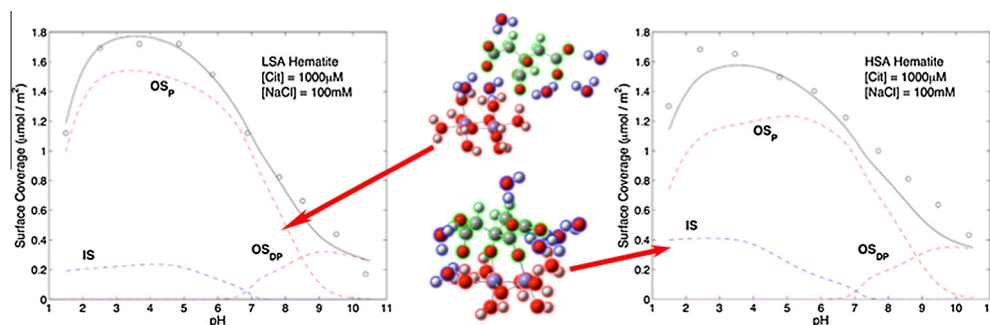# The impact of particle size on the adsorption of citrate to hematite

Matthew R. Noerpel, John J. Lenhart *

Department of Civil, Environmental, and Geodetic Engineering, The Ohio State University, Columbus, OH 43210, USA

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## ABSTRACT

We investigated the adsorption of citric acid on the surface of two different sized hematite nanoparticles using batch adsorption experiments, Fourier-transform infrared spectroscopy, surface complexation modeling and computational molecular modeling. Citrate adsorption reached a maximum between pH approximately 2.5 and 5.5 and declined as the pH was increased or decreased from that range. At high surface loading conditions, the dominant adsorbed citrate structure was outer-sphere in nature with a protonation state that varied with pH. At low pH, there was also evidence of an inner-sphere complex consistent with a binuclear, bidentate structure where the hydroxyl group was deprotonated and played an active role in the adsorption. An inner-sphere complex was also detected at low citrate surface loading conditions. Surface-area normalized surface coverages were similar for both sizes of hematite, however, the inner sphere complex appeared to be slightly more prevalent on the smaller hematite. Based on these structures, a triple layer surface complexation model comprised of two outer-sphere complexes and one inner-sphere complex was used to describe the adsorption data for both hematite sizes across a range of solution conditions with a single set of surface area dependent equilibrium constants.

## 1. Introduction

Organic acid interactions with metal oxide surfaces are a ubiquitous presence in natural soils and play an important role in many biological and geochemical processes [1]. When bound to an oxide surface, organic acids can alter the surface properties of the underlying mineral, which modifies its solubility and interactions with other solutes [2]. Organic acids also influence particle fate in the environment by altering the steric and electrostatic interactions that control aggregation and transport [2–4]. In addition to the effect organic acids have on particle surface reactivity they also bind metals in solution, either preventing or enhancing the metal's adsorption [5] and thus organic acids can impact metal transport through soil [4,6–8]. Therefore, understanding the conditions that control organic acid adsorption to metal oxide surfaces and the coordination modes of those acids will lead to a better understanding of metal transport in contaminated soils.

* Corresponding author.
  E-mail address: lenhart.49@osu.edu (J.J. Lenhart).

There are a wide variety of organic acids present in natural soils that can bind to metal oxides. Humic and fulvic acids are among the most prevalent and they are comprised of large polyelectrolytic, polyfunctional acids heterogeneous in size and structure [9,10]. While these humic substances are ubiquitous in soils and play an important role in soil chemistry, elucidating their fundamental adsorption mechanisms remains a challenge [11]. One alternative is to instead use low molecular weight organic acids of known structure that share common functional groups (e.g., carboxylic acid) with heterogeneous humic substances [10,12]. In this study, citric acid was used as a representative organic acid due to its prevalence in the environment and functional group similarities with humic substances [13]. Citric acid is used by plants and microorganisms as a metal chelator in iron and phosphate deprived soils to more efficiently extract the iron and phosphate necessary for growth [14,15] and in low pH soils to prevent aluminum toxicity [16]. Citric acid has three carboxylic acid functional groups, with intrinsic $pK_a$s of 3.13, 4.76, and 6.40 [17], and one hydroxyl group that deprotonates at pH values estimated to be between 11 and 14.4 [18]. The pK value for the hydroxyl group is out of the range of this study; however, that does not preclude it from deprotonating and playing an active role in the adsorption process as it does when complexing aluminum or gallium [19].

Hematite ($\alpha$-Fe$_2$O$_3$) is thermodynamically very stable and it is a common end result of the transformation of other less stable iron oxides [20]. As such it is commonly found in natural soils, especially older soils, in both nanoscale and larger forms [20]. Hematite readily binds organic and inorganic species and in a colloidal form it is implicated in the larger than anticipated transport of heavy metals through sediment and subsurface systems [21,22]. The different crystalline faces of hematite display varying reactivity and available binding sites. For example, the (001) face, considered the most common face, has a net neutral surface charge between pH 2 and 10 [23] while the $pH_{pzc}$ of whole hematite particles is reported to be between 8.5 and 9.5 [24,25]. This lack of surface charge in the environmentally relevant pH range results in the (001) surface being less reactive than other common surfaces and makes aggregation and adsorption processes on the (001) surface less dependent on pH [23].

The size of the hematite particles is expected to play an important role in adsorption processes as the relative abundance of the different crystalline faces and their associated binding sites may change with particle size [26,27]. For example, Madden et al. [26] determined that the affinity of Cu(II) to hematite changed with particle size as the smaller hematite had a higher proportion of irregular octahedral binding sites preferred by Cu(II). This occurred even though both particles exhibited the same pseudo hexagonal morphology. Similar results were also demonstrated with the iron hydroxide goethite, which displays a better defined crystal morphology than does hematite [27]. To isolate the role of different crystalline faces of goethite, atomic force microscopy was used to determine the (001) face made up 70% of the surface of larger crystals versus 30% of that for smaller crystals [27]. Thus, the adsorption capacity of the goethite crystals will not scale directly with available surface area if the adsorbate has a preference for sites in the (001) face [27]. In this study we use two different sizes of hematite to investigate the effect of particle size, and by inference, crystal face distribution on the adsorption of citrate to hematite.

In comparison to the extensive literature of citrate adsorption on goethite and other oxides, details of citrate adsorption on hematite are limited. For example, Zhang et al. [28] used macroscopic adsorption and iron dissolution experiments to conclude that citrate adsorbed as both doubly and triply deprotonated species. As part of the same study, Kallay and Matijevic [29] used zeta potential measurements and surface complexation modeling to determine that citrate is bound directly to the hematite surface

via a bidentate structure and that both singly protonated and fully deprotonated citrate surface species exist. Additional research has been performed on the iron oxyhydroxide, goethite, and the isostructural aluminum oxide, corundum. For example, Hidber et al. [30] used a variety of methods, including Fourier transform infrared (FTIR) spectroscopy, to investigate citric acid adsorption on corundum ($\alpha$-Al$_2$O$_3$). They reported citrate adsorbs in an inner sphere manner, but not with all three carboxyl groups. Hidber et al. [30] did not find direct evidence for the involvement of the hydroxyl group in citrate binding but assume it is involved due to differences between its adsorption and that for tricarballylate, which differs from citrate by lacking the additional hydroxyl group. Results with goethite are more extensive, with early investigators primarily invoking inner-sphere surface complex modes, such as one involving the citrate ion adsorbing in a triply coordinated manner using all three carboxyl groups [31]. More recent results have increasingly found outer-sphere adsorption modes, with Lackovic et al. [32] indicating inner-sphere complexation at low- to mid-pH gives way to outer-sphere complexation at elevated pH. This interpretation was based on FTIR spectroscopy coupled to batch adsorption and goethite dissolution experiments [32]. Lindegren et al. [33] reported finding multiple inner- and outer-sphere surface structures using 2-D correlation infrared spectroscopy, including two previously unreported structures. These new structures included a protonated outer-sphere complex at low pH and an inner-sphere structure at high pH where the hydroxyl group deprotonated and played an active role in the adsorption process. Most recently, Yeasmin et al. [34] used batch adsorption experiments with ^{14}C-labeled organic acids and infrared spectroscopy and came to a similar conclusion as Lindegren et al. that citrate adsorbs on goethite (and ferrihydrate) as mono- and bidentate inner sphere complexes as well as outer-sphere complexes. Unfortunately, they did not further specify the structure of the adsorbed citrate.

The main method of investigation in this study to determine the structure of adsorbed citrate onto hematite was Attenuated Total Reflectance FTIR (ATR-FTIR) spectroscopy. As the different structural features of the citrate molecule absorb infrared energy at specific frequencies, the changes in frequency and magnitude of that absorption can indicate changes in the coordination of the molecule [32,33,35]. These experimentally determined infrared spectra were compared with those produced through computational methods. Calculating the theoretical infrared spectra of different potential structures allows us to assign specific vibrations to the peaks visible in the experimental FTIR spectra and compare the experimental results of the adsorbed structure to those generated theoretically based upon different potential structures [35]. Based on these constraints, a surface complexation model was derived based on the Triple Layer Model of hematite developed by Hwang and Lenhart [24] and utilized to simulate the experimental adsorption data. Our results suggest that citrate adsorbs predominantly as an outer-sphere complex on both sizes of hematite studied, with a minor addition of a bidentate inner-sphere complex that adsorbs preferentially with respect to the outer-sphere complex, but in lower concentrations due to a limited number of available surface sites. The smaller hematite particles allowed for more inner sphere adsorption suggesting it carried a greater proportion of sites that prefer to directly bind citrate.

## 2. Materials and methods

### 2.1. Hematite synthesis and characterization

Two sizes of hematite were synthesized and used in this research. The first, with a nominal 10 nm diameter was synthesized