



# High molecular weight components of natural organic matter preferentially adsorb onto nanoscale zero valent iron and magnetite

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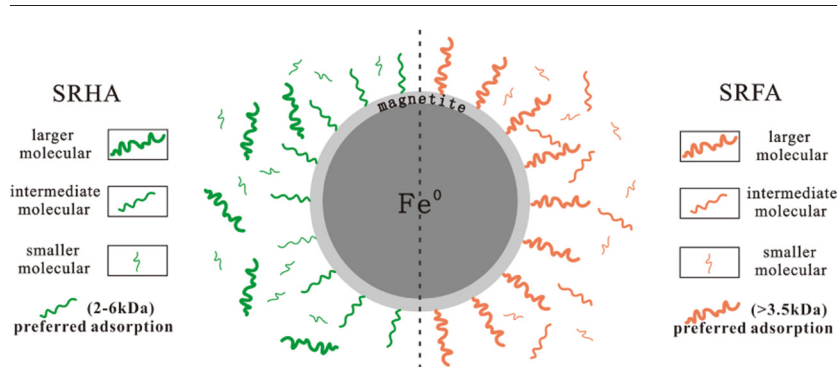
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## HIGHLIGHTS

- Adsorption capacity of nano-Fe<sup>0</sup> is 3 times more than nano-Fe<sub>3</sub>O<sub>4</sub> for SRHA and SRFA.
- Similar amounts of SRHA and SRFA were adsorbed onto nano-Fe<sup>0</sup>.
- Nano-Fe<sup>0</sup> preferentially adsorbed intermediate molecular weight fractions of SRHA.
- Nano-Fe<sup>0</sup> preferentially adsorbed larger molecular weight fractions of SRFA.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Nanoscale zero valent iron particles (nano-Fe<sup>0</sup>) are attractive for in-situ groundwater remediation due to their high reactivity and ability to degrade many different classes of environmental contaminants. It is expected that adsorbed natural organic matter (NOM), which is heterogeneous and typically has a wide molecular weight (MW) distribution, will affect the reactivity and performance of nano-Fe<sup>0</sup> as a remediation agent. However, the interaction of NOM with nano-Fe<sup>0</sup> has not been well-studied. In this study, we used high performance size exclusion chromatography (HPSEC) to determine if there was preferential sorption of the high MW fraction of NOM onto nano-Fe<sup>0</sup> that have a Fe<sup>0</sup> core and a Fe-oxide shell (predominantly magnetite). Adsorption of two types of NOM, Suwannee River Humic Acid (SRHA) and Fulvic Acid (SRFA), to nano-Fe<sup>0</sup> was compared to magnetite of similar size (nano-Fe<sub>3</sub>O<sub>4</sub>) to also assess the effect of the Fe<sup>0</sup> core on adsorption of NOM. The results showed that the surface area normalized adsorbed mass (mg/m<sup>2</sup>) of both SRHA and SRFA onto nano-Fe<sup>0</sup> is almost three times than that of nano-Fe<sub>3</sub>O<sub>4</sub>. This is attributed to a greater number of reactive sites on nano-Fe<sup>0</sup> compared to nano-Fe<sub>3</sub>O<sub>4</sub>, and indicates that the surface properties of nano-Fe<sup>0</sup> are different that nano-Fe<sub>3</sub>O<sub>4</sub> despite the shell of magnetite on nano-Fe<sup>0</sup>. The sorption capacity of both SRHA and SRFA onto nano-Fe<sup>0</sup> were similar. However, the intermediate sized MW fractions (2–6 kDa) of SRHA were preferentially adsorbed onto the nano-Fe<sup>0</sup> surface, whereas the large MW fractions (>3.5 kDa) of SRFA were preferentially adsorbed. These results suggest that NOM interaction with nano-Fe<sup>0</sup> are a function of the MW distribution of the NOM in the system studied and indicate that the MW distributions of NOM should be taken into consideration when predicting the fate and performance of nano-Fe<sup>0</sup> in environmental remediation.

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## 1. Introduction

For the past fifteen years, nanoscale zero valent iron (hereafter referred to as nano-Fe<sup>0</sup>) has been promoted for its high reactivity with a

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large variety of environmental contaminants, including halogenated organic compounds (Liu et al., 2005; Lim et al., 2007), heavy metals (Kanel et al., 2006; Xu and Zhao, 2007), nitroaromatic compounds (Choe et al., 2001; Zhang et al., 2010), nitrates (Yang and Lee, 2005), pesticides (Thompson et al., 2010) and dyes (Moon et al., 2011). Nano-Fe<sup>0</sup> has an intrinsic core-shell structure, in which 'the thin and distorted oxide layer allows electron transfer from the metal core (1) directly through defects such as pits or pinholes, (2) indirectly via the oxide conduction band, impurities or localized band, and (3) from sorbed or structural Fe<sup>2+</sup>, thus sustaining the capacity of the particles for reduction of contaminants' (Li et al., 2006). Nano-Fe<sup>0</sup> can remediate a broad range of environmental contaminants and has the potential to be delivered in situ for remediation of contaminated groundwater, making it popular worldwide (Glazier et al., 2003).

When nano-Fe<sup>0</sup> is injected into the subsurface for remediation, it interacts with natural organic matter (NOM). NOM is ubiquitous and plays a central role in the biogeochemical cycling of the elements, and in the fate and reactivity of nanoparticles (NPs). NOM usually contains a skeleton of alkyl and aromatic units decorated with carboxylic acids, phenolics, hydroxyls, and quinone functional groups (Sparks, 2003). The effect of NOM on the mobility, toxicity, reactivity and fate of nano-Fe<sup>0</sup> has been discussed (Johnson et al., 2009; Chen et al., 2011; Dong and Lo, 2013). During the process of pollutant removal by nano-Fe<sup>0</sup>, NOM may compete with target pollutants for iron surface area and lower the removal efficiency (Chen et al., 2011). On the other hand, NOM may serve as an electron-transfer mediator in the chemical degradation of compounds. Both the inhibitory (Giasuddin et al., 2007; Niu et al., 2011) and stimulatory effects (Feng et al., 2008) of humic acid (HA) on nano-Fe<sup>0</sup> reactivity have been reported. Additionally, NOM has also been used as 'green' surface coating on the surface of NPs due to its abundance, low cost, and environmentally friendly characteristics. It is proposed that coating NPs with NOM could enhance NPs stability against aggregation through electrostatic repulsions (Illes and Tombacz, 2006; Hu et al., 2010). It has been found that magnetite NPs coated by NOM are considerably more stable and have higher removal efficiency for heavy metals (Liu et al., 2008) and organic dyes in wastewater (Peng et al., 2012; Zhang et al., 2013).

NOM and NPs primarily interact via adsorption of NOM onto the NP's surface. Numerous studies have investigated the adsorption of NOM by various Fe-oxides in soil such as goethite (Kang and Xing, 2008; Zhou et al., 2001), hematite (Hur and Schlautman, 2003; Vermeer and Koopal, 1998; Gu et al., 1995), showing that the Fe-oxide surfaces have particular affinities for specific structural and functional moieties of NOM. Although adsorption of NOM onto minerals and Fe-oxides has been investigated in detail, the adsorption of NOM to nano-Fe<sup>0</sup> has not been investigated widely. Giasuddin et al. (2007) reported a HA adsorption capacity of synthetic nano-Fe<sup>0</sup> of 2.5 mg/m<sup>2</sup> at pH 7, and demonstrated that the surface adsorption of HA prevented arsenic removal by nano-Fe<sup>0</sup>. Lee et al. (2009) found that a maximum of 0.8 mg/m<sup>2</sup> HA was adsorbed onto synthesized nano-Fe<sup>0</sup>, and showed that adsorbed HA inhibited TCE degradation. The adsorption affinity and capacity of nano-Fe<sup>0</sup> for NOM differs in different studies. Such differences might be a result of different types of NPs and hence surface properties, and different types of NOM or NOM molecular weight fractionations (Louie et al., 2013). For instance, MW fractionated NOM had different stabilizing effects toward gold (Louie et al., 2013), fullerene NPs (Shen et al., 2015), and silver NPs (Yin et al., 2015). The different types of NOM, e.g. HA and FA, affected gold NP aggregation (Louie et al., 2015) and goethite NP reactivity and aggregation (Vindedahl et al., 2016) differently. These studies suggest that the heterogeneity of NOM, which consists of heterogeneous components with a wide range of molecular weight (MW) from several hundred to 10's of thousands of Daltons, and contain different chemical moieties, may interact with and affect nano-Fe<sup>0</sup> reactivity differently. This may explain why different NOM types had different effects on the reactivity of nano-Fe<sup>0</sup> (Giasuddin et al., 2007; Lee et al., 2009).

Most core-shell nano-Fe<sup>0</sup> have a layer of surface oxide (predominantly magnetite when in water). It is therefore possible that NOM sorption will follow that observed for magnetite (Scott et al., 2010). However, it is also possible that the highly reducing underlying zero valent iron core may affect the sorption behavior, making it diverge from that expected for magnetite. The overall objectives of the study are to 1) determine if there are differences in sorption between nano-Fe<sup>0</sup> having a magnetite shell, and nano-magnetite, and 2) to determine if there is preferential sorption of different MW fractions of NOM onto these particles. To assess the role of the Fe<sup>0</sup> core on adsorption of NOM, the adsorption on NOM onto nano-Fe<sup>0</sup> was compared to nanoscale magnetite (hereafter referred to as nano-Fe<sub>3</sub>O<sub>4</sub>). The experiments used two model NOM isolates, Suwannee River Humic Acid (SRHA) and Fulvic Acid (SRFA) because they have different MW distributions. Both of them were mixed with aqueous dispersions of commercially available nano-Fe<sup>0</sup> and nano-Fe<sub>3</sub>O<sub>4</sub>. To better understand the interactions of specific MW components of NOM with nano-Fe<sup>0</sup>, high-performance size-exclusion chromatography (HPSEC) was used to assess the NOM molecular weight distribution before and after adsorption onto the two particle types.

## 2. Materials and methods

### 2.1. Materials

Nanoscale zero valent iron (nano-Fe<sup>0</sup>) was purchased from Toda Kogyo Corp. (Onoda, Japan). The Fe<sup>0</sup> content in nano-Fe<sup>0</sup> was 55 ± 2 wt%, as determined from acid digestion using the methods described by Liu et al. (2005). Magnetite nanoparticles (nano-Fe<sub>3</sub>O<sub>4</sub>) were obtained from Sigma Aldrich (≥97% trace metal basis, <50 nm particle size). Suwannee River Humic Acid and Fulvic Acid were purchased from the International Humic Substances Society (IHSS). Stock solutions were prepared at 1 g/L in DI water and dissolved overnight on an end-over-end rotator at room temperature and then filtered through a 0.45 μm syringe filter (polyethersulfone) and stored at -4 °C in the dark.

### 2.2. Methods

#### 2.2.1. Characterization of iron NPs

2.2.1.1. TEM. The nanoparticle sizes and TEM images of nanoparticles were obtained before and after adsorbing NOM with a Hitachi H-8100 transmission electron microscope (TEM) at 200 kV. Nanoparticle samples were prepared by allowing a drop of the nanoparticles suspended in ethanol to dry on 200-mesh holey carbon coated copper grids. The reported sizes were determined from counting particles in at least three different TEM images.

2.2.1.2. XRD. X-ray diffraction (XRD) patterns of nano-Fe<sup>0</sup> and nano-Fe<sub>3</sub>O<sub>4</sub> were collected on a Japan Rigaku D/Max 2500 (generator voltage of 40 kV; tube current of 30 mA) with a CuK<sub>α</sub> radiation source. Fe<sup>0</sup> and Fe-oxide phases were identified by matching diffraction peaks from 2θ angles of 10–90° with a step size of 0.02°.

2.2.1.3. XPS. X-ray photoelectron spectroscopy (XPS) was performed for nano-Fe<sup>0</sup> and nano-Fe<sub>3</sub>O<sub>4</sub> before and after adsorbing NOM using a Thermo Scientific Escalab 250 Xi instrument. The dried samples were irradiated using an Al K<sub>α</sub> source.

2.2.1.4. Specific surface area. The N<sub>2</sub>-BET specific surface area of the nanoparticles was measured (4-point isotherm) using an Autosorb-iQ2-MP BET-surface area analyzer (Quantachrome). All samples were degassed for 2 h at 300 °C prior to the BET measurement at 77 K.

2.2.1.5. Zeta potential. The Zeta potential of nano-Fe<sup>0</sup> and nano-Fe<sub>3</sub>O<sub>4</sub> was measured before and after adsorbing NOM using a Brookhaven

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