

Adsorption and Precipitation of Aqueous Zn(II) on Hematite Nano- and Microparticles

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Abstract. As part of a study of the effect of particle size on reactivity of hematite to aqueous metal ions, the sorption of Zn(II) on hematite nanoparticles and microparticles was examined over a wide range of Zn(II) concentrations using Zn K-edge EXAFS. When reacted with nanoparticles at pH 5.5 and low Zn(II) sorption densities ($0.04 \leq \Gamma < 2.76 \mu\text{mol}/\text{m}^2$), Zn(II) formed five-coordinated or a mixture of four- and six-coordinated surface complexes with an average Zn-O distance of $2.04(\pm 0.02)\text{\AA}$. At pH 5.5 and high Zn(II) sorption densities ($2.76 \leq \Gamma \leq 3.70 \mu\text{mol}/\text{m}^2$), formation of surface precipitates is suggested based on the presence of second-shell Zn and multiple scattering features in the Fourier transform (FT) of the EXAFS spectra. EXAFS fitting of these high Γ samples yielded an average first-shell Zn-O distance of $2.10(\pm 0.02)\text{\AA}$, with second-shell Zn-Fe and Zn-Zn distances of $3.23(\pm 0.03)\text{\AA}$ and $3.31(\pm 0.03)\text{\AA}$, respectively. Qualitative comparison between the EXAFS spectra of these sorption samples and that of amorphous zinc hydroxide and Zn-bearing hydrotalcite indicates the development of surface precipitates with increasing Γ . EXAFS spectra of Zn(II) sorbed on hematite microparticles under similar experimental conditions showed no evidence for surface precipitates even at the highest Zn surface coverage ($\Gamma = 4 \mu\text{mol}/\text{m}^2$). These results indicate that reactivities of hematite nanoparticles and macroparticles differ with respect to Zn(II)_{aq}, depending on Zn(II) sorption density. We suggest that the degree of hematite crystallinity affects the reactivity of hematite surfaces toward Zn(II)_{aq} and the formation of the Zn(II) surface complexes.

Keywords: Zinc, hematite, nanoparticles, sorption, XAFS

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INTRODUCTION

Sorption of toxic metal ions on the surfaces of oxides plays an important role in the fate of metal ions in soils, sediments, and aquatic environments because the concentrations of dissolved metal ions in aqueous systems are controlled to a large extent by the partitioning of solutes to solid phase (i.e., sorption).

Zinc is a relatively common metal ion in soils and aquatic environments, and excess concentrations of Zn are introduced to these geomedia from smelting operations, sulfidic mine tailings, and agricultural applications of sewage sludge and pesticides. Zn forms a number of different complexes at the surfaces of metal oxides, often dependent on reaction conditions, such as solution pH, ionic strength, reaction time, Zn surface loading and types of mineral substrates. Among the Fe-oxides present in natural environments, hematite ($\alpha\text{-Fe}_2\text{O}_3$) is one of the most abundant. The

objectives of this research were to determine if (1) different types of Zn complexes (e.g., inner- or outer-sphere, mono- or polynuclear structures) formed at the surfaces of hematite nanoparticles vs. microparticles, and (2) surface precipitates form at high Zn surface loadings as reported by others for different types of iron oxides.

METHODS AND MATERIALS

Hematite nanoparticles were prepared according to the method of Madden and Hochella [1]. The N_2 BET surface area of synthesized hematite nanoparticles was $218 \pm 1.3 \text{ m}^2/\text{g}$. XRD verified that the synthesized particles are hematite. SEM and TEM images (not shown) indicate that the individual particles are spherical and in aggregated states, with an average diameter of $10.5 \pm 1.6 \text{ nm}$. Hematite microparticles were purchased from Sigma-Aldrich (99.98% pure)

and their N_2 BET surface area is 18 ± 0.8 m^2/g . XRD verified phase purity, and TEM and SEM images indicated an average particle size of 800 ± 3 nm.

All sorption experiments were carried out at $25^\circ C$ in a N_2 -purged glove box to minimize CO_2 contamination. Stock solutions of 10 g/L of hematite nano- and microparticle suspensions were prepared in 0.01 M NaCl. 10 mM $ZnCl_2$ solution was added in a dropwise manner to hematite nano- and microparticle stock solutions to yield selected total $Zn(II)$ concentrations (Fig. 1). pH was adjusted to 5.5 by manual addition of 0.1 M HCl or NaOH and was checked periodically during 48 hours of equilibration. Solid-to-liquid ratios were 0.0023 g/mL for the hematite nanoparticle systems and 0.007 g/mL for the hematite microparticle systems. Sorption samples were centrifuged, and the filtered supernatants were analyzed with inductively coupled plasma (ICP) spectrometry. $Zn(II)$ uptake was calculated as the difference between total and measured metal concentration. Zn K-edge XAS spectra of wet pastes were collected at Stanford Synchrotron Radiation Laboratory on wiggler beam line 10-2 at $25^\circ C$ in fluorescence mode using a 30-element Ge detector. A Si(220) double crystal monochromator was detuned 40%, and energy calibration was monitored using a Zn-metal foil. EXAFS data analysis was performed using SIXPACK [2]. Phase and amplitude functions were simulated using the FEFF8.0 code [3]. During EXAFS fitting, the amplitude reduction function, S^2_0 , was set at 0.90. For some samples, the third cumulant expansion term, C_3 , was varied to account for anharmonicity in the EXAFS spectra [4]. The presence of multiple scattering was identified using continuous Cauchy wavelet transform analysis (CCWT) [5].

RESULTS AND DISCUSSION

Figure 1 shows that more Zn sorbs on hematite microparticles than on the nanoparticles after normalization for differences in surface area. All samples are undersaturated with respect to formation of $ZnO(s)$ or $Zn(OH)_2(s)$. Samples for EXAFS experiments were chosen based on the adsorption isotherms in order to assess the effect of Zn surface loading on the types of surface complexes formed.

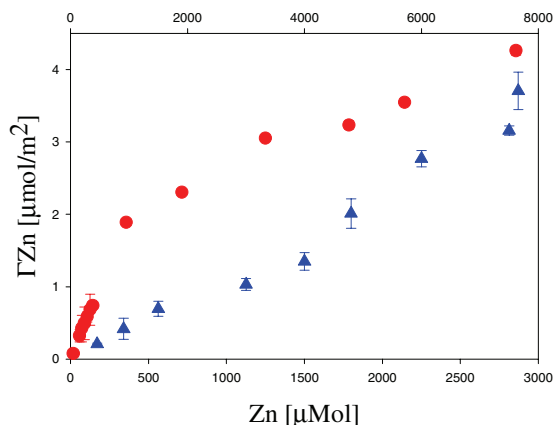


FIGURE 1. Surface-area normalized $Zn(II)$ uptake on hematite microparticles (●) and nanoparticles (▲) at pH 5.5 as a function of total $[Zn(II)]$. Bottom x-axis is for microparticles and upper x-axis is for nanoparticles.

The normalized, k^3 -weighted EXAFS and Fourier transforms (uncorrected for phase shift) of $Zn(II)$ sorbed to hematite nanoparticles (HN) and hematite microparticles (HM) are presented in Figs. 2 and 3, respectively, together with model compound spectra. FT's of the Zn K-edge EXAFS of adsorption samples in the HN systems at low Zn surface loading ($\Gamma < 2.76$ $\mu mol/m^2$) do not contain strong 2nd-neighbor peaks; in contrast, strong 2nd-neighbor peaks do occur for samples with higher Zn surface loading (Fig. 2). The EXAFS spectra of adsorption samples at $\Gamma = 2.76$ and 3.70 $\mu mol/m^2$ are similar to that of synthesized amorphous zinc hydroxide or Zn-bearing hydrotalcite. Unlike the HN systems, no strong 2nd-neighbor peaks indicative of surface precipitates are observed in the HM systems even at the highest Zn surface loadings. However, CCWT analysis suggests the possible presence of 2nd-neighbors for the HM sorption samples.

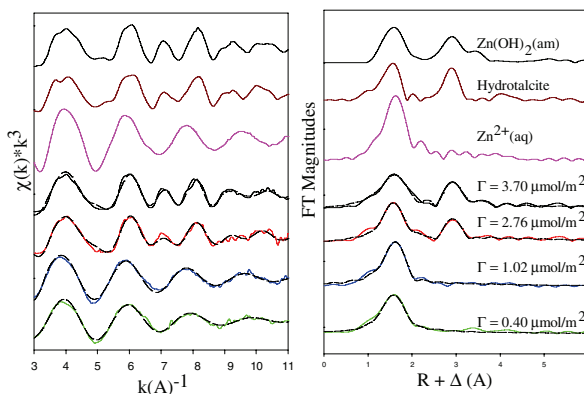


FIGURE 2. EXAFS spectra and Fourier transforms (not phase corrected) of Zn reference and sorption samples in hematite nanoparticle systems (solid lines = experimental spectra; dashed lines = fitted spectra).

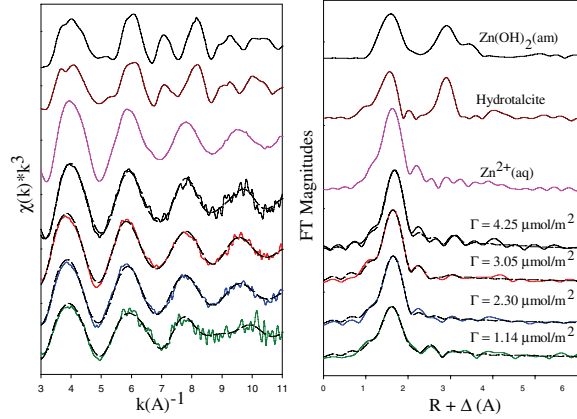


FIGURE 3. EXAFS spectra and Fourier transforms (not phase corrected) of Zn reference and sorption samples in hematite microparticle systems (solid lines = experimental spectra; dashed lines = fitted spectra).

Table 1 shows that Zn-O distances change from 2.04 to 2.09 Å and coordination numbers increase from 5.2 to 6.8 in HN systems as Zn surface loading increases. The short distances (2.04 Å) in HN sorption samples with $\Gamma < 2.76 \mu\text{mol/m}^2$ suggest either a mixture of octahedral and tetrahedral Zn coordination or pentagonal Zn coordination by oxygen. It is possible that highly disordered oxygens are present in the 1st-coordination shell of Zn sorbed on hematite nanoparticles, leading to a distorted five- or six-coordinated 1st-shell. Fitting the 2nd-FT feature of these samples did not improve the fit significantly, suggesting that Zn(II) sorbs on hematite nanoparticles as an outer-sphere complex under these conditions.

TABLE 1. Results of EXAFS Fits for Zn-Hematite Sorption Samples.

HN samples	Zn-Z ^a	N	R ^a (Å)
$\Gamma = 0.40 \mu\text{mol/m}^2$	Zn-O	5.2	2.04
$\Gamma = 1.02 \mu\text{mol/m}^2$	Zn-O	5.4	2.04
$\Gamma = 2.76 \mu\text{mol/m}^2$	Zn-O	6.2	2.08
	Zn-Fe ^b	4.1	3.15
$\Gamma = 3.70 \mu\text{mol/m}^2$	Zn-O	6.8	2.10
	Zn-Fe	3.2	3.32
	Zn-Zn ^c	4.8	3.28
HM samples	Zn-Z	N	R (Å)
$\Gamma = 1.14 \mu\text{mol/m}^2$	Zn-O	6.2	2.08
	Zn-Fe	1.1	3.55
$\Gamma = 2.30 \mu\text{mol/m}^2$	Zn-O	6.1	2.10
	Zn-Fe	1.1	3.38
$\Gamma = 3.05 \mu\text{mol/m}^2$	Zn-O	6.3	2.09
	Zn-Fe	1.2	3.34
$\Gamma = 4.25 \mu\text{mol/m}^2$	Zn-O	6.2	2.11
	Zn-Fe	1.1	3.37

^a Uncertainties in N_{av} and R_{av} are estimated to be $\pm 20\%$ and 0.02 Å.

^b No significant difference in the goodness of fit was observed between Fe and Zn in the second shell.

^c Fitting two second shells (Zn-Fe/Zn) significantly improved the goodness of fit.

It is possible that undercoordinated oxygens at the surface of hematite nanoparticles result in a lower coordination of Zn(II) in order to more closely satisfy Pauling's electrostatic valence rule.

At higher Zn loading ($\Gamma \geq 2.76 \mu\text{mol/m}^2$), strong multiple scattering features are observed at $R + \Delta$ of 4.5-6.5 Å in the FT's, suggesting that longer range order exists in these samples.

No significant changes in the 1st-shell Zn-O distance or Zn coordination environment were observed in the HM samples throughout the range of Zn surface loading on hematite (Table 1). The lack of distinctive frequencies in the EXAFS spectra, such as those present in the EXAFS of zinc hydroxide, Zn-hydrotalcite, and HN sorption samples at high Zn surface loading, indicates that no Zn-containing precipitates formed under these experimental conditions. Mononuclear inner-sphere sorption complexes of Zn are proposed based on the fitting results. Our results also indicate that 1st-shell Zn coordination remains octahedral for the HM samples. Schlegel *et al.* [6] found that Zn(II) sorbs as an inner-sphere complex in distorted six-fold coordination by oxygen, with an average Zn-O distance of 2.10 Å. Nachtegaal *et al.* [7] also found Zn(II) sorbed on goethite as inner-sphere complexes with octahedral coordination. In this study, we have demonstrated that hematite particle size and Zn surface loading affect the mode of sorption of Zn(II)aq on hematite particles.

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