

Forces of interaction between fresh iron particles and iron oxide (magnetite): Effect of water chemistry and polymer coatings



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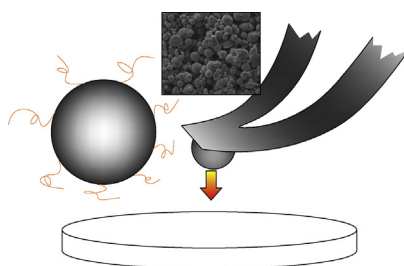
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HIGHLIGHTS

- Attachment of iron particles onto magnetite was studied in different chemistries.
- Attachment of bare and CMC coated iron particles was favorable at pH 4 and 5.5.
- Attachment of bare iron particles was favorable in 100 mM NaCl and CaCl₂ at pH 8.
- Attachment of bare and CMC coated iron was hindered in water at pH 8.
- Attachment of bare and CMC coated iron was hindered in 10 mg/l humic acid.

GRAPHICAL ABSTRACT



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ABSTRACT

Atomic force microscopy-based force spectroscopy (AFM) was employed to probe the forces of interaction between iron oxide (magnetite) surfaces and fresh zero-valent iron particles, either bare or coated with carboxymethyl cellulose polymer. Experiments were conducted at different pH values (4, 5.5 and 8), ionic strengths (water, 100 mM NaCl and 100 mM CaCl₂), and in 10 mg/l humic acid solutions (pH 6.75). pH values of 4 and 5.5 produced attraction between magnetite and iron particles (either bare or polymer coated), promoting attachment. Attractive forces between uncoated particles and magnetite were also measured in 100 mM NaCl and CaCl₂ at pH 8. Attachment of uncoated and CMC-coated iron particles was unfavorable in water at pH 8 and in humic acid solutions, as the forces upon approach were repulsive and, in addition, adhesive forces were on average weaker than in the other chemistries. A quartz-crystal microbalance with dissipation monitoring was used to probe humic acid sorption onto magnetite, and assess its impact on the forces of interaction.

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1. Introduction

Zero-valent iron nanoparticles have potential use in treating water contaminated by chlorinated compounds and heavy metals [1–12]. A key issue when applying this technology is related to iron particle delivery to the polluted areas. An accurate assessment of

particle transport in the subsurface is therefore needed to ensure remediation success. In order for the particles to travel far enough in the subsurface, their retention on geological substrates should be minimal. Particle retention is largely affected by the forces of interaction between particles and substrate, as attractive interactions favor particle attachment onto the substrate, while the presence of repulsive or neutral interactions would inhibit retention. Iron particles tend to form large aggregates that may be trapped in the soil pores, unless they are adequately stabilized with surfactants or polymers [10,13,14], such as carboxymethyl-cellulose [15,16].

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Understanding how polymer coatings influence the interactions between the particles and the geological substrates is crucial to engineer coatings that produce repulsive interactions, thus limiting particle attachment and promoting transport.

A range of minerals exists in the subsurface including magnetite, which is commonly found in the coarse fraction of soils [17]. The water chemistry can affect the interactions between approaching surfaces. To probe the effect of chemistry on the interactions between iron particles and magnetite, experiments were conducted at different pH, ionic strength and in humic acid (HA) solutions. HA are major constituents of organic matter [18] and are present in the subsurface as a result of the bacterial and chemical degradation of plant tissue [19,20].

To date, meso-scale sand column experiments have been conducted to probe the role of humic acids [21–23], polymeric coatings [22,24–26], pH [27] and ionic strength [28] on iron particle transport, while molecular-scale studies are limited [29]. AFM was used to investigate the interactions between bare iron particles and silica [30,31], between iron particles and mica [32], and between iron particles and silicon wafers [33], while the interactions between iron particles and magnetite have not been previously probed. The goal of this study is to understand the molecular-scale mechanisms involved in the interactions between magnetite and bare iron particles, filling existing knowledge gaps. In this study both micron- and nano-sized particles were employed. This is the first AFM study to investigate the effect of CMC coatings on the forces of interaction between iron particles and magnetite. Such forces include electrostatic, van der Waals, Born and hydration forces, as well as steric forces in the presence of CMC polymer coatings. Humic acid sorption onto zero-valent iron [6], hematite [34,35], goethite [36,37], commercial iron oxide powder [38] and magnetite [39] was studied using batch tests and atomic force microscopy [6,34–41], but this is the first study in which a quartz crystal microbalance with dissipation monitoring (QCM-D) system was employed to analyze humic acid sorption onto magnetite.

2. Materials and methods

2.1. Carbonyl iron particles

Micron-sized carbonyl iron particles (CIP) were purchased from Alfa Aesar (product number 10214). In a previous study, the particles were analyzed to assess their purity, their morphology, their composition and their point of zero charge (PZC) [32]. This study highlighted the presence of zero-valent iron and iron oxides due to partial iron oxidation in the presence of atmospheric oxygen, and a point of zero charge (PZC) that was expected to be $> \text{pH } 10$.

2.2. Magnetite substrates

Substrates sputter-coated with magnetite used for the AFM and QCM-D experiments (Q-Sense: QSX 326). The atomic percent of the elements constituting the sensor surface, as determined by XPS analyses performed by the supplier, were as follows: Fe = 41.6, O = 58.4. The point of zero charge for the magnetite could not be determined, as analyses would have required the material to be in powder form. The point of zero charge for magnetite is expected to be approximately between pH 6 and 7 [42,43], although values as high as 9.9 were found in previous studies [44].

2.3. Solutions

Experiments were conducted in water from a Millipore system (milli-Q water) at pH 5.5 from equilibration with atmospheric CO_2 , in milli-Q water buffered to pH 4 and 8, in 100 mM NaCl and CaCl_2 solutions having pH 5.5 and 8 and milli-Q water amended with

10 mg/l humic acid sodium salt (Aldrich, H16752), which had a pH of 6.75. Buffering to pH values of 4 was accomplished with 1 ml of acetate buffer per liter of solution (Ricca Chemicals: UA106000). Buffering to pH 8 was obtained with 0.2 mM NaHCO_3 . The solutions were stored at 23 °C for 24 h before each experiment.

2.4. Quartz-crystal microbalance with dissipation monitoring (QCM-D)

A QCM-D system (Q-Sense, Biolin Scientific, Sweden) was used to analyze sorption of humic acid (HA) onto magnetite. In our study, the magnetite-coated sensor was located at the bottom of a laminar flow cell. The sensor was oscillated at a range of frequencies (resonant frequency and its odd multiples, called overtones). Changes in these parameters can be related to film deposition at the sensor surface, as described in greater detail elsewhere [45–50].

Experiments were conducted at a flow rate of 10 ml/min and at 23 °C. The cell was first flushed with milli-Q water until stable baselines for the curves representing the dissipation and overtones were obtained. A 10 mg/l humic acid (HA) solution was then flushed through the cell for approximately 5 min followed by rinsing with milli-Q water for 15 min. The overtones and their dissipation were compared before and after the injection of HA solution to probe HA sorption onto the magnetite-coated sensor.

2.5. AFM cantilever characteristics and functionalization

Tipless silicon nitride AFM cantilevers were purchased from Bruker (NP-O10). Their average spring constant (k_c), determined with the end mass method [51], varied between 0.064 nN/nm and 0.096 nN/nm, depending on the wafer. Micron-sized carbonyl iron particles (CIP) were mounted onto these cantilevers using a micro-manipulator and their size was determined at the end of each experiment using scanning electron microscopy. Once the CIP were mounted onto the probes, polymer coatings were obtained by immersing the probes in a 10 g/l solution of sodium salt of carboxymethyl cellulose polymer (CMC) solution buffered with acetate to pH 4. The CMC polymer used (Sigma-Aldrich, product ID 419273) had a molecular weight of 90,000 g/mol and a degree of substitution per mole of cellulose of 0.7.

Conventional cantilevers with integral pyramidal tips were also purchased from Bruker (NP-10) and their experimentally determined spring constant was 0.051 nN/nm. Single nano-iron particles were electrodeposited onto the apex of these cantilevers (Fig. 1) using a previously published protocol [52]. Cantilevers were passivated with silicone oil and paraffin, and rinsed with milli-Q water to eliminate the excess oil. The tip apex was then exposed by imaging a stainless steel surface in contact mode. When hard substrates are imaged in this way, the tip's apex is abraded due to the friction with the substrate. Finally, the tips were subjected to a ~ 75 s 1.2 mA current pulse in a 0.01 M Fe_2SO_3 /0.05 M H_2SO_4 solution using a Pt wire counter-electrode. Energy dispersive spectroscopy (EDS) analyses showed the presence of iron at the tip's apex (Fig. 1a). It is noted that silicon and gold peaks appear in the EDS spectrum given in Fig. 1b, due to the fact that silicon AFM cantilevers were used and that the reflective back coating of such cantilevers was gold. The presence of these materials was detected when collecting the spectra because of matrix effects.

2.6. AFM working conditions and data analysis

Experiments were conducted with a Nanoscope Multimode AFM equipped with a Nanoscope IIIA controller using a glass fluid cell and a J-scanner. Data were acquired using the Nanoscope software (version 5.30a). In all experiments, the applied load was less than or equal to 16.5 nN and the scan rate of the AFM tip was 27.9 Hz. The

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