



Goethite surface reactivity: A macroscopic investigation unifying proton, chromate, carbonate, and lead(II) adsorption

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ARTICLE INFO

Article history:

Received 22 January 2008

Accepted 13 June 2008

Available online 14 July 2008

Keywords:

Goethite

Chromate

Surface saturation

Site density

Specific surface area

Site occupancy

Anion

Pb(II)

Adsorption

Surface charging

ABSTRACT

The goethite surface structure has been extensively studied, but no convincing quantitative description of its highly variable surface reactivity as inversely related to its specific surface area (SSA) has been found. The present study adds experimental evidence and provides a unified macroscopic explanation to this anomalous behavior from differences in average adsorption capacities, and not in average adsorption affinities. We investigated the chromate anion and lead(II) cation adsorption behavior onto three different goethites with SSA varying from 50 to 94 m²/g, and analyzed an extensive set of published anion adsorption and proton charging data for variable SSA goethites. Maximum chromate adsorption was found to occupy on average from 3.1 to 9.7 sites/nm², inversely related to SSA. Congruency of oxyanion and Pb(II) adsorption behavior based on fractional site occupancy using these values, and a site density analysis suggest that: (i) ion binding occurs to singly and doubly coordinated sites, (ii) proton binding occurs to singly and triply coordinated sites (ranging from 6.2 to 8 total sites/nm², in most cases), and (iii) a predominance of (210) and/or (010) faces explains the high reactivity of low SSA goethites. The results imply that the macroscopic goethite adsorption behavior may be predicted without a need to investigate extensive structural details of each specific goethite of interest.

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1. Introduction

The mineral solid–water interface plays a central role in regulating the concentrations of a large number of reactive elements in natural aqueous systems by influencing their biogeochemical cycles, and also in engineered aqueous systems such as those in water treatment technologies [1–3]. Models that describe the physicochemical processes that occur at this interface have reached a considerable level of development and sophistication in so-called “surface complexation models” (SCMs). Goethite is the most abundant iron oxide in nature [4], whose surface reactivity has been extensively studied and its synthetic preparations have served as references for the development of many of the SCMs noted above. Particularly, multisite complexation (MUSIC) models [5,6] have identified the participation to varying degrees of three differently coordinated oxygen-terminated groups at the surface of this mineral, namely singly, doubly, and triply coordinated oxygens to central Fe atoms, as well as specific distributions of different crystalline faces [5–11].

Notwithstanding all this theoretical development, it was recognized, early on, that goethite preparations of relatively large par-

ticle size [specific surface areas (SSA) below ca. 60 m²/g] showed a considerably higher surface reactivity toward protons when normalized to surface area [5,10–15], as well as toward carbonate [14], and higher adsorption capacities for anions such as phosphate [6] and fluoride [16–19]. This anomalous behavior presumably arises from morphological features of surface roughness that result from multidomain crystal formation [10,12,19,20], and that in turn do not translate to an increase in the BET measurement of SSA. However, there are no adequate explanations that relate it to quantitatively measurable surface structural features, and that would allow a generalized quantitative description of the goethite adsorption behavior.

Rustad and Felmy [21] found, through a molecular dynamics simulation study of goethite nanoparticles, a larger proton charging behavior at acute angles between crystal faces, than in other crystalline locations. They speculated that this behavior was caused by dielectric effects arising from an improved water solvation at such an asperity, favoring proton accumulation at these sites, and proposed that surface roughness present in larger particles may show such kind of behavior on a larger scale. Boily et al. [10] were able to simulate the enhanced experimental proton adsorption behavior of a 37 m²/g goethite preparation by increasing the Stern-layer capacitance, while maintaining a constant affinity for protons in a 1-pK MUSIC model formulation. Very recently, Lutzenkirchen

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et al. [15] successfully modeled a large series of proton charging data in different electrolytes for goethites with low SSA (25 to 40 m²/g) and high SSA (90 m²/g). They used simplified versions of MUSIC model formulations, and increased both the electrolyte binding constants 0.4–0.5 log unit and the Stern-layer capacitance to more than 0.1 unit difference for the low SSA goethites, while maintaining the total site density approximately constant for both types of goethites. However, the assumptions of higher capacitance and affinities, exclusively, are not consistent with the higher maximum adsorption capacities observed for phosphate [6] and for fluoride [16–19].

In another MUSIC modeling study, to be able to simulate the proton charging behavior of a 49 m²/g goethite preparation, Gaboriaud and Ehrhardt [11] were forced to empirically increase the value of the total reactive site density to almost twice (12 sites/nm²) the value of the one calculated theoretically (6.50 sites/nm²), while simultaneously increasing the Stern-layer capacitance from the one used for a 95 m²/g goethite. The theoretical calculation was performed through specific assumptions of crystal face contributions, obtained from interpretations of atomic force microscopy (AFM) images, which varied between the two different goethites used. In previous work [14,20] we found an inverse relationship between SSA and surface reactivity for protons and for carbonate, of three different goethite preparations (of 50, 70, and 94 m²/g). We showed that congruent carbonate adsorption behavior among goethites was possible by assuming fixed proportions of empirically obtained average site densities among them (in inverse relationship to SSA), after normalizing the data to molar fraction site occupancy.

Considering that few investigations have been conducted on surface reactivity of goethites with different SSA, the goals of the present work were (i) to ascertain via experimental data the hypothesis of a variable average reactive site density of goethite toward anions, as opposed to a variable average surface affinity, that would explain its variable surface reactivity; (ii) to investigate if an adsorption variability behavior exists as well toward a heavy metal cation [Pb(II)], and to compare it to the variability toward anions; and (iii) to propose, based on these and previous data, a unified macroscopic SCM-independent description of goethite surface reactivity toward protons, anions, and possibly metal cations.

2. Materials and methods

2.1. Preparation and calibration of reagents

Reagents used were analytical grade, and solutions and suspensions were prepared using high-purity ion-exchanged (nanopure, 17.5 Ω cm) water. When necessary, CO₂ content was minimized by previous boiling and maintaining under a nitrogen atmosphere. All aqueous reagents and experimental preparations were performed by gravimetric (not volumetric) measurements, using measured or reported densities of solutions used. Standard NaOH solutions were prepared from “carbonate-free Dilut-it” (J.T. Baker) solutions. Calculations of adsorbed concentrations were performed by subtracting the aqueous concentrations left after proper equilibration times, from the initial total concentrations added to the reactor systems.

2.2. Preparation and characterization of the goethite samples

All goethite preparations used in the present study were synthesized more than a decade ago at the Civil and Environmental Engineering Department, Stanford University, and characterized both then and again recently by X-ray diffraction (XRD), confirming their crystallographic identity and stability. All were prepared using the same procedure based on the method by Atkinson et

al. [22], in which a solution of Fe(NO₃)₃ is neutralized with excess NaOH until a pH of 12, while stirring and bubbling with N₂, followed by aging at 60 °C for 24 h, acid neutralization, and dialysis. The only difference between preparations was on the speed of initial NaOH solution addition: GOE94 (94 m²/g) was obtained with an addition rate close to 5 mL/min [23], GOE50 (50 m²/g) with a very quick NaOH addition (rate unmeasured) [24], and GOE70 (70 m²/g) with an intermediate rate (unmeasured) [25].

BET N₂ SSA measurements were performed at Stanford University at the time when the goethite preparations were synthesized, and again recently to detect any variation after 10+ years in suspension. The latter were performed at the George E. Brown Jr. Salinity Laboratory, Riverside. For the more reactive goethite (GOE50), additional samples were analyzed at the Department of Chemical Engineering, Chemistry School, Universidad Nacional Autónoma de México, using a Quantachrome Autosorb-1-C (Quantachrome Instruments) surface area analyzer. GOE50 was dried from water suspensions at pH ~ 6 and at pH ~ 4, after sonicating and removing CO₂ by vigorous N₂ gas bubbling. This latter was done to discard possible lower SSA measurements than would actually be available when in suspension, that would arise from high particle aggregation on drying from near neutral pH, since at low pH, particles are highly positively charged and should repel each other strongly and presumably remain disaggregated.

Goethite samples dried at 105 °C were gold-covered using a JEOL fine coat ion sputter JFC-1100, and processed on a JEOL JSM-6360LV scanning electron microscope (SEM), at the Institute of Ocean Sciences and Limnology, Universidad Nacional Autónoma de México. SEM images were obtained at 15,000×, 25,000×, and 40,000× magnifications.

2.3. Chromate adsorption

Goethite preparations were previously acidified to pH 4 with HClO₄, and gaseous, humidified N₂ (previously purified through a concentrated NaOH solution to remove any possible trace of CO₂) was bubbled through them at high flux for 24 h to remove all carbonate ions dissolved and adsorbed. For the pH adsorption-edge experiments, only suspensions of GOE50 and GOE70 were used. A volume of 150 mL of 10 g/L carbonate-free goethite suspensions was placed in 250-mL polycarbonate bottles and an ionic strength (*I*) of 0.1 M was established with NaClO₄. A starting pH above 7 was adjusted with carbonate-free NaOH under a headspace N₂ atmosphere. A total concentration of Cr(VI) of 5 × 10⁻⁶ M was added to the suspensions and pH values were sequentially adjusted up to pH 11. After each adjustment, 10-mL aliquots were transferred to 50-mL polycarbonate centrifuge tubes sealed under a nitrogen atmosphere and shaken to 14 G (250 rpm) for 2 h. A total of approximately 10 samples was withdrawn from each suspension equally spaced in the pH interval 7–11. After shaking, the equilibrium pH in each tube was measured, and the suspension was centrifuged to 2033g (3000 rpm) for 10 min. The supernatant was filtered through 25-mm-diameter nitrocellulose membranes of 0.05 μm pore diameter (Millipore 9004-70-0 filter type on Millipore SX0002501 Swinnex Gaskets). The concentration of Cr(VI) left in solution was determined by differential pulse polarography using a Stand VA 694 Metrohm polarograph with a dropping-mercury working electrode, an Ag/AgCl reference electrode, and a Pt auxiliary electrode. For this technique a supporting electrolyte composed of a buffering 0.25 M NH₄OH and 0.25 M NH₄Cl mixture was used at 5% in each sample. The quantification parameters were potential interval imposed = -150 to -400 mV, potential scan speed = 20 mV/s, measurement time = 20 ms, pulse time = 40 ms, measurement potential = 320 ± 15 mV.

Maximum concentrations of chromate adsorbed were determined also to calculate total reactive goethite site densities. For

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