LETTER

Size distribution of ferrihydrite aggregate and its implication for metal adsorption and transport

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Adsorption experiments of Zn onto ferrihydrite were carried out at different initial Fe concentrations and pH, and at room temperature. Zinc-adsorbed ferrihydrite was fractionated to examine Zn adsorption among different-size aggregates of ferrihydrite. Primary ferrihydrite particles were as small as 5–7 nm in diameter and they formed aggregates of <0.25 to >32 μm in size. The dominant size of the aggregates decreased with a decrease in the initial Fe concentrations and pH. Zinc was adsorbed on the surface of individual ferrihydrite nano-particles but not on that of ferrihydrite aggregates, indicating that ferrihydrite nano-particles were so loosely attached to one another in aggregates that individual nano-particles could adsorb Zn. The size distribution of ferrihydrite aggregates and the Zn adsorption on individual ferrihydrite nano-particles can change the sedimentation rate of ferrihydrite aggregates and the behavior of Zn during the transformation of ferrihydrite to goethite and hematite. Therefore, our results will give a deeper understanding of metal transport by ferrihydrite.

Keywords: Ferrihydrite, Adsorption, Size distribution, Nano-particle, Metal transport

INTRODUCTION

Ferrihydrite is ubiquitous in natural environments and characterized by its nano-size, large specific surface area and high adsorption capacity; ferrihydrite is metastable and transformed to goethite and hematite, and further, it forms aggregate (e.g., Cornell and Schwertmann, 2003). Because of the important roles of ferrihydrite in element transport (e.g., Cornell and Schwertmann, 2003; Hasselöv and von der Kammer, 2008), the sorption onto ferrihydrite has been intensively investigated for both cations such as Cu, Zn, Cd, Pb and U and anions such as P, As and I (e.g., Scheinost et al., 2001; Waychunas et al., 2002; Trivedi et al., 2004; Song et al., 2008; Nagata et al., 2009; Rossberg et al., 2009; Antelo et al., 2010; Carabante et al., 2010; Rout et al., 2012). Ferrihydrite aggregates made from a solution of ~ 0.2 mM Fe exhibits a significant size range from <1 μm to a few hundreds of μm (Lo and

Waite, 2000). The sedimentation time depends on their size; for instance, it is estimated to take a few thousand days and a few days for 5- and 200-nm ferrihydrite aggregates, respectively, to sediment by 10 mm in depth (Tsukimura et al., 2010). Ferrihydrite particles can transport adsorbed elements when they are dispersed (Novikov et al., 2006). On the other hand, adsorbed elements can be immobilized if ferrihydrite aggregates sediment or if adsorbed elements form precipitates during the transformation of ferrihydrite to hematite and goethite (Murakami et al., 1997, 2005). For elemental transport, therefore, the size distribution of ferrihydrite particles and aggregates and the reaction pathways posterior to adsorption are important factors, in addition to adsorption itself.

The present study aimed to elucidate Zn adsorption among different-size aggregates of ferrihydrite, which can give deeper understandings of metal transport. Zinc was chosen for an adsorbate because it is simply adsorbed on the surface of ferrihydrite at less than tens of μM of Zn (Waychunas et al., 2002).

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Table 1. Experimental conditions and Fe and Zn concentration in fractions

Run 1			Run 2			Run 3			Run 4		
IS ^a (mM)/pH 4.6/7.5			IS(mM)/pH 4.5/7.0			IS(mM)/pH 4.4/4.2			IS(mM)/pH 7.6/7.0		
Diameter μm	Fe ppm ^b	Zn ppm	Diameter μm	Fe ppm	Zn ppm	Diameter μm	Fe ppm	Zn ppm	Diameter μm	Fe ppm	Zn ppm
Initial ^c	11.26	4.90	Initial	1.12	0.490	Initial	11.26	0.499	Initial	11.21	4.90
< 20	10.26	5.32	< 10	0.84	0.412	< 5	9.12	0.494	< 32	9.79	5.20
< 10	10.02	5.13	< 7.5	0.85	0.429	< 3	9.01	0.490	< 16	9.54	5.14
< 7.5	9.84	5.09	< 5	0.82	0.415	< 2	9.40	0.503	< 8	7.78	4.80
< 5	9.27	4.90	< 3	0.70	0.397	< 1	8.86	0.496	< 4	1.07	2.90
< 1.8	2.99	2.52	< 1.8	0.65	0.389	< 0.75	7.48	0.442	< 2	0.25	2.45
< 0.5	0.66	1.76	< 0.75	0.28	0.365	< 0.5	7.17	0.438			
< 0.25	0.22	1.58	< 0.5	0.12	0.354	< 0.3	7.94	0.484			
			< 0.3	0.04	0.358	< 0.25	6.62	0.486			
			< 0.25	0.02	0.354						

^a IS stands for ionic strength; the range of the present IS values does not change the Zn adsorption significantly (e.g., Trivedi et al., 2004).

^b The uncertainties of measurements by ICP-AES were 5% of relative standard deviation.

^c Concentrations before fractionation. The initial concentration of Fe was 0.2 or 0.02 mM and that of Zn 75 or 7.5 μM.

EXPERIMENTAL

Ferrihydrite was synthesized from a $\text{Fe}(\text{NO}_3)_3$ solution by adding 1 M NaOH solution until pH 7–8 and aged for 2 hours (modified from Davis and Leckie, 1978; Schwertmann and Cornell, 2000). Synthesized ferrihydrite was confirmed to be two-line ferrihydrite by X-ray diffraction (XRD, data not shown). The morphology of ferrihydrite particles and aggregates were observed by transmission electron microscopy (TEM). The TEM sample was prepared from a solution made similar to experimental run 2 (Table 1) and passed through a 0.22 μm membrane filter.

After adding a 1 M NaNO_3 background electrolyte solution to aliquots of the ferrihydrite suspension, $\text{Zn}(\text{NO}_3)_2$ solution was poured to be 8–75 μM of Zn in resultant solutions. The pH of the samples was adjusted by 0.01, 0.1 and 1 M of NaOH and HNO_3 . The Zn adsorption reached equilibria in 2 hours (data not shown), and therefore, all adsorption experiments were conducted with more than 2-hour reaction time. All experiments were carried out in Ar atmosphere and at 22 ± 1 °C of temperature. The experimental conditions are given in Table 1.

Centrifugation was used to fractionate ferrihydrite aggregates (runs 1, 2 and 3 in Table 1). In addition, gravitational sedimentation was employed to fractionate larger aggregates (run 4 in Table 1). The suspension of Zn-adsorbed ferrihydrite aggregates was dispersed ultrasonically for three minutes before fractionation. For fractionation by centrifugation, 45 mL of each lot of the suspension was centrifuged for an assigned time and rotation rate as given in Table 2, which were calculated based on the assumption that ferrihydrite particles and aggregates were spherical, the viscosity of the solution 1 Pa s, the density

Table 2. Conditions for centrifugation

Diameter μm	Rotation time min	Rotation per min (rpm)
< 20	1.15	400
< 10	5	400
< 7.5	9	400
< 5	4	900
< 3	11	900
< 2	2	3200
< 1.8	2.4	3200
< 1	7.9	3200
< 0.75	14	3200
< 0.5	31	3200
< 0.3	87	3200
< 0.25	125	3200

of water 1.0 g/cm³, and the density of ferrihydrite 3.96 g/cm³ (for 6-line ferrihydrite, Towe and Bradley, 1967). A supernatant was sampled after each centrifugation run. For fractionation by gravitational sedimentation, the suspension solution was put in a graduated cylinder of about 30 cm height and sampled with pipette from 5-cm depth at assigned settling time calculated by Stokes law. Analytical grade HNO_3 was added to the sampled solutions to dissolve all ferrihydrite. Then, the Fe and Zn concentrations of the solutions were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES, Scientific Instruments, SPS-7700). The uncertainties of measurements by ICP-AES were 5% of relative standard deviation. All measurement data are given in Table 1. The difference in the concentration of Zn or Fe between one fraction and the next one corresponds to its concentration

in the fraction range.

RESULTS AND DISCUSSION

Synthesized ferrihydrite formed aggregates, and therefore, individual ferrihydrite particles were difficult to be observed (Fig. 1a), partly because the TEM specimen was prepared by drying a droplet of the suspension solution on a TEM grid. The enlarged image indicates the presence of isolated, spherical ferrihydrite particles of 5 to 7 nm in diameter in the left side of Figure 1b (see examples of ferrihydrite particles shown by arrows in Fig. 1b). The XRD and TEM examinations strongly suggested that nano-sized ferrihydrite primary particles formed aggregates.

The size distribution of ferrihydrite aggregates was obtained from the Fe concentrations in the fractions by centrifugation and sedimentation (Table 1); this was calculated by $C_{\text{Fe},i} - C_{\text{Fe},i+1}$, where $C_{\text{Fe},i}$ is the Fe concentration in the i -th fraction. The data with $(C_{\text{Fe},i} - C_{\text{Fe},i+1})/C_{\text{Fe},i+1} < 0.05$, the uncertainty of ICP-AES measurements, were not used for the size-distribution calculations. The solubility of ferrihydrite is so low ($\log K_{\text{sp}} \cong -39$, Cornell and Schwertmann, 2003) that we can neglect dissolved Fe in aqueous phase. With a decrease in Fe concentration at similar pH (from 0.2 to 0.02 mM Fe corresponding to runs 1 and 2, respectively), the dominant size of ferrihydrite aggregates decreased (Figs. 2a and 2b); about 60% of aggregates were present in the 1.8–5 μm fraction for

the 0.2 mM Fe solution while about 50% in the 0.5–1.8 μm fraction for the 0.02 mM Fe solution. On the other hand, with a decrease in pH at similar Fe concentration (from pH 7.5 to pH 4.2 corresponding to runs 1 and 3, respectively), the dominant size of ferrihydrite aggregates drastically decreased (Figs. 2a and 2c); about 70% of aggregates were present in the $<0.3 \mu\text{m}$ fraction at pH 4.2. This is consistent with the size distribution of ferrihydrite aggregates in soil where positively charged ferrihydrite at low pH results in aggregate instability (Rhoton et al., 2003). Our results show that the size distribution of ferrihydrite aggregates changes with chemical conditions.

We can reasonably assume that Zn is distributed among different-size ferrihydrite fractions as adsorbed and dissolved Zn (Table 1). Thus, the difference in the Zn concentration between the i - and $(i+1)$ -th fractions, $C_{\text{Zn},i} - C_{\text{Zn},i+1}$, was thought to be the concentration of Zn adsorbed on ferrihydrite aggregates having the corresponding size range. In the similar way to the ferrihydrite size distribution, the data with >0.05 of $(C_{\text{Zn},i} - C_{\text{Zn},i+1})/C_{\text{Zn},i+1}$ were used for the following examination for the amount of Zn adsorbed on ferrihydrite. We calculated the number of Zn atoms adsorbed on the unit surface of ferrihydrite assuming that Zn is adsorbed either on the surface of individual 5-nm particles or on aggregate surface. Both particles and aggregates were assumed to be spherical. A median diameter was adopted for the size of a given fraction

Figure 1. TEM images of ferrihydrite aggregates at relatively low (a) and high (b) magnifications. Isolated, spherical ferrihydrite particles of 5 to 7 nm in diameter are observed (e.g., those shown by arrows in Fig. 1b).

Figure 2. Variations of size distribution of ferrihydrite aggregates: (a), (b) and (c) are for runs 1 (0.2 mM of initial Fe and 7.5 of pH), 2 (0.02 mM and 7.0) and 3 (0.2 mM and 4.2), respectively, in Table 1.

of the aggregates; for instance, the median diameter for the <20 μm fraction was 15 μm . The number of adsorbed Zn atoms per unit area (nm^{-2}) in a fraction is given:

$$\begin{aligned} & \frac{\text{Total number of Zn atoms}}{\text{Total surface area of particles or aggregates}} \\ &= \frac{M(\text{Zn}) \times A / M_{\text{Zn}}}{M(\text{Fe}) \times 4\pi r^2 / ((4/3)\pi r^3 \times \rho)} \\ &= \frac{M(\text{Zn}) \times A \times r \times \rho}{3M(\text{Fe}) \times M_{\text{Zn}}} \\ &= 12.15 \frac{C_{\text{Zn},i} - C_{\text{Zn},i+1}}{C_{\text{Fe},i} - C_{\text{Fe},i+1}} r \end{aligned}$$

where $M(\text{Fe})$ and $M(\text{Zn})$ are the masses of Fe and Zn, respectively, in the fraction, A the Avogadro number (6.02×10^{23}), M_{Zn} the atomic weight of Zn (65.4), r the radius of the particle or aggregate, ρ the density of ferrihydrite, and $M(\text{Zn})/M(\text{Fe}) = (C_{\text{Zn},i} - C_{\text{Zn},i+1})/(C_{\text{Fe},i} - C_{\text{Fe},i+1})$. The calculated results are shown in Figure 3. The number of Zn atoms assumed to be adsorbed on aggregate surface increased drastically with an increase in the aggregate

Figure 3. The number of Zn atoms adsorbed on ferrihydrite per unit surface as a function of median diameter of ferrihydrite aggregate (see Table 1), assuming Zn is adsorbed on aggregate surface (a) and on the surface of individual 5-nm particles (b). Solid and open squares, triangles, diamonds and circles corresponds to the data points of runs 1, 2, 3 and 4, respectively. Note that the pH dependency of Zn adsorption can be seen in Figure 3b where the number of Zn atoms per unit surface at pH 7.5 (solid squares) is larger by one order of magnitude than that at pH 4.2 (solid diamond).

diameter (Fig. 3a), whereas that assumed to be adsorbed on the surfaces of individual 5-nm ferrihydrite hardly changed with the aggregate diameter, 1 to 16 per unit surface (Fig. 3b). The small number, 1.2, for run 3 (solid diamond in Fig. 3b) was probably due to low adsorption of Zn at relatively low pH (Trivedi et al., 2004). As the ionic radius of Zn^{2+} is 0.083 nm, about 40 Zn^{2+} cations at maximum might be packed on a given unit surface. The formation of bidentate complexes of Zn on ferrihydrite surface (Waychunas et al., 2002) would further reduce this number. Therefore, it is impossible to pack more than hundred Zn atoms in the unit surface area as shown in Figure 3a. On the other hand, Dzombak and Morel (1990) suggested that ferrihydrite has 4–40 surface sites per unit surface area, and Stumm (1992) 2–12 hydroxyls per unit surface areas of oxides. These values well agree with the number of Zn cations that are assumed to adsorb on the surfaces of primary ferrihydrite surfaces. Thus, our results strongly indicate that Zn is adsorbed on the surface of individual ferrihydrite nano-particles but not on the (external) surface of ferrihydrite aggregates. This may reflect that ferrihydrite nano-particles are so loosely attached to one another in aggregates. Slight changes of the density of aggregates or the size of primary ferrihydrite particles do not affect the number of Zn atoms significantly (see the equation above).

For adsorption experiments, ferrihydrite is usually prepared at tens of μM to mM of Fe (e.g., Violante et al. 2003; Trivedi et al., 2004; Nagata et al., 2009), which is much larger than dissolved Fe concentration estimated from the ferrihydrite solubility (Stefansson, 2007). Although ferrihydrite forms aggregates, metal ions are adsorbed onto the surface of individual nano-particles (Fig. 3b), and therefore, such adsorption experiments with high Fe concentrations will provide appropriate estimates of adsorbed amounts of metal ions. The concentration of Fe does not affect the estimates of adsorbed metal ions even if a suspension is filtered through a 0.2- μm pore-size membrane filter because an amount of ferrihydrite aggregates with <0.2 μm is not significant (Figs. 2a and 2b). However, when adsorption experiments are carried out at low pH, filtration of a ferrihydrite suspension with 0.2- or 0.4- μm pore-size membrane filters will give wrong results on the amount of adsorbed metals due to the dominant size distribution at the <0.3 μm fraction (Fig. 2c).

Transport of trace metals by ferrihydrite is a complex process including adsorption, aggregation, sedimentation, transformation and co-precipitation (e.g., Buffle and Leopard, 1995; Hassellöv, and von der Kammer, 2008; Raiswell, 2011), where adsorbed metal ions can be mobilized, immobilized or remobilized, depending on the processes involved. It was reported that amorphous Fe hy-

droxide (probably ferrihydrite) of <50 nm in diameter transported Pu more than 3 km from the source area through groundwater of pH 6–8 (Novikov et al., 2006). Our results of the size distribution (Fig. 2) predict that there might be amorphous Fe hydroxide aggregates of larger sizes present in the upstream, which are removed from the groundwater by sedimentation in much shorter time due to the size (Tsukimura et al., 2010). Sedimentation associated with phase transformation will change the behaviors of adsorbed metal ions further. In fact, nano-crystals (~ 10 nm in diameter) of metatorbernite, Cu uranyl phosphate, are found to form between goethite and hematite nano-crystals in the downstream of the Koon-garra uranium mine, Australia (Murakami et al., 1997, 2005). The formation of nano-crystalline metatorbernite, called as post-adsorption phenomena, is explained as follows (Murakami et al., 1997, 2005); ferrihydrite formed by weathering adsorbs U, Cu, P and so on, is sedimented to form ferrihydrite veins and nodules, and U, Cu and P are concentrated in a nano-area as the surface area is reduced by about one order of magnitude during the transformation of ferrihydrite to goethite and hematite. Finally, the concentrated U, Cu and P form metatorbernite between goethite and hematite, and consequently, the U concentration in groundwater ~ 200 m from the area where metatorbernite occurs decreases to 10^{-10} M from 10^{-8} M. Our results on Zn adsorbed on the surface of individual ferrihydrite nano-particles strongly support the explanation although post-adsorption phenomena are possibly different between adsorbed metals.

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