

Reductive Dissolution of Iron Oxyhydroxides by Different Fractions of Natural Organic Matter

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Abstract

Because of the polydispersity of natural organic matter (NOM), different components or fractions of NOM contain varying structural and functional properties and were hypothesized to play different roles in the adsorption, reduction, and dissolution of ferric iron oxyhydroxides. Two fractions of an aquatic NOM and a soil humic acid (HA) were obtained and studied for their adsorption and effectiveness in reductive dissolution of an amorphous ferrihydrite and a well-crystallized hematite sample. Results indicate that all three NOM fractions were strongly sorbed by iron oxyhydroxides, particularly the amorphous ferrihydrite at a low pH (~4). Different NOM fractions were able to reduce ferric iron and, in particular, the polyphenolic-rich NOM fraction (NOM-PP) was among the most reactive in reducing iron oxides. At pH about 4, we observed ~4 times higher amount of dissolved ferrous iron in the presence of the NOM-PP than in the presence of soil HA in solution. Under the same experimental conditions, a higher amount of ferrous iron was observed in the amorphous ferrihydrite system than in the hematite system by all three NOM fractions. In addition, the reductive dissolution of iron oxyhydroxides appeared to be both pH and time dependent and is correlated to the chemical and functional properties of these NOM fractions. Results of this study demonstrate the electron donating capabilities of different NOM components, which may be potentially utilized for contaminant metal reduction and immobilization in soil.

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Introduction

Natural organic matter (NOM) or humic substances are widely distributed in soil and aquatic environment and known to play a significant role in the complexation and redox reactions with many environmental contaminants (Lovley, 1995; Lovley and Phillips, 1986; Deiana et al., 1995; Gu et al., 1994, 1995, 1996; Banwart, 1999). In particular, NOM has recently been demonstrated to mediate electron transfer reactions by dissimilatory microorganisms for metal reduction (Lovley et al., 1996). For example, numerous studies have been conducted on the reduction of iron oxyhydroxides either directly by NOM or indirectly (NOM as a mediator) by microorganisms although few studies have paid particular attention to the adsorption and reductive capabilities of NOM or NOM subcomponents. Additionally, because of the polydispersity of NOM, little is known about the fractional adsorption and thus the reductive dissolution of ferric iron or iron oxides by different NOM fractions. The objectives of this study were therefore to investigate the adsorption and reductive dissolution of iron oxyhydroxides by two fractions of an aquatic NOM and a reference soil humic acid as a function of pH, reaction time, and organic carbon concentrations.

Materials and Methods

The iron oxide powder sample was obtained from J.T. Baker, Inc. (100.3% assay) without further purification; it consists of primarily hematite with an average particle size of ~200 nm on the basis of previous studies (Gu et al., 1994). The amorphous ferrihydrite was synthesized by forced hydrolysis of 0.05M ferric nitrate with 2M KOH solutions. The ferrihydrite sample was then purified by repeated wash with deionized water before use.

Two fractions of an aquatic NOM (NOM-PP, NOM-CH) obtained from Georgetown, South Carolina (Gu et al., 1994, 1995) and a soil humic acid (HA) were used for the present experiment. Previous studies have indicated that the NOM-PP fraction contains a relatively high amount of the polyphenolic-rich organic components whereas the NOM-CH fraction consists of primarily low-molecular weight carbohydrate materials (Chen et al., 2000). For comparison, a soil humic acid was obtained from the International Humic Substance Society (IHSS) and studied in parallel for its adsorption and reductive dissolution of iron oxyhydroxides.

The time-dependent adsorption of NOM fractions and the reductive dissolution of iron oxides were performed as follows. First, stock solutions of the Soil HA, NOM-PP, and NOM-CH fractions were prepared with 0.05M NaCl as supporting electrolyte. While stirring, stock iron oxide suspensions were added, and pH was adjusted at either 4 or 7. The final solid concentration was 2 g/L, and NOM concentration was either 10 or 60 mg C/L. The NOM-iron oxide suspensions were then divided and transferred into 40-mL polyethylene centrifuge tubes (25 mL); they were kept anoxic by purging with ultra-pure N₂ gas for ~20 min, which resulted in a dissolved oxygen content of less than 2 µg/L in solution. The sample suspensions were shaken end-by-end for ~3 weeks at room temperature and, at a given time interval, duplicate samples were centrifuged at 13000 rpm for 30 min. The clear supernatant solution after centrifugation was analyzed for UV/Vis absorbance, ferrous ion, and total organic carbon (TOC) concentrations.

The UV/Vis absorbance spectra of NOM fractions after reactions with iron oxyhydroxides were collected with a Hewlett Packard 8453 spectrophotometer. The TOC concentrations were determined on a Shimadzu Total Organic Carbon 5000 Analyzer equipped with an autosampler. The detection limit was ~10 µg C/L. Ferrous ions (Fe²⁺) were determined by the colorimetric method

using ferrozine reagent (Fukushima and Tatsumi, 1999). Briefly, a 5-mL aliquot of the sample solution was placed in a test tube and mixed with 100 μL of H_2SO_4 (3.6M), 400 μL of ferrozine (4.9 mM), and 165 μL of ammonium acetate buffer. After color development, the Fe^{2+} concentration in each sample was analyzed by the measurement of UV/Vis absorbance at 562 nm.

Results and Discussion

All three NOM fractions show strong adsorption onto iron oxyhydroxide surfaces, particularly the soil HA and NOM-PP fractions on ferrihydrite at pH ~4 (Figure 1). Greater than 95% of the added soil HA and NOM-PP were adsorbed by ferrihydrite at pH ~4 and at an initial NOM concentration of as high as 60 mg C/L. On the other hand, sorption of these NOM fractions was about 2–5 times lower on hematite than on ferrihydrite (data not shown). These observations are anticipated because of its lower surface areas and active sorption sites on the well-crystallized hematite than on amorphous ferrihydrite. On a C weight basis, more soil HA was adsorbed on both hematite and ferrihydrite than that of the NOM-PP or NOM-CH fractions. Adsorption of these NOM fractions was also found to be pH dependent as reported previously by other investigators (Gu et al., 1994; 1995; Davis, 1982). Such pH dependent sorption of NOM by iron oxides has been attributed

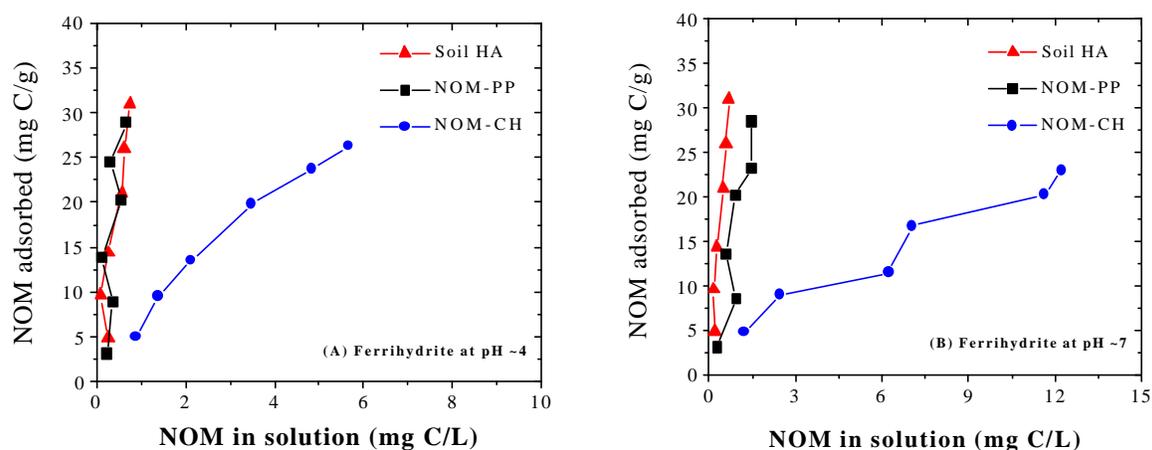


Figure 1. Adsorption isotherms of the soil HA, NOM-PP, and NOM-CH fractions on ferrihydrite at pH 4 (A) and 7 (B) in a background electrolyte of 0.05M NaCl.

to the surface complexation between negatively charged NOM compounds and positively charged iron oxide surfaces.

Figure 2 shows the ferrous ion concentrations as a result of reductive dissolution of hematite and ferrihydrite by the soil HA, NOM-PP, and NOM-CH fractions at pH ~4. Results indicated a time-dependent reduction and dissolution (consequently the release of ferrous ions) of hematite and ferrihydrite. However, ferrous ion concentrations were more than an order of magnitude higher in the ferrihydrite than in the hematite suspensions. These observations are attributed to the amorphous nature of ferrihydrite so that more surface areas and reaction sites are subjected to attack by the NOM macromolecules. The reduction rates were the fastest initially (within the first 2 days) although the reduction did not appear to reach an equilibrium after ~3 weeks. In addition, the reductive dissolution of both hematite and ferrihydrite was found to depend on pH and the initial concentration of NOM in the system. The amounts of ferrous ion released were directly proportional to the TOC concentration of NOM added (data not shown). At an initial TOC concentration of 10 mg C/L, the amounts Fe^{2+} released in both hematite and ferrihydrite systems were about 4–6 times less than that at an initial TOC concentration of 60 mg C/L. These observations may be anticipated because the reducing capacity of NOM or NOM fractions should be directly proportional to the concentrations of NOM.

Among the three NOM fractions, the NOM-PP fraction was found to be the most reactive with respect to the reductive dissolution of both hematite and ferrihydrite (Figure 2). On the other hand, the soil HA was the least effective in reducing iron oxyhydroxides despite the fact that the soil HA was adsorbed more than the NOM-PP and NOM-CH fractions by both ferrihydrite and hematite

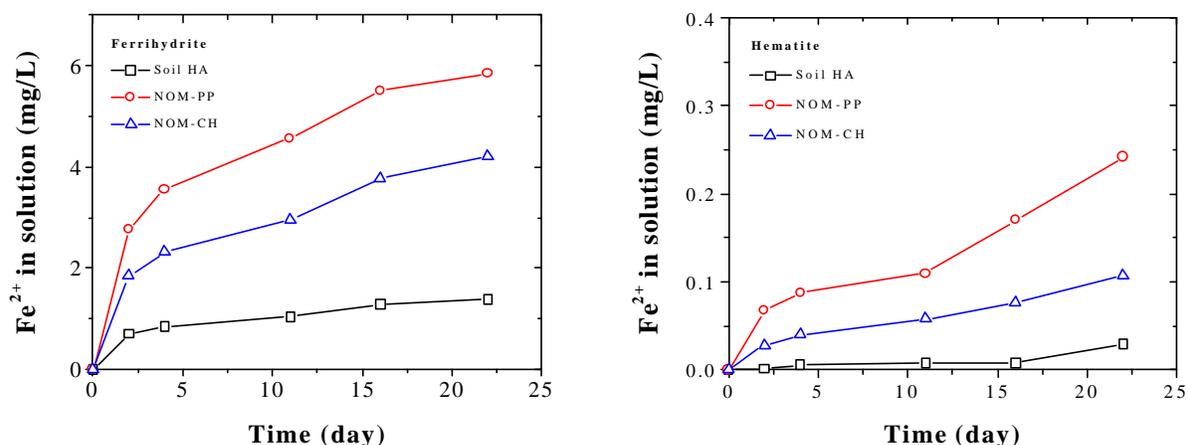


Figure 2. Effect of NOM fractions on the reductive dissolution rates of ferrihydrite and hematite at pH ~4 and a background electrolyte of 0.05M NaCl (the initial NOM concentration = 60 mg C/L).

(Figure 1) and exhibited the highest aromatic carbon content by the NMR and FTIR spectroscopic analyses (Chen et al., 2000). These observations may be partially attributed to the high molecular size and its condensed polyaromatic structure of the soil HA which make it less reactive in dissolving and reducing iron oxyhydroxides. It therefore appears that the reducing power of NOM fractions is not directly proportional to the aromatic carbon contents but to the contents of reactive NOM components or functional groups within NOM (such as the NOM-PP fraction). Nevertheless, results of this study demonstrate that NOM is redox reactive and capable of directly reducing Fe(III)-oxyhydroxides to Fe(II) species (without addition of microorganisms) although the electron donating capabilities vary greatly among different NOM fractions. Further studies are in progress to evaluate the roles of microorganisms and NOM fractions (as mediators) in reducing iron oxyhydroxides or some contaminant metals or radionuclides.

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