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

Walter J. Weber
University of Michigan
181 EWRE Building
1351 Beal Avenue
Ann Arbor, Michigan 48109-2125
Phone: 313-763-2274
E-mail: wjwjr@engin.umich.edu

Alok Bhandari
Kansas State University
Manhattan, Kansas 66506-2905
Phone: 785-532 1578
E-mail: bhandari@ksu.edu

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Walter J. Weber, University of Michigan

Alok Bhandari, Kansas State University

Research Objective

Hydroxylated aromatic compounds (HAC's) and their precursors are common contaminants of surface and subsurface systems at DOE facilities. The environmental fate and transport of such compounds, particularly in subsurface systems, is generally dominated by their sorption and desorption by soils and sediments. Certain secondary chemical reactions, most specifically abiotic and/or enzymatic oxidative coupling, may be significant in controlling the sorption and subsequent desorption of such hydroxylated aromatics by soils and sediments. The principal objectives of this study are to investigate: 1) the role of abiotic/enzymatic coupling reactions on the immobilization of HAC's; 2) the effects of environmental factors on such immobilization; and 3) preliminary engineering approaches utilizing enhanced abiotic/enzymatic coupling reactions to immobilize hydroxylated aromatics in-situ. 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.

Research Progress and Implications

Over the first two years of this three-year project, we have developed a significantly improved understanding of the mechanisms of hydroxylated aromatic compound sorption and immobilization by natural soils and sediments. Immobilization in this context is attributed to oxidative coupling of the hydroxylated aromatics subsequent to their sorption to a soil or sediment, and is quantified in terms of the amount of a sorbed target compound retained by a sorbent after a series of sequential water and solvent extractions. The presence of oxygen, metal oxides, and organic matter, all of which can potentially catalyze/facilitate the abiotic oxidative coupling of HAC's [1], were investigated during these first two years. Three different HAC's: phenol, trichlorophenol and *o*-cresol were included in the experimental program. Inorganic soil matrices were represented by a glacial wash sand (Wurtsmith sand) having very low organic content. Because the chemical nature of soil organic matter may potentially affect the extent of coupling or immobilization [2], sorbents having different organic matter compositions are being investigated. Two of the three studied to date are near-surface soils, characterized by geologically younger organic material (Fox Forest soil and Fox Grassland soil). The third sorbent is an older and diagenetically altered soil (Lachine Shale). Sorbent preparation, characterization and experimental protocol development were completed in the first year of the study while the second year of the project has focused primarily on experiments with natural systems, as planned. Preliminary work with engineered systems has been initiated earlier than scheduled in order to integrate and relate all aspects of the study.

Three different experimental approaches were used to demonstrate the occurrence of oxidative coupling in the immobilization of the HAC's: 1) determination of extractable and non-extractable fractions of the contaminant, 2) comparison of oxic/anoxic isotherms, and 3) evaluation of sorption/desorption hysteresis indices. Our initial hypothesis that soils and sediments having organic matter comprised of geologically younger organic materials are more likely to have potential for immobilization of hydroxylated aromatic contaminants is supported by the experimental results. As presented in Fig.1, up to 75 % of sorbed phenol is immobilized by Fox Forest Soil. A similar trend

was observed for the Fox Grassland Soil. In contrast, diagenetically altered materials such as Lachine Shale, although having higher sorption capacity and higher total iron concentration did not promote phenol immobilization (Fig. 2).

Sorption/Desorption experiments were conducted under oxic/anoxic conditions to verify the hypothesis that oxidative coupling and contaminant immobilization can be induced by the presence of oxygen in subsurface systems (Fig. 3). If oxidative coupling is the primary mechanism, we can expect a difference in sorption behavior under these two different conditions. Indeed, it was demonstrated that the significant immobilization observed for phenol on Fox Forest soil (Fig. 1) translated into detectable differences between its oxic and anoxic isotherms (Fig. 3). Conversely, for the soil for which no significant immobilization was observed (Fig. 2), there was no significant difference in the oxic and anoxic isotherms.

Iron and manganese oxides have been known to catalyze the oxidative coupling of HAC's [3]. Preliminary work with the four natural sorbents described above revealed, however, that total iron and manganese contents are not good predictors of immobilization. This suggests that the oxidative

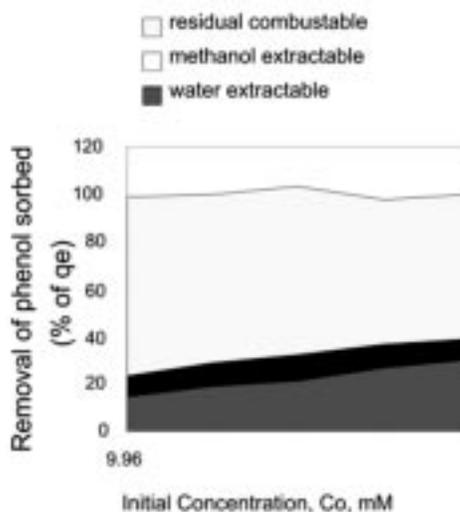


Figure 1 Distribution of phenol sorbed by Fox Forest Soil.

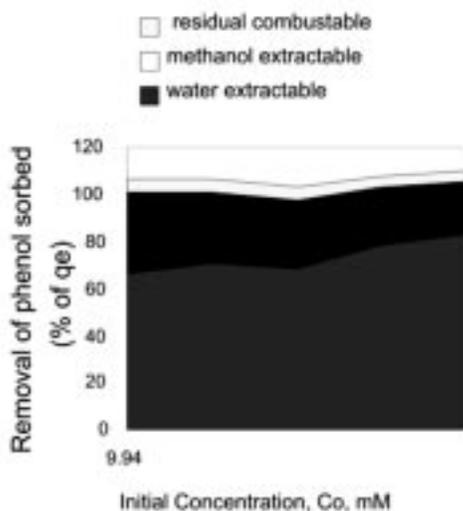


Figure 2 Distribution of phenol sorbed by Lachine Soil.

state or/and crystal structure of the metal oxides might be important. Detailed characterization of metal oxides associated with various soils will be performed as a part of the on going study.

One generally accepted method of quantifying irreversible sequestration of solutes by adsorbents is to measure aqueous phase sorption/desorption hysteresis and express the results in terms of a hysteresis index (H.I.) [4]. As demonstrated in Fig. 4, for the systems studied to date, several types of interactions appear to be responsible for the hysteresis observed. For low values of H.I. both hydrophobic interactions and hydrogen bonding appear to be important contributors (solvent extractable fraction). However, for high values of H.I immobilization by oxidative coupling dominates.

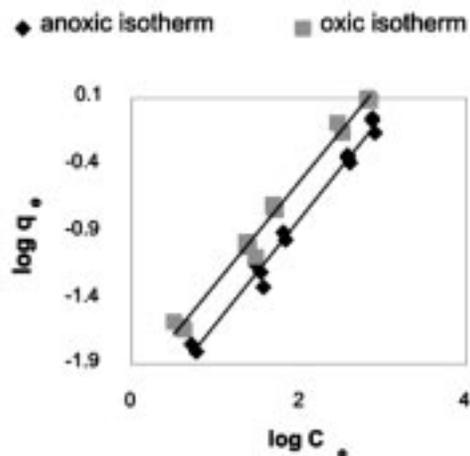


Figure 3 Oxic/anoxic isotherm of phenol sorption on Fox Forest soil.

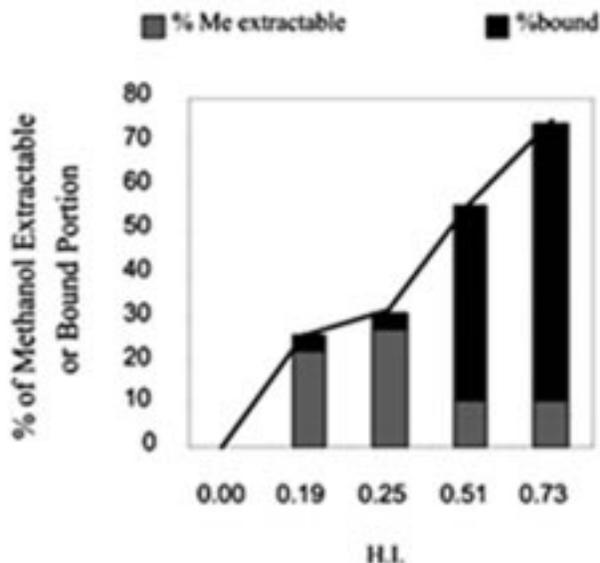


Figure 4 Sources for phenol sorption on Lachine Shale, Forest and Grassland Soils (H.I. = 0.19, 0.73, and 0.51, respectively) and 0-cresol sorption on Lachine Shale (H.I. = 0.25).

Planned Activities

Pursuant to the project schedule, all work associated with the model (Phase II) and engineered (Phase III) systems will be completed. Phase II includes evaluation of the efficiency of immobilized enzymes and transition metal oxides in promoting oxidative polymerization of the target hydroxylated aromatics compounds. Phase III involves addition of immobilized enzymes, metal oxides, and possibly organic matter to the four selected natural sorbents to evaluate the efficacy of oxidative coupling induction. Immobilization of the three HAC's in these amended soil systems will be also evaluated in a flow-through multi-port column systems. This will simulate in-situ applications of the research in reactive wall configurations.

Other Access To Information

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