THE EFFICACY OF OXIDATIVE COUPLING FOR PROMOTING IN-SITU IMMOBILIZATION OF HYDROXYLATED AROMATICS IN CONTAMINATED SOIL AND SEDIMENT SYSTEMS

DOE-EMSP Project 54548. DOE-EMSP Workshop, April 25-28, 2000; Atlanta, GA

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Abstract

Our current research on abiotic and enzymatic coupling reactions of hydroxylated aromatic compounds (HACs) in natural geosorbent systems expanded our understanding of the processes involved, and demonstrated that induction of oxidative coupling by addition of catalysts is a subsurface remediation option worth exploring further. Oxidative coupling of HACs on natural sorbents by addition of mineral or enzymatic oxidative coupling catalysts is shown to be an effective immobilization approach by promoting either coupling to the soil organic matter and/or formation of polymers with strong sorption tendencies. Our results reveal that natural sorbents containing diagenetically young organic matter are more likely to promote coupling to soil organic matter in the presence of naturally occurring or added catalysts. The role of catalyst concentration was evaluated demonstrating that the catalyst activity and concentration of parent HAC compound control the distribution of coupling products between soluble and insoluble polymers. Moreover, oxidative coupling to soil organic matter is apparently predominant at low catalyst activities where formation of insoluble polymers is decreased.

Introduction

Sorption processes often dominate the fate and transport of organic contaminants in the subsurface. A significant emphasis has been placed on characterizing sorption onto and desorption from natural sorbents, however, for these same systems, there has been comparatively little investigation of the coupling reactions that are known to occur with phenolic compounds and how this coupling affects sorption processes. Theoretically, these coupling reactions can result in the formation of covalent linkages with soil surface functionalities, immobilizing the contaminants on the soil matrix, a process similar to humification, the natural formation of soil organic matter. (shown schematically in Figure 1). Formation of less mobile polymeric products, which could strongly interact with solid surfaces, can also result from oxidative coupling reactions. In either case, the contaminants could be sequestered, less subject to migration, and, therefore, virtually innocuous to the subsurface environment and would not be transported to a water source or surface water. Artificially inducing these coupling reactions could prove to be a novel in situ approach to soil and groundwater remediation that would result in reduced treatment times and costs. Studies were conducted in three thrust areas of concentrated research: i) natural systems, ii) mineral oxide-induced coupling, and iii) enzyme-induced coupling.

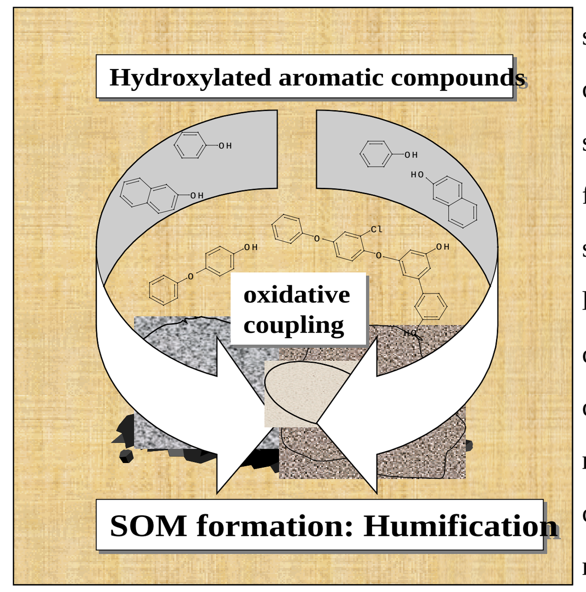

Figure 1: Schematic representation of humification of contaminants via oxidative coupling onto soil organic matter .

Research Objectives

We proposed to investigate i) the role of abiotic/enzymatic coupling reactions on the sequestration of hydroxylated aromatic compounds (HACs) by natural geosorbents, ii) the effects of sorbent structure and chemical compositions on such processes; and iii) the conditions for induction of these abiotic/enzymatic coupling reactions by addition of suitable catalysts and sorbents. Information gathered from the study will be useful in quantifying the behavior of this class of organic compounds in various subsurface contamination scenarios relevant to DOE facilities, and in specifying strategies for the selection and design of remediation technologies

Experimental

Sequestration and Sorption/Desorption Isotherms

The equilibrium sorption, desorption and sequestration of phenol, o-cresol, and p-chlorophenol in five natural sorbents with varying types of organic matter were investigated (Table 1). Standard bottle-point, fixed sorbent dosage technique were utilized for the equilibrium isotherms in completely mixed batch reactors. Scintillation counting techniques were used for assessing concentrations. Abiotic conditions were maintained by gamma irradiation of the sorbent and addition of sodium azide. Sequestration of HACs was quantified and operationally defined in terms of the mass of compound retained by the sorbent after a series of sequential water and solvent extractions. The remaining fraction in the sorbent was measured by combustion of the soil and entrapment of $^{14}CO_2$. Mass balance closure within 5 % of the total mass of HAC added to the systems was obtained with this experimental procedure.

Table 1. Relevant characteristics of the selected natural sorbents used in this study

SORBENT	[1]S_A, m^2/g	% ORGANIC MATTER	TYPE OF ORGANIC MATTER	[2]CHEMISTRY OF ORGANIC MATTER	Mn, ppm	Fe, ppm
Lachine shale	15.0	12.6	Kerogen	Aliphatic, aromatic	23.2	840
Wagner III	1.5	0.15	Kerogen	n/d	n/d	n/d
Fox Forest	4.5	5.9	Humus	O-aliphatic, phenolic, aromatic	44.8	9
Fox Grassland	8.9	2.5	Humus	O-aliphatic, phenolic, aromatic	24.2	16
Canadian Pea	2.3	99.1	Peat	O-aliphatic	13	91

[1] S_A = BET surface area determined by N_2 adsorption, [2] predominant groups determined by solid state ^{13}C NMR spectra, n/d = not determined

Manganese oxide-induced coupling

Birnessite, an amorphous manganese oxide of mixed oxidation state (III/IV) was selected as the mineral catalyst due to its abundance in natural materials and high catalytic activity. Manganese-induced coupling was studied in a) soil-free birnessite-phenol systems in CMBR to characterize the self-coupling (phenolic polymer formation) phenomena at different phenol and catalyst concentrations and b) birnessite-catalyzed coupling in non-equilibrium flow-through column systems packed with different geosorbents to evaluate the cross-coupling to the soil organic matter in non-equilibrium conditions. The reactor columns consist on 8mm ID, 150 mm long glass columns, equipped with Teflon tubing and fittings for in-flow and out-flow ports and lines. Columns are packed dry, spiked with set amounts of ^{14}C-labeled phenol solution, and incubated isothermally for a determined contact time. Aqueous and organic solvents are delivered with a multiple port (4) syringe pump equipped with airtight glass syringes. Effluent is collected automatically in two Fraction Collectors in scintillation vials containing scintillation cocktail. Blank runs (e.g., no column) with a set amount of phenol, were performed to evaluate possible losses in the collection systems. A set of eight columns can be operated simultaneously with current set-up. Aqueous desorption is performed until no ^{14}C activity is detected in the effluent. This is followed by methanol extraction until no ^{14}C activity is detected in the effluent. Columns are then ultra-sonicated for 1 hour to improve extractability, and methanol flush is continued. Water and methanol are delivered through two- four channel syringe pumps with gas-tight glass-Teflon syringes. Flow conditions were maintained at 1 mL/hr (superficial velocity = 2 cm/hr).

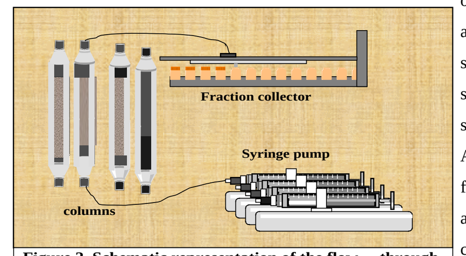

Figure 2. Schematic representation of the flow -through column system

Enzyme-induced coupling

Horseradish peroxidase (HRP) was selected as the enzymatic coupling catalyst and phenol as the model compound to study the kinetics of coupling and enzyme inactivation. HRP inactivation experiments in selected geosorbent systems were carried out at variable sorbent and initial enzyme concentrations in excess H_2O_2, in completely mixed batch reactors (CMBRs). After enzyme sorption equilibrium is attained, the target HAC substrate is added to start the coupling reaction and the enzyme inactivation as well. At predetermined time intervals, an aliquot of the sample is withdrawn to analyze for enzyme activity using the ABTS method. Coupling rate experiments were carried out in identical CMBRs as those for the enzyme inactivation study. Quantification of ^{14}C-phenol in solution was performed with scintillation counting techniques. Solid-liqiud separation was performed with centrifugal filtering devices (Spin-X, 10,000rpm for 10 min) that have a 1.0ml insert with 0.22 mm membrane filter. The fraction remaining in the Spin-X filter insert is transferred to a new 2.0 ml micro-centrifuge tube. to procede to methanol extraction. Sorbent-free control and blank control without catalyst were used to confirm the mass balance and evaluate the efficiency of the extraction method. Triplicates for each experiment were conducted for statistical quality control.

Oxidative Coupling by Natural Geosorbents

Sequestration and SOM

More than 70 % of sorbed phenol was non extractable in the diagenetically young humus-type Fox Forest soil (Figure 3). The organic fraction of these soils contains relatively high concentrations of phenolics (Table 1), which are the reactive groups more likely to participate in oxidative coupling reactions. However, diagenetically altered materials such as Lachine shale, although having higher sorption capacity, exhibits complete phenol extractability (Figure 4). Absence of cross-coupling reactions in kerogen-type SOMs may be limited by the availability of reactive coupling sites in this chemically reduced and physically condensed SOM type.

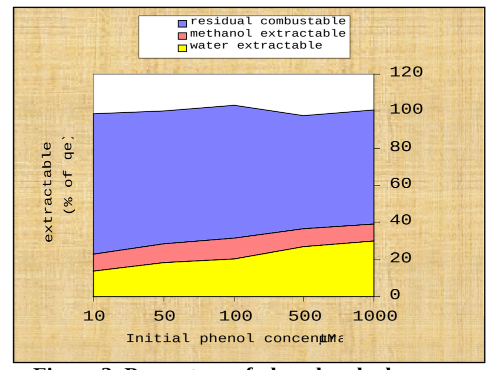

Figure 3. Percentage of phenol sorbed on Fox Forest soil that was water and so lvent extractable, and non extractable (residual combustable).

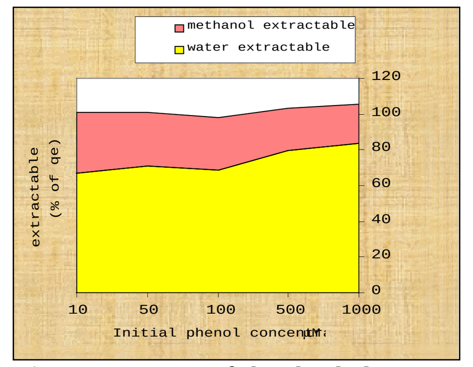

Figure 4. Percentage of phenol sorbed on Lachine shale that was water and solvent extractable, and non extractable (residual combustable).

Sorption Behavior

Isotherm nonlinearities and sorption-desorption hysteresis was significant for both humus- and kerogen- type SOMs but not for the peat type (Table 2). However, the non-extractable fraction (% Seq.) was only significant in the diagenetically young near-surface Fox Forest and Grassland soils (Table 2). Almost total extractability of all three contaminants was observed on Lachine shale and Wagner III soil (kerogen-type). Absence of sequestration and hysteresis was also evident in Canadian Peat, a very young soil with little diagenetic alteration (Table 2). Addition of mineral catalysts to peat resulted in significant sequestration (data not shown), suggesting that this anoxic material with ultra low mineral content (99% organic matter) may not contain sufficient mineral oxides to catalyze oxidative coupling reactions. These results suggest that oxidative coupling induced sequestration depends on the availability of reactive sites, function of the SOM structure and composition (i.e., diagenesis) and the presence of oxidative coupling catalysts in the system.

Table 2. Selected parameters that illustrate the sorption linearity (n), sorption -desorption hysteresis (H.I.250) and extractability (% Seq) of phenol, o -cresol, and p -chlorophenol in natural sorbents described in Table 1.

	PHENOL			O-CRESOL			P-CHLOROPHENOL		
	[1]n	[2]$H.I._{250}$	[3]%Seq	[1]n	[2]$H.I._{250}$	[3]%Seq	[1]n	[2]$H.I._{250}$	[3]%Seq
Lachine Shale	0.80	0.18	4.5 ± 1.1	0.74	0.25	4.6 ± 1.1	0.54	0.31	2.1 ± 0.3
Canadian Peat	n/d	n/d	n/d	0.91	0.05	4.6 ± 1.6	0.85	0.001	1.0 ± 0.07
Fox Forest	0.76	0.67	74 ± 10	0.87	0.49	19 ± 3	0.61	0.24	61 ± 18
Fox Grassland	0.78	0.51	48 ± 6	n/d	n/d	n/d	0.65	0.49	n/d
Wagner III soil	n/d	n/d	n/d	0.82	0.22	4.7 ± 0.2	0.74	0.29	1.3 ± 0.2

[1] n = Freundlich n ($q_e = K_F C_e^n$), [2] $H.I._{250}$ = hysteresis index at C_e = 250 µM. H.I.= $(q_{e,des} - q_{e,ads})/ q_{e,ads}$, [3] % Seq is the percentage of the sorbed fraction (q_e) that remains in the solid after water/solvent extraction averaged for all organic concentrations tested 10 µM ≤ C_o ≤ 1000 µM.

Manganese Oxide-Induced Coupling

Catalyst Activity and Sequestration

The most significant finding of this thrust area is the unfolding of the role of catalyst activity on the reaction rate and composition of coupling products (oligomers/polymers) and its effect on promoting SOM coupling and/or polymerization. As exemplified in figures 1 and 2, manganese oxide (birnessite) concentration controls the nature and rate of the coupling reactions so that:

i) at low birnessite concentrations phenol polymerization is minimal (Fig. 5) and oxidative coupling onto SOM is promoted (Fig. 6, peat and shale in a lesser extent),

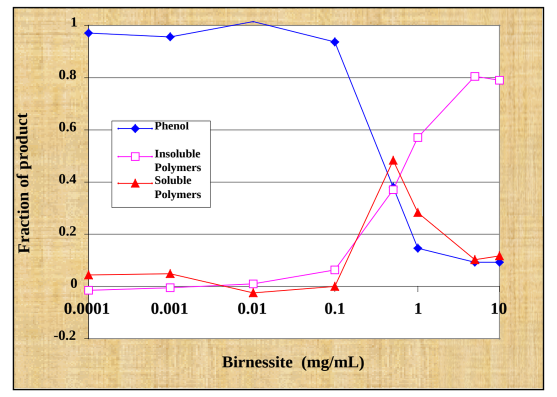

Figure 5. Coupling product distribution as a function of birnessite concentration. Initial [phenol] = 800 µM, reaction time =1 week. Products are expressed as fraction of total phenol reacted.

ii) at increasing birnessite concentrations, soluble and insoluble polymer formation increases (Fig. 5) and coupling to SOM decreases (Fig. 6, peat and shale) and

iii) at high birnessite concentrations, insoluble polymer that become strongly associated to the birnessite particles are preferentially formed, resulting in low extractabilities (Fig. 5 and Fig. 6, all conditions).

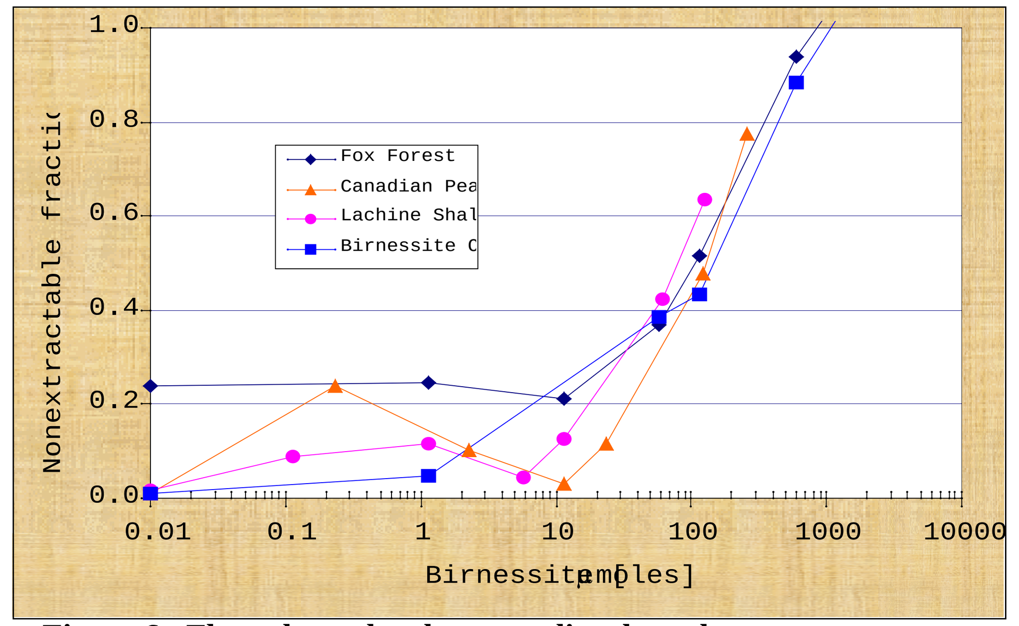

Figure 6. Flow-through column studies show the non - extractability of phenol in both soil and soil -free birnessite amended systems as a function of mass of birnessite

While both phenomena have the net effect of reducing the mobility of HACs, inducing SOM coupling is desired. Polymer sorption onto birnessite particles shortens their catalytic activity. Model simulations of birnessite-induced coupling (data not shown) show that it follows retarded first order rate equation, in which the retardation factor is related to catalysts inactivation that increases with increasing polymerization. Investigations with other coupling catalysts with lower coupling activities, such as iron (III) oxides will be explore.

Enzyme-Induced Coupling

Enzyme Inactivation

Studies on the kinetics of horseradish peroxidase (HRP)-catalyzed oxidative coupling revealed that enzyme inactivation was an important process controlling the rates and extent of coupling. A significant finding of this study is to show that the inactivation of the enzyme is reduced in the presence of geosorbents, which suggests that enzyme sorption may prevent inactivation (Figure 7).

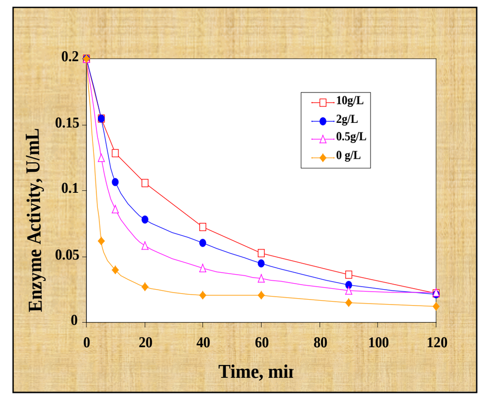

Figure 7. Rates of enzyme inactivation at various concentrations of Lachine shale. Initial [HRP] = 0.2 U/mL and [phenol] = 50 µM. Similar results were obtained with the humic -type Chelsea soil.

Kinetics of Coupling

A mechanistic model was developed to describe the involved processes: HAC polymerization and coupling with SOMs, enzyme and phenol sorption, and enzyme inactivation. The concentration of reacted phenol, $S_{coupled}$, at time t is given by:

$$S_{coupled} = K \ln(1 + E_0 k_{in} t)$$

where K is a constant, E_0 the initial enzyme activity, and k_{in} is the inactivation rate constant.

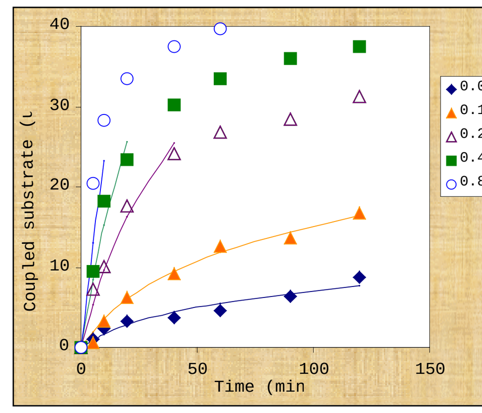

Figure 8. Simulation of coupled phenol on L. shale systems at various initial HRPactivities. Symbols indicate measured values and so lid lines are model predictions. Sorbent concentration = 7g/L, Phenol] = 50 µM, and $[H_2O_2]$ =1 mM

The model describes very well the data at lower enzyme activities and at the initial stages of the higher range of enzyme activities, but deviates at later times (Figure 4). This deviation could be caused by the depletion of substrate

Summary

Major highlights of this study include a) elucidation of the role of composition and structure of the SOM to mediate oxidative coupling; b) evaluation of the effect of oxidative coupling on equilibrium sorption/desorption processes, c) elucidation of the role of catalyst activity in the type of coupling reaction (i.e., SOM coupling and/or polymerization), and d) development of descriptive models for enzyme-induced oxidative coupling on natural geosorbents.In light of these significant findings, we strongly believe that induction of oxidative coupling reactions for the immobilization of HACs in selected sorbents can be an effective remediation strategy for HACs contaminated groundwater. A natural course of action would be to continue exploring this area by determining optimal sorbent materials based on their surface chemistry, type and dosage of catalyst, and expanding our modeling efforts to describe coupling rates on engineered system configurations.

Acknowledgements

We would like to thank Tom Yaravaski for his technical support and the U of M students that helped us in the lab: Ray Malewitz, Kristi Jurey, Jung Wook, Pete Hill, and Debbie Ross. Thanks also to Hong Fang for his technical aid.