GRAPHICAL ABSTRACT

SURFACE COMPLEXATION MODELING OF PROTON AND METAL SORPTION ONTO GRAPHENE OXIDE

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ABSTRACT

The objective of this investigation was to develop a surface complexation modeling approach to account for proton and metal (Cd, Pb) binding onto many-layered graphene oxide (MLGO) across a range of pH and ionic strength conditions. MLGO particles exhibit large buffering capacities between pH 3 and pH 10 and the buffering behavior is only nominally influenced by ionic strength. In contrast, batch metal sorption experiments illustrate that the striking capacity of MLGO to sorb metals substantially diminishes with increases in ionic strength. X-ray absorption spectroscopy measurements were used to establish reaction stoichiometries and indicate that both Cd and Pb associate with single sites on the MLGO surface. The difference in sorption behaviors for protons and metals is best modeled using a 4-site non-electrostatic surface complexation model that accounts for ionic strength effects as a competition between Na from the background electrolyte and Cd/Pb for available MLGO sorption sites. Using this approach, titration data are used to constrain the site concentrations and pK_a values for MLGO binding sites. The pK_a values ($\pm 1\sigma$) are calculated as 4.55 (± 0.91), 6.52 (± 0.49), 8.48 (± 0.21), and 9.98 (± 0.21). We then use these parameters and the metal sorption data to determine thermodynamic stability constants for each important Cd- and Pb-MLGO surface complex. The site concentrations and equilibrium constants provided herein are critical for developing and testing remediation strategies for specific water chemistries.

KEYWORDS

Surface complexation modeling; graphene oxide; metal sorption; potentiometric titration.

1. INTRODUCTION

Graphene oxide (GO; also called graphite oxide [1-4]) is typically synthesized via the oxidation and exfoliation of the graphene laminations that comprise natural flake graphite [5]. GO exhibits an extremely large surface area to mass ratio and a high concentration of covalently-bonded functional groups, including epoxide, ketone, and hydroxyl groups on the basal planes, and carboxylic, lactol, and phenolic groups at the edges [6-9]. The combination of these two surface properties results in a significant capacity to sorb various compounds present in the environment, including humic acid [10], cationic dye [11], ammonia [2], antibiotics [12], and organic [13-15] and metal [16] contaminants. In fact, GO has higher maximum sorption capacities for Pb (II), Cd (II), Zn (II), Cu (II), Co (II), and U(VI) than any other currently-reported material [17-21].

The extraordinary capacity of GO to sorb metal cations from solution suggests potential uses in water treatment and contaminant remediation. However, in order to make optimal use of GO in these applications, equilibrium thermodynamic modeling is needed to determine material dose, reactor size, and operational parameters. Nearly all previous studies in the literature demonstrate GO sorption capacities by applying non-mechanistic models, such as Langmuir/Freundlich isotherms, which result in partitioning coefficients that vary as a function of the solution composition for which they were determined. Consequently, the parameters calculated from these sorption models cannot be applied with confidence to natural and engineered treatment environments that vary much more widely in pH, ionic strength, sorbate concentration, and/or concentrations of competing cations and metal-binding ligands than those directly studied in the laboratory. In contrast, *intrinsic* equilibrium constants determined by surface complexation modeling are invariant with respect to most parameters that affect

partitioning coefficients [22, 23], and would therefore yield a more flexible and mechanistic model of metal-GO sorption. Using this approach, one can calculate discrete equilibrium constants in relatively simple systems that isolate specific sorption reactions and then combine the results with computational models to quantify the effects of GO sorption reactions on the distribution and speciation of metals in more complex engineered or natural geologic systems.

Hence, in this study, we tested several different surface complexation modeling approaches for their abilities to account for proton and metal binding onto GO surfaces. We conducted acid/base potentiometric titrations as a function of ionic strength and used the results to provide constraints on the number of discrete proton-active site types on the GO surface, their acidity constant (K_a) values, and their site concentrations. After defining reaction stoichiometries for the metal-GO surface complexes using X-ray absorption spectroscopy (XAS) measurements, we also utilized bulk metal (Cd/Pb) sorption experiments as a function of pH under three or four ionic strength conditions to constrain the number of sites involved in metal binding, their pH ranges of influence, and the thermodynamic stability constants (K_{ads}) for important metal-GO surface complexes. In order to best fit our experimental data, we ultimately devised a non-traditional surface complexation modeling approach that accounts for the influence of ionic strength on sorption behaviors as a competition between the background electrolyte (Na) and Cd/ Pb at available sorption sites.

Throughout this study, we focus primarily on many-layered GO (MLGO) particles, which are stacked arrangements of exfoliated single-layered GO (SLGO) nanosheets. Relative to SLGO nanosheets, MLGO particles are more practical for use in engineered treatment and remediation systems, as they are more easily sedimented and recovered from aqueous solutions. However, some potentiometric titrations and metal sorption experiments were also conducted

using SLGO nanosheets to address specific research questions. In this way, we demonstrate the relative utility of both SLGO nanosheets and MLGO particles in treatment applications.

2. MATERIALS AND METHODS

2.1 Potentiometric Titrations

We synthesized MLGO particles and SLGO nanosheets from natural flake graphite (Alfa Aesar, 99.9995%) using the method of Hummers and Offerman [5] and characterized their physical properties with atomic force microscopy (AFM), as described in the Supplementary Material (SM) Section S.1. We performed potentiometric titrations on ~1 g MLGO L⁻¹ suspensions using an automated acid-base titrator (MT-70, Mettler-Toledo, Columbus, OH). To buffer ionic strength, we added appropriate quantities of NaClO₄ to each suspension, such that the resulting initial ionic strength in the titrated solutions was 1 mM, 10 mM, 100 mM, or 300 mM. These suspensions were then purged with N₂ for more than 20 minutes and analyzed. All titrations were performed under a positive pressure of N₂ gas in the reaction vessel headspace. We completed between three and seven titrations for each ionic strength. We also performed three titrations of SLGO nanosheets suspended in a 100 mM solution of NaClO₄ using an identical approach.

The titrator utilizes an automatic burette assembly to deliver precisely measured quantities of standardized 1.0 M HCl and NaOH solutions. During continuous stirring with a Teflon-coated magnetic stir-bar, the 100 mM and 300 mM ionic strength MLGO suspensions were first acidified to pH ~2.5, at which point a *forward* titration commenced by slowly basifying the suspension to pH ~10, followed by a *reverse* titration that returned the solution to pH ~2.5. In order to minimize the change in ionic strength caused by the added titrant over the

course of the titration, the 1 mM and 10 mM ionic strength treatments were titrated from their initial pH (~3.2) forward without acidification to pH 2.5 and we generally did not perform reverse titrations for these systems. Even with this methodological amendment, we note that the forward titrations added ~4 mM (in the form of Na⁺ ions) to the initial ionic strength.

The known concentration of MLGO in suspension and the continuous monitoring of added titrant volumes and pH (i.e., a measure of the activity of free H⁺ in solution in mol L⁻¹) combine to result in a mass balance of acid and base in a system per gram of MLGO [(C_a – C_b) / (g MLGO L⁻¹)] along a continuum of pH. The net excess/deficit of protons then serves as input for surface complexation models to determine individual site concentrations for distinct proton-active functional groups, as well as their respective pK_a values, as described in Section 4.2.

2.2 Batch Metal Sorption Studies

Suspensions of MLGO particles (200 mg L⁻¹ for Cd; 20 mg L⁻¹ for Pb) were evaluated for their abilities to sorb aqueous Cd (1 ppm; 8.9 × 10⁻⁶ M) or Pb (1 ppm; 4.8 × 10⁻⁶ M) from solution. Ionic strengths (1 – 300 mM for Cd; 1 – 100 mM for Pb) were buffered by addition of appropriate concentrations of NaClO₄, while pH values (2.0 – 9.5 for Cd; 2.0 – 8.0 for Pb) were adjusted using ≤ 1.0 M NaOH or HNO₃. The pH adjustment altered the ionic strength of the suspension (though addition of H⁺ or Na⁺ ions) by as much as 10 mM, particularly for low pH systems. MLGO-free control experiments across the experimental pH range indicated considerable loss of Pb from solutions above pH 8.0, likely due to Pb-hydroxide precipitation and subsequent filter losses. Hence, batch Pb sorption analyses were limited to pH conditions below 8.0. Final Cd and Pb concentrations were achieved by adding appropriate quantities of a parent metal stock solution consisting of pH-neutralized inductively coupled plasma optical

emission spectroscopy (ICP-OES) standards [$\text{Cd}(\text{NO}_3)_2$ or $\text{Pb}(\text{NO}_3)_2$ dissolved in 5% HNO_3]. Starting with freshly-prepared parent MLGO and metal solutions, we conducted two replicate batch studies for each ionic strength treatment.

Exposure of the dissolved metal to the MLGO particles occurred for at least 4 hours, as kinetic studies associated with similar batch metal sorption studies indicated a sorption steady state occurs within this length of time. After the equilibration period, a final pH was measured and the MLGO particles were removed from suspension by centrifugation ($4000 \times g$ for 5 minutes) and filtration of the supernatant through $0.2 \mu\text{m}$ PTFE syringe filters. The resulting solutions were acidified and analyzed via ICP-OES (Optima 2000DV, Perkin-Elmer, Waltham, MA) against aqueous metal standards diluted into the same matrix utilized during the sorption experiments. Using an approach identical to the one presented above, we also conducted batch Cd sorption experiments for SLGO nanosheets suspended in either 1 mM or 100 mM solutions of NaClO_4 to buffer ionic strength.

2.3 XAS Measurements

Complete details regarding the extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) experiments are provided in SM Section S.2. The Cd- and Pb-sorbed MLGO materials used for EXAFS and XANES measurements were obtained from batch metal sorption experiments similar to those described above. Briefly, a 500 mL solution of 420 mg L^{-1} MLGO particles was adjusted to an ionic strength of 100 mM using NaClO_4 and exposed to 6.5 ppm Cd [$5.5 \times 10^{-5} \text{ M}$ as $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$] or 10 ppm Pb [$4.8 \times 10^{-5} \text{ M}$ as $\text{Pb}(\text{NO}_3)_2$] via end-over-end rotation or stirring for at least 4 hours. pH values were continuously maintained at pH 4.9, 6.4, and 8.1 in Cd systems and pH 4.9, 6.0, and 6.8, and 8.3

in Pb systems using NaOH. After equilibration, samples were centrifuged at $4000 \times g$ for 10 minutes and the supernatants were discarded. The resulting hydrated pastes were transferred to Teflon cells, sealed with adhesive Kapton tape, and stored until analysis. Solid (Pb/Cd-oxides) and solution (dissolved acetate, nitrate, and/or perchlorate salts) standards were also prepared and mounted using the procedures outlined in SM Section S.2.

Pb L(III) edge and Cd K-edge XAS measurements were performed at the Materials Research Collaborative Access Team (MR-CAT) sector 10-ID [24] and sector 10-BM [25] beam lines located at the Advanced Photon Source of Argonne National Laboratory (USA). All samples were measured at room temperature, with powder standards measured in transmission mode and solution standards and experimental samples measured in fluorescence mode. Data analysis involved the UWXAFS/FEFFIT package (SM Section S.2). As applied in this study, the EXAFS and XANES measurements assisted in determining the stoichiometry of Pb- and Cd-MLGO complexation reactions and establishing whether inner- or outer-sphere binding mechanisms dominate metal-MLGO interactions.

3. RESULTS

3.1 Potentiometric Titrations of MLGO Particles

The concentration-normalized forward and reverse potentiometric titrations for a representative MLGO treatment are depicted in Figure 1a. Forward and reverse (when present) titrations generally overlapped illustrating that proton sorption onto MLGO particles is rapid and reversible. In order to compare the curves from different replicates and treatments on the same scale without regard to initial protonation state (see details in SM Section S.3), each replicate titration curve was normalized to its own negative-mean value over the pH range evaluated and

curves from identical treatments were subsequently averaged (Figure 1b). Variability between replicates (as indicated by the 1σ error bars) within a given ionic strength treatment is relatively low and approximately equivalent to the differences observed between ionic strength treatments. Similarities in the normalized titration curves depicted in Figure 1b suggest that protonation reactions at the MLGO surface are only nominally influenced by ionic strength. Still, we do evaluate the potential influence of ionic strength on the titration results in Section 4.2.1 using electrostatic surface complexation models.

3.2 Batch Metal Sorption of MLGO Particles

Respectively, Figure 2 and Figure 3 illustrate the sorption of Cd and Pb onto MLGO particles across a range of pH and ionic strength conditions, while SM Section S.4 provides additional details regarding the sorption behaviors of each metal as a function of ionic strength. For both Cd and Pb, the sorption edges for each ionic strength treatment contain two replicates, which largely overlap and are therefore not distinguished in these figures. In each system, MLGO particles exhibit a significant capacity to sorb Cd and Pb across a wide range of pH values. However, in marked contrast to the proton sorption/desorption experiments, batch metal sorption experiments for both Cd and Pb illustrate that ionic strength dramatically influences the sorption of these metals onto MLGO particles. For example, the point at which 50% of the initial Cd concentration is sorbed by MLGO particles shifts from pH ~3 to pH ~6.7 in the 1 mM and 300 mM ionic strength systems, respectively (Figure 2). Similarly, 50% of the initial Pb concentration is sorbed to MLGO particles at pH ~3.5 in the 1 mM ionic strength systems and at pH ~5.3 in the 100 mM ionic strength systems (Figure 3).

3.3 XAS Measurements

XAS analysis suggests that the dominant mechanism for Pb-MLGO binding varies as a function of pH. The presence of isosbestic points in the XANES region (Figure 4a) indicates that the reaction stoichiometry remains constant, with a probable mixture of two species that change in ratio as a function of pH [26]. Comparison with Pb^{2+} standard indicates that at least one of these species is likely Pb sorbed to the surface via an outer-sphere bond (Figure 4a). As discussed below, the EXAFS analysis for the Pb-MLGO complexes (Figure 4b) suggests a mixture of outer-sphere and monodentate inner-sphere binding, with outer-sphere binding dominating at low pH and inner-sphere binding becoming more prevalent at high pH. A similar transition in metal binding mechanisms associated with increasing pH has been observed in systems containing aluminum oxide [27], diatomite [28, 29], and titanate nanotubes [30].

The aqueous standard compounds were used extensively to characterize the Pb-bearing systems because there were a limited number of free parameters. The details for the EXAFS standards are provided in SM Section S.5. The multi-dentate aqueous Pb standards (acetate and EDTA) include a shorter first shell Pb-O bond distance than the first shell Pb-O bond in the hydrated aqueous Pb ion. The shorter inner sphere Pb-O bonds are accompanied by a second shell C/N bond, with contributions from each of these indicated by the arrows in Figure 4b (EXAFS is unable to determine the difference between the C and N in the EDTA structure). The real part of the Fourier-transformed EXAFS data of the Pb-MLGO complexes in Figure 4b show an increasing amount of inner sphere Pb-O bonds with increasing pH. In conjunction, there is an amplitude reduction trend with pH that appears at about 2.2 Å and corresponds to increased interference due to a Pb-C bond, with a higher contribution from Pb-C leading to a reduced overall amplitude. As modeled by the standards, three separate paths (short O, long O and C)

were used in the Pb-MLGO fitting. The Debye-Waller factors for each path and the third cumulant for the long Pb-O path were held fixed according to their values from the standards.

The fits for the Pb-MLGO systems, provided in Table 1, show that the Pb^{2+} ions are attached to the MLGO surface mainly by an electrostatic attraction at low pH and mainly by a monodentate bond at high pH. For this fit, the distances for each bond (short O for inner sphere, long O for outer sphere, and C for inner sphere) were constrained to be the same, with the Debye-Waller factors fixed for each path. The lowest pH value fit best without any inner sphere contributions, and as the pH increased, the contribution from the inner sphere oxygen and carbon increased in importance. The bond length between Pb and C varies in the standards depending on the type of bond (mono- vs. multi-dentate), with the multi-dentate bonding having a shorter (2.9 – 3.0 Å) distance than the mono-dentate bond (3.1 – 3.25 Å). Because the fitting places the Pb-C bond length at 3.20 ± 0.04 Å, this would indicate a mono-dentate bond is the prevalent mode of sorption at high pH values. In addition, the maximum number of Pb-C bonds remains less than one, even at the highest pH value measured where inner sphere sorption dominates, indicating that the Pb is attached to the surface via a single site. Overall, the Pb:site ratio for the MLGO surface is 1:1.

In contrast to the Pb-MLGO treatments, the Cd-MLGO systems shows only subtle differences in both the XANES and the EXAFS regions, which likely indicates a single mode of sorption. The XANES data for the aqueous standards matches that of the Cd-MLGO complexes, but differs for the solid powder standard shown in Figure 5a. The EXAFS analysis indicates that the single mode of sorption is outer sphere sorption. Figure 5b shows the similarities between the Cd-MLGO data and the hydrated Cd^{2+} standard. The aqueous standards, detailed in SM Section S.5, show that the first shell oxygen parameters are nearly identical across all standards.

The second shell for carbon (where relevant) shows that the bidentate inner sphere bond (Cd-acetate) has a shorter bond length (3.00 ± 0.04 Å) than the monodentate inner sphere bond (Cd-EDTA) Cd-C bond length (3.20 ± 0.05 Å). As such, the second shell analysis will be critical to determine the binding mechanism of the Cd. Analysis of the data is given in Table 2, including only the first shell oxygen. Inclusion of a carbon path in the Cd-MLGO fitting leads to worse values for reduced X^2 and R-factors, indicating that the best fit includes only the oxygen path. This means that the primary binding mechanism for Cd to the MLGO surface is outer sphere sorption. Thus, each Cd is associated with a single site on the MLGO surface.

4. DISCUSSION

4.1 Influence of pH and Ionic Strength on Proton and Metal Sorption

The potentiometric titration data indicate that MLGO particles exhibit a large buffering capacity throughout the experimental pH range and this capacity is only nominally influenced by ionic strength. Contrary to our findings, Szabó et al. [4] observed an increase in the buffering capacity of graphite oxide when ionic strength increased from 5 mM to 500 mM (using NaCl as the background electrolyte). However, Szabó et al. only presented one titration for each ionic strength considered and did not provide information regarding the variability of replicates within a given ionic strength treatment and/or the magnitude of these values in relation to the measured differences in the buffering capacity. Other studies have provided potentiometric titration results for different forms of GO at one ionic strength [18, 20, 31]. To our knowledge, this study is one of the first to quantify the variability in the buffering capacity of MLGO particles for multiple replicates at different ionic strength values.

The results of the batch metal sorption experiments indicate that MLGO particles also exhibit a striking capacity to sorb metals, particularly at moderate to high pH values. The relatively low sorption of metals at low pH is attributed the presence of greater numbers of protonated sorption sites, while sorption extents increase at higher pH values as sorption sites deprotonate. However, in contrast to our titration results, the batch metal sorption data suggest that ionic strength substantially impacts the interactions between Cd/Pb and the MLGO surface sites. The influence of ionic strength on metal sorption is particularly pronounced at relatively low to moderate pH values, where our XAS measurements indicate that outer-sphere sorption mechanisms dominate metal-MLGO interactions. The decrease in metal sorption extents with increasing ionic strength likely results from a compression of the electric double layer at the MLGO surface, which effectively diminishes the reach of the attractive charge for metal ions from each MLGO particle.

Our metal sorption results are in marked contrast with those of Zhao et al. [18, 19] who observed that the sorption of Cd(II) and Pb(II) onto few-layered GO (FLGO) was only negligibly influenced by ionic strength. While the direct comparison of sorption extents between studies is complicated by differing pH ranges and sorbent:sorbate ratios, the difference in behavior is significant and may have resulted from slight disparities in synthesis procedures. For example, the procedure utilized by Zhao et al. exposed the bulk graphite to an identical oxidizing solution, relative to our own, but over a significantly longer period of time. An extended oxidation period can change the overall extent of graphene oxidation [7], resulting in a distinctive collection or ratio of discrete surface site types, which could respond differently to changes in ionic strength.

We also tested the hypothesis that differences in GO exfoliation extents could explain the distinction between the metal sorption behaviors we observed and those from previous studies.

Under this theory, metals in MLGO-bearing systems would not have access to interlayer sorption sites and these basal groups would be differentially-influenced by ionic strength, relative to the edge groups. This effect could result from differences in the chemical identity of the basal and edge sorption sites or from the relationship between the Debye length for a given ionic strength and the interlayer spacing of an MLGO particle. Hence, we conducted internally-consistent Cd batch experiments using SLGO nanosheets and found that the sorption extents were nearly identical to those for MLGO particles in both the 1 mM and 100 mM ionic strength treatments (SM Section S.6). Our data suggest that functional groups present within the interlayers of the MLGO particles are likely accessible to metal sorption, although these data could also indicate that metal-active functional groups on both MLGO and SLGO surfaces are predominantly located on the edges of each material.

4.2 Chemical Equilibrium Modeling

4.2.1 Traditional Surface Complexation Modeling Approaches

Collectively, the potentiometric titrations and batch metal sorption experiments illustrate a dramatic and unexpected difference in sorption behaviors for protons and metals at the MLGO particle surface. While the titration data indicate very little influence of ionic strength on MLGO buffering, the batch metal sorption data suggest that ionic strength substantially impacts the interactions between Cd/Pb and the MLGO surface. Hence, we evaluated several traditional surface complexation modeling approaches, including 1- to 5-site non-electrostatic models (NEM), constant capacitance models (CCM), and diffuse layer models (DLM), for their abilities to account for the variation in proton and metal sorption behaviors as a function of ionic strength (SM Section S.7). The two electrostatic sorption models tested in this study, namely the CCM

and DLM, have been successfully employed in previous studies to account for the influence of ionic strength on proton and metal sorption at environmental surfaces (see reviews by Goldberg [32] and Koretsky [23]). Using the chemical equilibrium modeling program FITEQL 2.0 [33], we applied the evaluated models to the potentiometric titration data to obtain both pK_a values and individual site concentrations for each of the discrete types of functional groups present on the MLGO surface and active in the pH range of this study. Because different functional groups have distinct pK_a values, our metal sorption measurements conducted as a function of pH then place constraints on which sites are involved in the metal sorption reactions and the modeling of these data results in calculated K_{ads} values for each important metal-MLGO sorption reaction.

We evaluated the success of an individual model using its visual fit to the experimental data and its FITEQL-generated goodness-of-fit or variance value, $V(Y)$ (SM Section S.7). The optimal $V(Y)$ value is 1.0, although experimental evidence suggests that values between 0.1 and 20 are common for reasonably good model fits [33]. As importantly, we also defined a successful model as one that yields calculated equilibrium constant (pK_a and K_{ads}) values from the experimental data that do not show a consistent trend with changes in ionic strength. Consistency in these equilibrium constants across ionic strength indicates that the model alone adequately accounts for the electrostatic effects occurring at the MLGO surface and that single values for the pK_a or K_{ads} could be utilized to model the sorption of protons and metals, respectively, throughout a range of environmental conditions.

The methods and findings for the traditional surface complexation modeling approaches are thoroughly discussed in SM Section S.7. In summary, each of these approaches yielded calculated equilibrium constants from the experimental data that significantly vary as a function of ionic strength, indicating that these models are not capable of accurately representing

electrostatic effects at the MLGO surfaces. Hence, we instead devised and tested a non-traditional model that accounts for ionic strength effects as a competition between Na from the background electrolyte and Cd/Pb for available MLGO surface sites, as described below.

4.2.2 Modeling the Competitive Interactions between Protons, Cd/Pb, and Na

The traditional modeling approaches tested above implicitly assume the absence of site-specific complexation reactions between the surface being modeled and the background electrolyte [34]. However, Alessi et al. [35] illustrated that the influence of ionic strength on metal-surface complexation can be considered a competition for available sorption sites between the divalent cation of interest and the monovalent cations present in the background electrolyte. We tested whether the observed ionic strength effects for Cd/Pb sorption can be modeled by invoking a similar approach and explicitly accounted for the competitive interactions between protons, Cd/Pb, and Na at available binding sites on the MLGO surface. We assumed that the Na-MLGO interaction is an intrinsic property that can occur in the presence or absence of metals, and as such, we must also consider the effect of Na competition on MLGO protonation reactions, even though we did not see a strong ionic strength effect in our potentiometric titration data. By assuming the same affinities for Na-MLGO interaction in the modeling of both the titration and metal sorption data, we can calculate a suite of equilibrium constants that account for the observed sorption behaviors under all of the conditions studied here.

We utilized a traditional 4-site NEM as the base model for this investigation (SM Section S.7.2) and supplemented it with the Na-MLGO interactions described above. The NEM defines the complexation reactions between the protons (H^+) or metals (M^{2+}) and the MLGO surface using the following chemical reactions:

and

where L_i is assumed to be the discrete surface functional group type (or ensemble of functional group types with chemically-indistinguishable sorption behaviors) at which a surface complexation reaction occurs and $MLGO-$ represents the remainder of the MLGO particle to which the functional group is attached. We note that all sites are designated herein by number in order of increasing pK_a value. We assume surface sites are not capable of being doubly-protonated and also assume a 1:1 stoichiometry between MLGO surface sites and the target metals based on the results of our XAS measurements (Section 3.3). In each model, FITEQL uses the measured extents of proton and metal sorption to constrain acidity constants (K_a) for Reaction 1 and metal-surface stability constants (K_{ads}) for Reaction 2. Respectively, these equilibrium constants are given by the following equations:

$$K_{a(i)} = \frac{[MLGO-L_i^-] * a_{H^+}}{[MLGO-L_iH^0]} \quad (3)$$

and

$$K_{ads(i)} = \frac{[MLGO-L_iM^+]}{[MLGO-L_i^-] * a_{M^{2+}}} \quad (4)$$

where brackets represent the molal concentration of surface species, and a_x represents the activity of the species in the associated subscript. FITEQL uses the Davies equation to calculate activity coefficients for aqueous ions. The pH values utilized in this model are the final equilibrium pH values from a given sorption measurement.

Additional model inputs include a complete system of equations for each experimental treatment that accounts for all possible aqueous complexation reactions (SM Table S.3) and the known equilibrium constants for these reactions [36]. As mentioned previously, a traditional NEM approach would not include an interaction between the background electrolyte (Na) and the MLGO surface in this system of equations. However, in our modeling, we explicitly use the influence of Na-MLGO surface interactions as a proxy for electrostatic effects on the potentiometric titration and batch metal sorption results. Hence, we incorporate into the system of equations the following reaction:

Because the potentiometric titration data do not exhibit a significant or consistent trend with respect to ionic strength, we cannot use these data to constrain an optimal value for the Log K_{ads} for Reaction 5 (herein denoted as Log K_{Na-ads}) at each surface site. Rather, our approach is to assume a value for Log K_{Na-ads} that is applicable to all of the surface sites and to find the value that yields the best fit to both the potentiometric titration and the Cd/Pb sorption data. We begin by testing Log K_{Na-ads} values between 0.5 and 2.0 at 0.5-step intervals. By using the same Log K_{Na-ads} value for each site, we are applying the interaction of the background electrolyte uniformly amongst all sites, rather than allowing a different degree of influence at each specific

site type. We propose that this approach is more consistent with the way that traditional electrostatic models integrate the influence of ionic strength across a surface. In addition to the above approach, for comparison we also model our potentiometric titration and metal sorption data without incorporating Reaction 5.

4.2.3 Potentiometric Titration Modeling with Na-Binding

Using our Na-binding approach, we calculated site concentrations and pK_a values for Site 1 through Site 4 for each experimental replicate based on an assumed fixed value of $\text{Log } K_{Na-ads}$ (SM Table S.6). In general, for any given site, pK_a values increase with increasing values of $\text{Log } K_{Na-ads}$ (Figure 6) indicating that for a model to attain the same buffering capacity despite the competition with Na at surface sites, the affinity for protons at the MLGO surface must increase. As previously stated, we define a successful model with an optimal value of $\text{Log } K_{Na-ads}$ as one that would show minimal ionic strength dependence to the calculated pK_a values. We evaluated the ionic strength dependence of each model by calculating a difference or residual between each ionic strength-specific pK_a value and the average pK_a value across all ionic strengths for a given site (i.e., the horizontal lines in Figure 6). We observed from our data that as $\text{Log } K_{Na-ads}$ increases, the calculated ionic strength-specific pK_a values at all surface sites begin to show a trend with respect to ionic strength and the sum of the squared residuals (SSR) across all sites for a given $\text{Log } K_{Na-ads}$ model increases (Figure 7).

These data clearly indicate that as the assumed $\text{Log } K_{Na-ads}$ value incorporated into our potentiometric titration modeling increases, our ability to obtain a successful model of the titration data by our definition becomes increasingly compromised. However, for $\text{Log } K_{Na-ads}$ values up to 1.0, much of the variation in pK_a values that contributes to the increasing SSR is

concentrated in the residuals for Site 1 and Site 2 (SM Figure S.5) and we discern only a moderate degree of overall trend in these pK_a values with respect to ionic strength. In addition to pK_a values, the potentiometric titration modeling yields calculated site concentrations and $V(Y)$ values. Neither of these model parameters change in response to incorporation of Reaction 5 into the system of equations (SM Table S.6). The total proton-active site concentration for MLGO particles, averaged across all of the ionic strength treatments, is 2.8×10^{-3} mol sites g^{-1} . Hence, the value of $\text{Log } K_{Na-ads}$ does not affect the ability of the each model to fit an individual titration replicate, but to do so the pK_a value must increase as $\text{Log } K_{Na-ads}$ increases.

4.2.4 Metal Sorption Modeling with Na-Binding

We modeled Cd/Pb sorption by expressing the formation of a generic metal-MLGO surface complex (Reaction 2) and calculating its associated stability constant (Equation 4) while including the Na-binding reaction (Reaction 5) in the respective systems of equations. The average surface site concentrations and the pK_a values for each protonation/deprotonation reaction used in this metal sorption modeling were obtained from the results of the potentiometric titration models that utilized the same $\text{Log } K_{Na-ads}$ value (SM Table S.6). Because we observed extensive sorption of both Cd and Pb below pH 5, where we presume only Site 1 is deprotonated, each surface complexation model that we tested involved metal sorption onto the deprotonated form of Site 1. This was our only modeling restriction, and we tested all possible combinations of sites as long as metal binding onto Site 1 was included. In our modeling of the Cd systems, we allowed only the Cd^{2+} ion to sorb to the MLGO surface, as MLGO-free Cd speciation modeling indicates that $CdOH^+$ is a minor (<15%) component of these systems below pH 9.5 (SM Figure S.6). However, due to the substantial presence of $PbOH^+$ above pH ~7.0

(SM Figure S.7), we evaluated the potential interactions between PbOH^+ and the MLGO surface at Site 2 through Site 4.

Surface site combinations that converged on stability constant values for either Cd- or Pb-MLGO surface complexation reactions are provided in SM Table S.7 and SM Table S.8, respectively. For each site combination evaluated, increasing values of $\text{Log } K_{\text{Na-ads}}$ caused an increase in the calculated stability constant for the Cd- or Pb-MLGO surface complexes because in order for the model to fit the observed concentrations of sorbed Cd/Pb when considering Na competition, a greater affinity between the metal and the site is needed. We defined a successful metal sorption model with an optimal value of $\text{Log } K_{\text{Na-ads}}$ in a very different manner than the previously-discussed titration modeling evaluation. Here, for each value of $\text{Log } K_{\text{Na-ads}}$ that we tested, we calculated an average stability constant value from the ionic strength dependent stability constants for each metal sorption model. These average stability constants were then used to predict the metal sorption behaviors that would be consistent with each model in each ionic strength treatment. We then calculated the residuals between these model predictions and the actual data, and summed the squares of the residuals (SSR) for each experimental point across all ionic strengths. Hence, the calculation of the SSR for the metal sorption modeling yields an overall measure of the goodness-of-fit for a specific model to our measured metal sorption data from each pH and ionic strength condition, rather than measuring the variation in the equilibrium constant value with respect to ionic strength (as done for the titration modeling). In general, our findings indicate that within a given site combination, the models with the largest $\text{Log } K_{\text{Na-ads}}$ values best predicted the observed metal sorption behaviors across all ionic strengths (SM Table S.7; SM Table S.8).

4.2.5 Selection of a Model for Proton and Metal Sorption onto MLGO Particles

Our goal with this modeling effort was to converge on a set of equilibrium constant values that describe the interactions between MLGO surfaces and protons (K_a), target metals (K_{ads}), and Na (K_{Na-ads}). We defined a successful model as one that would yield a consistent set of calculated equilibrium constants that simultaneously accounts for the measured extents of proton and metal sorption across a range of pH and ionic strength conditions. However, our data define two conflicting trends. Models with the smallest Log K_{Na-ads} values yielded the least variation in calculated pK_a values across ionic strength at each site, but also yielded the poorest fits to the metal sorption data. Conversely, models with the highest Log K_{Na-ads} values yielded the most variation in calculated pK_a values across ionic strength at each site, but yielded the best fits to the metal sorption data.

Here we attempt to balance these two effects and select a model that exhibits a reasonable adherence to the criteria presented above. Because the SSR values from the titration and metal sorption modeling describe substantially different properties of the model outputs, we cannot simply combine these parameters to estimate an overall model fit. Instead, we use a two-step approach for selecting the model that best fits both the potentiometric titration data and the Cd/Pb sorption data. First we consider the potentiometric titration modeling, as this establishes the pK_a values that are used as a fundamental input for subsequent metal sorption models. Figure 7 indicates that SSR values for the titration modeling increase exponentially with increases in the value of Log K_{Na-ads} , resulting in a marked change in the rate of increase for SSR values above Log $K_{Na-ads} = 1.0$. We previously observed that, for Log K_{Na-ads} up to 1.0, only a moderate degree of overall trend in the calculated pK_a values occurs with respect to ionic strength, with much of the variation in pK_a values concentrated in Site 1 and Site 2 (SM Figure

S.5). Knowing that we must maximize the $\text{Log } K_{\text{Na-ads}}$ value to best fit the metal sorption data, we believe that a maximum value of $\text{Log } K_{\text{Na-ads}}$ of 1.0 still provides reasonable adherence to the titration modeling criteria.

Selection of this model results in calculated mean pK_a values ($\pm 1\sigma$) for Site 1 through Site 4 of 4.55 (± 0.91), 6.52 (± 0.49), 8.48 (± 0.21), and 9.98 (± 0.21), respectively (Table 3). In order to assign an identity to each of the MLGO surface sites, spectroscopic studies are required. However, by comparing the pK_a values determined via titration to typical protonation constants for functional group types, we can infer that the sites with pK_a values of between 4.0 and 6.0 are likely associated with short-chained carboxylic acids, while pK_a values of between 9.0 and 11.0 may be hydroxyl/phenolic acid groups. Using this assumption, the most abundant functional group (Site 4; SM Table S.6) would be a hydroxyl group, which is consistent with GO structural models that indicate a dominant hydroxyl presence at the GO surface [6-8]. In addition, Konkena and Vasudevan [37] combined titration experiments and infrared spectroscopy of GO samples to designate surface-associated functional groups with pK_a values of 4.3 and 6.6 as carboxyl groups and pK_a values of 9.8 as phenolic groups.

Next, because we previously defined a $\text{Log } K_{\text{Na-ads}}$ value of 1.0 as the maximum value that can still adhere to the titration modeling criteria, and because we know we must maximize the $\text{Log } K_{\text{Na-ads}}$ value to best fit the metal sorption data, we evaluate only the metal sorption models that incorporate a value of $\text{Log } K_{\text{Na-ads}} = 1.0$. Of these models, SSR values associated with the metal sorption data are minimized for the models that involve the binding of Cd^{2+} at Sites 1, 2, and 4 (SM Table S.7) and the binding of Pb^{2+} at Site 1 and PbOH^+ at Site 2 (SM Table S.8). We note that the Cd models that involve sorption of Cd^{2+} to Sites 1, 2, and 3 did not converge, which may indicate that, relative to Site 3, the abundance or structural placement of

Site 4 could contribute to its selective sorption of metals. In addition, the SSR value for the Pb model that involves Pb^{2+} sorbing to Site 1 and PbOH^+ sorbing to Site 3 is nearly identical to the selected Pb model. In general, several models resulted in similar fits, which illustrates the need for complimentary spectroscopic studies.

Table 3 provides calculated stability constants for these reactions and illustrates that MLGO particles have a strong affinity for Cd and Pb. For example, Log K_{ads} values describing the complexation between Pb^{2+} and Cd^{2+} and deprotonated Site 1 of MLGO, previously suggested as a carboxyl group, are between two and three orders of magnitude larger than the corresponding stability constants for aqueous Pb^{2+} - and Cd^{2+} -acetate complexes [38]. However, the stability constant values for important metal-GO surface complexes calculated herein are generally comparable to those found in many other corresponding metal-bacteria and metal-mineral systems [39-41]. Hence, the exceptional sorptive capacity of MLGO is most likely a function of its very high surface site concentration, relative to other sorbents of similar size, rather than a higher affinity of each site for metal binding. In fact, the total proton-active site concentration of $2.8 \times 10^{-3} \text{ mol g}^{-1}$ calculated for MLGO via our NEM approach is approximately an order of magnitude higher than the NEM-calculated site concentrations for bacterial cell walls or quartz surfaces, and between 2.5 and 6 times higher than NEM-calculated site concentrations for hematite, goethite, muscovite, and clinocllore [19, 39, 42, 43].

Figure 2 and Figure 3 illustrate the predicted model fits from the selected model applied to the actual metal sorption data. The selected Pb model provides a reasonable fit to the experimental data through pH 8.0, with only small misfits for some pH values in each ionic strength treatment. Relative to the Pb model, the selected Cd model exhibits a greater degree of misfit to the actual sorption data. In particular, the Cd model underestimates the extents of

sorption in the 1 mM and 10 mM ionic strength treatments, while overestimating sorption extents between pH ~4 and pH ~7 in the 100 mM and 300 mM ionic strength treatments. However, after testing multiple models, we determined that these selected models best distribute the misfits between the potentiometric titration data and the various metal and ionic strength treatments.

5. CONCLUSIONS

Using potentiometric titrations and batch metal sorption experiments, these studies illustrate that the binding behaviors of protons and metals onto MLGO surfaces are not similarly influenced by ionic strength. Titration data exhibit no consistent or significant trend as a function of ionic strength, suggesting that electric field effects on the protonation behavior are minimal. Conversely, we observed a large effect of ionic strength on the extents of Cd/Pb sorption across a range of pH conditions, which suggests that electrolyte interactions with the metal binding sites are not negligible. This disparity creates a significant challenge for traditional models of surface complexation. Hence, we derived a Na-binding model that accounts for the observed ionic strength effects while yielding a reasonable fit to both the titration and metal sorption data sets. Using a non-traditional surface complexation modeling approach, we calculated MLGO site concentrations and pK_a values, as well as $\text{Log } K_{ads}$ values for the important metal-GO surface complexes. This approach suggests that MLGO can be a highly efficient environmental sorbent, but that both protons and metals may compete with Na from the background electrolyte for sorption sites.

The observed difference in proton and metal sorption with respect to changes in ionic strength is not typical and suggests that the mechanisms associated with proton and metal binding at MLGO particle surfaces are quite different. It is possible that protons and metals bind

to sorption sites with different identities that are unequally influenced by ionic strength, but our data illustrate that this differential binding cannot simply be attributed to differential access to binding sites based on structural placement. In fact, we observed that sorption extents are not impacted by the degree of GO exfoliation, which suggests that both protons and metals have access to the same basal- and edge-associated functional groups. Instead, we hypothesize that the functional groups involved with proton and metal binding have a differing affinity for each sorbate, such that protons tend to sorb covalently to these sites, while metals tend to form outer-sphere complexes, at least at relatively low to moderate pH values. As the particle surface becomes more electronegative with increases in pH, metals too could then form covalent inner-sphere bonds with these sites, as suggested by our XAS studies. While the difference between proton and metal binding behaviors is generally inconsistent with typical sorption patterns for carboxyl and hydroxyl functional groups, little is known about the interaction between protons/metals and the ketone or epoxide groups present on the MLGO surfaces. We are currently devising and conducting additional sorption and spectroscopic experiments to further our understanding of these mechanisms.

The data presented herein suggest that MLGO particles, which settle from suspension much faster than SLGO nanosheets, could dominate metal budgets in natural and engineered geochemical systems, and may offer higher removal efficiencies in contaminated environments than sorption approaches using other materials. As a result, MGLO particles offer significant potential for water treatment and remediation applications. The surface complexation modeling parameters that we determine in this study enable extrapolation of our experimental measurements to quantitatively estimate metal budgets in GO-bearing systems throughout a range of environmentally-relevant conditions.

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Table 1

Fitting Results from the EXAFS Data for Pb-MLGO.

pH	N-O-IS	R-O-IS (Å)	N-O-OS	R-O-OS(Å)	N-C-IS	R-C-IS (Å)
4.9	1.0 ± 0.3	2.29 ± 0.01	10.3 ± 0.4	2.48 ± 0.02	---	3.20 ± 0.04
6	1.5 ± 0.4	2.29 ± 0.01	8.7 ± 0.7	2.48 ± 0.02	0.4 ± 0.9	3.20 ± 0.04
6.8	1.9 ± 0.3	2.29 ± 0.01	6.8 ± 0.8	2.48 ± 0.02	0.8 ± 0.8	3.20 ± 0.04
8.3	2.7 ± 0.2	2.29 ± 0.01	3.2 ± 0.6	2.48 ± 0.02	0.7 ± 0.5	3.20 ± 0.04

Notes:

- N = coordination number; R = distance from central scatterer; OS = outer sphere; and IS = inner sphere.
- Distances for each path were constrained to be the same and Debye-Waller factors were fixed to the best fit from standards ($\sigma^2=0.010 \text{ Å}^2$ for O-IS, $\sigma^2=0.028 \text{ Å}^2$ for O-OS and $\sigma^2=0.008 \text{ Å}^2$ for C-IS).
- All fits had R-factors below 0.02, indicating a good fit.

Table 2

Fitting Results from the EXAFS Data for Cd-MLGO.

pH	N-O	R (Å)	σ^2 (Å²)	R-factor
4.9	7.0 ± 0.7	2.29 ± 0.01	0.012 ± 0.002	0.0129
6.4	6.9 ± 0.8	2.28 ± 0.01	0.012 ± 0.002	0.0145
8.1	6.9 ± 0.8	2.28 ± 0.01	0.012 ± 0.002	0.0097

Notes:

- N-O = coordination number of oxygen; R = distance from central scatterer; σ^2 = Debye-Waller factor.
- R-factor is a goodness of fit parameter, with values below 0.02 indicating a good fit.

Table 3Equilibrium Constants Calculated by the Selected Model^a

for the Designated Surface Sorption Reactions

Reaction	Log K
<u>H: Site 1 through Site 4</u>	
$GO-L_1^- + H^+ \rightleftharpoons GO-L_1-H$	4.55 (± 0.91) ^c
$GO-L_2^- + H^+ \rightleftharpoons GO-L_2-H$	6.52 (± 0.49) ^c
$GO-L_3^- + H^+ \rightleftharpoons GO-L_3-H$	8.48 (± 0.21) ^c
$GO-L_4^- + H^+ \rightleftharpoons GO-L_4-H$	9.98 (± 0.21) ^c
<u>Pb: Site 1 & Site 2OH^b</u>	
$GO-L_1^- + Pb^{2+} \rightleftharpoons GO-L_1-Pb^+$	6.01 (5.60-6.40) ^d
$GO-L_2^- + PbOH^+ \rightleftharpoons GO-L_2-PbOH$	8.42 (8.11-8.81) ^d
<u>Cd: Site 1, Site 2, & Site 4</u>	
$GO-L_1^- + Cd^{2+} \rightleftharpoons GO-L_1-Cd^+$	5.03 (4.50-5.80) ^d
$GO-L_2^- + Cd^{2+} \rightleftharpoons GO-L_2-Cd^+$	4.44 (4.40-4.80) ^d
$GO-L_4^- + Cd^{2+} \rightleftharpoons GO-L_4-Cd^+$	6.81 (6.70-6.90) ^d

Footnotes:^a The selected model incorporates a $\text{Log } K_{Na-ads} = 1.0$ for Na-MLGO interactions.^b *Site 2OH* refers to the site combination from SM Table S.8 that includes $PbOH^+$ binding to Site 2.^c Uncertainty values are defined as the calculated standard deviations of the ionic strength specific pK_a values presented in Table S.6.^d Uncertainty ranges for each stability constant are defined as the range of values that encompass approximately 95% of all measured experimental data points presented in Figure 2 for Cd and Figure 3 for Pb.

Figure 1: (a) Concentration-normalized forward (filled) and reverse (open) potentiometric titrations for a representative $\sim 1 \text{ g L}^{-1}$ MLGO system suspended in a 100 mM ionic strength solution. Some data points have been removed for clarity. Note that reverse titrations were not obtained for 1 mM and 10 mM ionic strength treatments; and (b) Average potentiometric titration curves (and 1σ error bars) for between three and seven treatment replicates normalized to their own negative-mean value throughout the entire pH range. Collectively, these curves illustrate the relatively small influence of ionic strength on MLGO protonation behaviors.

Figure 2: Sorption of Cd (8.9×10^{-6} M) by MLGO (200 mg L^{-1}) as a function of both pH and ionic strength. Points are experimentally-measured data. The direct comparison of these data across ionic strength is illustrated in SM Figure S.3. Curves are sorption behaviors predicted by the selected non-electrostatic model that incorporates a $\text{Log } K_{\text{Na-ads}} = 1.0$ for Na-MLGO interactions and assumes the following site combination and equilibrium constants: Site 1- Cd^{2+} ($\text{Log } K_{\text{ads}} = 5.03$; $\text{pK}_a = 4.55$), Site 2- Cd^{2+} ($\text{Log } K_{\text{ads}} = 4.44$; $\text{pK}_a = 6.52$), and Site 4- Cd^{2+} ($\text{Log } K_{\text{ads}} = 6.81$; $\text{pK}_a = 9.98$). See Table 3 for further details regarding reactions. Note that the y-axis on each figure is %Cd sorbed.

Figure 3: Sorption of Pb (4.8×10^{-6} M) by MLGO particles (20 mg L^{-1}) as a function of both pH and ionic strength. Points are experimentally-measured data. The direct comparison of these data across ionic strength is illustrated in SM Figure S.4. Curves are sorption behaviors predicted by the selected non-electrostatic model that incorporates a $\text{Log } K_{\text{Na-ads}} = 1.0$ for Na-MLGO interactions and assumes the following site combination and equilibrium constants: Site 1-Pb²⁺ ($\text{Log } K_{\text{ads}} = 6.01$; $\text{pK}_a = 4.55$) and Site 2-PbOH⁺ ($\text{Log } K_{\text{ads}} = 8.42$; $\text{pK}_a = 6.52$). See Table 3 for further details regarding reactions. Note that the y-axis on each figure is %Pb sorbed.

Figure 4: XAS data for Pb-MLGO showing: (a) the near-edge (XANES) region with arrows indicating the isosbestic points; and (b) the extended fine structure (EXAFS) region with arrows indicating spectral features of inner vs. outer sphere contributions. The hydrated Pb ion modeling pure outer sphere adsorption is shown for comparison.

Figure 5: (Caption on the following page)

Figure 5: XAS data for Cd-MLGO showing: (a) the near-edge (XANES) region with the hydrated Cd ion representing the aqueous standards matching the data and the CdO powder representing a different signature typical of a precipitant; and (b) the extended fine structure (EXAFS) region with the hydrated Cd ion for comparison. Note that the samples at different pH values are nearly identical and show similar features to the hydrated Cd ion with slightly smaller amplitudes.

Figure 6: (Caption on the following page)

Figure 6: Calculated pK_a values for Site 1 through Site 4 as a function of ionic strength assuming: (a) no Na competition at the surface site; or (b) a $\text{Log } K_{\text{Na-ads}} = 2.0$. The horizontal line is the mean of the four ionic strength-specific pK_a values in each panel, while the red arrows provide example residuals. Note that the range and mean of the ionic strength-specific pK_a values increases after incorporating Na competition into the titration modeling. Identical plots for each site and $\text{Log } K_{\text{Na-ads}}$ value are provided in SM Figure S.5. Each point on these figures represents the mean pK_a value calculated from between three and seven potentiometric titration replicates for each ionic strength (Table S.6).

Figure 7: Sum of the squared residuals (SSR) between the site-specific pK_a values calculated for each ionic strength and the mean pK_a value across all ionic strengths for each site. These values are plotted as a function of $\text{Log } K_{\text{Na-ads}}$. See SM Figure S.5 for the complete data set from which these values are calculated.