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An integrated flow microcalorimetry, infrared spectroscopy and density functional theory approach to the study of chromate complexation on hematite and ferrihdyrite

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An approach to constructing comprehensive predictive models for contaminant interactions with mineral surfaces is to obtain multiples lines of evidence for surface properties and the types of complexes formed under different geochemical conditions. In this study, we used flow adsorption microcalorimetry (FAMC), attenuated total reflection infrared (ATR FTIR) spectroscopy, and density functional theory (DFT) calculations to study chromate complexation on ferrihydrite (FH) and hematite (HT). Under the experimental conditions used, chromate binds via an exothermic inner-sphere complexation on both surfaces, with similar enthalpy values that do not reveal dramatic differences in the sorption mechanism. Due to their underlying surface structure, FH favors more monodentate and HT more bidentate complexation. Chromate complexes were found by ATR and FAMC to be completely reversible, with substantially slower desorption compared to sorption. Both the FAMC and DFT indicated the presence of surface sites with different energetics, whereby lower surface coverages corresponded to higher enthalpies on both FH and HT. Both flow-based ATR and FAMC yielded different surface coverages than batch isotherms under the same conditions, highlighting the need to assess contaminant sorption under realistic conditions. Overall, this integrated approach proved to be an improved paradigm to study ion sorption on mineral surfaces.

1. Introduction

Our ability to predict the fate and transport of contaminants under real environmental conditions in iron oxides - dominated systems hinges on our ability to adequately model interfacial chemical reactions – protonation, exchange, adsorption, desorption, precipitation, redox, etc. The prerequisite to constructing versatile and comprehensive predictive models is acquiring mechanistic information about mineral surface reactivity. A promising approach to formulate complex surface complexation models (SCMs) is to obtain multiple lines of evidence for the types of surface complexes that a compound forms under different geochemical conditions. Various types of spectroscopy combined with predictions of density functional theory (DFT) calculations can be used to narrow down the surface complexation reactions and constrain the number of parameters needed to adequately describe adsorption. Ultimately, thermodynamic constants are obtained by fitting the model to data from traditional batch isotherms and there is typically no experimental evidence to support the obtained thermodynamics for the adsorption reactions.

Thorough thermodynamic studies have been conducted for ferrihydrite (Snow et al., 2013) and goethite, lepidocrocite and maghemite (Majzlan et al., 2003a, 2003b) but these have focused on measuring thermochemical properties, heat capacity and entropy in the context of formation and stability of bulk phases. The literature on energetics and enthalpies of adsorption and protonation surface reactions, especially those coming from direct measurements remain scarce despite the usefulness of thermodynamic data in linking molecular-level structure with macroscopic properties of surface reactivity. This utility can be attested for by attempts to develop theoretical predictions of protonation enthalpies (Sverjensky and Sahai 1998), and consistent models describing the thermodynamics of adsorption (Estes et al., 2013).

Accordingly, the goal of this study is to introduce an integrative approach to study surface reactions using a combination of three complementary techniques: attenuated total reflection infrared (ATR FTIR) spectroscopy, flow adsorption microcalorimetry (FAMC) and DFT calculations. While ATR and DFT have often been combined to study sorption reactions, FAMC has been utilized only as a stand-alone technique and for a limited number of systems (Kabengi et

al., 2006 a,b; Rhue et al., 2002; Gale et al., 2015). Ultimately, the integration of all three techniques can provide a deeper understanding of interfacial processes.

We have chosen chromate as a model contaminant and ferrihydrite (FH) and hematite (HT) as the surfaces to apply these techniques. Chromate sorption on FH and HT has been previously studied by the authors (Johnston and Chrysochoou 2012, 2014) and thus there is a strong baseline understanding of their interactions at the molecular level. However, there are only two published surface complexation model for chromate on FH (Dzombak and Morel 1990; Veselskáa et al., 2016), no published surface complexation model for HT and no studies on the energetics of chromate adsorption on any mineral. Given that chromate is clearly an important contaminant, present in 50% of the Superfund sites, as well as in Department of Energy and Defence sites, there is a clear need to produce improved models to predict its fate and transport. Finally, while a multitude of studies exist on the surface properties and behavior of goethite, there is substantially less information available for FH and even less for HT, even though both minerals are widespread in the environment.

2. Materials and methods

2.1. Mineral synthesis

Synthetic 2-line FH was prepared according to Schwertmann and Cornell (2000). Specifically, a 0.2 M $Fe(NO_3)_3 \cdot 9H_2O$ solution was titrated to pH 7.5 with 1 M KOH. The FH suspension was dialyzed for several days to remove excess electrolytes until the conductivity of the supernatant dropped to less than ~20 μS/cm. HT synthesis was performed according to Method 1 of Schwertmann and Cornell (2000). Briefly, 2 L of 0.002 M HNO_3 were heated to 98 °C and then 16.16 g of $Fe(NO_3)_3 \cdot 9H_2O$ crystals were added with vigorous stirring. The suspension was kept sealed in the oven for seven days at 98 °C and then also subjected to dialysis. Both FH and HT solutions were freeze dried for use in the microcalorimetry experiments, while the suspensions were used to deposit the films for the spectroscopy experiments. The concentration of the initial suspensions was estimated gravimetrically to 4.9 g/L for FH and 9.7 g/L for HT.

2.2. Sample characterization

X-ray diffraction (XRD) patterns were acquired on a Panalytical X-Pert Pro MPD, operating at 45 kV and 40 mA using CuKα radiation, a 1/4° programmable divergent slit, a 1/2° anti-scatter slit on the incident beam and a graphite monochromator filter on the diffracted beam. Samples were mounted on a low background holder and were scanned in the 2θ range 0 to 60° at 1°/min. Specific surface areas (SSAs) on air-dried and freeze dried samples were obtained from multipoint Brunauer-Emmet-Teller (BET) N_2 adsorption isotherms with a Quantochrome NovaWin surface area analyzer. Samples were outgassed prior to measurements for 3 h at 150 °C. A FEI Quanta 600 FEG scanning electron microscope (SEM) was used to study the general morphology and surfaces of the samples. Samples were fixed on an aluminum stub and sputter-coated with carbon paint to prevent electron build up on surfaces. High resolution transmission electron microscopy (HRTEM) characterization was carried out using a JEOL 2100F operating at 200 kV (JEOL, Ltd. Tokyo Japan). Samples were prepared by depositing 1–3 drops on a copper specimen grid coated with an ultrathin layer of carbon (Ted Pella, Inc.) and allowing the water to evaporate in a hood. Information on the sample elemental composition was collected using energy dispersive X-ray spectroscopy (EDS; Oxford detector). Additionally, electron diffraction patterns were captured from selected areas on the samples for crystallinity and mineral verification.

2.3. Calorimetric measurements

The flow adsorption microcalorimeter (FAMC) used in this study was custom-designed and fabricated in the Kabengi laboratory at Georgia State University. A description of the instrumentation and basic operation of the FAMC has been detailed previously (Rhue et al., 2002; Kabengi et al., 2006 a,b). An outline of the basic principles of experimental procedures is provided in the Supporting Information provided (Section 1 and Fig. SI-1).

The mechanisms of chromate sorption with the Fe-oxides surface was probed calorimetrically by 1) measuring the energetics of their respective interactions with the Fe-oxides at various surface loadings, and 2) measuring the surface positive charge before and after chromate exposure to probe any change to the charge-bearing surface hydroxyls functional groups from chromate complexation. This was done by using two anions, chloride (Cl^-) and nitrate (NO_3^-), that were previously reported to undergo a completely reversible outer-sphere ion exchange reaction on various Al- and Fe-oxides (Kabengi et al., 2006a,b, Harvey and Rhue 2008). Due to the congruence of their thermal signature in terms of reactions times, peak areas, and enthalpies of exchange on both FH and HT (See Fig. SI-2 for representative C/N and N/C thermal responses), they prove to be a calorimetric probe of the surface positive charge. The anions exchange cycles were obtained as described below.

Between 1 and 35 mg of the FH and HT sample was homogeneously packed inside the sample holder and equilibrated with a 0.05 M NaCl. The input solution was then switched to 0.05 M $NaNO_3$ resulting in an exothermic heat of NO_3^- replacing exchangeable Cl^- (N/C) on the surface. When the thermal signal returned to baseline, the input solution was reverted to 0.05 M NaCl and the resulting endothermic replacement of NO_3^- with Cl^- ions (C/N) recorded. This was repeated until the thermal signature of 3–5 replicates of each N/C and C/N was obtained. Similarly, several ion exchange cycles were recorded after the chromate exposure. Because these anions exchange cycles are inherently flow-through, time-based measurements, they also assess the reversibility of the chromate surface complexes and were also used as a mean to study chromate desorption.

The samples were exposed to chromate by changing the input solution from 0.05 M NaCl to one in which 5×10^{-4} M NaCl had been replaced with 5×10^{-4} M chromate, i.e. keeping the total concentration of Na at 0.05 M and ionic strength (I) constant. When the thermal signal returned to the initial baseline, indicating that the reaction between the surface and the chromate has come to completion, the input solution was reverted back to 0.05 M NaCl. The chromate complexation was also assessed as a function of surface coverage. For these experiments, FH and HT samples were incrementally loaded with chromate by injecting a known mass of chromate administered through a series of 1.8-ml injections of a 1×10^{-3} M chromate and 0.049 M NaCl solution. These experimental conditions were chosen based on results from preliminary tests conducted to ensure that an adsorption maximum would be reached (in a reasonable time frame) and an accurate mass balance was possible. During chromate injections and subsequent ion exchange cycles (when the experimental protocol required such cycles), effluent samples were collected for analysis. The amount of chromate retained at the surface was determined by a mass balance calculation between the total mass injected and the mass recovered from effluent samples, which were analyzed for chromate using EPA7196A. This information is necessary for the calculation of the integral molar enthalpy (ΔH_{ads}) obtained at thermal equilibrium or maximum obtainable coverage and differential sorption enthalpies (δH_{ads}) obtained as a function of incremental surface coverage, both in units of kJ/mol. All salts used in the microcalorimetry experiments were ACS certified and used as received. All solutions were prepared using ultra-pure water (>18.2 MΩ), were weakly buffered, in equilibrium with CO_2 in the atmosphere and had solution pH values of ~5.8 ± 0.2. All chromate solutions were carefully adjusted to pH of 5.8 ± 0.1 using dropwise addition of 6 M HCl. Analysis of