.09	8.65	24.2	59.4	15.2
Aged Soil +10% ZE	7.14	0.65	10.5	14.5	65.5	11.0
Aged Soil +10% MT	52.6	2.33	29.7	14.8	56.0	13.3
Aged Soil+5% MP0+5%ZE	14.4	1.26	10.4	21.9	61.1	17.8
Aged Soil+5% MP1+5%ZE	8.88	0.97	8.75	20.5	62.6	17.3
	B. Different Amounts of ENOS					
Aged Soil [b] (No ENOS)	46.5	1.88	14.3	13.6	70.8	7.57
Aged Soil +2.5% MP1	31.4	1.69	7.64	16.6	71.4	8.13
Aged Soil +5.0% MP1	27.6	1.50	7.42	18.2	74.0	7.44
Aged Soil +10% MP1	19.1	1.14	6.83	20.4	70.9	5.43
Aged Soil +15% MP1	14.8	1.04	6.65	22.3	70.1	9.94
	C. Different Initial Cd^{2+} Concentrations[c]					
Cd^{2+} @ 39.6 (μg/g)	25.8	2.00	13.6	28.9	52.5	16.6
Cd^{2+} @ 72.2 (μg/g)	20.5	1.49	8.93	18.6	63.3	12.6
Cd^{2+} @ 111.7 (μg/g)	19.7	1.34	6.81	14.0	73.5	10.7
Cd^{2+} @ 195.9 (μg/g)	16.4	0.99	4.41	10.8	75.3	8.60

a. Cadmium at 100 μg/g was aged in NC soil amended with different ENGs for 127 days.

b. Cadmium at 100 μg/g was aged in soils amended with treated CP for 216 days

c. Cadmium at different concentrations was aged in NC soil amended with 10% treated MP for 216 days.

Table 21. Effects of ENOS on the Bioavailability of Cadmium in North Campus Soil

	Worm Uptake		Plant Uptake	
Soil Treatment	**Conc. (μg/g)**	**BSAF**	**Conc. (μg/g)**	**BSAF**
	A. Different Types of ENOS			
Fresh Soil (No aging or ENOS)	848.6	7.69	201.4^{d}	1.71
Aged Soil [a] (No ENOS)	764.4	7.75	147.5	1.75
Aged Soil +10% PN0	990.9	8.84	113.6	0.86
Aged Soil +10% PN1	401.6	3.64	28.8	0.23
Aged Soil +10% MP0	549.3	4.86	119.3	0.96
Aged Soil +10% MP1	395.9	3.45	43.7	1.15
Aged Soil +10% ZE	Worm died		Corn died	
Aged Soil +10% MT	707.2	6.18	132.7	3.63
Aged Soil +5% MP0+5%ZE	452.1	3.88	27.9	0.24
Aged Soil +5% MP1+5%ZE	438.3	4.39	17.6	0.16
	B. Different Amounts of ENOS			
Aged Soil [b] (No ENOS)	511.6	4.89	122.1^{e}	0.83
Aged Soil +10% MP1	446.5	4.12	58.8	0.41
Aged Soil +10% MP1	354.2	3.23	45.8	0.27
Aged Soil +10% MP1	271.2	2.38	17.4	0.10
Aged Soil +10% MP1	174.4	1.42	10.1	0.06
	C. Different Initial Cd^{2+} Concentrations [c]			
Cd^{2+} @ 39.6 (μg/g)	130.0	3.32	6.01^{e}	0.15
Cd^{2+} @ 72.2 (μg/g)	181.6	2.54	20.4	0.22
Cd^{2+} @ 111.7 (μg/g)	240.8	2.17	41.8	0.26
Cd^{2+} @ 195.9 (μg/g)	419.4	2.15	52.8	0.20

a. Cd^{2+}at 100 μg/g was aged in NC soil amended with different ENGs for 127 days.
b. Cd^{2+} at 100 μg/g was aged in soils amended with treated MP for 216 days
c. Cd^{2+} at different concentrations was aged in NC soil amended with 10% treated MP for 216 days
d. Corn uptake and e. Soybean uptake

C. Implications and Future Research

The results from this study show that significant changes in the physical and chemical properties of a number of raw organic materials result from superheated water treatment, i.e., as temperatures and associated pressures are increased the overall aromatic character and state of condensation of the treated materials increases. Spectroscopic analyses confirm that fractions of alkyl and aromatic carbons increase, while oxygen-associated functional organic carbons decrease. Changes in elemental compositions and molecular structures indicate that the organic fractions of the raw materials become less polar, increasingly condensed, and more aromatic as a result of accelerated diagenetic-like reactions effected by this treatment. The experimental results confirm that the long-term biogeochemical processes, which in nature result in geologically slow advances in the chemical states of organic carbon along a continuous spectrum of transformations from simple biopolymers through humus, kerogens, and eventually various forms of coal-like "black carbon" species, can be simulated and markedly accelerated by superheated water treatment.

The sorption capacities of these treated organic materials for hydrophobic organic contaminants, such as DNAPL components TCE, PCE, and DCB, and heavy metals are significantly increased. The results obtained in this study provide direct evidence that the sorption capacities and isotherm nonlinearities of different types of NOMs are functions of the degree of condensation and aromatization that they undergo under superheated water processing. The environmental mobility and bioavailability of both organic and inorganic contaminants were remarkably reduced when the soils were amended with treated organic materials as geosorbents more contaminants became sequestrated and immobilized in soils as the amounts of these sorbent materials increased. The study shows that is feasible to produce smart natural organic sorbents by modifying and restructuring readily available and low-cost natural plant materials.

The *in-situ* irreversible immobilizations and inactivation of chlorinated aliphatic hydrocarbon DNAPLs, other organic contaminants, and heavy metals by ENOS demonstrated in this study are expected to provide an innovative, cost-effective and non-intrusive solution to these difficult remediation problems at most contaminated DOE sites, and should effectively eliminate both production of secondary wastes and the necessity for off-site treatment/disposal approaches. Such specially designed and engineered ENOS materials should not only be environmentally benign, but should in fact improve the structure and quality of soils and sediments via their gradual incorporation therein through natural humification processes. In addition to having tailored sequestration properties, ENOS materials can be designed to improve environmental conditions for the growth of indigenous microorganisms by providing nutrients/substrates and by reducing the toxicities of contaminants at high concentrations. This should lead to enhanced ongoing natural attenuation and eventual complete detoxification of sites contaminated with DNAPL compounds, polycyclic aromatic hydrocarbons (PAHs), energetic compounds (e.g., NT, RDX, etc.) that commonly present at DOE and other federally owned energy and defense related facilities. Future studies with field contaminated soils are recommended to verify the results obtained from the bench-scale reactor studies described herein.

D. Publications and Presentation

1. Journal Papers

1) Weber, W.J., Jr. , J. Tang, and Q Huang 2006. “Development of Engineered Natural Organic Sorbents for Environmental Applications: I. Materials, Approaches, and Characterizations”. *Environmental Science and Technology , 40* (5),1650-1656 (2006).

2) Tang, J. and W. J. Weber, Jr. 2006. “Development of Engineered Natural Organic Sorbents for Environmental Applications: II. Sorption Characteristics and Capacities with Respect to Phenanthrene”. *Environmental Science and Technology ,40* (5), 1657-1663 (2006).

3) Tang, J., E. Peterson, Q. Huang and W. J. Weber, Jr. 2006. “Development of engineered natural organic sorbents for environmental applications. 3. Reducing PAH mobility and bioavailability in contaminated soil and sediment systems" Submitted to *Environmental Science & Technology*. (in review).

4) Tang, J., and W. J. Weber, Jr. 2006. “The Effects of Engineered Natural Organic Sorbents on the Sorption and Sequestration of Pyrene in soil. II: Microbial Degradation and Environmental Fate”. *Environ. Sci .Technol.* (in preparation).

5) Qingguo Huang, Roger A. Pinto, Daniel J. Burlingame, Jixin Tang and W. J. Weber, Jr., 2005. "Enhanced Removal of Natural Organic Matter via Molecular Reconfiguration: Peroxidase- Mediated Oxidative Coupling", *Water Science and Technology: Water Supply !4* (4), 33-40 (2005).

6) Huang Q.G and W. J. Weber, Jr. 2004. "Peroxidase-catalyzed Coupling of Phenol in the Presence of Model Inorganic and Organic Solid Phases". *Environ. Sci .Technol.* 38 (19): 5238-5245 (2004).

7) Weber, W.J., Jr. and Q. Huang 2003. "Inclusion of Persistent Organic Pollutants in Humification Processes: Direct Chemical Incorporation of Phenanthrene via Oxidative Coupling", (with Q. Huang) *Environmental Science and Technology, 37*, 18, 4221-4227 (2003).

2. Abstracts and Presentations

1) Tang, J. and W.J. Weber, Jr. 2003. Engineered Natural Organic Sorbents: Characterization of Their Properties and Sorption/desorption Behaviors. 226th Annual Meeting of American Chemical Society, New York City, New York, September 7-11, 2003.

2) Weber, W.J., Jr. 2003. Organic Contaminant Bioavailability in Groundwater and Subsurface Systems. Water Purification and Reuse, Engineering Conferences International, Potsdam, Germany, June 9-13, 2003.

3) Huang, Q. and W.J. Weber, Jr. 2003. Reactive Inclusion of Phenanthrene in the Oxidative Coupling Reactions of Phenol: Implications for Irreversible Sequestration *via* Humification. 226th Annual Meeting of American Chemical Society, New York City, New York, September 7-11, 2003.

4) Tang, J. and W.J. Weber, Jr. 2004. Competitive Sorption and Desorption of Chlorinated Organic Solvents (DNAPLs) in Engineered Natural Organic Matter. 227th Annual Meeting of American Chemical Society, Anaheim, CA, March 28 – April 1, 2004.

5) Huang, Q.G. and Weber, W. J. Jr 2004. Transformation of bisphenol A in peroxidase-mediated oxidative coupling reactions: Pathway and mechanisms”. 228th Annual Meeting of American Chemical Society, August 22-26, 2004, Philadelphia, PA

6-10) Regular presentations by invitation at several DOE-Sponsored Conferences over the Research Project duration.

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Weber, W.J.,,Jr, L.E.Katz, and P.M. McGinley "A Distributed Reactivity Model for Sorption by Soils and Sediments: 1. Conceptual Basis and Equilibrium Assessments" *Environmental Science and Technology*, ***26*** (10), 1955-1962 (1992).

Appendix

Table A- 1. FTIR Radiation Bands and Bond Actions for Specific Organic Functional Groups and Biomolecules (1-4)

Wavenumber (cm^{-1})	Bond Action	Functional Group	Biomolecule
1100 - 1020	C-O stretch	Carbohydrate or aliphatic alcohol	Cellulose
1290 - 1240	C-O stretch	Aromatic ether or epoxide	Lignin
1180-1120			
1380-1350			
1485 -1445	C-H stretch	Saturated aliphatic C	Cellulose
1515-1480			Lignin or hemicellulose
1615-1580	C=C-C stretch	Aromatic ring	
1740-1700	C=O stretch	Carboxylic C or carbonyl C	Humic acid
2860-2840			
2930-2910	C-H stretch	Aliphatic C with CH_2 or CH_3	Cellulose
3600-3200	O-H stretch	Carboxylic C or hydroxy group	Carbohydrate or alcohol

Table A-2. Relative Percentages of NMR Signals of Specific Organic Carbon Functional Groups and Calculated Hydrophobicity and Aromaticity Indices of MI peat by ^{13}C NMR Analysis

Temperature (^{o}C)	Aliphatic 0-45*	Carbohydrate 50-95*	Aromatic 100-165*	Carboxyl 165-195*	Carbonyl 190-210*	I_H	I_{AR}
			%				
22 (Raw)	23.1	29.1	37.2	6.9	2.9	0.83	0.65
50	23.9	30.8	36.3	5.9	2.8	0.81	0.66
100	27.9	22.1	40.2	5.9	2.9	1.57	0.80
150	32.3	16.9	43.6	5.5	2.7	1.80	0.89
200	32.4	11.7	48.7	4.8	2.2	3.14	0.99
250	35.6	4.52	56.2	2.8	1.2	4.19	1.18

*** ppm range**

I_H: hydrophobicity index

I_{AR}: aromaticity index

Table A-3. Effects of ENOS on the Distribution of Aged and Biodegraded Pyrene in NC and Chelsea Soils – by Sequential Extraction

Soil Treatment	Water %	MeOH & Water %	MeOH %	Non-Extractable[c] %	Humic & Fulvic Acids %	Humin %
			NC Soil			
Fresh Soil (No aging or ENOS)	4.52	9.62	58.66	27.20	9.39	17.81
Aged Soil[a] **No ENG**	3.54	6.16	57.69	32.60	7.54	25.06
Aged Soil **+ MP0[b]**	4.64	4.10	47.59	43.67	8.39	35.28
Aged Soil **+ MP1[b]**	1.27	2.04	43.75	52.94	3.26	49.67
Aged Soil **+ SS0[b]**	2.83	7.49	54.26	35.43	6.47	28.96
Aged Soil **+ SS1[b]**	1.00	2.49	56.23	40.29	2.92	37.37
			Chelsea Soil			
Fresh Soil (No aging or ENOS)	5.09	6.81	42.07	46.03	17.49	28.53
Aged Soil[a] **No ENOS**	4.26	4.28	39.35	52.11	12.68	39.43
Aged Soil **+ MP0[b]**	4.58	4.37	38.61	52.43	12.08	40.36
Aged Soil **+ MP1[b]**	1.48	1.33	36.92	60.27	2.86	57.41

a. Soils were aged for 105 days and degraded for 122 days

b. MP: MI peat, SS: soybean stalks. 0: untreated, 1: treated

c. Non-extractable fraction included both humic and fulvic acids and humin

Table A-4. Effects of Different ENOS Amounts on the Distribution of Aged Pyrene in NC Soil – by Sequential Extraction

ENG Amounts	Water %	MeOH & Water %	MeOH %	Non-Extractable[c] %	Humic & Fulvic Acids %	Humin %
			Untreated MI Peat –MP0			
Aged Soil[a] No ENOS	3.54	6.16	57.69	32.60	7.54	25.06
Aged Soil[a] +5% MP0[b]	4.16	4.61	48.89	42.34	8.57	33.77
Aged Soil + 10% MP0	4.64	4.10	47.59	43.67	8.39	35.28
Aged Soil + 20% MP0	6.33	4.70	44.71	44.25	7.89	36.36
			Treated MI Peat –MP1			
Aged Soil[a] +5% MP1[b]	1.93	1.88	48.51	47.68	3.53	44.15
Aged Soil + 10% MP1	1.27	2.04	43.75	52.94	3.26	49.67
Aged Soil + 20% MP1	0.93	1.23	41.26	56.58	1.89	54.69
			Untreated Soybean Stalks – SS0			
Aged Soil[a] +5% SS0[b]	4.78	7.52	50.99	36.71	7.82	28.88
Aged Soil + 10% SS0	2.83	7.49	54.26	35.43	6.47	28.96
Aged Soil + 20% SS0	3.16	5.43	54.10	37.30	4.97	32.33
			Treated Soybean Stalks – SS1			

Aged Soil[a] +5% SS1[b]	1.18	2.17	67.37	29.28	3.23	26.04
Aged Soil + 10% SS1	1.00	2.49	56.23	40.29	2.92	37.37
Aged Soil + 20% SS1	1.11	1.56	49.27	48.06	2.84	45.22

a. Soils were aged for 105 days

b. MP: MI peat, SS: soybean stalks. 0: untreated, 1: treated

c. Non-extractable fraction included both humic and fulvic acids and humin

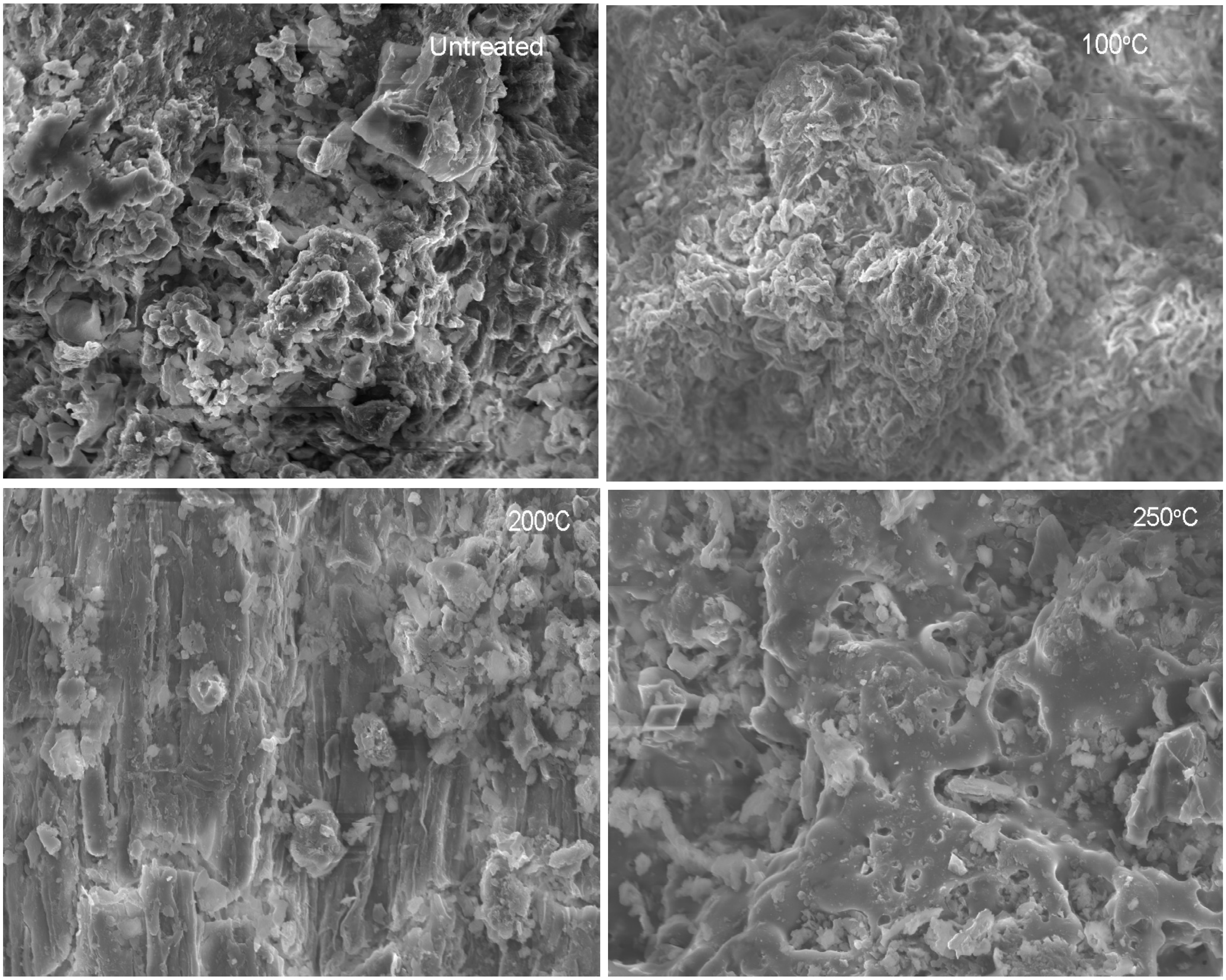
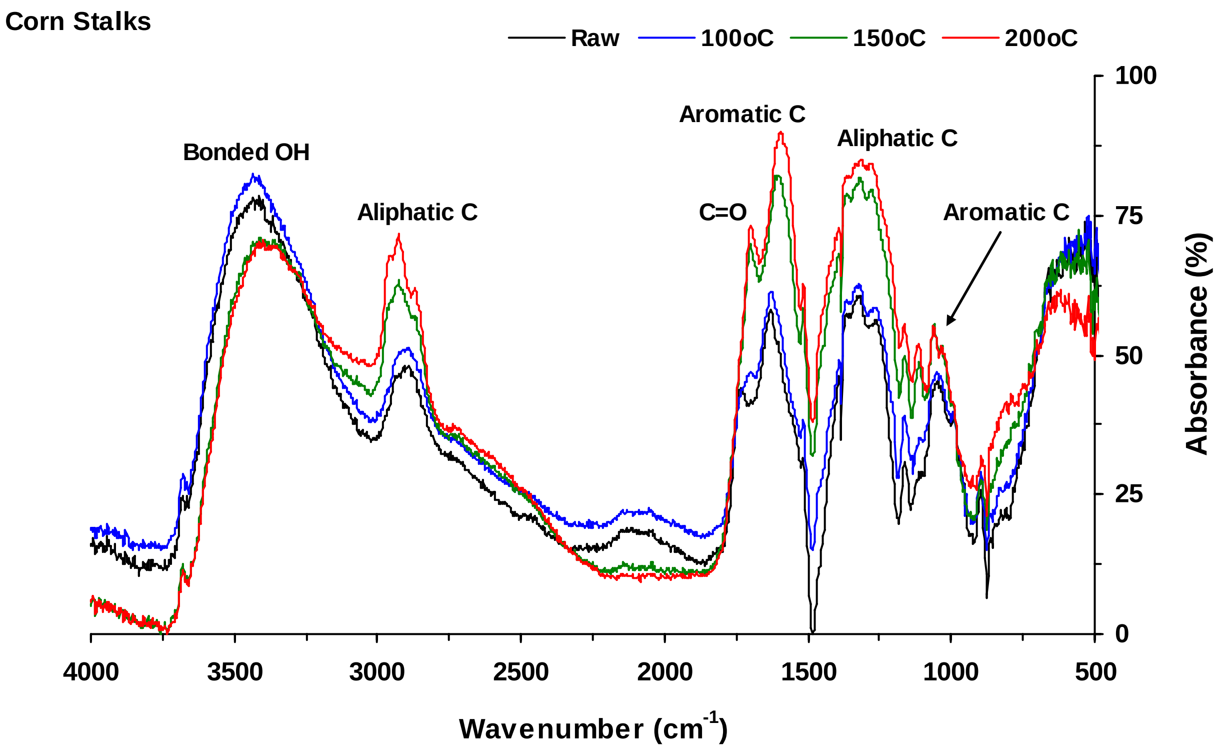

Untreated
100°C
200°C
250°C

Figure A-1. SEM images of MI peat treated at different temperatures in superheated water (50μm)


Corn Stalks
Raw
100oC
150oC
200oC
Bonded OH
Aliphatic C
C=O
Aromatic C
Aliphatic C
Aromatic C
Absorbance (%)
0
25
50
75
100
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

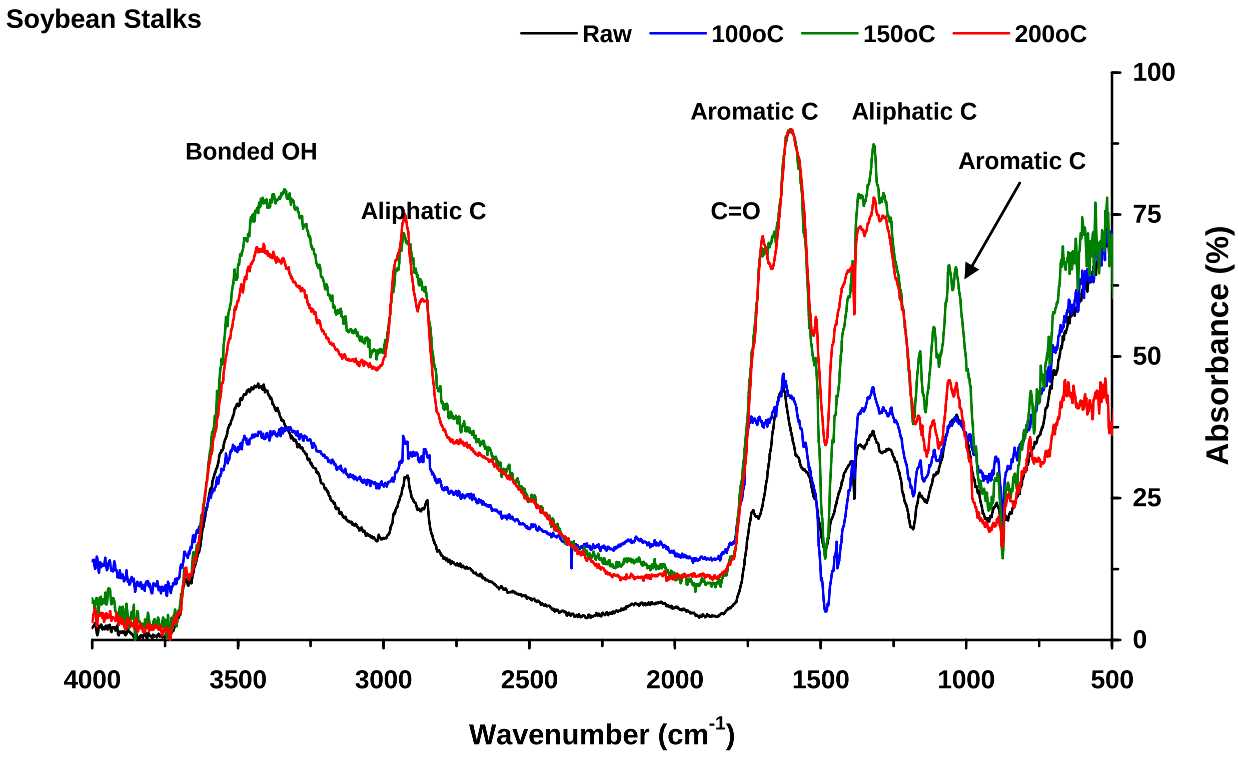
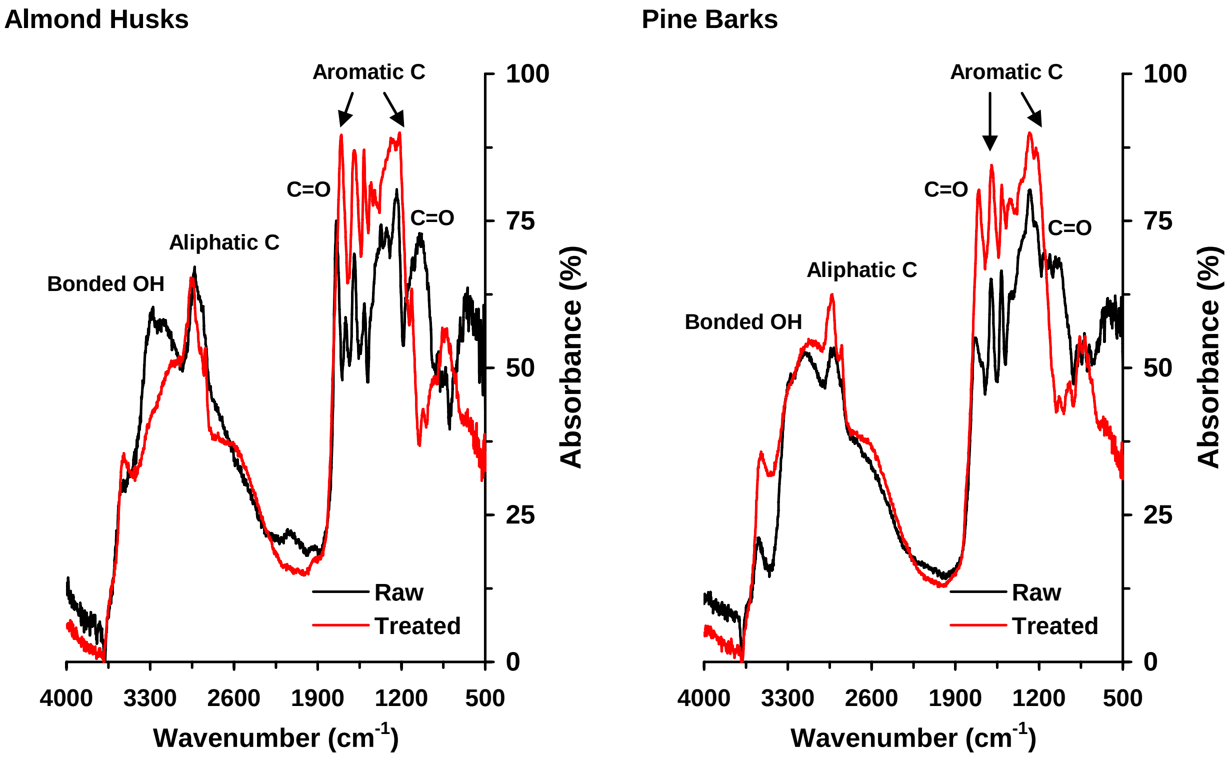

Soybean Stalks
Raw
100oC
150oC
200oC
Bonded OH
Aliphatic C
C=O
Aromatic C
Aliphatic C
Aromatic C
Absorbance (%)
0
25
50
75
100
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})

Figure A-2. FTIR spectra for corn stalks and soybean stalks treated at different superheated water temperatures


Almond Husks

Pine Barks

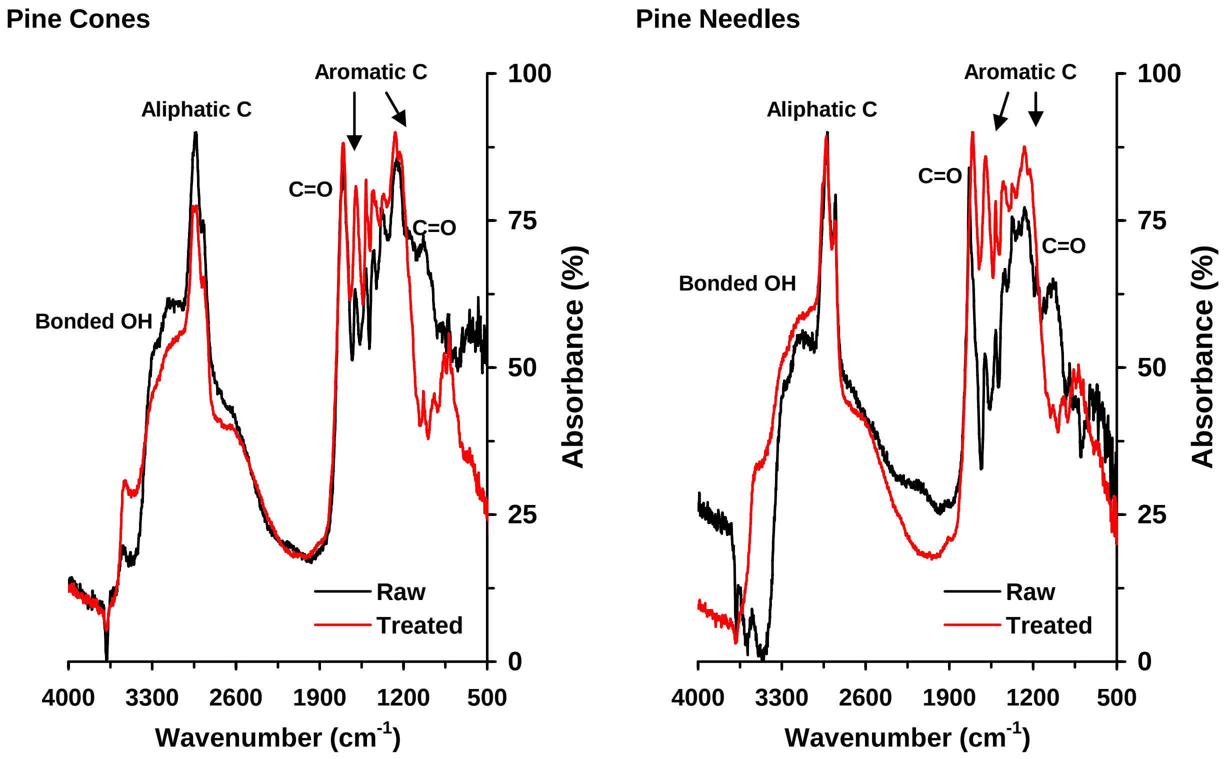
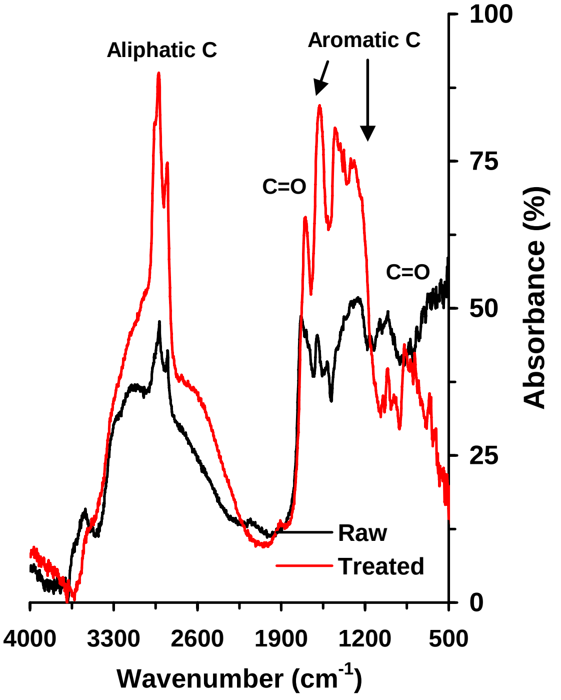
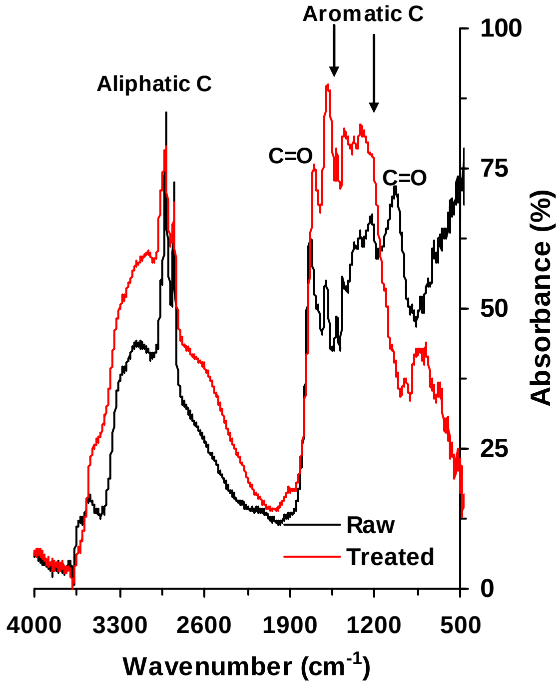


Figure A-3. FTIR spectra for almond husks, pine barks, pine cones, and pine needles before and after superheated water treatment (250°C)

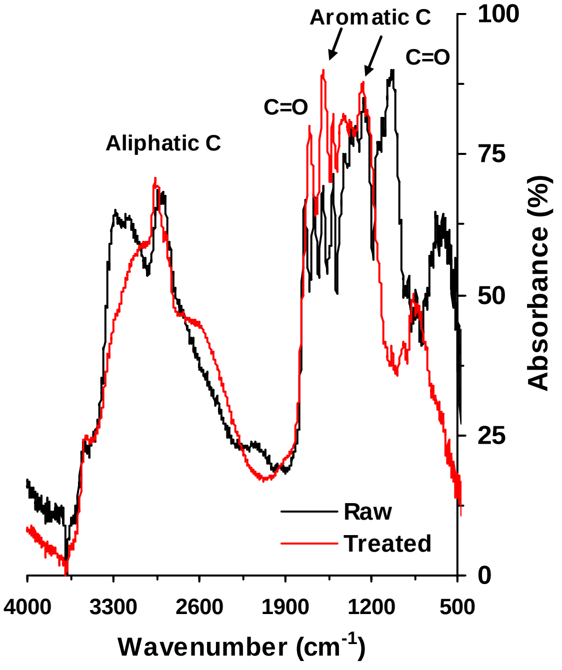
Ash Leaves



Oak Leaves



Peanut Husks



Wheat Straws

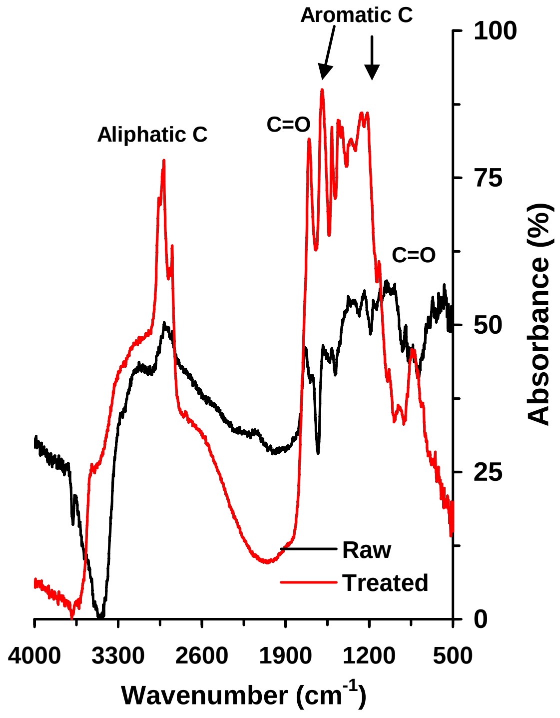


Figure A-4. FTIR spectra for ash leaves, oak leaves, peanut husks, and wheat straw before and after superheated water treatment (200^{o}C or 250^{o}C)

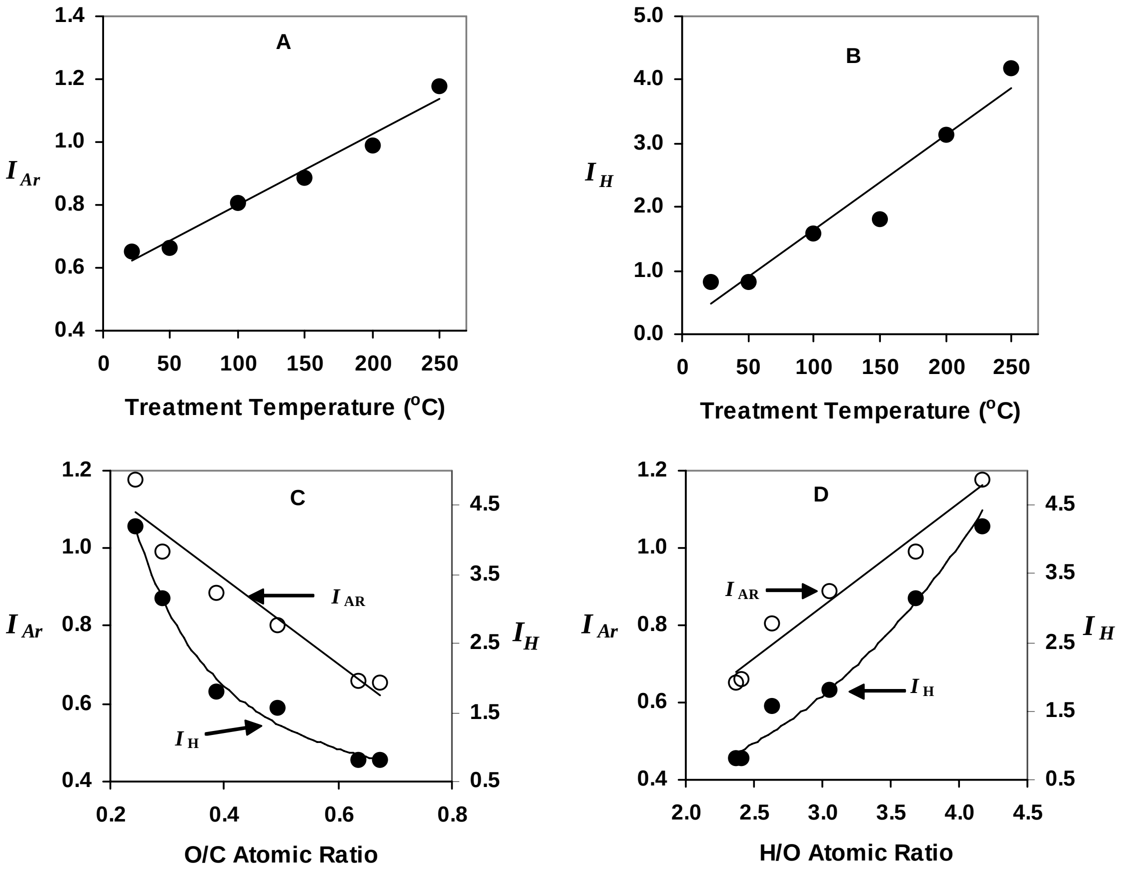

A
B
C
D
I_{Ar}
I_H
Treatment Temperature (°C)
O/C Atomic Ratio
H/O Atomic Ratio
I_{AR}
I_H
1.4
1.2
1.0
0.8
0.6
0.4
5.0
4.0
3.0
2.0
1.0
0.0
0
50
100
150
200
250
0.2
0.4
0.6
0.8
4.5
3.5
2.5
1.5
0.5
2.0
2.5
3.0
3.5
4.0
4.5

Figure A-5. Hydrophobicity and aromaticity index (I_{AR} and I_H) relationships to treatment temperatures and elemental atomic ratios

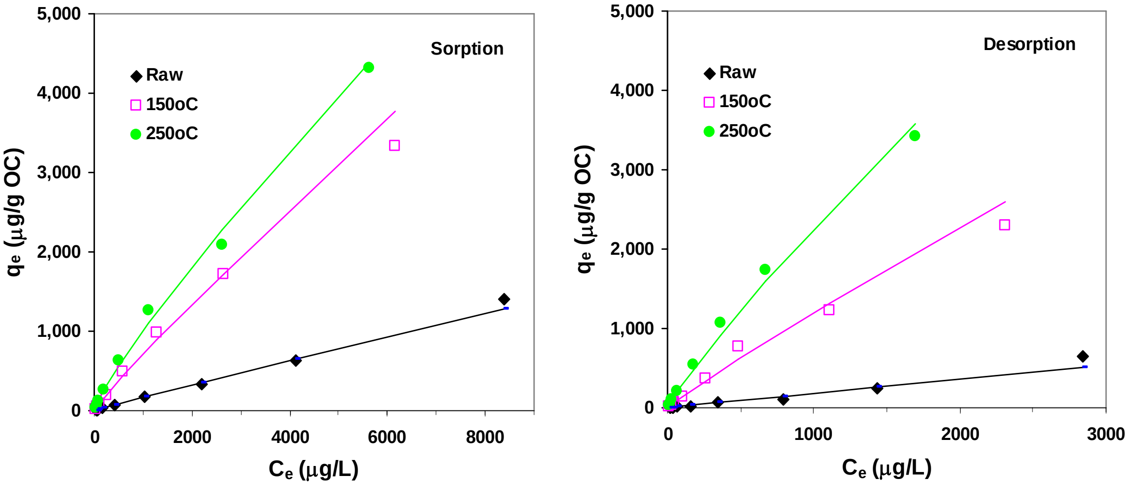
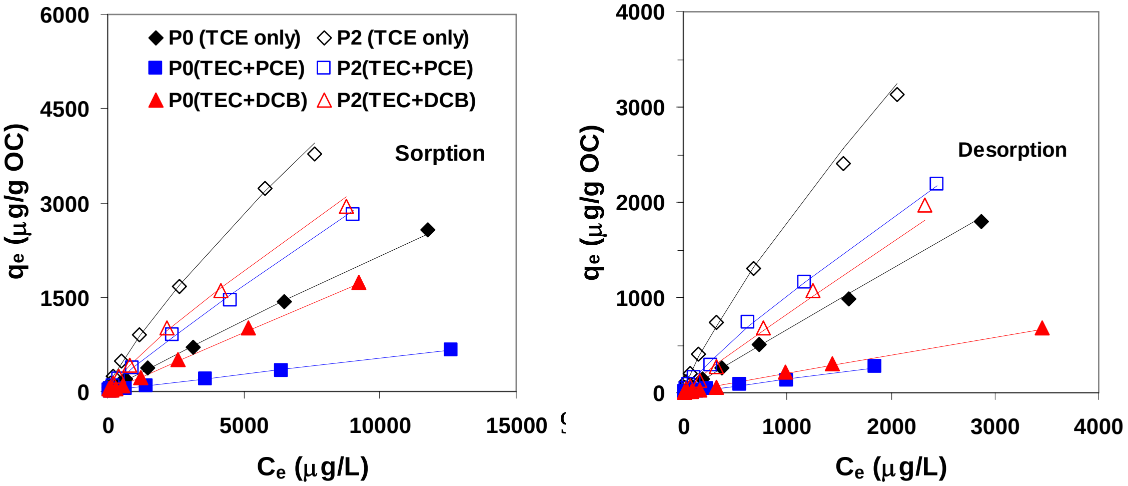


Figure A-6. Isotherms for the sorption and desorption of PCE by MI peat treated with superheated water at different temperatures



rption

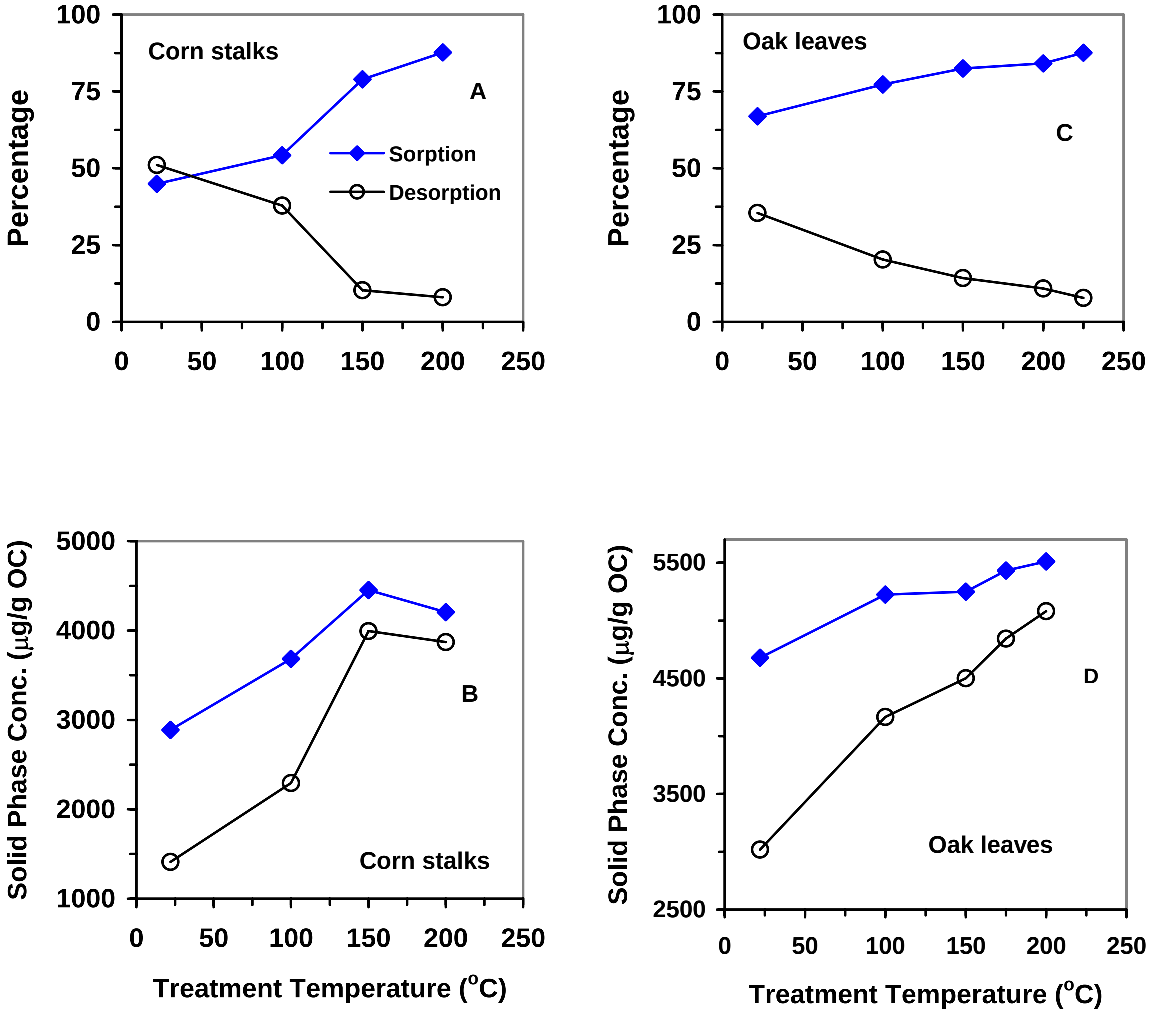


Figure A-8. Effects of treatment temperature on the sorption and desorption of phenanthrene by corn stalks and oak leaves treated in superheated water

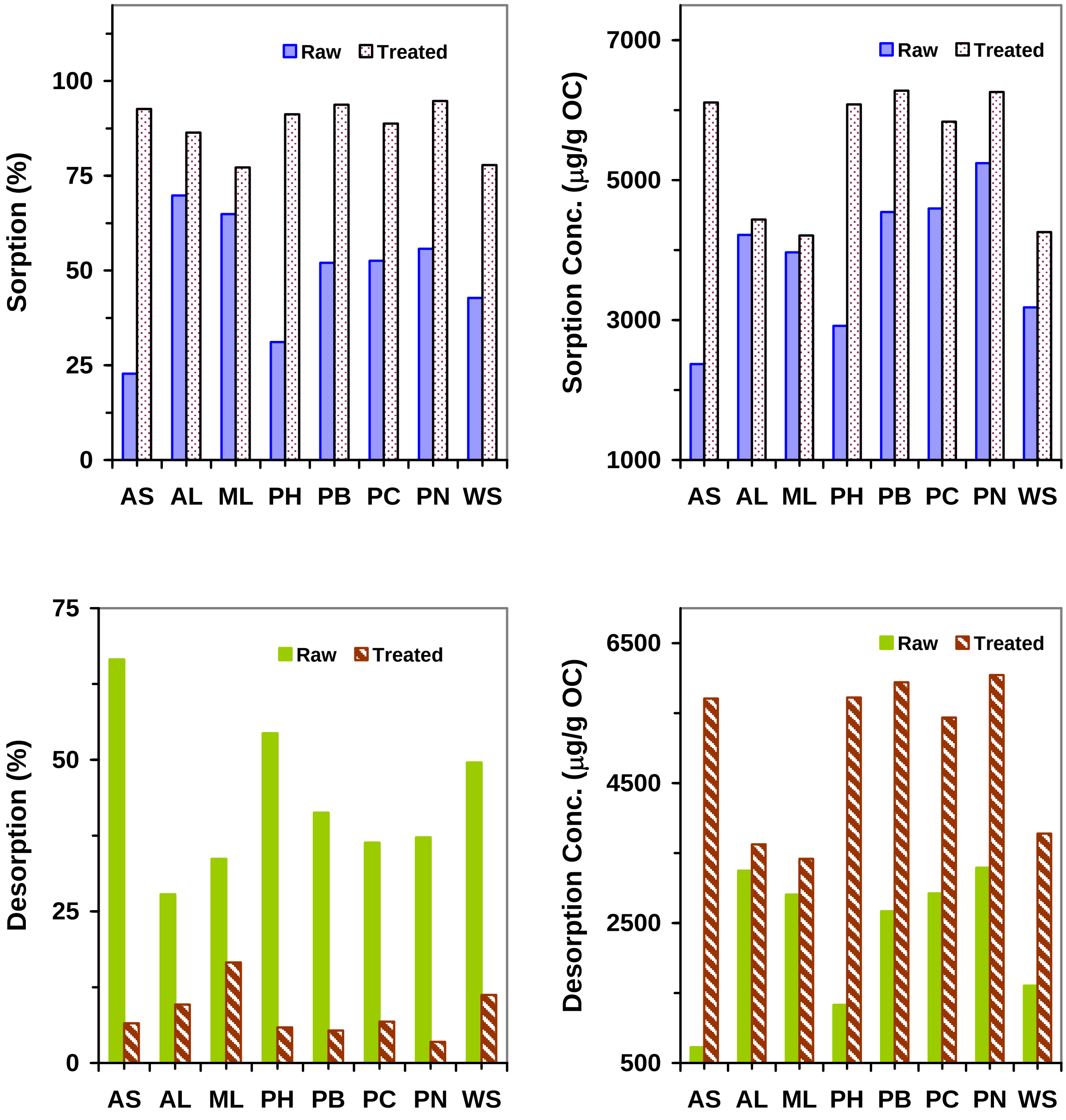


Figure A-9. Effects of thermal treatment on the sorption and desorption of phenanthrene by natural organic materials before and after treatment with superheated water at 250oC for 5 hrs (AS: almond shell, AL: ash leaves, ML: maple leaves, PH: peanut husk, PB: pine bark, PC: pine cone, PN: pine needle, and WS: wheat straw)

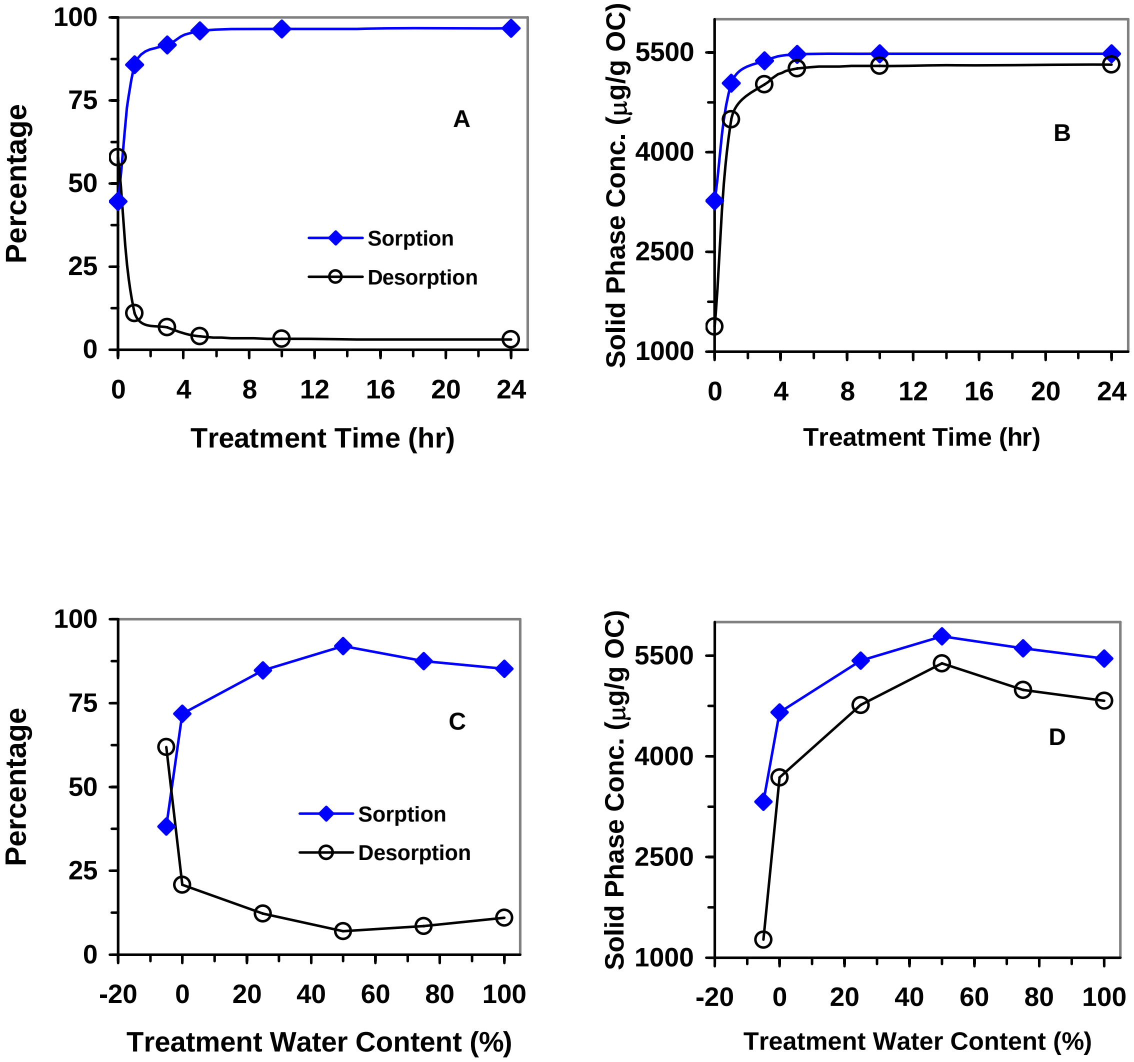


Figure A-10. Effects of treatment time (A and B) and water content (C and D) on sorption and desorption of phenanthrene by MI peat treated in superheated water at 250 ^{o}C.