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The reduction of 4-chloronitrobenzene by Fe(II)-Fe(III) oxide systems - correlations with reduction potential and inhibition by silicate

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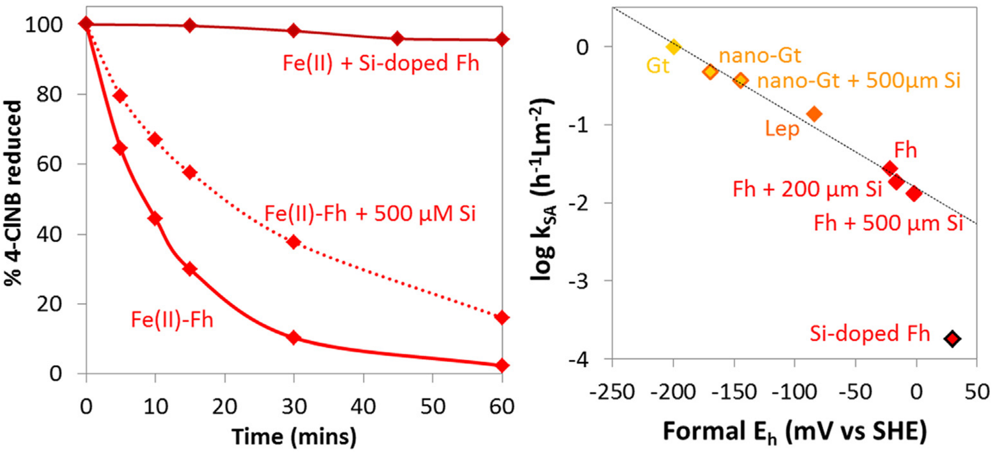
GRAPHICAL ABSTRACT



HIGHLIGHTS

- The impact of silica on Fe(II)-Fe(III) oxide reduction potentials is unknown.
- Reduction potentials determined using mediated open circuit potentiometry.
- Reduction kinetics and measured reduction potentials generally well correlated.
- Kinetics slower than predicted from reduction potential for Si-doped ferrihydrite.
- Contaminant degradation in high silicate groundwaters may be less effective.

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ABSTRACT

Recent studies have demonstrated that the rate at which Fe(II)-Fe(III) oxyhydroxide systems catalyze the reduction of reducible contaminants, such as 4-chloronitrobenzene, is well correlated to their thermodynamic reduction potential. Here we confirm this effect in the presence of Fe(III) oxyhydroxide phases not previously assessed, namely ferrihydrite and nano-goethite, as well as Fe(III) oxyhydroxide phases previously examined. In addition, silicate is found to decrease the extent of Fe(II) sorption to the Fe(III) oxyhydroxide surface, increasing the reduction potential of the Fe(II)-Fe(III) oxyhydroxide suspension and, accordingly, decreasing the rate of 4-chloronitrobenzene reduction. A linear relationship between the reduction potential of the Fe(II)-Fe(III) oxyhydroxide suspensions and the reduction rate of 4-chloronitrobenzene (normalized to surface area and concentration of sorbed Fe(II)) was

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Mediated electrochemistry
Redox potential
Contaminant degradation

obtained in the presence and absence of silicate. However, when ferrihydrite was doped with Si (through co-precipitation) the reduction of 4-chloronitrobenzene was much slower than predicted from its reduction potential. The results obtained have significant implications to the likely effectiveness of naturally occurring contaminant degradation processes involving Fe(II) and Fe(III) oxyhydroxides in groundwater environments containing high concentrations of silicate, or other species which compete with Fe(II) for sorption sites.

1. Introduction

Previous studies have demonstrated that Fe(II), when adsorbed onto an Fe(III) oxyhydroxide (herein termed Fe(III) oxide) or Fe mineral surface, displays enhanced reducing abilities towards environmental contaminants [1–9]. This enhancement has been attributed to a change in Fe(II) speciation following coordination of Fe^{2+} to oxygen atoms on the surface of the Fe(III) oxide [10], in much the same way as occurs for hydrolyzed Fe(II) species such as $FeOH^+$ [11]. As Fe(II) associated with Fe(III) oxides occur naturally in anoxic or sub-anoxic groundwaters, this redox-active assemblage can induce the degradation of reducible contaminants in the soil, with abiotic reactions shown to be an important component of such reduction processes [12,13].

The one-electron reduction potential of dissolved Fe(II) species which results following complexation by a particular ligand greatly impacts the rate at which various organic contaminants undergo reduction, with increased rates associated with an increase in the Gibbs free energy of the particular Fe(II) species formed [14]. Fe(II) species bound to Fe(III) oxide surfaces are expected to follow a similar trend, however obtaining the analogous Gibbs free energy of surface bound Fe(II) species is more difficult. Reduction potential is the most likely descriptor of the Gibbs free energy for heterogeneous reductants as it dictates the driving force of reduction reactions with contaminants [15,16]. However, it is difficult, or even impossible, to obtain reliable reduction potential measurements for Fe(II) species adsorbed on Fe(III) oxides using conventional methods [5,16,17], with researchers instead relying on theoretical predictions generally based on mineral solubility [17–19]. With calculated values varying by up to 100 mV, however, it is difficult to determine the most appropriate value [17–19]. A direct, yet reliable, means of measuring the reduction potential of Fe(II)-Fe(III) oxides systems in therefore preferable. The recent application of electron shuttles, or electrochemical mediators, paves the way to obtain reliable reduction potential measurements of such Fe(II)-Fe(III) oxide systems following recent pioneering studies investigating the reduction potential of Fe(II) within Fe-rich smectites [16,20,21]. Most recently Fan et al. (2016) [16] employed electron shuttling redox indicator compounds to measure the reduction potentials of a range of Fe(II)-Fe(III) mineral systems at pH 7.2. It was found that the measured reduction potentials of the Fe(II)-Fe(III) mineral systems correlated well with the reduction kinetics of model contaminants by the analogous Fe(II)-Fe(III) mineral system [16]. A similar methodology was employed by Orsetti et al. (2013) to determine the reduction potential of Fe(II) when adsorbed to goethite (Gt) at pH 7.0 [21], whereby reduction potentials were derived from spectrophotometric measurements of redox indicator compounds which display distinct spectrophotometric properties in their reduced or oxidized forms. The present study builds upon these recent studies [16,21] but instead employs mediated open circuit potentiometry (OCP) to measure the reduction potential of a range of Fe(II)-Fe(III) oxide systems in the presence and absence of Si. Mediated electrochemistry relies on the rapid transfer of electrons to and from the Fe(II)-Fe(III) oxide substrate by an electron shuttling compound known as the mediator [20,22]. Reduction potentials measured potentiometrically are expected to be equivalent to those determined spectrophotometrically following equilibration of a mediator with the substrate of interest [16].

Silicon species are ubiquitous in groundwaters with total Si concentrations typically ranging from 0.12 to 0.75 mM [23], although concentrations as high as 2.7 mM (or 75 mg/L) have been recorded in acid sulfate soil groundwaters [24]. As silicate, the soluble oxyanion form of Si, is a well-known corrosion inhibitor of zero valent iron present in steel [25] that readily adsorbs to Fe(III) oxides [26], it is expected to inhibit the reduction of contaminants by Fe(II)-Fe(III) oxide systems. Indeed, many studies have demonstrated that silicate retards the reduction of environmental contaminants in the presence of Fe(II)-Fe(III) oxide or zero-valent iron reductants [27,28]. In addition to its inhibitory effect towards corrosion, silicate can also compete with contaminants for sorption sites [29]. The impact of silicate on the reduction potential of Fe(II)-Fe(III) oxide systems and its associated effect on contaminant reduction kinetics has not yet been explored, with this issue forming the basis of this study. The organic compound 4-chloronitrobenzene (4-ClNB) is examined in this study as, from its reduction potential at circumneutral pH (approx. 420 mV vs. SHE at pH 7) [19], it is expected to readily undergo degradation by a range of Fe(II)-Fe(III) oxide systems. Furthermore 4-ClNB has been widely employed as a model nitroaromatic compound; a common class of explosive and agricultural pollutants known to undergo reductive degradation in the presence of Fe(II) and Fe(III) oxides [5,16,30].

2. Materials and methods

2.1. Materials

All chemicals employed are listed in the Supplementary material (S1). Experiments were conducted in pH 7.00 solutions containing 25 mM of the non-complexing buffer TEED (pKa = 6.58) [31] and 25 mM NaCl with the pH constant (to within ± 0.01 units) over the course of each experiment (S1). A 100 mM stock solution of Fe^{2+} was prepared by dissolving ferrous ammonium sulfate hexahydrate in de-aerated Milli-Q water adjusted to pH 2, filtered (0.22 mm; PVDF) and stored in the glovebox. Iron concentrations of all stock solutions were confirmed using ICP-OES (720, Agilent Technologies). Measurements of pH were performed using a Thermo Scientific Orion 8172BNWP ROSS glass combination pH probe calibrated with NIST compliant buffer solutions (pH 4.00 and 7.00 at 25 °C).

2.2. Anaerobic conditions

All experiments were conducted in an anaerobic glovebox (<0.1 ppm O_2) which employs a 5% H_2 in N_2 atmosphere (Type A, Coy Lab Products, MI, USA). All aqueous solutions were purged with 99.999 % Ar gas for 2 h prior to use. Solutions were then stirred overnight in the anaerobic chamber to ensure dissolved oxygen