



## Characterization and surface reactivity of natural and synthetic magnetites

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### ABSTRACT

Magnetite is an Fe (II/III) oxide mineral that occurs naturally and potentially as small particles with significant surface reactivity, and although much work is reported on synthetic material, little work exists for natural samples. The goal of the present work was to carefully characterize four natural magnetite samples from an iron ore deposit and two synthetic commercial reference samples, and to compare their surface characteristics and reactivity with the aim of evaluating their geochemical behavior towards adsorption of environmentally relevant ions, as well as their potential for use as environmental remediation sorbents. The techniques used were wet chemistry, X-ray diffraction, Raman spectroscopy, magnetic measurements (hysteresis curves), dynamic light scattering, scanning electron microscopy, low and high resolution transmission electron microscopy, BET Nitrogen adsorption, and electrophoresis. In addition, their As(V) adsorption behavior was measured at pH 6, and was analyzed as related to the surface characteristics and particle aggregation behavior determined. The analyses revealed high magnetite purity in the natural samples, and specific surface areas (SSA) ranging from 1 to 8 m<sup>2</sup>/g. Small alumino-silicate impurities were found in natural magnetites, apparently occurring at the particle surfaces and thus significantly lowering their isoelectric points as compared to the pure synthetic materials. All samples are composed of aggregates of 39–52 nm magnetite particle units, but highly aggregated with very large size dispersions. The synthetic sample with the smallest particle size (30 nm in average – 39 m<sup>2</sup>/g) showed its entire surface area available for adsorption, despite its highly aggregated state observed, suggesting an open and highly dynamic aggregate framework. The other larger samples showed more complex aggregation behavior, which produced: (1) a widely variable As(V) adsorption behavior with no clear predictable pattern among samples; and (2) a large decrease of the As(V) adsorption maxima with increasing solids concentration imposed in the experimental set-up for any one particular sample. Therefore, we recommend high caution in using the BET-SSA and solids concentration parameters when performing experimental adsorption work with micro-sized magnetite, especially when extrapolating laboratory results to field geochemical or engineered conditions for evaluating contaminant adsorption.

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## 1. Introduction

Iron oxides are commonly found in soils and aquatic sediments as discrete particles or coatings on other minerals and interspersed with organic materials and clays, and their presence can significantly

influence the chemistry of surface waters, groundwater, sediments and soils through adsorption processes (Trivedi et al., 2003; Gilbert et al., 2009). Among these oxides, magnetite, an Fe(II,III)-containing inverse spinel, can be found concentrated in beach sands, in large mineral deposits (such as those in Russia, Canada, China, Chile, Sweden, Australia, U.S., Norway, Brazil, and Mexico) (Kennedy, 1990; Rivas et al., 2006, 2009), in weathered clays and soils, in atmospheric aerosols, and in marine and freshwater sediments. This mineral can efficiently adsorb aqueous cations and anions, including Co(II), Ni(II), Cs(I), Yb(III), U(VI), Pu(V), Np(V), selenate, selenite, chromate, carbonate, phosphate and arsenate (Peterson et al., 1996; Marmier et al., 1999; Kendelewicz et al., 2000; Nakata et al., 2000; Missana et al., 2003; Powell et al., 2004; He and Traina, 2005; Ohe

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et al., 2005; Martínez et al., 2006; Uheida et al., 2006; Daou et al., 2007; El Aamrani et al., 2007; Missana et al., 2009; Das et al., 2010; Iltou et al., 2010; Roonasi and Holmgren, 2010), some of which may subsequently reduce upon interacting with the Fe(II) on the magnetite surface [e.g., U(VI) and Cr(VI)]. This adsorption capacity may be valuable for natural and engineered remediation of soils and waters contaminated by these and other species, because the enriched magnetite particles can later be removed from the cleaned matrix through relatively simple magnetic methods.

Most previous characterization and adsorption work on magnetite has been performed on pure and homogeneous synthetic preparations of this mineral, and several different experimental procedures are offered to synthesize pure magnetite. However, little work has been reported for naturally-occurring materials rich in this mineral. The goal of the present work was to investigate the composition and reactivity of magnetite concentrates from a currently active iron ore in the West Coast of Mexico, which were previously shown to be composed of aggregated nanoparticles (Rivas et al., 2006, 2009). Magnetite, with its characteristic black-colored grains, is pervasive in an extensive area around this mine, and is an important component of the mineral fraction of soils and tourist beach sands of the zone (Rivas et al., 2006, 2009). The purity, composition, and particle morphology of the mine concentrates were determined, placing particular focus on their surface characteristics and reactivity. Ultimately, the aim of this type of work is to provide information of the potential geochemical role of magnetite in the retention and biogeochemical cycles of ionic species, in areas where it is a prevalent mineral.

In aqueous systems, magnetite nanoparticles behave like magnetic colloids, for which particle interactions are governed by both magnetodipole and van der Waals forces and may cause the formation of multiparticle aggregates in suspension (Buzmakov and Pshenichnikov, 1996). Additionally, factors such as magnetic field, pH and ionic strength can influence morphology and size of the aggregates (Buzmakov and Pshenichnikov, 1996; Gilbert et al., 2009). Because of these interactions, multiparticle aggregates of differing sizes may form, which in turn are expected to impact significantly the adsorption behavior shown by magnetite. Although the effect of magnetite particle size on its adsorption behavior and capacity has been previously studied in the nanometric range (Yean et al., 2005; Yavuz et al., 2006), the influence of the different modes of aggregation of magnetites with a wider particle size range (be it synthetic or natural) has not been investigated. In the present work the differences in adsorption behavior among samples were related to differences in aggregation, and a strong dependence of the adsorption maxima was observed on the solids concentration imposed. Our findings have important implications in the environmental geochemical behavior of this particular iron oxide mineral.

Arsenate oxyanions were chosen for this work because they have been shown to bind strongly to the magnetite surface forming inner sphere, bidentate binuclear corner-sharing surface complexes (Jönsson and Sherman, 2008; Wang et al., 2008; Morin et al., 2009). Therefore, arsenic adsorption on this mineral is expected to be an important process of arsenic removal from aqueous solution in natural and engineered environments. In the present study we investigated the influence of particle and aggregate sizes on the adsorption behavior of magnetite towards As(V), for samples with a range of SSA values from approximately 1 to 40 m<sup>2</sup>/g. In addition, the effect of impurities and of size heterogeneity was analyzed by comparing the behavior of synthetic and natural samples.

Natural and synthetic reference magnetite samples were carefully characterized for composition and structure, magnetic behavior, particle size and aggregation, and surface parameters (SSA, surface composition and isoelectric point), by using wet-chemical, X-ray diffraction (XRD), surface Raman, magnetic cycle measurements, dynamic light scattering analysis (DLS), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), optical microscopy of transmitted and reflected light, BET-nitrogen adsorption, and

electrophoretic potential techniques. As(V) adsorption behavior was investigated at pH 6, and related to the magnetite surface characteristics and particle aggregation behavior investigated. From the results obtained, the geochemical role of natural magnetite in oxyanion retention is discussed, as well as its potential use as an adsorbent material for environmental remediation efforts.

## 2. Materials and methods

### 2.1. Reagents

All chemicals were reagent grade and were used without additional purification. Arsenic stock solutions were prepared using a High Purity Standards solution of 1000 mg/L of As(V) in 2% HNO<sub>3</sub> and sodium arsenate dibasic heptahydrate ≥98%, and iron stock solutions were prepared using a Accu Trace™ Reference Standard ICP multi-element standards solution with 1000 mg/L of Fe in 2% HNO<sub>3</sub>. NaOH and HNO<sub>3</sub> used to adjust pH for all experiments were purchased from J.T. Baker, NaNO<sub>3</sub> used to adjust ionic strength was purchased from Sigma Aldrich. Water used to prepare all solutions was obtained from an Ultrapure Water System (NANO pure) with 17.2 Ω cm.

### 2.2. Materials

The natural magnetite samples investigated were collected from the Peña Colorada iron ore deposit located in the Colima State, in Mexico. A detailed study on the magnetic and microscopic properties of this iron-ore deposit has been reported by Rivas et al. (2006, 2009) who found the presence of nanoparticulate magnetite. Five highly pure magnetite minerals from four different mining fronts were used, four of which were ground by a magnetic concentration procedure at the mine for 45 min (996, 910, 963 and 948), and one of them additionally for 100 h (948-fine). After grinding, the magnetite in each sample was separated using low-intensity magnetism with a magnetic permanent core, obtaining concentrates of micrometer-sized magnetite aggregates. From these concentrates aggregates smaller than a specific cut-off size value were additionally separated using hydro-cycle procedures, by an equipment called cyclosizer and subsieve sizer Warman model M8. This instrument generates hydro-cycles programmed at specific conditions of operation (density, flux source, elutriation time). During each hydro-cycle, a mineral pulp formed by magnetite particles suspended in water circulates continuously, following a spiral movement (like a cyclone) that separates, selects and accumulates magnetite particles. The cut-off size value for the four samples ground for 45 min was <38 μm, and <7 μm for the sample ground for 100 h.

In addition, two commercial synthetic magnetite samples were used as reference materials and were purchased from Sigma Aldrich as “<5 μm” and “<50 nm”.

### 2.3. Characterization techniques

For quantifying total Fe, and insoluble and soluble impurities in magnetite samples, approximately 0.50 g was accurately weighed in an Erlenmeyer flask and 70 mL of concentrated HCl was added. The flasks were placed under reflux conditions at 70 °C for 10 h, after which the resulting solutions were left to cool down. Subsequently, the solutions were transferred to 250 mL volumetric flasks and brought to the mark with nanopure water. The remaining solids were left to settle overnight. The samples were then filtered using Millipore polycarbonate membrane filters of 0.2 μm pore size. The retained solids were weighed after a couple of washes with nanopure water and drying. Solids were analyzed by XRD and SEM–EDX, and the solution was analyzed for dissolved Fe, and other cations, using ICP–AES.

Identification of crystalline magnetite phases and impurities in the natural samples was performed using a Siemens D5000 X-ray diffractometer with CuKα radiation. Diffraction patterns were collected at

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