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The Efficacy of Oxidative Coupling for Promoting In-Situ Immobilization of Hydroxylated Aromatics in Contaminated Soil and Sediment Systems

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RESEARCH OBJECTIVES

Hydroxylated aromatic compounds (HACs) are common subsurface contaminants at many industrial sites, including DOE facilities. Under certain conditions, HACs can undergo oxidative coupling reactions that may lead to their sequestration, reducing their environmental mobility and toxicity. Mineral oxides and enzymes naturally present in most soils can catalyze these coupling reactions. 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 this 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.

RESEARCH PROGRESS AND IMPLICATIONS

During the fourth and final year of this project, two interrelated areas of research were investigated as planned: i) soil-free model experiments to determine coupling rates and composition of reactive products at different catalyst and organic concentrations, and ii) sorbent-packed flow-through columns amended with tested catalyst/organic ratios and organic residence time to determine HAC sequestration. Results obtained from these experiments were expected to aid with the selection of coupling catalysts and sorbent materials as potential components of reactive barrier remediation strategies. The studies and analyses conducted so far demonstrate that induction of oxidative coupling by addition of catalysts is a subsurface remediation option worth exploring further.

Summary of Findings

It was established in previous years that

- Natural sorbents containing diagenetically young organic matter of humus-type are more likely to promote cross coupling (the coupling of HACs to the soil organic matter) in the presence of naturally occurring or added catalysts. Oxidative coupling reactions of HACs in natural geosorbents appear to be controlled by the existence of reactive sites in the soil organic fraction, such as phenolic and methoxy groups found in humic materials, and presence of oxidative coupling catalysts.
- Induction of oxidative coupling reactions by addition of catalysts (manganese oxide and horseradish peroxidase) resulted in increase sequestration of HACs on all natural sorbent tested. HACs' sequestration appears to take place by coupling to the soil organic matter and by formation of polymers with strong sorption tendencies.

The most significant findings during the fourth year of this project can be summarized as follows:

- The rate, extent, and product composition of induced coupling reactions can be controlled by selecting appropriate dosages of the coupling catalysts. This is an important finding for development of design criteria for sub-surface remediation applications.
- Flow-through column systems that simulate desorption on subsurface conditions were shown to be an efficient experimental system to study sequestration of HACs by oxidative coupling reactions. Oxidative coupling to soil organic matter is apparently predominant at low catalyst activities where formation of insoluble polymers is decreased.
- Enzyme inactivation, one of the main setbacks in the use of enzymes for detoxification of phenolics, is apparently reduced upon sorption to natural sorbents. Thus, additions of horseradish peroxidase (HRP) to induce oxidative coupling in natural systems appears to be a plausible HAC remediation strategy

Catalyst activity and coupling products

The most significant finding of this thrust area is the unfolding of the role of catalyst activity on the reaction rate and composition of oxidative 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

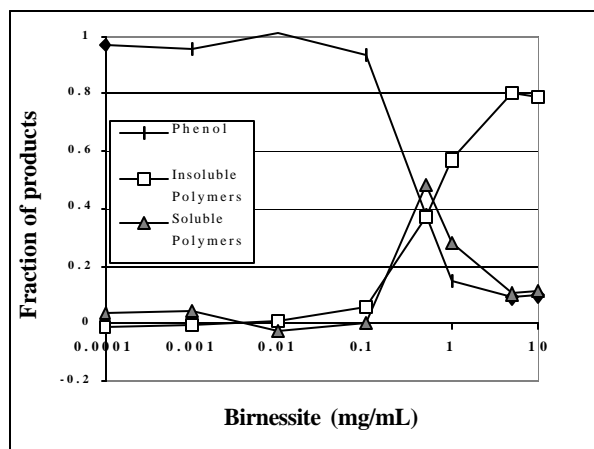


Figure 1. Coupling product distribution as a function of birnessite concentration. Initial [phenol] = 800 μ M, reaction time = 1 week. Products are expressed as fraction of total phenol reacted.

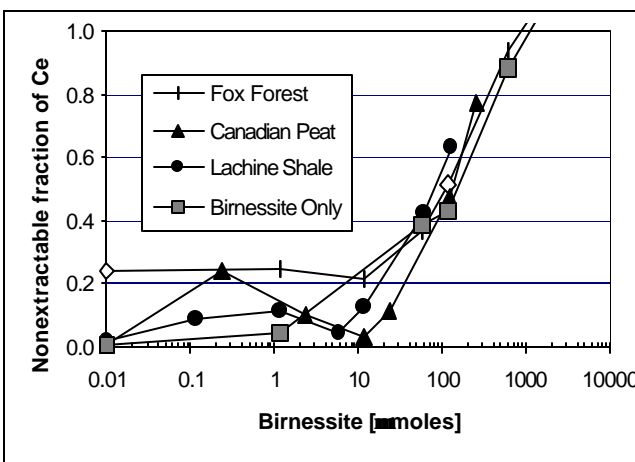


Figure 2. Flow-through column studies show the non-extractability of phenol in both soil and soil-free birnessite amended systems as a function of mass of birnessite

controls the nature and rate of the coupling reactions so that: i) at low birnessite concentrations phenol polymerization is minimal (Fig. 1) and oxidative coupling onto SOM is promoted (Fig. 2, peat and shale), ii) at increasing birnessite concentrations, soluble and insoluble polymer formation increases (Fig. 1) and coupling to SOM decreases (Fig. 2, peat and shale) and iii) at high birnessite concentrations, insoluble polymer that become strongly associated to the birnessite particles are preferentially formed, also resulting in low extractabilities (Fig. 1 and Fig. 2, all conditions).

Enzyme induced coupling

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

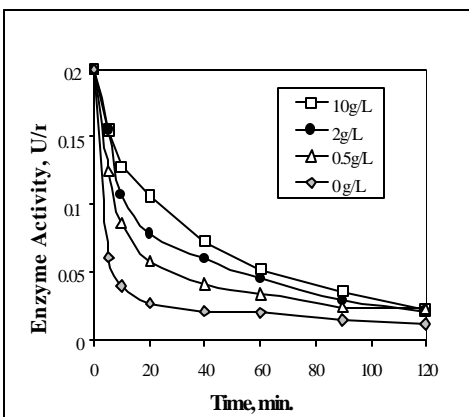


Figure 3. Decrease rates of enzyme inactivation at increasing Lachine shale conc. Initial [HRP] = 0.2 U/mL and [phenol] = 50 μ M. Similar results were obtained with the humic-type Chelsea soil.

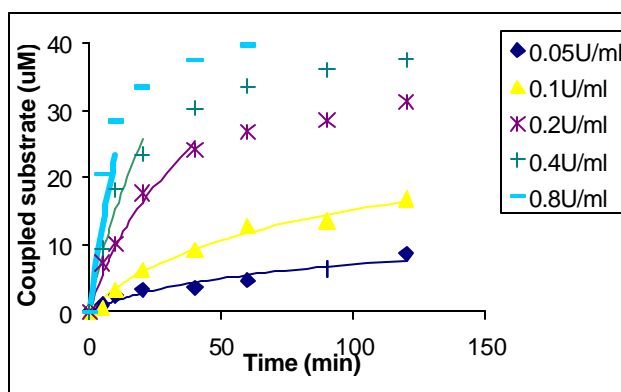


Fig 4. Simulation of coupled phenol on L. shale systems at various initial HRP activities. Symbols indicate measured values and solid lines are model predictions. Sorbent concentration = 7 g/L, [Phenol] = 50 μ M, and $[H_2O_2]$ = 1 mM

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 3). 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. The model describes very well the data at lower enzyme activities and at the initial stages of the higher range of enzyme activities (Figure 4). Deviations from the model only occur after depletion of the substrate, which makes the saturated enzyme assumption (i.e., $K_m \ll \text{substrate}$) not valid.

PLANNED ACTIVITIES

The principal objectives of our current project have been successfully met at its closing year. In light of the significant findings summarized here, 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.