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Organic matter interactions with natural manganese oxide and synthetic birnessite

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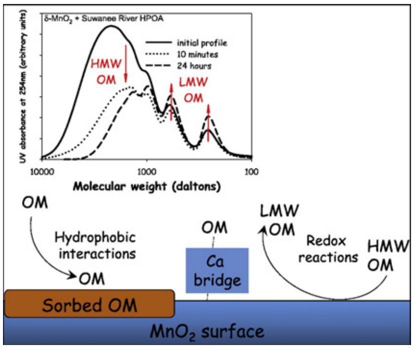
HIGHLIGHTS

- NOM adsorption on both manganese oxides increased with decreasing pH (pH 7 to 5).
- Calcium enhanced the rate of NOM adsorption.
- High molecular weight molecules enriched in aromatic moieties are preferentially adsorbed.
- Hydrophobic interactions may explain the adsorption of organic matter on manganese oxides.
- Low MW structures are produced during NOM oxidation by birnessite.

GRAPHICAL ABSTRACT



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ABSTRACT

Redox reactions of inorganic and organic contaminants on manganese oxides have been widely studied. However, these reactions are strongly affected by the presence of natural organic matter (NOM) at the surface of the manganese oxide. Interestingly, the mechanism behind NOM adsorption onto manganese oxides remains unclear. Therefore, in this study, the adsorption kinetics and equilibrium of different NOM isolates to synthetic manganese oxide (birnessite) and natural manganese oxide (Mn sand) were investigated. Natural manganese oxide is composed of both amorphous and well-crystallised Mn phases (i.e., lithiophorite, birnessite, and cryptomelane). NOM adsorption on both manganese oxides increased with decreasing pH (from pH 7 to 5), in agreement with surface complexation and ligand exchange mechanisms. The presence of calcium enhanced the rate of NOM adsorption by decreasing the electrostatic repulsion between NOM and Mn sand. Also, the adsorption was limited by the diffusion of NOM macromolecules through the Mn sand pores. At equilibrium, a preferential adsorption of high molecular weight molecules enriched in aromatic moieties was observed for both the synthetic and natural manganese oxide. Hydrophobic interactions may explain the adsorption of organic matter on manganese oxides. The formation of low molecular weight UV absorbing molecules was detected with the synthetic birnessite, suggesting oxidation and reduction processes occurring during NOM adsorption. This study provides a deep insight for both environmental and engineered systems to better understand the impact of NOM adsorption on the biogeochemical cycle of manganese.

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1. Introduction

The adsorption of NOM on manganese oxide (MnO_2) is an important process that significantly influences the fate and transport of inorganic and organic pollutants in aquatic systems. Manganese oxides are involved in a wide range of redox processes because of their high redox potential ($E^o_H = 1.23$ V) (Stumm and Morgan, 1996). The reductive dissolution of MnO_2 by inorganic (Allard et al., 2009; Fox et al., 2009; Landrot et al., 2010; Scott and Morgan, 1995, 1996) or organic compounds (Huguet et al., 2013; Stone, 1987a, 1987b; Stone and Morgan, 1984; Stone and Ulrich, 1989; Ulrich and Stone, 1989; Wang and Stone, 2006) has been extensively studied since the 1980's. Two steps are involved in these surface redox processes: 1) surface complex formation (adsorption), and 2) electron transfer (Morgan, 1964; Stone and Morgan, 1984). Birnessite (δ-MnO_2) with a pH of zero point charge varying from 1.4 to 4.5 (Stone and Ulrich, 1989) is negatively charged in the pH range of natural waters. Although the adsorption of NOM onto metal oxides is mostly controlled by electrostatic attraction, within the aquatic environment, NOM (i.e., also negatively charged at environmentally relevant pH) can be adsorbed onto MnO_2 (Bernard et al., 1997; Tipping and Heaton, 1983), competes with other inorganic/organic compounds for surface reactive sites, and decreases the oxidation rate of contaminants (Chen et al., 2010; Feitosa-Felizzola et al., 2009; Klausen et al., 1997; Zhang and Huang, 2003). NOM adsorption can alter the chemical surface properties of the metal oxide and thus affect the redox processes. Therefore, oxidation and mobility of inorganic and organic pollutants in the aquatic environment, as well as mineral dissolution, may be drastically impacted by the physicochemical properties of the NOM and NOM-mineral interactions.

In addition to affecting the redox behavior of contaminants via competition for adsorption sites, NOM can also be fractionated and oxidized by manganese oxides (Chorover and Amistadi, 2001; Sunda and Kieber, 1994). This adds to the complexity of the system because NOM reactivity evolves upon reaction with manganese oxide. Adsorption and oxidation of NOM and inorganic components of the water matrix can simultaneously occur and form undesirable transformation products. A previous study demonstrated that the treatment of iodide-containing water by natural manganese oxides (i.e., used as catalytic material) leads to the formation of iodoform (and other unidentified adsorbable iodinated organic molecules) (Gallard et al., 2009) which is toxic (Richardson et al., 2008) and responsible of medicinal taste (Cancho et al., 2001). Furthermore, Allard and Gallard (2013) and Allard et al. (2010) showed that MnO_2 can also induce the formation of methyl iodide, potentially resulting in damage to the ozone layer. In both studies, the interactions between NOM and synthetic or natural manganese oxides were found to produce undesired iodinated organic compounds.

Although a significant number of studies have been conducted on iron and aluminum oxides (Gu et al., 1996; Gu et al., 1995; McKnight et al., 1992; Ochs et al., 1994), very few investigations have focused on NOM adsorption onto manganese oxide. Tipping and Heaton (1983) showed that the adsorption of humic substances decreases with increasing pH (pH 4 to 11) and decreasing point of zero charge due to electrostatic repulsion. Furthermore, cationic species like Ca^{2+} or Mg^{2+} enhance the adsorption capacity of manganese oxide because they reverse the surface charge of manganese oxide and thus facilitate NOM adsorption through its dissociated carboxyl groups (Tipping and Heaton, 1983). Bernard et al. (1997) showed that negatively charged organic compounds were poorly adsorbed onto manganese oxide (pyrolusite β-MnO_2), probably due to electrostatic repulsion. In a more recent study, Johnson et al. (2015) showed that birnessite can trap and stabilize organic carbon within the bulk mineral through bridging and/or bidentate bonds between carboxylate groups of NOM molecules and birnessite mineral surface sites.

Nevertheless, the mechanisms behind NOM adsorption/oxidation affecting the reactivity of both metal oxides and contaminants remain unclear (Polubesova and Chefetz, 2014). This phenomenon represents an important research gap that needs to be addressed for better understanding its further impact on contaminants transformation and, more generally, their environmental behavior. Therefore, this current study investigates NOM adsorption on a natural manganese oxide used in drinking water treatment. NOM adsorption on synthetic birnessite was also studied for comparison purposes and because birnessite is one of the most common Mn oxide in the environment. The first part of the manuscript focused on the characterization of the manganese sand. The second part investigates the adsorption of different NOM fractions using DOC measurements and high-pressure size exclusion chromatography coupled with UV absorbance (HPSEC-UV). The objectives of this investigation were to better understand the mechanisms of adsorption, fractionation, and oxidation of NOM by MnO_2 under various experimental conditions (e.g., pH, MnO_2 concentration, NOM structural characteristics, and the presence of inorganic cations).

2. Material and methods

2.1. Characterization of mineral phases

A commercial natural manganese oxide sand approved for drinking water treatment was used in this investigation. The 300–700 μm size fraction was selected for this study. This manganese oxide sand (Mn sand) was rinsed with ultra-pure water in a sieve to remove fine residues before experiments. Elemental composition was determined by energy dispersive X-ray spectrometry (Quantax, Bruker). The isoelectric point (pH_{iep}) was determined by electrophoretic mobility measurement (Malvern Zetasizer) on a sample fraction < 1 μm.

The organic carbon (OC) associated with the Mn sand was quantified using a TOC-VCSH analyzer (Shimadzu, Japan) equipped with a Particulate Organic Carbon (POC) module. NaOH treatment was performed to extract the organic matter associated with the Mn sand. Two liters of 0.2 M NaOH solution were pumped through a 300 mL low-pressure chromatography column filled with Mn sand at a 3 V/V/h flow rate. After a 0.45 μm filtration procedure, the NaOH solution was then acidified to pH 2.0 with HCl. The resulting solution contained 8.8 mg L^{-1} DOC that was further extracted within XAD-8 and XAD-4 resins used in series (Leenheer and Croue, 2003). The recovered XAD-8 and XAD-4 resin fractions were freeze-dried and characterized by pyrolysis gas chromatography/mass spectrometry (pyrolysis - GC/MS) according to the protocol described by Christy et al. (1999). The manganese oxide sample resulting after NaOH treatment will be termed as NaOH-treated sand for the rest of the study. In addition, an ultrasonication procedure was conducted on the Mn sand. After ultrasonication, the larger particles were left to settle, and the supernatant was filtered through a 0.45 μm membrane to collect Mn micron-sized particles dispersed by the sonication treatment. The Mn sand after the sonication procedure was termed as sonicated sand.

Time-Resolved Dynamic Light Scattering (TR-DLS) was used as a sensitive tool to provide additional evidence of the presence of NOM on the Mn sand, and of the lower NOM content on the sonicated sand and the NaOH-treated sand. These three Mn samples were ground using a BTRM-1A equipment (Rocklabs, New Zealand), dispersed in ultra-pure water (Millipore), and filtered through a 0.45 μm membrane (i.e., stock suspension preparation). A ZS ZEN3600 Zetasizer (Dispersion Technology Software v5.10, 2008, Malvern, UK) and low volume plastic disposable cuvettes (ZEN112, Malvern, UK) were used to measure the initial hydrodynamic diameter (D_{ho}) of each Mn sample before every experiment. The aggregation kinetic experiments of the Mn samples in electrolyte solution were conducted following the procedures previously described (Gutierrez et al., 2015). A Mn sample (i.e., Mn sand or sonicated sand or NaOH-treated sand) was added to a 10 mM $NaClO_4$ (pH 5) solution to a final concentration of 1 mg L^{-1}. After a gentle shake, the cuvette was immediately placed in the Zetasizer for measurement. The measurements extended over 1 h to allow an increase in the

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