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Oxidation of Recalcitrant Organics in Subsurface Systems

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ABSTRACT

In contrast to remedial techniques for contaminated subsurface systems that simply transfer hazardous wastes from one part of the environment to another (e.g., off-site landfilling), in-situ transformation (to less hazardous products) or destruction of recalcitrant organics may offer a safe and cost effective solution. Biochemical and chemical biotic/abiotic immobilization and detoxification of recalcitrant organics, including polynuclear aromatic hydrocarbons (PAHs), associated with soil humification is a process that may serve as a basis for in-situ treatment of soils contaminated with wood-preserving or oily wastes. This paper addresses the potential for recalcitrant organic immobilization/humification as influenced by enzymatic (biotic) and metallic (abiotic) catalysis. Chemical stoichiometry and kinetic information are presented for abiotic catalysis of the PAH intermediate naphthalenediol using manganese. A simple model is presented for investigating the reductive-dissolution/auto-oxidation of manganese and the potential polymerization of naphthalenediol as influenced by manganese chemistry, and an illustrative experiment is presented demonstrating the near complete oxidation of 2,3-naphthalenediol by manganese oxide particles.

INTRODUCTION

Subsurface remediation of active and inactive waste sites generally includes activities related to the 1) identification, quantification, and control of contaminant sources; 2) consideration of clean-up levels for protection of human health and the environment; and 3) selection of treatment technologies. However, lack of methods and approaches for evaluating and selecting remedial technologies represents a major deficiency in the area of subsurface remediation [1]. One challenge is to relate more effectively site-characterization activities to the selection of the most appropriate remediation technologies. Site-characterization information that directly affects subsurface-remediation selection includes chemical distribution, transport, reaction kinetics, identification and amount of electron acceptors present, and redox and pH information to determine the chemical form and reactivity of electron acceptors [1].

The concept of chemical mass balance can be used for integrating site-characterization and treatment-selection decision-making. By evaluating the distribution of chemicals among air, water, solid, and organic phases of a soil, fate can be comprehensively assessed and used in the selection and design of remedial options. Chemical mass balance represents a rational and fundamental approach upon which specific
questions can be asked and specific information can be obtained, thereby simultaneously addressing site characterization and remediation. Although a mass balance provides only information on mass quantities involved, a mass-balance approach can be correlated to other pertinent information at the waste site (e.g., when the waste was originally disposed and the form of the original waste) to provide a more comprehensive picture of how the waste became distributed at the site.

Recalcitrant and hydrophobic organics, including halogenated aromatics and polynuclear aromatic hydrocarbons (PAHs), tend to partition from water to solid phase (e.g., adsorption) in a soil environment [2]. One fate mechanism for these organics is immobilization through the natural soil humification process. Although contact may exist between the organic chemical and soil surface, there is currently a lack of information on how natural humification functions to immobilize these chemicals. This information is useful in the evaluation of chemical degradation, transformation, and detoxification processes that form the basis for using in-situ, prepared-bed, or in-tank (composting) reactors [1,3].

Humic materials are natural organic substances that are common in the environment and are involved in a nonstop polymerization process with organic molecules [4]. Polymerization of humus material (humification) involves the breakdown, convolution, and transformation of organic matter into long, complex, amorphous organic molecules with numerous reactive functional groups and bridges that are similar to the reactive groups added to aromatic compounds by microbial enzymatic action. Functional groups include hydroxyl, carboxyl, ketonic, phenolic, quinone, ester, ether, carbonyl, imino, and amino groups, with dihydrodiol and dione (e.g., quinone) structural formations showing promise in promoting polymerization. Figure 1 illustrates a typical structure of humus. During humus formation, reactive compounds are linked through biotic-enzymatic and/or abiotic-chemical reactions, resulting in complexes of polymerized molecules. Biotically induced polymerization, for example, can result in oxidative coupling of nonreactive organics (e.g., anilines) into active organic polymerization processes (e.g., using dichlorophenols) [6,7]. More recently, scientists have noted that abiotically catalyzed polymerization may also represent an important aspect of humification [8-11]. For example, manganese-bearing silicates have demonstrated catalytic effects in enhancing the polymerization of polyphenols (e.g., hydroquinone) [11].
Biotic copolymerization of organics

Bollag and Myers [7] conclude that biotic polymerization of xenobiotics in the humification process is possible because many of the degradation products of pesticides result in the formation of reactive intermediates with structures and/or functional groups similar to those found in natural humus material (see Figure 1). To seriously consider biotic immobilization of xenobiotics in the humification process as an acceptable engineering practice, it must be demonstrated, for example, that by-products are less toxic than the parent compounds and that constituents are chemically bound (i.e., inner-sphere complexation) to the humic structure and immobile as opposed to being merely physically adsorbed (i.e., outer-sphere complexation). Chemical binding could result in 1) no future release of any constituent from the soil macromolecular structure, 2) insignificant release of toxic parent or transformation material from the structure, or 3) release of nontoxic degradation/transformation/intermediate products of the humification process.

Bollag and Liu [12] reported experiments in which halogen-substituted phenols (e.g., tri-, tetra-, and penta-chlorinated) were incubated with humus derivative syringic acid \([C_6H_9OH(OCH_3)_2COOH]\) or 3,5-dimethoxy-4-hydroxybenzoic acid, in the presence of the phenooxidase enzyme laccase, to produce two types of hybrid oligomers: 1) quinonoid oligomers (dimers to trimers) in which the chlorophenols were bound through linkage to an orthoquinone derived from syringic acid or 2) phenolic oligomers (dimers to pentamers) in which the chlorophenols were bound through ether linkages to decarboxylated products of syringic acid. Figure 2 illustrates the cross coupling of 2,4,5-trichlorophenol \([2,4,5-C_6H_3Cl-OH]\) and syringic acid (forming dimer, trimer, and tetramer products). Bollag and Myers [7] noted that enzymatically-catalyzed bond formation between xenobiotics and humic materials is primarily of a covalent nature. Outer sphere complexation (i.e., physical adsorption) or trapping in the molecular lattice is also possible.

Bollag et al. [15] and Bollag and Liu [13] reported covalently bound copolymerized products. Bollag et al. [15] incubated humus derivatives with 2,4-DCP and laccase; from MS results, they proposed dimer, trimer, tetramer, and pentamer polymerized products, based on mass spectrometry m/z (mass to charge) ratios. Bollag and Liu [13]...
noted that quinonoid and phenolic oligomers were products that were formed and that they matched the mass spectra of respective monomers. They suggested dimer, trimer, tetramer, and pentamer polymerized products for phenols with one to five chlorine functional groups. Bollag et al. [16] extended the analysis by investigating substituted anilines. Based on the observation that the acyl group is readily removed by biological or chemical hydrolysis to result in the release of substituted anilines, they demonstrated that laccase was capable of cross-coupling aromatic amines and humus monomers (e.g., syringic acid). They proposed that the binding took place by nucleophilic addition of the amino group to a quinone molecule by way of an imine linkage.

Sarkar et al. [17] demonstrated that chlorinated phenols could be enzymatically bound to fulvic and humic acids [7,14]. They used the three oxidative enzymes laccase, peroxidase, and tyrosinase to humify $[^{14}C]2,4$-DCP. Incorporation of $[^{14}C]2,4$-DCP into the humic material was determined by measuring the radioactivity in fulvic and humic acids. They precipitated fulvic acid with FeCl$_3$·6H$_2$O. On repeated "extractions" with hexane, no appreciable amount of radiolabeled material was detected, indicating a binding of 2,4-DCP to the humus material.

Martin et al. [18] and Cheng et al. [19] reported similar results concerning chemical binding involving humus material. Martin et al. [18] demonstrated rapid polymerization of radiolabeled catechol [1,2-C$_6$H$_4$(OH)$_2$] as the result of soil-enzyme activity (although abiotic auto-oxidation could have influenced the polymerization process) by confirming the presence of the radioactivity in both fulvic and humic acids. Cheng et al. [19] reported 2,4-DCP being gradually incorporated into the soil organic matter matrix, resulting in a loss of 2,4-DCP in the soil. Abiotic auto-oxidation could have significantly influenced the polymerization process.

Liu et al. [20,21] showed that nonreactive organics could be induced into polymerization. Liu et al. [20] demonstrated that anilines could be "induced" into the humification process by incubating them with the enzyme laccase and 2,4-DCP. They suggested that the anilines were not directly oxidized by the enzyme but by an enzymatically formed orthoquinone derivative of the 2,4-DCP molecule, which is unstable and spontaneously polymerizes. They demonstrated that in the presence of enzymatically formed quinone derivatives of 2,4-DCP and in the absence of the enzyme itself, the anilines reacted with the 2,4-DCP molecule. Liu et al. [21] also performed experiments with glycine ethyl ester. When combined with laccase, no polymerization was noted. When combined with laccase and syringic acid, the ester was copolymerized. Bollag and Bollag [14] cite several additional examples.
Qiu and McFarland [22] studied degradation/transformation of radiolabelled benzo(a)pyrene ([14C]B(a)P) in two different soils with and without fungal inoculation (i.e., with and without *Phanerochaete* *chrysosporium*, respectively). Inoculated soils were amended with corn cobs as the primary organic substrate. They noted that 1) mass balance considerations suggested that the enhanced removal of B(a)P resulted in the formation of immobilized bound residues in soil and 2) humification rather than conversion to CO$_2$ was the major reaction observed. Figures 3 and 4 present the amount of 14C recovered in solvent extract and from soils with and without inoculum in sandy-loam McLauren and silty-loam Kidman soils, respectively. The two top increasing curves in each figure represent the percentage of the initial [14C]B(a)P activity recovered from a 1:1 dichloromethane/acetone solvent extract for sterile and active soils (expressed as percentage of disintegrations per minute per gram of soil), while the two bottom increasing curves represent the percentage of the initial [14C]B(a)P recovered from the combusted soil residue with and without inoculation. The amounts associated with the bound soil residues were calculated as the difference between the total and extractable activities. These results do not account for all removal mechanisms (e.g., volatilization) of the 14C; as such, the activity levels shown in Figures 3 and 4 only account for approximately 82 and 86%, respectively, of the original amount added to the systems (i.e., 100 µg [14C]B(a)P/g of soil). These figures illustrate, though, that over time more of the [14C]B(a)P (or intermediate/product) was associated with soil. Although the soil without inoculum might contain microbial activity, the effects of humification may be significant for certain soils and cannot necessarily be discounted as an important mechanism in catalyzed B(a)P degradation/transformation.

**ABBIOTIC COPOLYMERIZATION OF ORGANICS**

Research has also indicated that aromatic constituents might be abiotically humified [22-29]. For example, soil samples spiked with a [14C]B(a)P and pyrene [the structures of which are illustrated in Figure 5] have shown significant increased activity over time with soil samples previously extracted with methylene chloride [25,26]. The extraction procedure did not remove all of the radiolabelled carbon, suggesting some sort of binding process between the B(a)P molecule or a portion of it and the soil material. Bollag and Myers [7] noted that the most persistent complexes result in organic alterations followed by covalent bonding and that organics covalently linked to soil organic matter are often referred to as "bound residues."

Keck [25] combined radiolabelled B(a)P with microbially active and sterile silty-loam Kidman soil, while Abbott and Sims [26] combined radiolabelled B(a)P and pyrene with active and sterile sandy-loam soil, the results of which are presented in Figures 6, 7, and 8, respectively. The two top decreasing curves in each figure represent the percentage of the initial [14C]B(a)P recovered from the solvent extract for sterile and active soils (expressed as percentage of disintegrations per minute per gram of soil), while the two bottom increasing curves represent the percentage of [14C]B(a)P.

![Radiolabelled Benzo(a)pyrene](image1.png)

![Radiolabelled Pyrene](image2.png)

**FIGURE 5** Structures of Benzo(a)pyrene and Pyrene (* indicates location of 14C)
recovered from the combusted soil residue. Radiolabelled recovery efficiencies associated with Figures 6, 7, and 8 were approximately 95, 95, and 93%, respectively. These figures illustrate that over time more of the $\left[^{14}\text{C}\right]$B(a)P and $\left[^{13}\text{C}\right]$pyrene activities became associated with the soil. At day zero, approximately 25% of the $\left[^{14}\text{C}\right]$B(a)P and $\left[^{13}\text{C}\right]$pyrene (or intermediate/product) were associated with the soil, and at day 100, the percentage had increased to between 50 and 63%. These results occurred for both sterile and nonsterile samples and suggest that 1) B(a)P and pyrene were bound in some way to the soil material, 2) copolymerization of multiple-ringed constituents might be possible, and 3) abiotically catalyzed polymerization may also be occurring and may be as important as microbially mediated polymerization in humification. Bollag and Myers [7] comment that many chemicals and their degradation products are structurally similar to naturally occurring humic acid constituents with many of these compounds and their metabolites resembling humic acid precursors. Quinonoid and phenolic structures appear to be reactive forms for polymerization; as such, Figure 9 illustrates two B(a)P intermediates containing such functional groups, indicating that B(a)P might also have the ability to be involved in polymerization/humification processes.

Laha and Luthy [28] also noted polymerized products while investigating the oxidation of aniline with $\delta$-MnO$_2$ under sterile, anoxic conditions at low pH. They combined equal amounts and concentrations of aniline and manganese dioxide in an acetate buffer at pH of 4. Following analysis by GC/MS, the chromatogram identified aniline, and azobenzene and 4-aminodiphenylamine as major and minor polymerized products of the aniline, respectively.

Bollag and Myers [7], whose research focuses on enzymatically induced polymerization, state that abiotically mediated catalysis may also be important. A number of reactants appear to move through a transitional phenol-, aniline, or quinone-like structure prior to becoming part of the final humified product [12,14]. Senesi and Schnitzer [27] have proposed similar pathways for abiotically induced polymerization. They suggested that hydroquinone [1,4-C$_6$H$_4$(OH)$_2$] goes to the semiquinone radical $\cdot$[C$_6$H$_4$(OH)] and that this radical forms a quinone (1,4-C$_6$H$_4$O$_2$), where all reactions are reversible (Figure 10):

\[
\begin{align*}
\text{C}_6\text{H}_4(\text{OH})_2 & = \cdot\text{C}_6\text{H}_4\text{O(OH)} + \text{H}^+ + e^- \quad (1) \\
\cdot\text{C}_6\text{H}_4\text{O(OH)} & = \text{C}_6\text{H}_4\text{O}_2 + \text{H}^+ + e^- \quad (2)
\end{align*}
\]
Shindo and Huang [11,30] explained the polymerization of hydroquinone in the following manner, using oxidation-reduction potentials ($E^\circ$) for manganese dioxide ($\text{MnO}_2$) and hydroquinone [31]:

$$\text{MnO}_2 + 4 \text{H}^+ + 2 \text{e}^- = \text{Mn}^{2+} + 2 \text{H}_2\text{O} \quad E^\circ = +1.224 \text{ V}$$

$$C_\text{6}H_\text{4}(\text{OH})_2 = C_\text{6}H_\text{4}O_2 + 2 \text{H}^+ + 2 \text{e}^- \quad E^\circ = -0.6992 \text{ V}$$

Thermodynamically, the overall redox reaction is +0.525 V, indicating that the oxidation of diphenol (i.e., hydroquinone) by manganese dioxide is favorable.

Stone and Ulrich [32] note that Equation (4) is written such that one proton is transferred from the oxide surface with every electron that is transferred. Such hydrogen atom transfer reactions are common in the oxidation of organic compounds by metal complexes and have been postulated for the oxidation of hydroquinone by manganese(IV) dioxide [33,34]. Stone and Ulrich [32] also note that single-hydrogen transfer generates semiquinone radicals and surface Mn(III), and these reaction intermediates are subsequently consumed in the formation of the stable reaction products p-benzoquinone and Mn(II)(aq) under anoxic conditions. LaKind and Stone [35] stated that the formation of quinone as the major product is most likely under anoxic conditions; the presence of oxygen tends to promote oxidative coupling reactions, creating dimers, trimers, etc. Their brief analysis was based on the reductive dissolution of Fe(III) to Fe(II) coupled with suspected auto-oxidation of Fe(II) to Fe(III).

Shindo and Huang [36] took a different approach to explain the catalytic polymerization of hydroquinone by primary minerals, especially the olivine tephroite (Mn$_2$SiO$_4$). Schnitzer [37] suggested that the rate-determining step in the synthesis, by oxidative polymerization of humic acids from simple phenols and phenolic acids, is the formation of a semiquinone radical involving a one-electron transfer reaction. These relatively unstable and reactive semiquinone radicals will couple with each other to form a stable humic acid polymer. Shindo and Huang [11] noted that because the coupling of radicals requires no activation energy (in contrast to electron transfer reactions), coupling of semiquinones rather than the formation of quinones should be kinetically the preferred reaction path. Therefore, diphenols should be converted to humic acid through semiquinones during the reduction of Mn(IV) oxides. Senesi and Schnitzer [27] noted that the semiquinone radical can form a semiquinone radical ion [($C_6H_4O_2^-$)] and then a semiquinone dianion [($C_6H_4O_2^-$)], where all reactions are reversible (Figure 10):
In previous work, Kononova [38] and Schnitzer and Kahn [39] made statements similar to that of Shindo and Huang [11] regarding the polymerization of hydroquinone through a semiquinone radical [29,40]. Wang et al. [40] also reported that in the absence of an electrophilic substituent in the ring of the hydroquinone, phenolic hydroxyl groups act like weak acids, and with an increasing pH, the hydroquinone dissociates to a semiquinone anion ([C₆H₄O(OH)]⁻):  

\[ C₆H₄O(OH) \rightarrow [C₆H₄O(OH)]⁻ + H⁺ \]  

(5)

Upon oxidation by, for example, a manganese oxide [in which manganese acts as an electron acceptor and becomes reduced (acting as a Lewis acid)], the semiquinone anion is converted into a semiquinone radical (Figure 10).

\[ [C₆H₄O(OH)]⁻ \rightarrow \cdot C₆H₄O(OH) + e⁻ \]  

(6)

(7)

Under neutral or higher pH conditions and in the presence of air (i.e., oxygen, which acts as an electron acceptor) and MnO₂, the dissolved Mn²⁺ is oxidized to form MnO₂ through auto-oxidation:

\[ Mn²⁺ + \frac{1}{2} O₂ + H₂O \rightarrow MnO₂ + 2 H⁺ \]  

(9)

The terminal electron acceptor of the abiotic-catalytic process is free oxygen.
Stone [41] notes that rates of reductive dissolution of transition metal oxide/hydroxide minerals are controlled by rates of surface chemical reactions and that transition metal oxides/hydroxides differ in their ability to oxidize organic compounds. He listed reduction potentials for nickel, manganese, cobalt, and iron. Based on his thermodynamic data, oxidant strength decreased in the following order: \( \text{Ni}_2\text{O}_3 \), \( \text{Mn}_2\text{O}_3 \), \( \text{MnO}_2 \), \( \text{CoO}_2 \), \( \text{FeO}_2 \). Because manganese is a relatively strong oxidant commonly found in soil, its reductive dissolution and auto-oxidative characteristics are reviewed and used in the proposed analysis. Stone [42] notes that

"(r)actions involving manganese(III/IV) oxides differ in several important respects from analogous reactions of metal ion complexes in homogeneous solutions. Manganese(III) and manganese(IV) centers are incorporated within an oxide surface when reduction occurs; the flux of Mn(III) and Mn(IV) from the surface into overlying solution is negligible, given the exceedingly low solubility of oxidation states [43]. Specific interaction between reductant molecules and oxide surface sites is believed to be necessary for reaction, since adsorbed calcium and phosphate ions strongly inhibit reaction [43]. Small changes in reductant structure cause large differences in reaction rates, another indication of specific interaction [44]. Thus, reductive dissolution of manganese(III/IV) oxides is surface chemical reaction controlled and requires close association of reductant molecules with surface sites before electron transfer and metal ion release can occur."

Stone and Morgan [45] proposed a simple model for describing reductive dissolution of Mn(III) with phenol. Whelan and Sims [5] expanded on this effort by presenting a hypothetical model of reductive dissolution and auto-oxidation of Mn(IV) and hydroquinone. Based on their work, a simple illustrative model is presented herein for the reductive dissolution and auto-oxidation of Mn(IV) and transformation of naphthalenediol \([1,4\text{-C}_{10}\text{H}_6\text{(OH)}_2]\). The following assumptions apply to this analysis:

- Manganese(IV) represents the oxidized form of the metal, although manganese(III) most likely is also present.
- For illustration, similar reaction schemes based on hydroquinone are assumed where no information on abiotic oxidation of naphthalenediol exist.
- The oxidized organic product is represented as a radical because under aerobic conditions a radical represents the most likely product for polymerization reactions. Numerous research has noted that oxygen promotes oxidative coupling reactions, creating dimers, trimers, and other less soluble, more surface active oxidation products [11,29,30,35,36,40-42,45-5].
- Transport-controlled reactions are assumed not to occur [43]. The dissolution rate is controlled by the rates of surface chemical reactions (assuming for this paper inner-sphere complexation) and not by diffusion [52]. Stone and Morgan [43] performed experiments with manganese oxides and hydroquinone where they demonstrated that the reaction kinetics were not a function of the stirring rate. Stone [52] also notes that he experienced an eight-fold increase in the dissolution rate when catechol, as opposed to hydroquinone, was employed under exactly the same conditions, suggesting that the dissolution rate is controlled by surface chemical reactions and not by diffusion.
- The release of the reduced metal ion is independent of the product concentrations, indicating that the release of the reduced metal from the oxide surface is unidirectional. Stone and Morgan [43] performed experiments containing manganese oxides and hydroquinone. They varied the Mn\(^{2+}\) concentrations and illustrated that different dissolved manganese concentrations had no effect on the initial rates of dissolution.
The availability of the oxidized metal surface [i.e., MnIV(OH)2] is not limiting in the proposed reactions, and the total number of surface sites remains relatively constant as a new site is generated when a reduced manganese ion is released then auto-oxidized. This assumption does not address the potential for the oxide surface to readsorb reduced manganese (i.e., dissolved Mn2+) or dissolved oxidized organics. Stone and Morgan [43] investigated the potential for readsorption of Mn2+ and determined that the loss of Mn2+ was less than 2% of the amount of manganese added. Readsoorption of Mn2+ and organic products will depend on the type of manganese oxide present and could be significant.

The number of moles of surface sites is assumed to equal 6% of the number of moles of manganese added to the system. Stone and Morgan [43] estimated the number of manganese oxide surface sites in their experimental setup to be between 3.5 and 9.0% of the total oxide added to the system.

The naphthalenediol is assumed in excess, and its mass changes negligibly in the system. Although this illustrated example addresses one organic, other organics could also polymerize, which might induce the copolymerization of naphthalenediol. For example, Bollag and Liu [12] reports that anilines polymerize in the presence of Rhizoctonia laccase and 2,4-DCP but do not oligomerize in the presence of the enzyme only. Because aniline alone was not polymerized by the enzyme, the formation of cross-coupling products of 2,4-DCP and aniline may be due to a chemical reaction between aniline and a 2,4-DCP derivative [6].

In an approach similar to that presented by Whelan and Sims [5], a simple model is suggested herein for describing reductive dissolution of Mn(IV) and auto-oxidation of Mn(II); it illustrates the importance of oxygen and the impact of auto-oxidation on Mn2+ concentrations. Also presented are stoichiometric equations associated with the process and a brief analysis illustrating their application.

**Half Reactions and Inner-Sphere Mechanism for Reductive Dissolution of Mn(IV)**

The half-reactions associated with the reductive dissolution of Mn(IV) and the oxidation of 1,4-naphthalenediol [i.e., 1,4-dihydroxynaphthalene, Nap-(OH)2] are presented in Table 1 [53]. Stone and Morgan [45] have mechanistically described these equations in four steps: 1) precursor-complex formation (i.e., reductant adsorption), 2) electron transfer, 3) release of oxidized organic product, and 4) release of reduced metal ion. Precursor-complex formation may be either an inner-sphere reaction, when incoming organics bind directly to the surface metal centers, or an outer-sphere reaction, where a layer of coordinated hydroxyl groups or water molecules separate the organic from the surface metal centers [45,54]. Hydroxyl groups exist at the surface of the manganese dioxide mineral [i.e., MnIVO2(s)]; these hydroxyl groups are used to balance the charge at the surface-water interface and can be expressed as MnIV(OH)2, where "i" refers to the oxide surface. The following four steps can be used to describe the inner-sphere complex formation between Nap-(OH)2 and the manganese dioxide surface [45]:

<table>
<thead>
<tr>
<th>Table 1: Hypothetical Half Reactions for Reductive Dissolution</th>
</tr>
</thead>
</table>
| \[
| \text{Mn}^{IV}O_2(s) + 4 \text{H}^{+} + 2 \text{e}^{-} = \text{Mn}^{2+} + 2 \text{H}_2\text{O} \quad (1) \\
| 2 \text{Nap-(OH)}_2 = 2 (\cdot 0-\text{Nap-OH}) + 2 \text{H}^{+} + 2 \text{e}^{-} \quad (2) \\
| \text{net:} \quad \text{Mn}^{IV}O_2(s) + 2 \text{Nap-(OH)}_2 + 2 \text{H}^{+} = \text{Mn}^{2+} + 2 (\cdot 0-\text{Nap-OH}) + 2 \text{H}_2\text{O} \quad (3) \\
| \] |

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1. Precursor-Complex Formation (Reductant Adsorption):

\[ \text{Mn}^{IV}(\text{OH})_2 + 2 \text{Nap-(OH)}_2 \xrightleftharpoons[k_1]{k_{-1}} \text{Mn}^{IV}(\text{O-Nap-OH})_2 + 2 \text{H}_2\text{O} \] (10)

where \( k_1 \) and \( k_{-1} \) are rate constants in the forward and reverse directions, respectively.

2. Electron Transfer:

\[ \text{Mn}^{IV}(\text{O-Nap-OH})_2 \xrightleftharpoons[k_2]{k_{-2}} \text{Mn}^{II}(-\text{O-Nap-OH})_2 \] (11)

where \( k_2 \) and \( k_{-2} \) are rate constants in the forward and reverse directions, respectively.

3. Release of Oxidized Organic Product:

\[ \text{Mn}^{II}(-\text{O-Nap-OH})_2 + \text{H}_2\text{O} \xrightleftharpoons[k_3]{k_{-3}} \text{Mn}^{II}\text{OH}_2 + 2 (-\text{O-Nap-OH}) \] (12)

where \( k_3 \) and \( k_{-3} \) are rate constants in the forward and reverse directions, respectively, and \(-\text{O-Nap-OH}\) is a radical. By noting that \( \text{Mn}^{II} \) still resides on the oxide surface, the \( \text{Mn}^{II} \) products of Equation (12) can also be written as follows, because the right- and left-hand sides of Equation (13) are equivalent:

\[ \text{Mn}^{II}\text{OH}_2 = \text{Mn}^{IV}\text{O}_2-(\text{Mn}^{II}\text{OH}_2) \] (13)

4. Release of Reduced Metal Ion:

Stone and Ulrich [32] noted that protons frequently assist in the metal-detachment step of dissolution reactions and that studies have generally found the number of protons involved to be equal to the valence of the detached metal (i.e., 2) [55]. They continued to note that the actual number of protons involved in reductive dissolution is not known with certainty, because the presence of two or more oxidation states on the metal surface may alter the pH dependence of the metal-release step. The release of the reduced metal ion from the surface is expressed as follows:

\[ \text{Mn}^{IV}\text{O}_2-(\text{Mn}^{II}\text{OH}_2) + 2 \text{H}^+ \xrightarrow[k_4]{\text{ }} \text{Mn}^{IV}(\text{OH})_2 + \text{Mn}^{II} + \text{H}_2\text{O} \] (14)

where \( k_4 \) is a rate constant. In experiments to determine the effect of varying amounts of \( \text{Mn}^{II} \) on \( \text{MnO}_2 \) dissolution rates, Stone and Morgan [43] found that initial rates of dissolution with varying amounts of \( \text{Mn}^{II} \) in solution had no effect on the kinetics. Based on these results, one might conclude that Equation (14) is not rate limiting and can be considered to be unidirectional. The amount of \( \text{Mn}^{II} \) in solution does not influence the rate of its formation. This conclusion appears to be confirmed by the fact that \( \text{Mn}^{II} \) has a larger radius than \( \text{Mn}^{IV} \) (i.e., 0.80 Å versus 0.60 Å [31]) and does not appear to fit very well into the solid structure of \( \text{MnO}_2(s) \). As such, the \( \text{Mn}^{II} \) ion is readily released from the matrix.
TABLE 2

Half Reactions for Auto-Oxidation

\[
\begin{align*}
\frac{1}{2} \text{Mn}^{2+} + \frac{1}{2} \text{O}_2 + \frac{1}{2} \text{H}_2\text{O} & \quad \overset{\text{slow}}{\longrightarrow} \quad \frac{1}{2} \text{MnIVO}_2(\text{s}) + \text{H}^+ \quad (1) \\
\frac{1}{2} \text{Mn}^{2+} + \frac{1}{2} \text{MnIVO}_2(\text{s}) & \quad \overset{\text{fast}}{\longrightarrow} \quad \frac{1}{2} (\text{MnIVO}_2-\text{Mn}^{II}) \quad (2) \\
\frac{1}{2} (\text{MnIVO}_2-\text{Mn}^{II}) + \frac{1}{2} \text{O}_2 + \frac{1}{2} \text{H}_2\text{O} & \quad \overset{\text{slow}}{\longrightarrow} \quad \text{MnIVO}_2(\text{s}) + \text{H}^+ \quad (3)
\end{align*}
\]

\textbf{net:} \quad \text{Mn}^{2+} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} = \text{MnIVO}_2(\text{s}) + 2 \text{H}^+ \quad (4)

\textbf{Polymeric Products of Mn(IV) Reductive Dissolution/Auto-Oxidation}

Research has indicated that oxygen promotes oxidative coupling reactions, creating dimers, trimers, and other less soluble, more surface-active oxidation products [9,29,30,35,36,40-42,45-51]. These oxidative-coupling reactions could account for the removal of radical products that are consumed in the oxidation process. Taylor and Battersby [56] note that the rate of disappearance of phenolate radicals through dimerization has been clearly shown to follow second-order kinetics.

\textbf{Auto-Oxidation of Mn(II) to Mn(IV)}

Stumm and Morgan [57] presented reactions for the oxidation of Mn(II) to Mn(IV). They felt that the reactions might best be visualized as proceeding according to the reactions presented in Table 2. They also note that the Mn\textsuperscript{II} concentration decreases with time with an apparent autocatalytic effect. Based on Stumm and Morgan [58], Benefield et al. [59] describe the autocatalytic oxidation of Mn(II) in the following manner:

\[
d[\text{Mn}^{2+}]/dt = -k_5 [\text{Mn}_7] [\text{P}_0] [\text{OH}^-]^2 [\text{Mn}^{2+}] [\text{Mn}_7 - \text{Mn}^{2+}] \quad (15)
\]

where \(k_5\) is a rate constant, \(\text{Mn}_7\) is the total manganese in the system, and \([\text{P}_0]\) is the partial pressure of oxygen. Although Mn(II) is oxidized according to Equation (15), it is unclear what valence that manganese is oxidized to [i.e., Mn(III) or Mn(IV)]. To be a true catalyst, Mn\textsuperscript{2+} would have to be oxidized to Mn(IV) to regenerate the oxidative surfaces and maintain zero net change. Equation (14) and Table 2 indicate that the rates of reaction and production of Mn\textsuperscript{2+} and oxidized products are pH dependent. Wehrli [60] notes that thermodynamics indicate that manganese should be present in aquatic waters as Mn(IV) oxides; however, experiments and analyses by Diem and Stumm [61] and Wilson [62], respectively, have indicated that Mn\textsuperscript{2+} is not oxidized by oxygen within several years. Wehrli [60] continues to note that recent experimental evidence has shown that mineral surfaces provide accelerated pathways for redox processes such as the oxygenation of metal ions and organic pollutants. He also notes that manganese oxygenation is accelerated by iron oxide particles by a factor of more than 10,000.

\textbf{KINETICS OF REDUCTIVE DISSOLUTION AND AUTO-OXIDATION}

This section presents algorithms describing the kinetics of hypothetical reductive-dissolution and auto-oxidation reactions of manganese dioxide and naphthalenediol, assuming that Equations (10) through (15) are valid. Figure 11 presents a schematic
FIGURE 11 Schematic of the Reductive-Dissolution/Auto-Oxidation Process [5,45]

Illustration of the reductive dissolution and auto-oxidation processes, based on Equations (10) through (15). Assuming that the only species that contribute to the surface mass balance equation are $[^{IV}Mn](OH)_2$, $[^{IV}Mn](O-Nap-OH)_2$, $[^{II}Mn]OH_2$, and $[^{II}Mn](\cdot O-Nap-OH)_2$, and that other competing anions and cations are not considered, the surface mass balance equation can be written as follows:

$$S_t = [^{IV}Mn](OH)_2] + [^{IV}Mn](O-Nap-OH)_2] + [^{II}Mn](\cdot O-Nap-OH)_2] + [^{II}Mn]OH_2]$$  (16)
where \( S_t \) is the total moles of surface sites per liter of solution (M). Under the assumption that each reaction can be described as an elementary reaction, rate expressions are proposed for \( \text{Mn}^{IV}(\text{OH})_2 \), \( \text{Mn}^{IV}(\text{O-Nap-OH})_2 \), \( \text{Mn}^{II}(\cdot \text{O-Nap-OH})_2 \), and \( \text{Mn}^{II}\text{OH}_2 \), using Equations (4) through (7):

\[
\frac{d[\text{Mn}^{IV}(\text{OH})_2]}{dt} = -k_1 [\text{Nap(OH)}_2]^2 [\text{Mn}^{IV}(\text{OH})_2] + k_{-1} [\text{Mn}^{IV}(\text{O-Nap-OH})_2] + k_4 [H^+]^2 [\text{Mn}^{II}\text{OH}_2]
\]

\[
\frac{d[\text{Mn}^{IV}(\text{O-Nap-OH})_2]}{dt} = k_1 [\text{Nap(OH)}_2]^2 [\text{Mn}^{IV}(\text{OH})_2] - (k_1 + k_2) [\text{Mn}^{IV}(\text{O-Nap-OH})_2] + k_2 [\text{Mn}^{II}(\cdot \text{O-Nap-OH})_2]
\]

\[
\frac{d[\text{Mn}^{II}(\cdot \text{O-Nap-OH})_2]}{dt} = k_2 [\text{Mn}^{IV}(\text{O-Nap-OH})_2] - (k_2 + k_3) [\text{Mn}^{II}(\cdot \text{O-Nap-OH})_2] + k_3 [\cdot \text{O-Nap-OH}]^2 [\text{Mn}^{II}\text{OH}_2]
\]

\[
\frac{d[\text{Mn}^{II}\text{OH}_2]}{dt} = k_3 [\text{Mn}^{II}(\cdot \text{O-Nap-OH})_2] - (k_3 [\cdot \text{O-Nap-OH}]^2 + k_4 [H^+]^2) [\text{Mn}^{II}\text{OH}_2]
\]

The rate expressions for the remaining nonsurface-constituent concentrations (i.e., \( \text{Mn}^{II} \), \( \text{Nap(OH)}_2 \), and \( \cdot \text{O-Nap-OH} \)) are as follows:

\[
\frac{d[\text{Mn}^{II}]}{dt} = k_4 [H^+]^2 [\text{Mn}^{II}\text{OH}_2] - k_5 [\text{Mn}_2] [\text{P}_0] [\text{OH}^-]^2 [\text{Mn}^{III}][\text{Mn}_1 - \text{Mn}^{II}]
\]

\[
\frac{d[\text{Nap(OH)}_2]}{dt} = -2 k_1 [\text{Nap(OH)}_2]^2 [\text{Mn}^{IV}(\text{OH})_2] + 2 k_1 [\text{Mn}^{IV}(\text{O-Nap-OH})_2]
\]

\[
\frac{d[\cdot \text{O-Nap-OH}]}{dt} = 2 k_3 [\text{Mn}^{II}(\cdot \text{O-Nap-OH})_2] - 2 k_3 [\cdot \text{O-Nap-OH}]^2 [\text{Mn}^{II}\text{OH}_2]
\]

Solutions to the Kinetic Rate Expressions

This section presents an illustrative example of the effects of kinetic rate constants and other parameters in determining the importance of reductant adsorption, electron transfer, surface release of oxidized organics, surface release of reduced Mn\(^{II} \), and auto-oxidation. Responses to variations in parameters contained in Equations (10) through (15) are determined through solutions of Equations (16) through (24), which have been solved using Euler's method [63]. The solutions to these equations assume that the systems are well buffered (constant pH). If the pH was set at a lower value, then the rate of reductive dissolution would increase [see Equations (17) and (20) through (22)], and the rate associated with auto-oxidation would decrease [see Equation (22)]. Although many environmental systems are buffered, many are not; and the effects of pH can be seen in these equations though.

As noted earlier, Schnitzer [37] suggested that the rate-determining step in the synthesis, by oxidative polymerization of humic acids from simple phenolic constituents and acids, is the formation of a semiquinone radical involving one-electron transfer reaction. Following this reasoning, this illustrative example investigates the conditions when the formation and release of the naphthalenediol radical is rate-limiting. To meet this condition, either the electron transfer step (i.e., formation of the radical on the oxide surface, Equation (11)) or the release of the oxidized organic radical from the oxide surface [Equation (12)] is rate limiting. For illustrative purposes, the latter (i.e., release of radical from the surface) is assumed to be the rate-limiting step.

The assumptions associated with this analysis are presented in Table 3. Although temperature, ionic strength, and other parameters can play an important part in any scenario involving surface chemical reaction, they are not directly factored into the stoichiometric and kinetic equations outlined by Equations (10 through (15). Whelan and Sims [5] and Stone and Ulrich [32] arbitrarily assigned values for the
parameters presented in this table, which have been modified for this example. The initial concentrations for [S₄], [锰IV(OH)₂], and [Nap(OH)₂] are also given in Table 3. All other initial concentrations (i.e., [锰IV(OH)₄], [锰IV(O-Nap-OH)], [锰IV(O-Nap-OH)₂], and [锰IV(O-Nap-OH)₄]) are assumed as zero.

The results of the simulation are presented in Figure 12. When release of the oxidized organic from the metal surface is rate-limiting (i.e., small k₃), equilibrium conditions between MnIV(O-Nap-OH), Mn⁺(O-Nap-OH), and Mn₂⁺ may occur. MnIV(OH)₂ is converted to MnIV(O-Nap-OH), which in turn is converted to Mn₃⁺(O-Nap-OH). Under steady-state conditions, these concentrations do not change. Figure 12 also shows that the [MnIV(OH)₂] concentration is nearly zero, because once [MnIV(OH)₂] is formed it is immediately converted to Mn²⁺ [Equation (14)]. The Mn²⁺ concentration (theoretically) would continue to rise with time. Figure 13 illustrates that auto-oxidation would counterbalance the increase until steady-state conditions were reached between Mn²⁺ formation from reductive dissolution and its disappearance due to auto-oxidation.

![Figure 12 Fraction of Oxide Surface Occupied by Various Species](image1)

![Figure 13 Temporal Variation in Mn²⁺ Concentration during Reductive Dissolution/Auto-Oxidation When Release of Oxidized Organic is Rate Limiting](image2)
EXPERIMENTAL APPLICATION

A brief experimental analysis was performed to determine if a multiple-ringed aromatic compound could be effectively oxidized through abiotic catalysis using the reductive-dissolution process. This section briefly discusses the oxidation of 2,3-naphthalenedioid \([C_{10}O_6(OH)_2]\) by manganese-oxide particles. Although naphthalenedioid is strictly not a recalcitrant organic, it is a multiple-ringed aromatic that may reflect the behavior of larger, multiple-ringed aromatic compounds with diol/dione functional groups when involved in the reductive-dissolution process.

Materials and Methods

Unless otherwise stated all solutions were prepared from reagent grade chemicals [e.g., 2,3-naphthalenedioid (Aldrich 98%) and deionized distilled water (DDW)] and filtered with a 0.2-μm-pore-diameter, nylon membrane filter (Nylafo, Baxter Scientific Products) prior to use. All glassware was soaked in 2 M HNO₃ and 0.05 M NH₂OH·HCl, and thoroughly rinsed with DDW prior to use.

Manganese Oxide Particle Preparation. Manganese oxide particles were prepared using a procedure based on Murray [64]. An 18-L, manganese-dioxide solution was prepared using 0.016 N NaOH, 0.008 M KMnO₄, and 0.012 M MnCl₂ using the following procedure: Add 11.52 g NaOH and 22.76 g KMnO₄·H₂O to 16 L of DDW. Stir until dissolved. In a separate container, add 42.75 g MnCl₂·4H₂O to 2 L of DDW. Stir until dissolved. Under nitrogen purging, add the MnCl₂ solution to the NaOH/KMnO₄ solution at a pumping rate of 4 mL/min while gently stirring the entire solution. When complete, stop purging with nitrogen gas, and allow MnO₂ particles to settle out. Adjust pH to approximately 7 by adding dropwise 1 N NaOH without stabilizing the floc. Carefully decant supernatant. Place the remaining MnO₂ particles in an acid-washed, plastic container. Adjust the final pH to 7. Mix contents, centrifuge, decant, and mix with a DDW with a pH of 7 and an ionic strength of 0.01 M NaCl; repeat three times. After 37 days, the specific surface area was determined as 252 m²/g using a Brunauer-Emmett-Teller (BET) surface-area analyzer (Quantachrome Monosorb).

Sample Preparation. A series of triplicate 50-mL KIMAX centrifuge tubes with Teflon-lined septum (Thomas Scientific, 2390-H72) and screw caps were prepared under oxic conditions for each sample and control; no attempt was made to establish an anoxic environment. Sample tubes contained 3.0E-04 M MnO₂ (26 mg/L), 5.0E-05 M organic substrate (8 mg/L), 1.0E-03 M acetate-buffer (sodium acetate and acetic acid) solution (measured pH of 5.5), and 1.0E-03 M NaClO₃ (to fix ionic strength) in a 0.2-μm-filtered DDW solution. The filters were presoaked in 0.5 M HNO₃ and rinsed in filtered DDW. Triplicate controls were also prepared for manganese dioxide and organic substrate, in which triplicate tubes identical to the samples were prepared without MnO₂ particles and organic substrate, respectively. These controls were used to assess changes in the tubes not attributed to the interaction between the manganese oxide suspension and the organic substrate. All tubes were prepared under yellow light and stored in the dark to minimize photodegradation. Prior to analysis, the tubes were stored in the dark in an unmonitored constant temperature room (25°C) and tumbled at 30 rpm's. The characteristics of the manganese oxide (i.e., surface area, reactivity, etc.) change with time [43,44]. To minimize the effects of aging (as it slows with time), the particles were aged at least eight months and all analyses used particles from the same preparation batch.

Experimental Design. Because the experimental centrifuge tubes essentially contained only manganese oxide and organic substrate, the experimental design focused on monitoring manganese and the parent organic substrate. Dissolved manganese (Mn²⁺) and the parent organic substrate were monitored with Inductively Coupled Plasma (ICP, Perkin-Elmer ICP/6000) and High Performance Liquid Chromatography (HPLC), respectively. The HPLC was equipped with Shimadzu components consisting of an SCL-6A system controller, an SIL-6A Auto-Injector, two Shimazu LC-6A pumps, a Chromatopac C-R3A integrator, and an SPD-6A UV detector set at a wavelength of 230 nm. The columns used were a 25-cm by 4.6-mm-ID SUPELCOSIL LC-PAH (5-μm particle size) column (Supelco 5-8229) and a
2-cm cartridge guard column with filled-width 5-μm SUPELCO-FILL packing (100 À pores) LC-18 SUPELGUARD column (Supelco 5-9554). The mobile phase was 30:70 acetonitrile:water (v/v) at a flow rate of 1 mL/min with an injection volume of 30 μL.

Once the sample and control tubes were prepared and tumbled, they were sacrificed (i.e., no subsampling) at days 0, 1, 4, 7, and 14. The tubes were first centrifuged (Beckman J2-21) at 3000 rpms for 10 minutes. The supernatant was filtered through a 0.2-μm-nylon filter using a Millipore filtering apparatus. Twenty milliliters of the filtrate were dropwise acidified to a pH of 3 using 1 N NH₂OH·HCl and 0.1 N HNO₃ [65], the contents of which were diluted to 50 mL using an acetate-buffered/NaC10₃-DDW solution with a pH of 3 (acidified with 1 N NH₂OH·HCl and 0.1 N HNO₃). The final solution contained 1.0E-03 M NaC10₃ and a pH of 3 (i.e., acetate-buffered solution acidified with 1 N NH₂OH·HCl and 0.1 N HNO₃). All standards were prepared under the same conditions as samples and controls and at a pH and ionic strength consistent with samples and controls. The manganese in the filtrate [i.e., Mn(II)] is assumed to represent the dissolved manganese (i.e., [Mn⁶⁺]) and is reported without modification by the manganese control (i.e, blank). The manganese control is provided to demonstrate that it did not contain significant amounts of dissolved manganese and that [Mn⁶⁺] in sample tubes were due to oxidation of the organic substrate.

Results and Discussion

These experiments examined the effectiveness of employing manganese oxide particles to oxidize 2,3-naphthalenediol. The effectiveness is best illustrated in Figures 14 and 15. Figure 14 presents temporal variations in the dissolved manganese concentration with 95% confidence intervals, expressed as a fraction of the total manganese added to the reaction vessel. Correspondingly, to indicate the degree of oxidation of the parent organic by the manganese particles, Figure 15 presents the fraction of the organic oxidized (i.e., molar ratio of organic oxidized to organic control). For example, a 0.99 value in this figure indicates that 99% of the parent organic has been oxidized (either transformed or degraded); the possibility of sorption has been accounted for. The results in this figure assume that the sample controls are indicative of the initial concentration in the reaction vessel. Because separate reaction vessels are employed for all analyses (i.e., separate samples, controls, and blanks without subsampling), this assumption may not strictly be correct.

Figure 14 illustrates that dissolved manganese increased from zero to 34% of the total manganese over a 14-day period. The results show that after four days there was little change in the dissolved manganese fraction. Figure 15 illustrates that the reductive dissolution of the manganese was stopped by the absence of oxidizable substrate. Nearly all of the naphthalenediol was oxidized within the four-day sampling period. Although the curves look similar in Figures (13) and (14), the Mn⁶⁺ production was not stopped by the effects of auto-oxidation, as illustrated by the modeling simula-
tion presented previously. The simulation illustrated how auto-oxidation could impact the reductive-dissolution process, where as the experiment was designed to illustrate that reductive dissolution could be a viable approach for oxidizing certain aromatic constituents. These results suggest that multiple-ringed aromatic compounds with diol functional groups are susceptible to oxidation by the reductive-dissolution process.

SUMMARY/CONCLUSIONS

By understanding the environmental consequences of recalcitrant-chemical oxidation/polymerization and the incorporation of these compounds into the humification process, recalcitrant organics could become constituent parts of soil humus, resulting in immobilized and/or detoxified bound residues. Immobilization and detoxification could be a decontamination method for certain types of waste constituents. These wastes would then be accessible to engineer-designed cleanup alternatives. To evaluate this alternative, data are currently needed on abiotic/biotic reactions that affect oxidation of organics in natural soil systems. The experimental results suggest that multiple-ringed aromatic compounds with diol functional groups are susceptible to oxidation by the reductive-dissolution process. The framework reviewed in this paper 1) provides a rational basis for an assessment of potential mechanisms influencing oxidation at a waste site, 2) provides focus for the design of treatability studies to determine rates of reaction and management options for stimulating natural polymerization, and 3) identifies master variables influencing polymerization for monitoring.

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