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# Bidentate Complexation Modeling of Heavy Metal Adsorption and Competition on Goethite

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Accurate sorption modeling is critical for environmental risk assessment and development of sound remedial technologies. Adsorption to iron oxide phases is one of the important sorption processes regulating the bioavailability and toxicity of metal ions in natural systems. In this study, we used spectroscopically derived bidentate surface species to constrain surface complexation modeling in addressing Ni(II) and Zn(II) adsorption and competition on goethite surfaces. The 2-p$K_a$ triple layer model successfully predicted adsorption in single adsorbate systems. The curvature in adsorption isotherms was accurately depicted using two types of sites: high affinity and low affinity, and mononuclear bidentate surface complexes. A constrained set of parameters was found for each metal (log $K_L = -6.63$ and log $K_H = -2.45$ for Ni, log $K_L = -3.92$ and log $K_H = 2.14$ for Zn) that successfully described adsorption over a large range of experimental conditions, covering 6 to 7 orders of magnitude in concentration, ionic strength from $10^{-3}$ to $10^{-2}$, and environmentally relevant pH range between 4 and 6.5. Adsorption competition was predicted using the bidentate surface species with parameters calibrated using single adsorbate data.

## Introduction

Sorption of trace elements onto reactive mineral surfaces is an important process regulating contaminant mobility and bioavailability in natural systems (*1, 2*). Accurate description of the sorption process is critical for environmental risk assessments and the development of sound remedial technologies in contaminant management. Therefore, sorption modeling has received considerable attention. Surface complexation models (SCMs) are one of the most promising methods in modeling sorption. They offer a distinct advantage by representing surface chemical reactions with a set of quasi-thermodynamic constants, which are independent of changes in solution conditions (*3*). One requirement of using SCMs is that the controlling reactions and surface species must be known or assumed. A common practice is to assume that the surface is chemically homogeneous and a two-step protonation reaction accounts for the charging of metal (hydr)oxides (*4*). Adsorbate reactions are generally proposed based on adsorption edges, isotherms, and/or the number of $H^+$ released (e.g., *1, 5*). Although these approaches are usually successful, the surface species selected may not be unique or physically meaningful.

Fortunately, recent advances in addressing speciation using in situ spectroscopic techniques, such as X-ray absorption spectroscopy (XAS) and FTIR spectroscopy, have made it possible to overcome this drawback. Especially from XAS analysis, inner-sphere versus outer-sphere complexation, mononuclear versus multinuclear, or solid solution formation can be distinguished through a local structure analysis. For example, vanadium (V) adsorption on goethite at pH 1.5−12 could be better modeled with monodentate surface complexes, rather than bidentate species; however, based on XAS, only bidentate surface complexes formed (*6*). Also, a SCM was found to under-predict Co(II) adsorption on α-$Al_2O_3$ at high surface coverage (>10%) using mononuclear complexes; while based on XAS results, Katz and Hayes (*7*) successfully modeled this adsorption using polymer complexes. Therefore, spectroscopic techniques are needed to unambiguously fit data using surface complexation modeling.

On the other hand, although surface complexation models have been widely applied in describing the adsorption process (e.g., *4, 8, 9*), a unique set of parameters is difficult to achieve. Few studies have addressed isotherm and edge data with the same set of model parameters, and most models have been derived from adsorption edges (*8, 9*), the applicability of which may be questionable when there is an effect of adsorbate concentration. Moreover, a single set of SCM parameters could not predict Zn(II) sorption onto ferrihydrite over a wide range of conditions; the equilibrium "constant" was adjusted with pH to fit the isotherm data (*10*). Robertson and Leckie (*11*) also could not apply a unique model for Cu adsorption isotherms with goethite covering pH values 4−6 and ionic strengths $10^{-2}$−$10^{-1}$.

Goethite exists widely and exhibits a high affinity and large capacity for heavy metals (*12*). Ni(II) and Zn(II) are two common contaminants that may coexist due to release from historically poor waste management practices from industries such as electroplating. The objective of this work was to develop one set of parameters for the description of Ni and Zn adsorption on goethite, based on isotherm and edge data. Better constrained parameters were achieved by considering spectroscopic information and calibrating the SCM using a broad range of conditions. Also, Ni and Zn competition studies were used to test the predictive capability of the model.

## Materials and Methods

**Materials.** All solutions were prepared from Milli-Q Type I DI water and chemicals were of ACS reagent grade. Ionic strength, pH, and metal concentration were adjusted with $NaNO_3$, $HNO_3$, and NaOH, and metal nitrates, respectively. $Ni(NO_3)_2$ and $Zn(NO_3)_2$ stock solutions were prepared using Aldrich high-purity (99.999%) reagents and stored at pH 2. Goethite was synthesized and characterized in earlier work (*13*). The surface area of goethite measured with $N_2$ adsorption and BET model is 31 $m^2/g$ and the $pH_{PZC}$ is 8.8 ± 0.97 (Supporting Information).

**Sorption Studies.** One g $L^{-1}$ goethite suspension was diluted from 10 g $L^{-1}$ stock and adjusted to ionic strength $10^{-3}$ or $10^{-2}$. Adsorption edges covered the pH range 4−7, while isotherms were generated for initial metal concentrations ($[Me]_0$) ranging between $2.6 \times 10^{-8}$ and $2 \times 10^{-4}$ M. The 100 mL samples were equilibrated in 250 mL Nalgene containers for 4 h under a fully turbulent hydraulic condition

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($Re \geq 1.0 \times 10^4$) through shaking (C-1 Platform Shaker, New Brunswick Scientific). Systems were open to the atmosphere at room temperature. Sample $[Me]_0$ was undersaturated with respect to $\beta$-$Ni(OH)_2$ (theophrastite), $ZnCO_3$ (smithsonite), and $Zn(OH)_2$ based on simulations using MINEQL+ (*14*). Samples were filtered using 0.22 $\mu$m Millipore filters. The filtrate was analyzed for metal concentration with a Beckman Liquid Scintillation System (model LS6500), where an isotope-tagged ($Ni^{63}$ or $Zn^{65}$) metal-nitrate stock solution was used to adjust the initial concentration. The amount of metal adsorbed was calculated from a mass balance.

**Modeling Approach.** The nonlinear least-squares fitting program, FITEQL 4.0 (*15*) was used to model titration and adsorption data. This program solves the equilibrium model at each data point and optimizes adjustable parameters until the sum of the squares of the residuals (SOS/DF) between the measured data and the calculated values is minimized (*15*). Several forms of surface complexation models have been introduced and compared (*16*–*17*). The triple layer model (TLM) involves the most parameters; however, with the flexibility in cation and anion placement with respect to sorbent surface, it has been demonstrated to accurately depict a large range of conditions (*16*, *18*). Therefore, TLM was selected for this study (a comparison of the existing models is provided in the Supporting Information).

The titration data (Supporting Information) were used to calibrate the TLM. Surface reactions describing the goethite/water interface and corresponding reaction constants are the following:

Surface protolysis reactions:

$$SOH_2^+ = SOH + H^+ \log K_{a1}$$

$$SOH = SO^- + H^+ \log K_{a2}$$

Electrolyte binding reactions:

$$SOH + Na^+ = SO^- - Na^+ + H^+ \log K_{cat}$$

$$SOH + NO_3^- + H^+ = SOH_2^+ - NO_3^- \log K_{an}$$

The values of $\log K_{a1}$ and $\log K_{a2}$ were constrained based on the relationship that $pH_{PZC}$ is equal to $-(\log K_{a1}+\log K_{a2})/2$. As a result, $\Delta pK_a$ as well as the inner-layer capacitance ($C_1$) were optimized outside of the FITEQL program. The outer-layer capacitance ($C_2$) is traditionally set at 0.2 F/m$^2$ (*19*). For the total site density ($N_s$) of goethite, a value of ~6 sites nm$^{-2}$ was calculated based on crystallographic considerations proposed by Hiemstra and van Riemsdijk (*20*). This value was adopted for our work. The TLM parameters optimized in FITEQL were $\log K_{cat}$ and $\log K_{an}$. Ionic strength effects are accounted for in FITEQL using activity coefficients calculated with the Davies equation (*21*). From the TLM modeling results for the titrations, a $\Delta pK_a$ value of one ($\log K_{a1} = -8.3$ and $\log K_{a2} = -9.3$) was chosen with optimized constants of $\log K_{cat} = 9.94$, $\log K_{an} = -8.25$, and $C_1 = 2.0$ F/m$^2$. This set of parameters was therefore used in modeling adsorption.

**Defining Adsorption Mechanisms.** XAS information of Ni and Zn adsorption to mineral surfaces (Supporting Information) was used to constrain the TLM. Zn(II) has been found to form inner-sphere mononuclear edge- and corner-sharing complexes upon adsorption to goethite (*22, 23*). EXAFS analysis performed by the authors (*24*) suggest that Ni(II) forms inner-sphere mononuclear bidentate complexes along edges of $FeO_6$ octahedra with loadings up to $8.1 \times 10^{-3}$ mole Ni g$^{-1}$ hydrous ferric oxide (HFO) for ionic strengths $2.8 \times 10^{-3}$ to $10^{-1}$. Similar surface species are assumed to form on goethite as both HFO and goethite are composed of $FeO_6$ octahedral unit. For these reasons, bidentate surface complexes were used in this study, where SOH represents a surface hydroxyl group and the surface reaction for either Ni or Zn (Me) on goethite is the following:

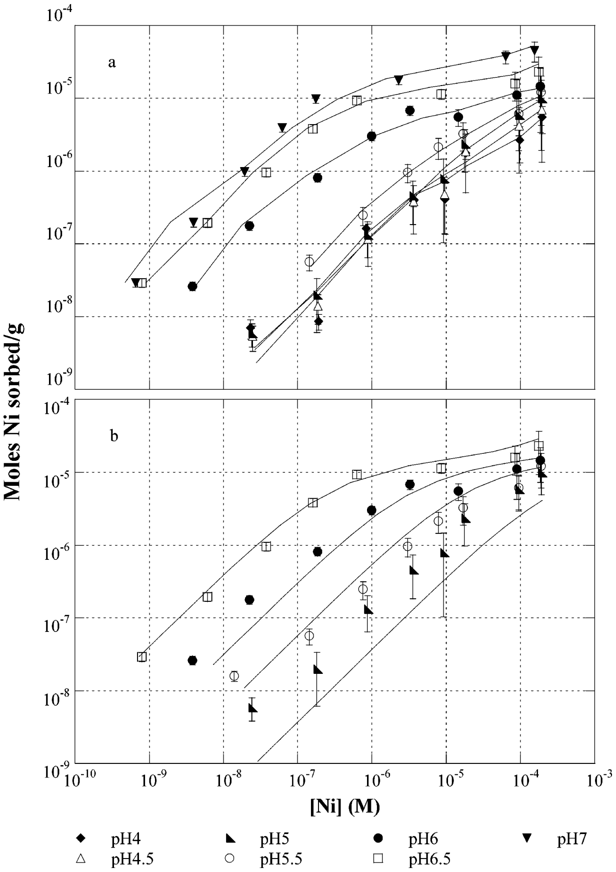

**FIGURE 1. Ni adsorption isotherms for an open system at room temperature using 1 g L$^{-1}$ goethite and $10^{-3}$ M ionic strength (adjusted with $NaNO_3$). Solid lines in (a) represent TLM best fits. Solid lines in (b) represent TLM predictions using the parameters obtained from modeling isotherm data at pH 6.5.**

$$2SOH + Me^{2+} = (SO)_2Me + 2H^+ \log K_{Me}$$

This reaction is consistent with the reported proton release for Zn adsorption on goethite (*1*). Although the systems were open to the atmosphere, there was no evidence of structural contributions from carbonate in XAS analyses (*23*, *24*). Carbonate species have not been reported to affect adsorption of Zn, Ni, Cd, and Pb under atmospheric conditions (*2*, *25*).

## Results and Discussion

**Ni Adsorption on Goethite.** Ni adsorption isotherms were conducted from pH 4 to 7 (Figure 1a). Although adsorption increases with pH, isotherms between pH 4 and 5 are almost equivalent and within the experimental error. This result may be due to very low adsorption and thus the error is large. Overall, Ni adsorption increases significantly between pH 5.5 and 6.5. These isotherms also show that below $10^{-6}$ M, the sorbed concentration is linearly related to the aqueous concentration with a slope approximately equal to one, suggesting one type of site. However, the slope of the isotherms became less than one for Ni concentrations greater than $10^{-6}$ M, suggesting surface site heterogeneity (*26*). Palmqvist et al. (*27*) did not observe a second type of surface sites in the sorption of Pb, Cd, Zn, and Cu onto goethite; this maybe because the concentrations were below ~$10^{-6}$ M in their study. Therefore, to predict metal adsorption under a variety of scenarios, the model needs to be calibrated using

**TABLE 1: Model Parameters for Ni and Zn Adsorption Isotherms for Goethite at Different pH Values**

| $2SO_LH + Me^{2+} = (SO_L)_2Me + 2H^+$ log $K_L$ | | | |
|---|---|---|---|
| $2SO_HH + Me^{2+} = (SO_H)_2Me + 2H^+$ log $K_H$ | | | |
| pH | Log $K_L$ | Log $K_H$ | $N_{sH}$ (mol/g) |
| | **parameters for Ni adsorption** | | |
| 4 | −1.93 | 3.73 | $2.5 \times 10^{-6}$ |
| 4.5 | −2.62 | 2.18 | $2.5 \times 10^{-6}$ |
| 5 | −3.34 | 0.39 | $2.5 \times 10^{-6}$ |
| 5.5 | −4.42 | −0.42 | $5.0 \times 10^{-6}$ |
| 6 | −5.34 | −1.15 | $2.0 \times 10^{-5}$ |
| 6.5 | −6.63 | −2.45 | $3.5 \times 10^{-5}$ |
| 7 | −6.89 | −3.04 | $6.0 \times 10^{-5}$ |
| | **parameters for Zn adsorption** | | |
| 4 | −2.10 | 4.18 | $5.0 \times 10^{-7}$ |
| 4.5 | −2.66 | 3.29 | $1.0 \times 10^{-6}$ |
| 5 | −3.56 | 2.34 | $3.1 \times 10^{-6}$ |
| 5.5 | −3.92 | 2.14 | $3.1 \times 10^{-6}$ |
| 6 | −4.36 | 0.86 | $7.3 \times 10^{-6}$ |
| 6.5 | −4.60 | 0.41 | $7.3 \times 10^{-6}$ |
| 7 | −5.00 | −0.29 | $7.3 \times 10^{-6}$ |

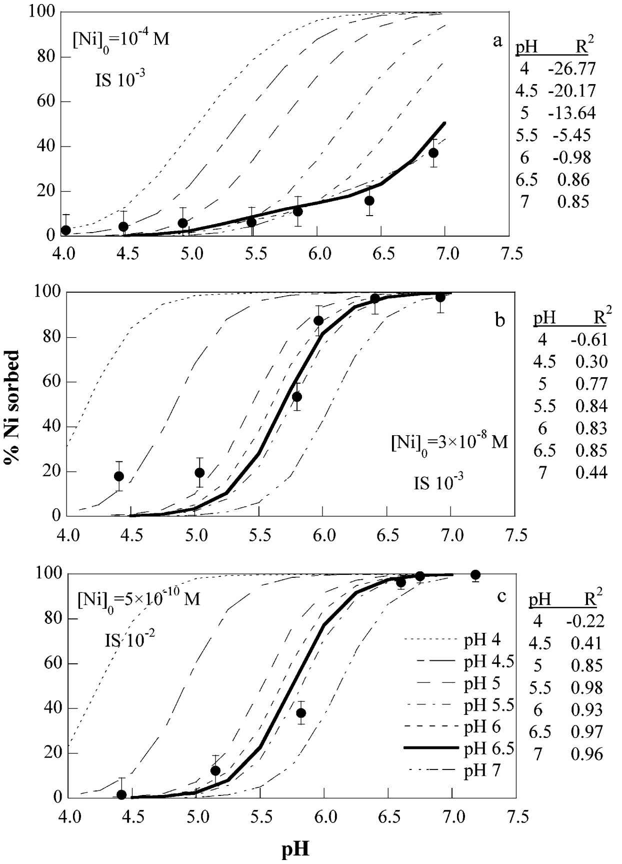

**FIGURE 2. Ni adsorption edges for 1 g L$^{-1}$ goethite conducted in air at room temperature; ionic strength adjusted with $NaNO_3$ (dots represent experimental data; lines represent TLM predictions using best-fit parameters obtained from modeling the isotherm data at different pH values).**

a wide concentration range to account for possible changes in adsorption mechanisms.

Surface heterogeneity was taken into account in modeling isotherms over the entire range of Ni concentrations tested. However, XAS analyses performed by the authors suggested only one type of site, that is, mononuclear bidentate surface complexes were formed on iron oxide surface (Supporting Information). Two explanations exist for the seeming discrepancy. First, XAS data are averaged over the entire surface; a small fraction of other site types may exist, but were not detected in the analysis. Another explanation is consistent with that proposed by Benjamin and Leckie (*5*) that the oxide surface exhibits a spectrum of binding energies; as the surface binds more ions, the higher energy sites may become limiting and the overall binding energy of the surface decreases. Also sites at corners and edges are not as electrochemically balanced as those on crystal planes and have higher energies. These sites are occupied first by the adsorbed ions. Although different binding energies exist on the goethite surface, the reaction stoichiometry may still reflect an equivalent surface complex. Therefore, a two-site model as employed by Dzombak and Morel (*8*) was used. XAS derived $(SO)_2Ni$ complexes were applied for both high affinity ($K_H$) and low affinity ($K_L$) sites.

Surface complexation modeling constrained with bidentate surface species at low and high affinity sites resulted in seven sets of best-fit parameters (Table 1). Overall, the TLM reproduced the isotherm data very well (Figure 1a). The results suggest that, although polynuclear surface complexes and/or precipitation can account for isotherms with slopes not equal to one (*16*), multisite adsorption is applicable when supported by spectroscopic data. More than one type of surface site has been experimentally observed on ferric oxyhydroxide (*28*) and supported in crystallographic analysis (*29*). As Robertson and Leckie (*26*) noted, even when slopes equal one, this does not guarantee that only one type of site is present; it is more likely that several site types exist.

Even if site density is a function of pH, it appears that, at least in this study, the high affinity site density falls within an order of magnitude of each other. Therefore, in terms of applying the TLM, a single set of parameters describing both adsorption edge and isotherm data would be more practical. Adsorption edges (Figure 2) suggest that the percent Ni sorbed increased significantly from pH 5 to 6.5 at low Ni concentrations (Figure 2b and c); however, at the highest $[Ni]_0$ (Figure 2a) the typical sigmoid curve was not observed, potentially due to site saturation. All seven sets of TLM parameters derived from isotherms were used to predict edge data (Figure 2). Based on the $R^2$ for the model, the pH 6.5 set of parameters predicted all edge data (Figure 2a–c) reasonably well. This set of parameters was selected and found to predict adsorption isotherms successfully (Figure 1b). Therefore, a single set of TLM parameters described Ni adsorption on goethite over a broad range of conditions, covering almost 7 orders of magnitude in concentration ($10^{-10}$ to $10^{-3}$ M), ionic strength from $10^{-3}$ to $10^{-2}$, and an environmentally relevant pH range from 5 to 6.5.

**Zn Adsorption on Goethite.** Regression of the Zn-goethite adsorption data using the TLM involved the same procedure as for Ni/goethite system. Adsorption isotherms (Figure 3a) also reveal decreasing slopes as concentration approaches $10^{-5}$ M, necessitating the use of high and low affinity sites for modeling. Seven sets of parameters were obtained (Table 1) from modeling (Figure 3a) and tested with edge data (Figure 4). For Zn, the pH 5.5 parameter set provided a reasonable fit for both the edge (Figure 4) and isotherm data (Figure 3b). Therefore, this better constrained set of parameters was found to describe Zn adsorption on goethite over a large range of conditions, covering 6 orders of magnitude in concentration ($10^{-10}$ to $10^{-4}$ M), ionic strength from $10^{-3}$ to $10^{-2}$, and an environmentally relevant pH range from 4 to 6.

For Zn sorption on ferrihydrite, Dzombak and Morel (*8*) obtained a group of log $K_H$ and log $K_L$ parameters by modeling a variety of edge and isotherm data; weighted averages of these log Ks were determined to be the best estimates. Similar work was also conducted for goethite (*9*). Although reasonable fits were achieved, the surface complexes used in modeling were not spectroscopically supported. Dyer et al. (*10*) used

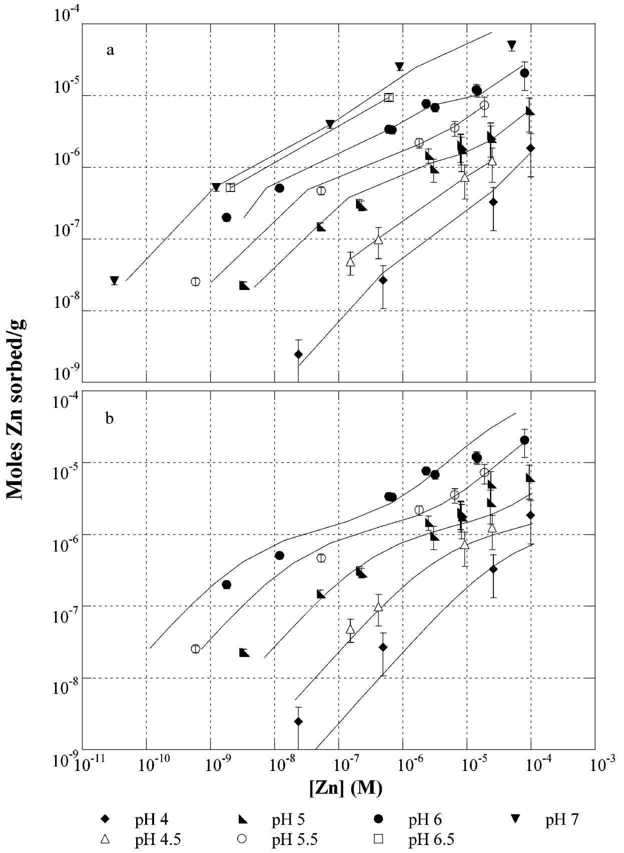

**FIGURE 3. Zn adsorption isotherms for an open system at room temperature using 1 g L$^{-1}$ goethite and 10$^{-3}$ M ionic strength (adjusted with NaNO$_3$). Solid lines in (a) represent TLM best fits. Solid lines in (b) represent TLM predictions using the parameters obtained from modeling isotherm data at pH 5.5.**

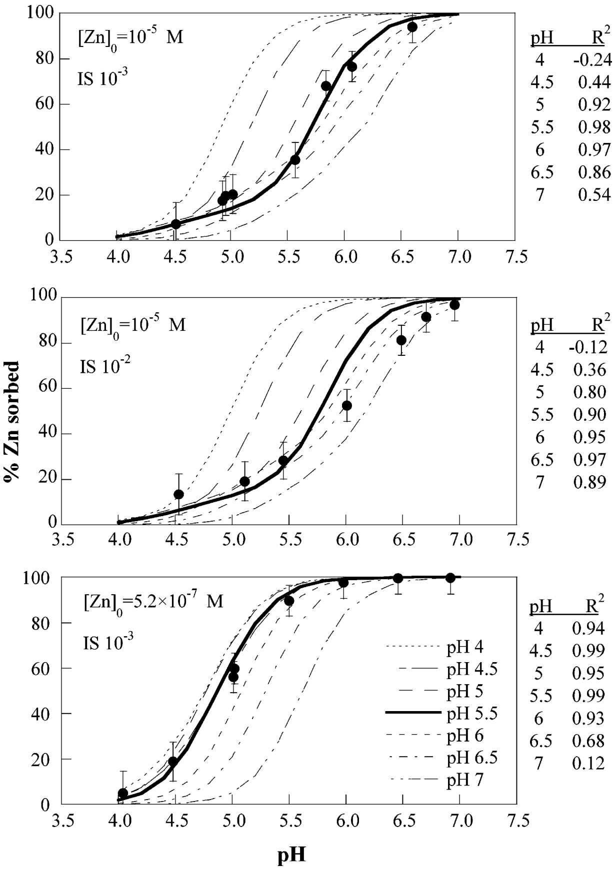

**FIGURE 4. Zn adsorption edges for 1 g L$^{-1}$ goethite conducted in air at room temperature; ionic strength adjusted with NaNO$_3$ (dots represent experimental data; lines represent TLM predictions using best-fit parameters obtained from modeling isotherm data at different pH values).**

an XAS-derived surface complex [(FeO)$_2$Zn] to fit Zn adsorption on 2-line ferrihydrite data over a pH range of 4–8 and a loading of $10^{-5}$ to $5 \times 10^{-1}$ moles Zn mole$^{-1}$ Fe. Both the site density and best-fit equilibrium "constant" had to be adjusted with pH to adequately fit the isotherm data. In this study, a two-site TLM resulted in improved predictions of Ni and Zn adsorption over a broad range of conditions (6 to 7 orders of magnitude in metal concentration, ionic strength ranging from $10^{-3}$ to $10^{-2}$ M, and an environmentally relevant pH range) using a single set of model parameters.

Calibrating the SCM using a wide concentration range and experimentally derived surface complexes are important for development of predictive models. For example, Cd adsorption shows complexity as a function of concentration (*30*) and XAS analysis suggests bidentate Cd complexes on goethite (*31*). Although Wen et al. (*32*) modeled Cu and Cd adsorption isotherms and edges on natural sediments with a CCM, DLM, and TLM using one set of parameters, their data covered only 2 to 3 orders of magnitude in concentration. Moreover, the sediment was treated as a homogeneous sorbent and the adsorbed surface complexes were assumed to be monodentate. The predictive capability of their model to a wider range of concentration conditions or different sediments may be limited. The Ni and Zn adsorption on goethite data in this study are overall consistent with those conducted by Kooner et al. (*33*) and Buerge-Weirich et al. (*34*). A direct comparison with other studies is not applicable due to significant differences in either ionic strength, surface area of goethite, and/or goethite concentrations (Supporting Information, Table S3). Furthermore, the data obtained in this study greatly extend the metal concentration ranges; these larger-range data were successfully modeled using TLM constrained with XAS-derived bidentate surface complexes.

**Ni and Zn Competition.** The modeling results for single adsorbate systems (Table 1) indicate that the reaction constants for Zn(II) adsorption are greater than that for Ni(II), suggesting Zn ions exhibit a higher affinity than Ni ions for the goethite surface. This observation is in agreement with other studies (e.g., *35, 36*). Therefore, competition is expected when both ions are present and the site density is limited. Competition has been investigated by many researchers, for example, Gadde and Laitinen (*37*) concluded that Pb sorbed more strongly than other ions (Zn, Cd, and Ti) on HFO and HMO surfaces; Balistrieri and Murray (*2*) found that Mg(II) tends to suppress the adsorption of trace metals (Cu, Pb, Zn, and Cd) on goethite; Christophi and Axe (*38*) observed that goethite has a greater affinity for Pb than Cu; Trivedi et al. (*35*) found that Zn and Ni bind more strongly than Ca to goethite; Bradl (*39*) observed that Cd adsorption is strongly influenced by the presence of competing cations, such as Ca and Zn; and, Kanungo et al. (*40*) found in a study on Co, Ni, Cu, and Zn sorption onto HMO that Ni experienced the greatest degree of displacement. However, competition between trace metals in other studies may have been difficult to demonstrate, because site density may not have been limiting (e.g., *41*).

The competition experiments were performed at pH 6. Compared to single adsorbate systems, Ni(II) adsorption decreased by approximately 23% due to the presence of Zn(II) (Figure 5a). With a higher affinity for goethite surfaces, Zn(II) competes with Ni(II) in occupying sites available for both metals. Ni(II) and Zn(II) competition was predicted using

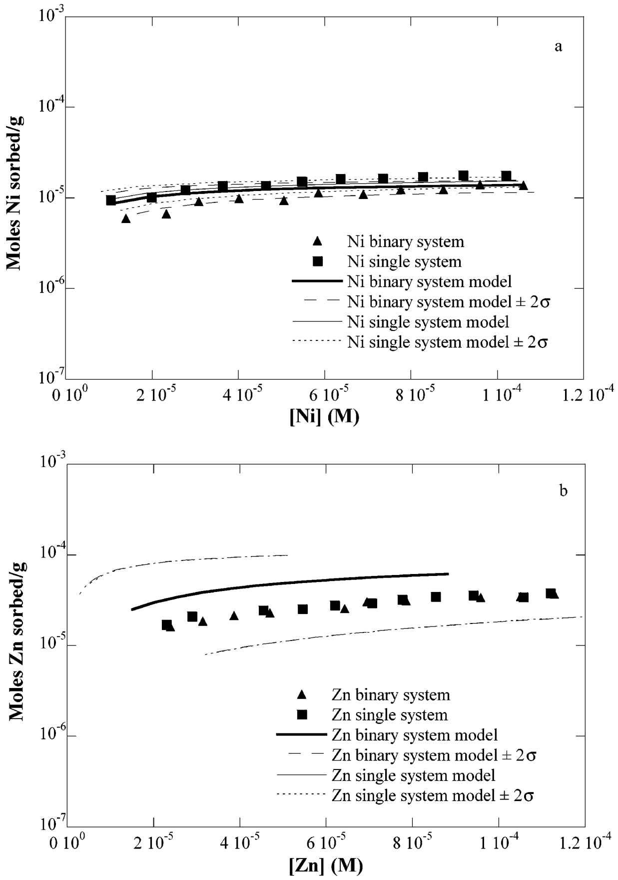

**FIGURE 5. Ni ($[Ni]_0 = 2 \times 10^{-5} - 1.2 \times 10^{-4}$ M) and Zn ($[Zn]_0 = 4 \times 10^{-5} - 1.5 \times 10^{-4}$ M) adsorption in Ni−Zn bisolute systems at 1 g $L^{-1}$ goethite, pH 6, and $10^{-3}$ M ionic strength. Symbols represent experimental data; solid lines represent TLM predictions using log $K_{a1} = -8.3$, log $K_{a2} = -9.3$, log $K_{anion} = 9.94$, log $K_{cation} = -8.25$, and fitting parameters obtained from single-adsorbate modeling: pH 6.5 parameters for Ni and pH 5.5 parameters for Zn. Dashed lines represent ± two standard deviations.**

Ni (pH 6.5 set) and Zn (pH 5.5 set) parameters and the experimental data were within two standard deviations of the model (Figure 5a); errors were calculated through error propagation in previous optimization. However, compared to the Zn(II) single adsorbate system, the presence of Ni(II) did not influence Zn(II) adsorption (Figure 5b), which is consistent with the lower affinity of Ni(II) for goethite. Model prediction resulted in similar amounts of Zn(II) adsorption with and without the presence of Ni(II); experimental data were within two standard deviations of the model prediction (Figure 5b). Therefore, the broadly calibrated TLM model constrained by XAS-derived bidentate surface complexes predicted adsorption of both high- and low-affinity metal ions onto goethite reasonably well.

Although SCMs have been employed to simulate multisolute adsorption competition, success has been mixed. Using a generalized two-layer model, Ali and Dzombak (*42*) predicted adsorption of sulfate and organic acids reasonably well based on single-adsorbate data over a wide range of conditions. Under prediction for the weaker adsorbate was explained by adsorbate-specific surface site heterogeneity and/or by inaccurate representation of Coulombic effects in the model. Gao and Mucci (*43*) predicted the shape of the competitive adsorption data for phosphate and arsenate on goethite, but failed to reproduce it quantitatively. Heidmann et al. (*44*) were able to predict Cu and Pb competition on kaolinite successfully using the combination of a 1-p*K* basic Stern model for edge sites and an extended basic Stern model for face sites; nevertheless the surface complexes were assumed without spectroscopic support. Hayes and Katz (*16*) pointed out that nonelectrostatic, diffuse layer, and constant capacitance models are likely to be less successful in modeling competition data, because they do not account for differences in inner- and outer-sphere complexes. Christl and Kretzschmar (*45*) demonstrated that surface site density is a key parameter in applying SCMs to multicomponent environments, and they obtained the best predictions with site densities between 5 and 10 sites $nm^{-2}$ for hematite. Palmqvist et al. (*41*) showed that single-adsorbate modeling predicted adsorption competition for Cu and Zn, but underestimated Pb(II) adsorption. Both the TLM and NEM predicted Cd and Ca competition on HFO; however, the model failed at the lowest ionic strength (0.005) studied (*18*). Results of this study indicate that, when coupled with spectroscopic data, parameters derived from single-adsorbate systems can be used to predict adsorption competition; experimental data lie within two standard deviations of the model prediction (Figure 5).

**Application of Experimentally Derived Surface Species.** One of the important features of this study is that XAS supported bidentate surface species were used for metal adsorption modeling. However, monodentate species (e.g., $SOMe^+$) are traditionally used (e.g., *8*, *46*). If $(SO)_2Me$ species were replaced with $SOMe^+$ in this study, modeling of Ni isotherms at pH 6−7 did not converge and the fitting for Zn was not satisfactory at high pH and lower concentrations (Supporting Information, Table S4 and Figure S2). Therefore, the spectroscopic information better constrains the model than traditional assumptions for the overall success of TLM in this study. The prediction results at higher pH (≥6) and concentrations ($>10^{-5}$ M), where competition studies were conducted, may suggest room for improvement potentially requiring discernment of any new or relatively less-dominating adsorption mechanism(s) under these conditions, which may be challenging with current available techniques.

Additionally, Dijkstra et al. (*46*) noted that model prediction for multi-metal leaching from natural, heterogeneous soils strongly relies on parameters derived from the laboratory for well-characterized materials. Therefore, soil composition and characterization of adsorbed species on corresponding materials are important in describing metal behavior in natural environments. The uncertainties introduced by assuming SOM surface species and using HFO as a "surrogate" for amorphous aluminum (hydro)oxides may be reduced if spectroscopic information for metal adsorption to iron and aluminum oxides had been taken into account by Dijkstra et al. (*46*).

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## Supporting Information Available

Potentiometric titration of goethite, comparison of SCM models, spectroscopic information, and additional tables and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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