

Non Oxidisable Sorbed Fe(II): Indicator of Strong and Weak Site Adsorption at the Goethite Surface

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Abstract

Experiments were conducted to study the behaviour of Fe(II) adsorbed to goethite at pH 4 with respect to exposure to dissolved O₂. Adsorption of Fe(II) onto the goethite surface was carried out under a nitrogen atmosphere, and the samples were subsequently exposed to the atmosphere for 48 hours. Adsorbed Fe(II) was determined by subtraction of the dissolved from the total Fe(II). It was found that a significant portion of the adsorbed Fe(II) did not oxidise and that this fraction increased with increasing goethite solids concentration. These results are consistent with the presence of strong and weak cation sorption sites on the goethite surface and with the strongly sorbed Fe(II) being most resistant to oxidation by dissolved O₂.

Introduction

Cardiff University has developed a system for the passive treatment of ferruginous, net-alkaline, circum-neutral, mine water using a Vertical Flow Reactor (VFR) (Dey et al, 2003). In the VFR, mine water is passed through an accreting bed of ochre on a gravel support. Highly efficient iron removal (greater than 95%) is achieved due to self filtration of suspended ochre particles, and by heterogeneous auto-catalysed oxidation and accretion of Fe(II) on ochre surfaces within the bed (Sapsford et al, 2006). During the performance monitoring of this system, a parallel study was undertaken into the rates and mechanisms of Fe(II) oxidation in the presence of Fe(III) (hydroxy)oxide surfaces. In this study the oxidation of Fe(II) was examined at pH 4 using the goethite surface as a catalyst. Goethite was used as it is an abundant precipitate throughout mine water systems, especially those of low pH (Williams et al, 2002).

Background

Recent studies of the adsorption of Fe(II) to the surface of goethite have found a one site, two species model best describes the observed adsorption characteristics (Liger et al, 1999; Dixit and Hering, 2006). Dzombak and Morel (1990), however, showed that adsorption of various divalent cations onto hydrous ferric oxide was best fit using both low affinity sites and high affinity cation sites. Appello et al (2002) used this two surface site approach to model the adsorption of Fe(II) to the hydrous ferric oxide surface.

In this study, a set of experiments were conducted to determine the characteristics of adsorption of Fe(II) on to goethite at pH 4. The experiment differed from a standard adsorption isotherm experiment such as those reported by Liger et al (1999), in that the pH and the total concentration of Fe(II) were constant, whilst the concentration of goethite solid was varied. Therefore, these experiments represent adsorption isotherms for Fe(II) on to goethite surfaces, with emphasis on the concentration of surface adsorption sites.

Materials and methods

The adsorption experiments were carried out in a glove box which was continuously purged with oxygen free nitrogen to maintain a positive pressure and prevent oxygen ingress. Reaction vessels consisted of 60 mL polypropylene centrifuge tubes with screw caps lids which were used as received. Experiments were run in triplicate and all reagent used were analytical reagent grade or better; where mentioned deionised water was Millipore MilliQ 18.2MΩ. Experiments were carried out in pH 4 sodium acetate / acetic acid buffer solutions prepared to an acetate concentration of 10 mM. Synthetic goethite (Bayferrox 930, Lanexess, Germany) was used after washing in 0.1N NaOH and 0.1N HCl before rinsing several times to remove any specifically adsorbed contaminants. The dried goethite solid was weighed directly into the reaction vessels using an analytical balance and 20 mL of pH 4

buffer was added to each of the reaction vessels making the resulting solids concentrations as shown in Table 1. A 1 g L⁻¹ anoxic Fe(II) stock solution was prepared by dissolving Fe(II)SO₄·7H₂O in N₂ purged deionised water. 0.2 mL of stock solution was then transferred to each of the 48 reaction vessels to an end concentration of approximately 10 mg L⁻¹ Fe(II). The tubes were then capped and mixed end over end for 24 hours.

Table 1 Experimental conditions

	goethite g L ⁻¹	Mean pH	Mean Temp °C
1 a, b, c	0.00	3.912	25.70
2 a, b, c	1.00	3.917	25.70
3 a, b, c	5.00	3.886	25.23
4 a, b, c	10.01	3.887	25.33
5 a, b, c	25.01	3.904	25.13
6 a, b, c	50.04	3.888	25.07
7 a, b, c	100.02	3.912	25.10
8 a, b, c	200.01	4.027	24.90

The letters a, b and c refer to the triplicate runs for each of the 8 goethite concentrations used at both pH.

After this time, a sub-samples was removed from each reaction vessel for the determination of both total (0.5 N HCl extractable), and dissolved (0.22 μm filterable) Fe(II). Fe(II) analysis was done using the modified Tamura et al (1974) 1,10-phenanthroline method as described previously (see Barnes et al, 2007). The reaction vessels were then removed from the glove box and the remaining 7.5 mL of reaction mixture was exposed to the atmosphere. The pH and temperature was determined (see Table 1) and the tubes were then re-capped and placed back on the rotational mixer and left aerated for a further 48 hours. After this time total and dissolved Fe(II) of the aerated mixture was determined.

Results and discussion

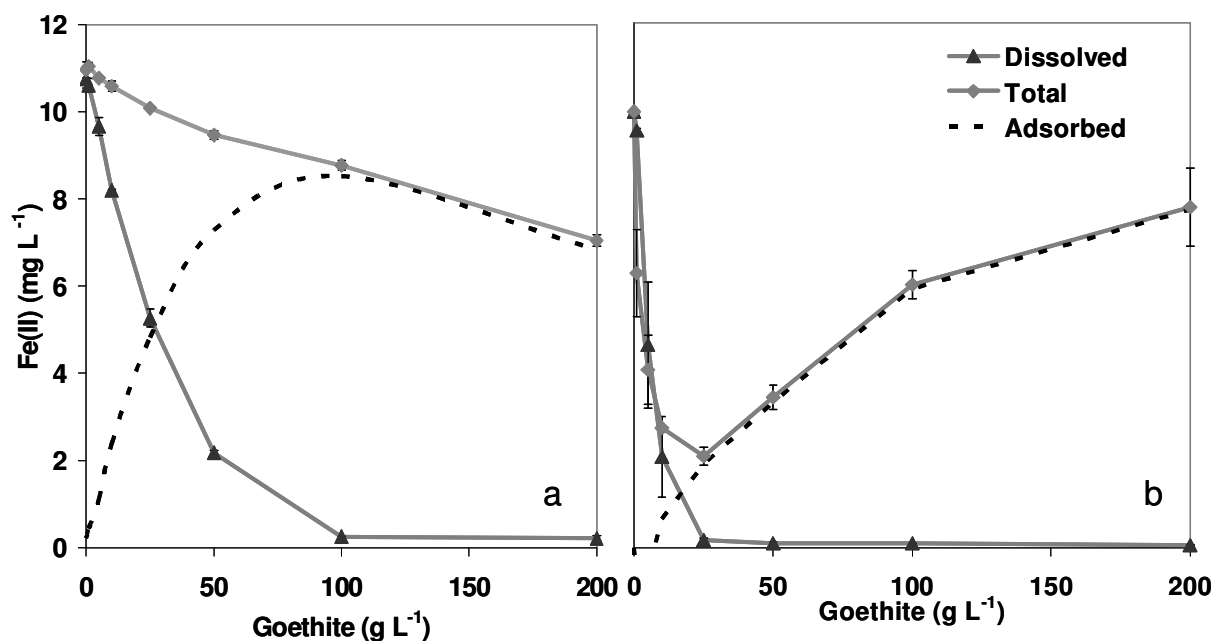
Figure 1(a) and (b) show the mean concentrations of dissolved and total Fe(II) in mg L⁻¹ against goethite concentration in g L⁻¹ in adsorption experiments before and after the 48 hour exposure to the atmosphere. Error bars where visible represent SD from the mean of singular readings from triplicate experiments. The calculated values of total minus dissolved Fe(II) are included for comparison and represents the recoverable sorbed Fe(II) portion.

Dissolved Fe(II) concentrations in Figure 1(a) are shown to decrease with increasing goethite concentration from an initial mean value of 10.75 mg L⁻¹ in the goethite free experiment to 0.25 mg L⁻¹ at 100 g L⁻¹ goethite and 0.21 mg L⁻¹ at 200 g L⁻¹ goethite. After 48 hours exposure to the atmosphere (see Figure 1(b)) no detectable dissolved Fe(II) is evident above a goethite concentrations of 50 g L⁻¹. It is also evident that complete oxidation of total Fe(II) did not occur at any goethite concentration as shown in Figure 1(b). Initial concentrations of total Fe(II) with no added goethite are shown to have decreased from 10.75 to 9.96 mg L⁻¹ a reduction of 0.79 mg L⁻¹ after 48 hours oxidation. Post oxidation total Fe(II) is shown to reduce with increasing goethite concentration to a minimum at 25 g L⁻¹ with total Fe(II) concentrations decreasing from 10.03 to 2.079 mg L⁻¹. It is evident that a significant portions of sorbed Fe(II) is not oxidised during the 48 hour oxidation period and that this proportion increases with increasing goethite concentration until, at 200 g L⁻¹, the non-oxidisable fraction represents 100 % of the HCl extractable Fe(II).

These results are consistent with adsorption of Fe(II) to both high and low affinity cation adsorption sites on the goethite surface, in which the Fe(II) adsorbed to the high affinity cation sites is not-available for the reduction of dissolved O₂. Rosso and Morgan (2002) predicted that the oxidation of hydrolysed Fe(II) solution species occurred via inner sphere electron transfer which Park and Dempsey (2005) assumed to hold true for surface Fe(II) species. Park and Dempsey (2005) state that

inner sphere reactions are more dependant on reorganisation energy, in which case the more strongly sorbed Fe(II) would be expected to be more resistant to oxidation by O₂.

Figure 1 Mean filtered and HCl extractable Fe(II) concentrations against goethite concentration at pH 3.92 in a) the adsorption experiments after 24 hours equilibration under N₂ and b) after 48 hours aerial oxidation. Error bars (where visible) indicate standard deviations from triplicate reading.



Previous studies of Fe(II) adsorption on goethite (Liger et al, 1999; Dixit and Hering, 2006) have not found high affinity cation sites to have been necessary to describe the adsorption data. However, to the authors knowledge, no previous studies have used such high concentrations of Fe(III) (hydroxy)oxide and determined both total and dissolved Fe(II). In addition to the presence of non-oxidisable adsorbed Fe(II), the actual total portion of Fe(II) oxidised is shown to increase with increasing goethite concentration. This demonstrates that goethite effectively catalyses the oxidation of Fe(II) even at pH 4. This opens up the possibility of using a VFR treatment system (or other “Ochre Accretion” based system) in the mildly acidic pH region.

Acknowledgements

This research was funded in the UK by research grant GR/S66978/01 from the Environmental and Physical Science Research Council (EPSRC).

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