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**Title**: Organic Matter and Iron Oxide Nanoparticles: Aggregation, Interactions, and Reactivity

**Authors**: Amanda M. Vindedahl[1], Jennifer H. Strehlau[1], William A. Arnold[2]*, R. Lee Penn[1]*

[1]Department of Chemistry, University of Minnesota, 207 Pleasant St. SE, Minneapolis, MN 55455-0431

[2]Department of Civil, Environmental, and Geo- Engineering, University of Minnesota, 500 Pillsbury Dr. SE, Minneapolis, MN 55455-0116

*corresponding authors (arnol032@umn.edu; rleepenn@umn.edu)

**Abstract**:

Understanding the fate and transport of engineered and naturally-occurring nanoparticles is vital to predicting their ecological and toxicological impacts. Much of the current literature details the effects of solution conditions, such as pH and ionic strength, on aggregation and reactivity. Such work has drastically improved our ability to predict how nanoparticles could impact chemistry occurring in natural waters. Recently, a focus on how organic matter (OM) impacts chemistry occurring at the solid-liquid interface has emerged. This review focuses on summarizing major findings of how OM affects iron oxide nanoparticle reactivity, with particular focus on the underlying processes. First, we review work focused on the chemical reactivity of iron oxide nanoparticles in aqueous environments. Second, the current state of knowledge regarding the adsorption of OM onto mineral surfaces and its effects on nanoparticle aggregation and ion adsorption is presented. Third, how OM impacts chemical and solid-state transformations, oxidative/reductive reactivity, and photocatalytic activity of iron oxide nanoparticles is reviewed. Finally, we provide our vision of future research directions, with particular focus on improving our ability to predict the fate, transport, and chemical behavior of nanoparticles in complex, environmental systems.

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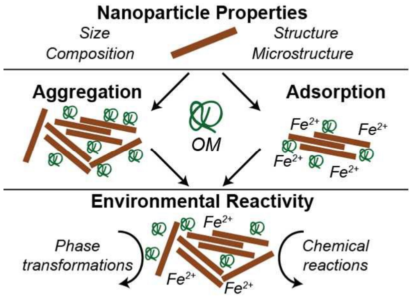

**Nano Impact:**

This critical review presents a summary of current literature focused on how organic matter impacts iron oxide nanoparticle reactivity. It provides an evaluation of knowledge gaps that should be filled to better predict fate and transport of both inorganic nanoparticles and environmental contaminants in complex environmental systems.

## 1. Introduction:

Nanoparticles, both naturally occurring and engineered, directly and indirectly impact element cycling and pollutant fate and transport.[1-8] Recently, concerns about the ecological and human health effects of metal-based nanoparticles released into or present in natural waters have spurred research aimed at elucidating what happens to nanoparticles in the environment, how those materials participate in environmental processes, and how they might perturb natural systems. Engineered nanoparticles, in particular, are a growing environmental concern; an estimated 10,000 tons of nanoparticles are produced annually for use in consumer products (e.g. cosmetics, paint, and electronics) worldwide.[9-11] As products containing nanoparticles become more common, the presence of engineered nanoparticles in the environment is expected to increase. While engineered nanoparticles are of concern, natural nanoparticles, such as iron oxide nanoparticles, are commonly found in a wide range of environments including sediments, natural waters, weathered rocks and minerals, and volcanic ash. Thus, it is also important to understand the fate, transport, and impacts of natural nanoparticles. By understanding natural

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nanoparticle behavior in the environment, elucidation of how engineered nanoparticles perturb natural systems can be achieved.

Nanoscale iron oxides represent a class of nanoparticles both produced by natural processes (e.g., products of weathering of iron-bearing minerals and biominerals) and introduced into the environment as engineered materials (e.g., iron oxides from pigments or nano-zero valent iron introduced for groundwater remediation purposes).[12, 13] The reactivity (oxidation/reduction (redox) and otherwise), solubility, surface chemistry, and aggregation state of iron oxide nanoparticles directly impact environmental fate and transport of a wide range of anthropogenic and natural species. When nanoparticles are released into or generated in surface and near-surface waters, they encounter a broad range of pH, ionic strength, and other solution conditions. These solution variables dramatically enhance or inhibit both reactivity and aggregation. The impact of ionic strength, pH, and other solution conditions has been extensively explored in colloid research,[14-19] and those findings contribute fundamental understanding of how nanoparticles behave in aquatic systems.

Indeed, the iron oxides in particular have been extensively studied, and their redox reactivity, solubility, surface chemistry aggregation state, and even phase stability vary greatly depending on the chemistry of their aqueous environments. A major challenge to understanding the behavior of nanoparticles of all kinds is the poorly understood nature of organic matter (OM) and how it impacts both the physical and chemical behavior of nanoparticles. This review summarizes the current understanding of how OM interacts with iron oxide surfaces, impacts particle aggregation and mineral transformations, and influences the adsorption and chemical reactions involving pollutants at the mineral–liquid interface. Given that the interaction between engineered inorganic nanoparticles and OM has been the primary focus of recent reviews

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elsewhere,[20, 21] this work specifically focuses on the effects of OM on iron oxide stability and reactivity. Finally, the ongoing challenges in OM/iron oxide characterization are highlighted.

## 2. A brief review on OM and nanoparticle interactions

Understanding interactions between OM and nanoparticles is critical to bridging the gap between the laboratory and the field as well as facilitating accurate predictions of environmental processes. OM is present in all natural waters but varies in content and concentration considerably. This poorly understood material is a heterogeneous mixture of molecular compounds formed by the decay of terrestrial organic material or produced in aquatic systems by microbiota. Molecular-level information about OM is only now coming to light,[22-32] with key molecular characteristics including aromaticity; functional groups like cathechol, carboxylate, and phenolic moieties; amino acid content; and overall composition (e.g., O and N content). The hydrophobic or hydrophilic character of the OM is also important. Recent advancements in instrumentation have enabled improved elucidation of OM molecular formulas. High-field Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS),[33-37] for example, is a technique that measures the mass-to-charge ratio of high molecular weight compounds with up to six decimal place precision. Exact elemental formulas are determined for compounds of the same molecular weight but different respective elemental and isotopic compositions,[38, 39] which is a significant step towards understanding the chemical nature of OM. OM presents an additional challenge, however, because it is spatially and temporally unique, which makes characterization of every OM impossible. Determination of OM elemental compositions falls far short of the definitive and exact molecular structures that are possible for small molecules and even large biomolecules like proteins.

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Of all OM components, humic substances are some of the most widely studied. Humic substances are the major organic fraction of natural OM from a wide range of environments, including soil, water, and peat. Humic and fulvic acids are two of the common fractions (soil humic substances also contain another fraction, called humin) and are isolated based on solubility in basic (humic and fulvic acids) and acidic (fulvic acids only) solutions. The International Humic Substances Society (IHSS) maintains a collection of humic substance samples and a database detailing source information (how and when samples were collected, isolated, fractionated, and purified) and what is known about the molecular characteristics of each humic substance standard. IHSS database entries include elemental compositions as well as heteroaliphatic carbon content, aromatic character, and mass fractions of amino acids. This invaluable collection of samples and their associated properties facilitates comparison of experiments directly with one another.

OM and inorganic nanoparticles primarily interact via adsorption of OM onto particle surfaces, and this adsorption dramatically impacts the adsorption of other ions and molecules.[40-50] These changes in surface chemistry may also dramatically influence aggregation state and thus accessible surface area.[15, 18, 51-58] In addition, the presence of OM may mediate or inhibit electron transfer reactions, which could substantially change the kinetics of reductive and oxidative reactions in environmental systems. All of these effects are expected to be sensitive to aqueous solution conditions, such as ionic strength, pH, as well as the concentration of OM and other reactive species.

Elucidating how OM interacts with nanoparticles (engineered or natural) is critically important to understanding fate and transport of nanoparticles as well as dissolved species like pollutant molecules in environmental systems. The current insight summarized here suggest the

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future of OM characterization is growing, yet at present, we have only begun to explore how OM specifically impacts reactions at iron oxide surfaces and the dynamics of such interactions at a fundamental level. Elucidating how various moieties found in OM interact with particle surfaces will enable predictions based on detailed characterization of OM from specific sites at specific times.

## 3. Iron Oxide Nanoparticles in Aquatic Systems

Revealing the influence of OM on the chemical and physical behavior of nanoparticles in environmental systems requires, first, an understanding of the role of other variables. The "iron oxide" family includes a broad diversity of crystal structures, chemical compositions, grain sizes, and morphologies.[59] In addition to iron(III) oxides, oxyhydroxides, and hydroxides, iron(II)-bearing minerals like green rust and mixed valence minerals, such as magnetite, exist in a number of environments.[60] The various chemical and physical properties of iron oxide nanoparticles have been extensively studied in a variety of aqueous environments through both controlled laboratory studies and field investigations. Properties relevant to aquatic systems include adsorption capacity, aggregate stability, and chemical reactivity. Due to the ubiquity of iron in the environment, major control parameters (e.g., pH) have been systematically investigated in colloids literature for many of the iron oxides, including goethite ($\alpha$-FeOOH), ferrihydrite ($Fe_{10}O_{14}(OH)_2$),[61] hematite ($\alpha$-$Fe_2O_3$), and magnetite ($Fe_3O_4$), as discussed below.

The surface chemistry of iron oxide nanoparticles in aqueous systems is exquisitely sensitive to the properties of hydroxyl groups that dominate the surface, which may be coordinated to one, two, or three structural iron atoms. The density and distribution of the three types of hydroxyl groups varies between the various iron oxides due to differences in crystal structure and crystal faces.[12] For example, all three types of hydroxyl groups are present on the

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goethite {100} and hematite {110} but only the singly and doubly coordinated groups are present on goethite {021} and hematite {100}.[62] Surface hydroxyl group density directly affects the acid dissociation constant and, thus, the point of zero charge and isoelectric point for a given sample of iron oxide nanoparticles. Literature values for these properties vary widely for each iron oxide mineral due to differences in experimental methods and site density value selection.[12] In general, $pK_{a1}$ values range from 4-8, $pK_{a2}$ from 8-11, and point of zero charge from 6-10.[12] In general, goethite nanoparticles have values that are in the higher range for each pKa, while magnetite and maghemite typically have values in the lower part of each of the ranges given.

Nanoparticle aggregation state and dynamics are critical considerations in environmental studies of nanoparticles. Iron oxides rarely exist as isolated particles in environmental systems and instead occur more commonly as aggregates (or heteroaggregates with other minerals) of varying size, size distribution, shape, and density.[18] With the variable charge of surface hydroxyl groups, pH and ionic strength are primary determinants of iron oxide surface properties and thus aggregation state.[15, 63-67] In the presence of other common soil minerals, such as clays and quartz, iron oxide surface charge becomes especially important. With points of zero charge generally lower than 6,[68] most clay minerals and quartz will heteroaggregate with positively charged iron oxides in circumneutral waters. This has led to several studies determining the effect of solution chemistry on heteroaggregation, as demonstrated by the recent works of Wei et al.,[69] Jung et al.,[70] and Wang et al.[71, 72] Such studies are critical to understanding accessible reactive surface area as aggregation and heteroaggregation could dramatically decrease accessible reactive surface area as compared to well dispersed nanoparticles.

To study transport and reactivity of iron oxide nanoparticles in environmental applications, particular attention to surface chemistry and aggregation state is essential.[73] For

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example, recent investigations have shown that open fractal or small aggregates of iron oxides are more colloidally stable and travels longer distances in aquatic systems.[14] Furthermore, certain metal(loid) contaminants (e.g. Cu, As, and Zn) often associate with iron oxide phases found in acid mine drainage.[74] Thus dispersed iron oxide nanoparticles or dispersed aggregates serve as carriers of contaminants.

Much has been learned through laboratory and theoretical studies of iron oxide surface chemistry in aqueous environments free of OM. The ubiquity of OM, however, means its interactions with nanoparticles must be elucidated to gain a holistic understanding of the chemical and physical behavior of nanoparticles in environmental systems. A major roadblock is the spatial and temporal heterogeneity of OM. Linking specific molecular and structural characteristics with specific impacts on chemical reactivity means that detailed characterization of field samples could facilitate accurate predictions of the roles native iron oxides play in the environmental geochemistry of a given site.

## 4. Iron Oxide Suspensions Containing OM

Much has been learned from experiments examining iron oxide properties in aquatic systems, and more recent work has included the presence of OM. In the 1980s, a large focus was on the adsorption and desorption of OM on iron oxide surfaces,[75, 76] and the results of these works improved understanding of how OM alters surface properties (such as electrophoretic mobility, zeta potential, and protonation state) of iron oxide particles. The chemical and physical behavior of iron oxide nanoparticles are considerably sensitive to adsorption that the ways in which OM perturbs these processes must be examined. Despite the detailed research in this area, the ubiquitous and evolving nature of OM in the environment leads us to emphasize its impacts on the evolving reactivity of iron oxide nanoparticles. In addition, recent advancements in

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experimental design and instrumentation should be highlighted to promote the progress towards elucidation of these complex systems.

### *4.1. OM Surface Interactions and Aggregation Effects*

#### *4.1.1. OM Adsorption*

Gu and coworkers[40] summarized six possible mechanisms for OM adsorption on mineral surfaces, which arise due to differences in chemical and structural features of both the OM and the mineral surface (Figure 1). They proposed the two primary mechanisms for most systems were electrostatic attraction and ligand exchange between the hydroxyl groups on the iron oxide surface and carboxyl or hydroxyl groups within the OM. This was verified through a combination of characterization techniques (quantifying adsorption/desorption by using total organic carbon analysis to quantify OM in the aqueous phase, Fourier transform infrared (FTIR) spectroscopy, and nuclear magnetic resonance (NMR) spectroscopy) of hematite nanoparticles that had been suspended in aqueous solutions of natural wetland OM and the Suwannee River fulvic acid humic substance standard.

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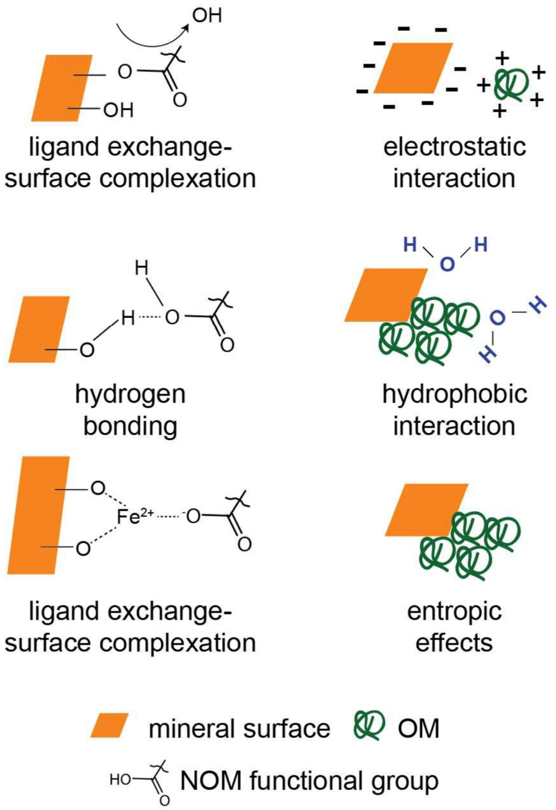

**Figure 1**: Schematic depicting the six mechanisms for OM adsorption on mineral surfaces as described by Gu et al.[40]

Some works have studied the adsorption of weak acid molecules on iron oxide nanoparticles to establish which molecular characteristics are most important in predicting how OM affects surface chemistry, aggregation state, and chemical behavior. Studies have both modeled and experimentally quantified adsorption capacity of weak acid molecules, including EDTA and metal-EDTA complexes,[77] benzoic acid, other simple carboxylic acids,[78, 79] citrate,[80] phosphonates,[81] and aminophenols[82] onto goethite and hematite nanoparticles. Typically, a maximum in adsorption of weak acid is observed at acidic pH (ca. 4 – 5), which decreases to minimal adsorption at circumneutral and alkaline pH. Also, some studies reported no dependence of adsorption of weak acid on solution ionic strength.[78, 79, 81] The mechanism of adsorption for goethite was modeled by Filius et al.,[79] and these results were consistent with adsorption governed by electrostatic forces. Many iron oxides are neutral at circumneutral pH

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and negatively charged at alkaline pH. The experimental work demonstrating minimal adsorption at circumnuetral and alkaline pH, at which weak acids would be deprotonated and negatively charged, is also consistent with this conclusion.

While the study of weak acid adsorption on iron oxide nanoparticles may provide some insight into OM adsorption, it does not fully describe or necessarily predict OM adsorption. Unlike simple weak acids, OM can contain large networks of hydrophobic content including aromatic, aliphatic, and heteroaliphatic character. OM with a greater hydrophobic content preferentially adsorbs onto an iron oxide due to the density and distribution of surface hydroxyl groups, which interact with the hydrophobic groups in OM as directly evidenced by Gu et al. with FTIR spectroscopy.[40] Several later studies demonstrated preferential adsorption of the hydrophilic and hydrophobic acid components to iron oxide surfaces.[41, 83, 84] In contrast, a clay mineral which only contains surface hydroxyl groups on edge faces would not have similar OM adsorption capacity. For example, Meier et al. demonstrated that Suwannee River natural organic matter adsorption on goethite was greater than for another OM with lower hydrophobic content.[85] Their results also indicated the strong preference for adsorption on goethite over kaolinite, a clay mineral. Hydrophobicity of OM, therefore, is an important characteristic to consider for future predictions of OM adsorption on iron oxides and their resultant aggregation state and surface-mediated reactions.

Electrostatic interactions between iron oxide nanoparticles and OM have also been observed. Increasing pH decreases surface charge density which decreases OM adsorption capacity if electrostatic interactions are primary mechanisms of adsorption. At pH values higher than the point of zero charge, iron oxide nanoparticles are negatively charged and OM adsorption is inhibited due to electrostatic repulsion and decreased ligand exchange between OM acidic

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functional groups and iron oxide surface sites. Carboxylic OM moieties have been shown to influence the OM adsorption capacity on iron oxides through coordination to surface hydroxyl groups.[86-88] Adsorption isotherms as a function of pH have revealed the pH sensitivity of OM adsorption on iron oxides. Illés and Tombácz reported significant decreases in the adsorption of a humic acid on magnetite with increasing pH, especially when pH neared the experimentally determined point of zero charge of 8.[89] Other studies with fulvic acids demonstrated comparable results.[79, 90] With the current trend in simulating groundwater systems and the variable surface charge (due to circumneutral point of zero charge values) of iron oxides, electrostatic interactions between OM and iron oxides become a major component of OM adsorption.

Finally, the adsorption of OM onto an iron oxide is a dynamic process and depends on several other factors, including the OM molecular weight and concentration. In a study examining the kinetics of humic substance adsorption onto hematite by Vermeer and Koopal, the rate of adsorption of small fulvic acids as compared to larger humic acids was time dependent, with adsorption dominated by the small fulvic acid at early times.[91] After equilibration, however, the relative amounts of the humic acids and fulvic acids had shifted, with more humic acids residing on the surface.[83, 92, 93] More specifically for iron oxides, Zhou et al. described adsorption isotherms on goethite composed of three regimes of preferential adsorption and the most important parameter was molecular weight.[93] At low added fulvic acid concentrations, most of the fulvic acid adsorbed onto goethite (i.e., the result was relatively independent of molecular weight) due to minimal competition for unoccupied surface sites. With increased fulvic acid concentration, all high molecular weight fulvic acid and a portion of low molecular weight fulvic acid had adsorbed, leaving some small molecular weight fulvic acid in solution. Finally, as the adsorption isotherm leveled off at higher initial fulvic acid concentrations, the

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larger fulvic acid molecules completely occupied the surface sites, leaving all the low molecular weight fulvic acid molecules in solution because there was insufficient adsorption capacity for all of the fulvic acid molecules. This trend of preferential adsorption of large molecular weight OM as compared to low molecular weight OM has been observed recently for other systems, as well.[94, 95]

While details of the fundamental mechanisms of OM-iron oxide interactions have been studied through batch experiments, future adsorption studies should include contact extent and duration as factors, considering that groundwater is a continuous and dynamic system. In an effort to better characterize OM adsorption properties and resultant iron oxide transport in natural environments, flow-through columns have been applied. McInnis et al. investigated the transport behavior of three different OM fractions within an iron oxide-coated sand column, finding that transport time decreased for the largest fractions of OM, which is in direct contrast to the previous studies.[96] They hypothesized that compositional characteristics (e.g. hydrophobicity) of the OM fraction (collected from the same water sample but via different extraction methods) overrode the effect of molecular weight. Kreller et al. performed similar column experiments with a similar conclusion, although molecular weight played a larger role.[97] These studies are unique for the coming shift in environmental studies involving OM, aimed at revealing not only fundamental mechanisms but long-term effects more relatable to natural environments.

### *4.1.2. Aggregation Effects*

The adsorption of OM on an iron oxide impacts the surface charge density and, therefore, the aggregation state of the iron oxides in aquatic systems, which means the presence, molecular characteristics, and concentrations of OM must also be considered when interpreting aggregation

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effects. The addition of small amounts of OM to suspensions of positively charged iron oxide nanoparticles at circumneutral pH may drop the surface charge dramatically,[98] which would favor aggregation and potentially result in a decrease in accessible reactive surface area. Furthermore, if the OM added has a large number of deprotonated weak acid moieties, charge reversal could also be possible. In fact, previous work has demonstrated aggregation upon addition of small amounts of OM,[45, 89, 99] and one study demonstrated charge reversal.[100] Aggregation may be inhibited because the adsorption of OM provides an organic macromolecular layer on the iron oxide causing electrostatic repulsion between the negatively-charged macromolecular layers coating the nanoparticles.[101, 102] The differences between low and high OM concentrations on goethite nanoparticle aggregation are highlighted in Figure 2. At low concentrations, the charge neutralization promotes aggregation. At high concentrations, steric stabilization and electrostatic repulsion inhibit aggregation. Comparing the two suspensions imaged by cryogenic transmission electron microscopy (cryo-TEM) in Figure 2, the same number of particles were imaged in either 2 or 50 ppm organic carbon (Suwannee River humic acid purchased from IHSS). In suspensions containing 50 ppm organic carbon (OC), the particle per OC ratio was 25 times larger than in 2 ppm OC, resulting in greater OM adsorption, steric stabilization, and electrostatic repulsion, correlating to the visibly smaller aggregate sizes and fewer particle interactions.

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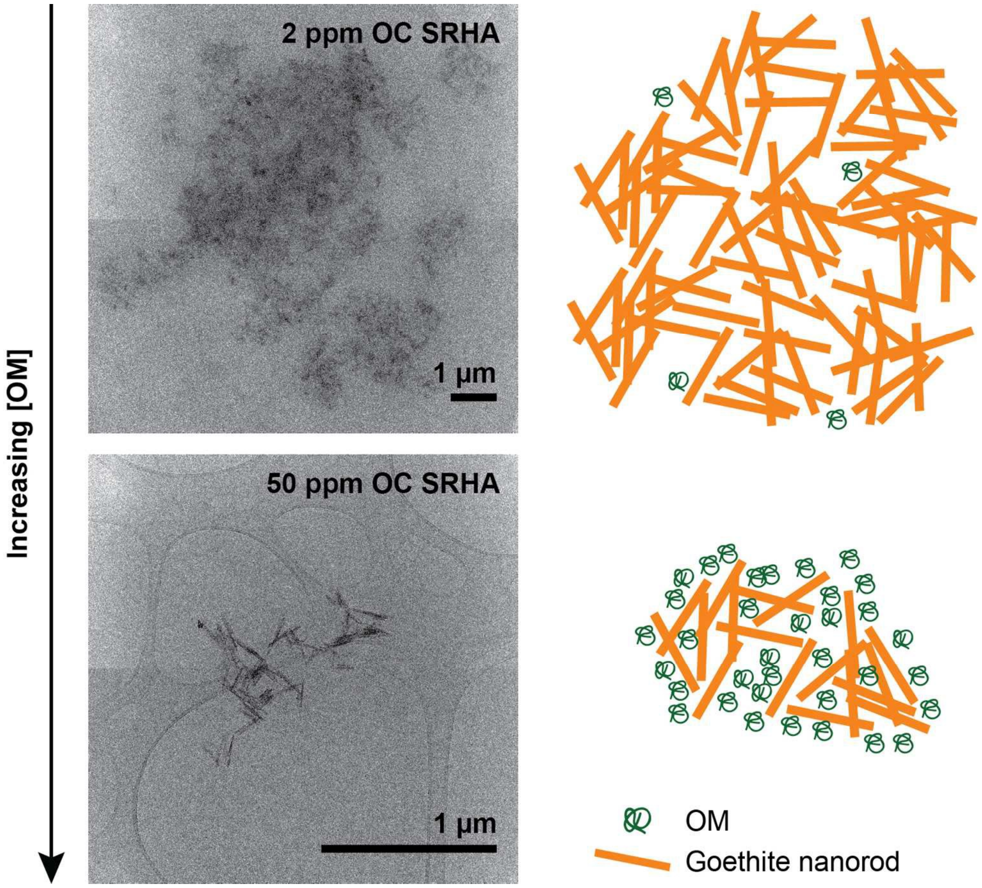

**Figure 2**: Representative cryo-TEM images of goethite nanorods suspended in 10 mM sodium bicarbonate buffer at pH 7 and either 2 or 50 ppm organic carbon (OC) of Suwannee River humic acid (SRHA).

### *4.2. Adsorption of Other Ions and Molecules Affected by OM*

The aggregation state and surface reactions of iron oxides are oftentimes dependent on the ionic strength and adsorption of ions, including heavy metal contaminants (e.g., Pb(II). U(VI)) and reactive ions (e.g., Fe(II)). The impact of OM on the adsorption of ions on iron oxide surfaces has been well studied. Mechanisms by which OM could inhibit ion adsorption include ion complexation by OM or competition for reactive surface sites. A variety of ions adsorb strongly to iron oxide nanoparticles, including Pb(II), Cu(II), Zn(II), U(VI), carbonate, phosphate, and sulfate, some of which are of environmental concern.[12, 103-108] In recent years, research has expanded to address more diverse environmental conditions and the mechanisms

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linking ion adsorption and resultant reactivity.[109-120] The addition of aqueous OM molecules leads to complex formation with common contaminant ions, such as Hg(II),[121] Cu(II),[122, 123] Fe(II) and Fe(III),[124, 125] Ag(I),[126] Ca(II),[123] U(VI),[127] under relevant environmental conditions. This process lowers dissolved ion activities and disrupts or limits their adsorption onto the mineral surface, as seen by depressed adsorption of U(VI) on hematite in the presence of humic acid.[128] In rare cases, some cations have been shown to not complex with OM, such as Cd(II).[122] This process leaves free ion activities unchanged, and the ions either remain in solution or adsorb onto the mineral surface. In other cases, the addition of OM that is able to complex with an ion may not affect ion adsorption on an iron oxide, as demonstrated at circumneutral and alkaline pH for Th(IV) adsorption on hematite.[128]

Several works have highlighted unique competitive OM adsorption on iron oxides or co-adsorption of ions between OM and iron oxides. For example, Diagboya et al. concluded that competition of OM with Cd(II) was greater than with either Cu(II) or Pb(II) on iron oxide-containing soil within 7 days of metal addition.[129] They demonstrated that OM determined initial metal ion distribution and that the iron oxide determined the redistribution of metal ions with increasing time. Mineral surface site competition has also been observed for a variety of systems, including less phosphate adsorption on goethite in the presence of soil OM.[130] Recently, Uwamariya et al. revealed that Suwannee River fulvic acid demonstrated little to no effect on the adsorption of chromate and arsenate onto iron oxide-coated sand and granular ferric oxide at pH 6 – 8.[131] The authors note that the controlling factor is likely the pH of the system, and thus recognition of the charged characteristics of the OM and the role of electrostatic interactions in competitive OM-ion adsorption is critical.

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In summary, there is strong evidence that the presence of OM perturbs the expected adsorption capacity of ions on iron oxides in heterogeneous systems. Systematic studies involving small organic molecules with similar functional groups (e.g., phenols, carboxylic acid) would provide a simplistic approach to monitoring adsorption processes on iron oxide surfaces. More studies are needed at a larger scale, however, to determine the dynamics of these heterogeneous systems for environmental predictions of transport. For example, certain ions may be mobilized in groundwater systems by adsorption on iron oxide colloids, followed perhaps by later desorption if OM concentration or identity fluctuates. Alternatively, OM may not affect ion adsorption but instead stabilize the iron oxide colloids, resulting in similarly localized ion concentration gradients. Future work on the interactions between ions, organic matter, and iron oxides are necessary to explain these unresolved questions, particularly studies that apply continuous-flow columns or similar designs to model groundwater gradients.

## 5. Reaction Processes

### *5.1. Mineral Transformation/Formation in the Presence of OM*

Iron oxide nanoparticles are capable of phase transformation in the environment. Ferrihydrite, a poorly crystalline iron(oxy)hydroxide with an elusive chemical formula and structure,[132-134] is often the first iron oxide formed in natural systems. Ferrihydrite readily transforms into other, more stable, iron(oxy)hydroxides, such as goethite and hematite,[135] and its transformation to other iron oxides (e.g. goethite, lepidocrocite, and magnetite) is catalyzed by Fe(II) ions.[105, 136-147] Previous work has demonstrated that the rates and products of phase transformation are dependent on surface chemistry including the amount of Fe(II) available and the presence of competing surface adsorbing ions.[148, 149] Thus, it seems highly probable that OM

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could impact the products and rates of iron oxide phase transformations. Few reports, however, describe iron oxide phase transformations in the presence of OM.

One such example reported that in the presence of Elliot Soil humic acid, Fe(II)-catalyzed ferrihydrite transformed to primarily lepiocrocite, whereas magnetite and goethite also formed over the same reaction time when the humic acid was absent.[147] Furthermore, mineral transformations in the presence of Elliot Soil humic acid catalyzed by *Shewanella putrefaciens* (Strain CN32) yielded more diverse phase compositions, including unreacted ferrihydrite (major product), goethite, magnetite, and green rust (with increasing green rust as carbon to iron ratios increased).[150] High concentrations of Suwannee River fulvic acid (150 mg/L) completely inhibited ferrihydrite transformation, presumably due to slower rates of exchange between the mineral Fe(III) and aqueous Fe(II), while complete transformation to lepidocrocite and goethite was observed at lower concentrations (25 mg/L) at constant ferrihydrite concentration (2.5 mM Fe(III)).[151] Mineral transformations, as well as the processes described in the next sections, are also dependent on iron oxide concentration, which makes direct comparisons between experiments challenging.

Lepidocrocite ($\gamma$-FeOOH), like ferrihydrite, undergoes phase transformation to other, more stable, iron oxide phases.[152] The kinetics and products of transformation depend strongly on the aqueous conditions.[151] Interestingly, the bioreduction products of lepidocrocite by *Shewanella putrefaciens* (Strain CN32) were dependent on the humic substance present in solution.[153] Magnetite was the dominant bioreduction product observed in experiments performed with the addition of Pony Lake fulvic acid and green rust was observed in the presence of Elliott Soil humic acid, Leonardite humic acid, Suwannee River fulvic acid, and Suwannee River humic acid. The physiochemical properties of Pony Lake fulvic acid are

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significantly different (lower aromaticity and average molecular weight) than the other four humic substance standards. These results suggest that OM character affects contaminant reactivity indirectly by perturbing iron oxide mineral formation and/or transformation, signifying major implications for the reactivity of iron oxide nanoparticles environmental systems.

Studies have also examined the relative properties and reactivity of iron oxides that were either coprecipitated in the presence of OM verses heterogeneous mixtures, i.e., iron oxide suspensions subject to OM adsorption after precipitation. For example, Mikutta et al. demonstrated that coprecipitation of iron oxides and OM resulted in larger particles and smaller aggregate sizes as compared to iron oxides prepared similarly except in the absence of OM and then later introduced to the same OM.[154] Iron oxide minerals precipitated in different OM environments, therefore, may exhibit drastically different transport behavior and surface reactions, but this needs to be confirmed experimentally.

### *5.2. Effects of OM on Contaminant Transformation*

Generally speaking, the colloidal stability of nanoparticles in the aqueous medium will dramatically affect the efficiency by which contaminant species adsorb or transform via reactions at the solid-liquid interface.[155] Sorbed OM could be exploited for its impact on aggregation and colloidal stability of iron oxide nanoparticles as well as its chemical behavior towards other dissolved species. Liu et al. demonstrated that a surface coating of humic acid improved the stability of magnetite nanoparticles in typical groundwater conditions, and these complexes could remove Hg(II), Pb(II), Cd(II), and Cu(II) from water.[156] Chekli et al. further argued that the coating of OM onto iron oxide nanoparticles, inducing an aggregate stabilization effect and increased mobility, is a “green” alternative to the use of other synthetic surfactants or engineered systems.[17]

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Few reports detail the effects of OM on hydrolysis of organic contaminants by iron oxides. Feitosa-Felizzola et al. observed that the presence of 10 mg/L Aldrich humic acid reduced the hydrolysis rate of two antibacterial agents (clarithromycin and roxithromycin) by approximately an order of magnitude in the presence of ferrihydrite.[157] The authors hypothesized that competitive adsorption between the humic acid and antibacterial agents resulted in the slower rates of hydrolysis. Results like these suggest that mineral reactivity would be reduced in natural environments as compared to the simple case of iron oxides suspended in aqueous solutions in the laboratory.

Iron oxide nanoparticles readily participate in the oxidation or reduction of organic compounds in environmentally-relevant systems.[2-4] Oxidized contaminants are reduced by surface-adsorbed Fe(II), which results in concurrent oxidative mineral growth, and reduced contaminants oxidized by mineral-bound Fe(III), which results in concurrent mineral dissolution. Changes in iron oxidation state (e.g. Fe(II) → Fe(III), or vice versa) occurs through both abiotic and biotic processes and can be facilitated by OM and/or the particle surface.[158-162] In general, the presence of OM inhibits the reduction of environmental contaminants (and, thus, oxidative mineral growth, Figure 3). Pentachloronitrobenzene reduction slowed in the presence of Pony Lake and Suwannee River isolates and Fe(II)-iron colloid complexes in comparison to conditions without OM.[163] Furthermore, rates of reduction depend strongly on the iron oxide mineral to which Fe(II) is bound. For example, the rate of nitrobenzene reduction by Fe(II) in the presence of humic acid was slowest in reactors containing magnetite as compared to goethite and hematite, which yielded the fastest rates.[164] Further studies with nitrobenzenes and goethite nanoparticles suggest that inhibition is directly related to the concentration of OM. Increased Suwannee River humic acid concentrations resulted in lower aqueous Fe(II) concentrations and

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slower reduction kinetics of *p*-cyanonitrobenzene.[165] The authors hypothesized that the humic acid prevented Fe(II) adsorption onto the mineral surface and/or oxidized or complexed with surface-bound Fe(II) and/or blocked the nitroaromatic compound from approaching surface-bound Fe(II).[164, 165] Recent work suggests that OM physiochemical properties, in addition to concentration, play key roles in the inhibition of contaminant reduction.[98] The authors determined that the reactivity of goethite nanoparticles was sensitive to eight quantifiable humic substance characteristics; increased OM molecular weight, carbon, nitrogen, and aromatic content and decreased OM carboxyl concentration, oxygen, aliphatic, and heteroaliphatic content yielded faster model contaminant degradation rate constants.

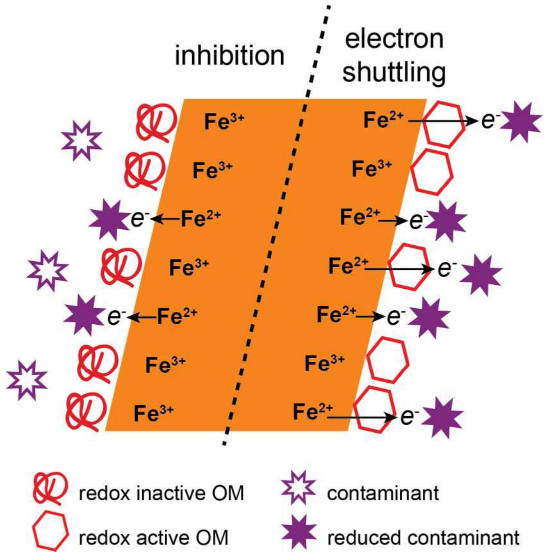

**Figure 3**: Model iron oxide nanoparticle with adsorbed OM that either inhibit (left) or enhance via electron shuttling (right) the transformation of contaminant.

Reductive dissolution of iron oxides is oftentimes driven or influenced by the presence of OM (Figure 3). Some functional groups present in OM, such carboxylic acids, phenols, or hydroxyl species, drive mineral dissolution through electron shuttling.[166-169] This is particularly important in water with little to no dissolved sulfide, which limits the favorable reduction pathway of Fe(III) by $H_2S$.[170, 171] The reactive character of the OM, or the capacity as an

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electron shuttle, therefore directly affects the rate of OM-driven reductive dissolution. On the other hand, OM also influences reductive dissolution through surface interactions with the iron oxide mineral. The capability to competitively adsorb on iron oxides and promote aggregation or disaggregation serves as an inhibitor or catalyst for these types of reactions. Eusterhues et al. found that the abiotic reduction rate of ferrihydrite decreased with increasing amounts of humic acids, concluding that surface passivation by the OM leads to slower rates of mineral dissolution.[172] The dynamic nature of OM (i.e., its variability in location and time), however, means that there remains a narrow understanding of the multiple mechanisms by which OM affects iron mineral dissolution in complex environmental systems.

Indirect degradation of organic contaminants by iron oxide nanoparticles has also been observed. Hydroxyl radicals formed through a photo-induced Fenton reaction enhance the photocatalyst ability of iron oxide nanoparticles, and this process could be exploited as a viable remediation technology.[173] Common hydroxyl radical sources include $H_2O_2$[174] and oxalic acid,[175-182] with successful contaminant degradation observed with goethite,[174, 178] hematite,[175-178, 180, 182] maghemite,[180-182] and lepidocrocite.[179] Rates of contaminant degradation may increase in the presence of OM due to the formation of hydroxyl radicals by photo-irradiation of the OM.[183] Other research groups have reported both no effect[184] or a reduction[185, 186] in contaminant phototransformation by iron oxides in the presence of fulvic and humic acid from Suwannee River. The mechanism of how OM could inhibit indirect degradation is not well understood (whether the dominant mechanism is binding to the contaminant or separation of hydroxyl radical and contaminant microenvironments, for example) and is an area of needed research.

## 6. Future Research Directions

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This vast body of literature, along with the multitude of studies focused on different minerals and nanoparticles, highlights the importance of incorporating natural OM into laboratory-simulated environmental studies. Iron oxides are some of the most commonly found minerals in the environment, and these minerals commonly occur as nanoparticles. There remain large gaps in our knowledge of iron oxide-OM interactions. Limited work on the formation and transformation of iron oxides in the presence of well characterized OM and knowledge gaps in iron oxide reactivity leave many unanswered questions that must be addressed to bridge between laboratory and field studies. Past work has demonstrated that the presence of OM affects mineral transformations, although the complexity of OM present, such as types and concentrations of OM, has not yet been fully examined.

On the other hand, recent work has clearly demonstrated that OM strongly impacts iron oxide reactivity towards ions, contaminants, and other organic molecules. The focus has shifted now to unveil the detailed roles OM plays during reactions involving iron oxide mineral surfaces. This includes detailed characterization of iron oxide–ion–OM complex formation, the dynamics of these complexes in environmental waters, and the dynamics of iron oxide surface chemistry in the presence of OM. The detailed and quantitative characterization of how aggregation state, including the mechanism and kinetics of aggregation and its reversibility, evolves in the presence of OM is essential to elucidating how OM influences these reactive systems. Fractal analysis and evolving aggregation studies from state-of-the-art characterization techniques like cryogenic microscopy and nanoparticle tracking will assist in connecting aggregation and reactivity to field studies.

OM is astoundingly heterogeneous, and its properties vary widely from location to location as well as a function of time. Thus, detailed characterization of how OM transforms and

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fractionates between the surface bound and dissolved states should have high priority. Identifying which fractions of OM adsorb onto an iron oxide and which remain in the aqueous solution as well as quantifying the dynamics of structure and conformation of OM during reaction will provide clues about how OM impacts reactivity as well as the fate of OM in the presence of iron oxides. The conditions in which redox transformations of OM are favorable and how that may alter the role of OM in contaminant fate and transport should be highlighted. Incorporation of techniques such as excitation-emission matrix fluorescence spectroscopy, attenuated total reflectance-FTIR, atomic force microscopy,[187] and the labeling of OM with electron dense substances (to assist with characterization by microscopy) are some future directions to exploring how OM directly and indirectly affects iron oxide colloidal stability and chemical reactivity. Excitation-emission matrix fluorescence spectroscopy can reveal fluorescence differences between different fractions of OM, such as adsorbed and aqueous portions, much like the study by Wu et al. where EEMs was used in tandem with high pressure liquid chromatography.[188] attenuated total reflectance -FTIR could similarly explore fractionation and properties of OM adsorbed onto iron oxides.[189] These analyses, in combination with results tracking rates of uptake or reaction, will provide insight into the mechanisms by which iron oxide–OM surface interactions influence the reactivity of iron oxides in environmental systems.

Despite the need for further exploration of iron oxide–OM interactions, in addition to other minerals in general, it should be noted the impressive amount of contextual literature available today. These studies have provided a basis to explain environmental processes in the field and could contribute to the development of viable solutions to global water issues.

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