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Adsorption of humic acids onto goethite: Effects of molar mass, pH and ionic strength

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Abstract

In this paper, the LCD (ligand charge distribution) model is applied to describe the adsorption of (Tongbersven) humic acid (HA) to goethite. The model considers both electrostatic interactions and chemical binding between HA and goethite. The large size of HA particles limits their close access to the surface. Part of the adsorbed HA particles is located in the compact part at the goethite surface (Stern layers) and the rest in the less structured diffuse double layer (DDL). The model can describe the effects of pH, ionic strength, and loading on the adsorption. Compared to fulvic acid (FA), adsorption of HA is stronger and more pH- and ionic-strength-dependent. The larger number of reactive groups on each HA particle than on a FA particle results in the stronger HA adsorption observed. The stronger pH dependency in HA adsorption is related to the larger number of protons that are coadsorbed with HA due to the higher charge carried by a HA particle than by a FA particle. The positive ionic-strength dependency of HA adsorption can be explained by the conformational change of HA particles with ionic strength. At a higher ionic strength, the decrease of the particle size favors closer contact between the particles and the surface, leading to stronger competition with electrolyte ions for surface charge neutralization and therefore leading to more HA adsorption.

Keywords: LCD; CD-MUSIC; NICA; ADAPT; Humic acid adsorption; Humic; Fulvic; Iron (hydr)oxides; Variable-charge particles

1. Introduction

Both natural organic matter (NOM) and iron (hydr)oxides are nanosize colloidal particles present in soils, sediments, and aquatic systems. Natural organic matter is operationally divided into humin, humic acid (HA), and fulvic acid (FA) fractions, based on their solubility differences in acid and base. Natural organic matter interacts strongly with various minerals including iron (hydr)oxides. Application of mechanistic models for ion adsorption to oxides in environmental systems requires that we be able to account for the effect of the presence of adsorbed organic matter on ion adsorption, an effect that can be very large in the case of adsorption of oxyanions [1–3].

Many studies on NOM–mineral interactions have been carried out using chemical experimental approaches [4–13], spectroscopic techniques [14–16], or modeling [12,17–22]. However, a clear picture of the state of NOM at the mineral surface and the mechanisms that determine the NOM–mineral interactions is still not available. Quantitative description and prediction of NOM adsorption onto mineral surfaces as a function of solution condition, while explicitly taking electrostatic effects into account, still remains a big challenge, especially for humic acid adsorption. The ill-defined, heterogeneous macromolecular nature of humic substances complicates the study.

In 2001, an advanced modeling approach for NOM–mineral interaction was proposed, known as the ligand and charge distribution (LCD) model [20,23,24]. One of the advantages of the LCD model is that it makes use of existing sophisticated surface complexation models for small ion adsorption onto respectively humics and iron (hydr)oxides. In the LCD model, the humic particles interact with small ions as well as surface sites according to the nonideal consistent competitive adsorption (NICA) approach [25–33]. The binding of small ions to oxides and the mutual electrostatic effects are calculated in the LCD approach using the charge distribution multisite complexation (CD-MUSIC) model [34,35], which has been developed

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over the years with special attention to the interfacial structure in the vicinity of the mineral surface.

The use of a surface complexation model such as NICA to calculate the speciation of humics is required due to the large number of reactive ligands that are present on one humic particle. In the NICA approach, the statistical distribution of the reactive ligands over their possible chemical states is calculated, rather than the concentration of each specific species. This character of the model demands another treatment than the classical stepwise reaction approach to calculate the equilibrium distribution of the humics between the solution and the adsorbed phase. Very recently, the LCD model approach has been improved by introducing a new formalism, the ADAPT model (adsorption and adaptation), to define the equilibrium condition of the phase distribution of humic substances [36,37]. This improved LCD model has been applied to describe the adsorption of FA onto goethite, which shows that the effects of the pH, ionic strength, and fulvic acid loading on the adsorption can be well reproduced with the model, using only one adjustable parameter, the mean affinity constant of a carboxylic type of ligand on humics for a surface site on goethite ($\tilde{K}_{s,1}$) [37].

In this paper, the LCD model will be applied to describe the adsorption of HA to goethite. Compared to FA, the relatively large size of the HA particle is one of the complicating factors in extending the model from FA to HA, while the polydispersity of the material is another complicating factor. In this paper, we will make several simplifying assumptions. The aim of the paper is to investigate the major factors that affect the adsorption behavior and to test how far a relatively simple approach, given all the complexities of the system, can reproduce a rather extensive data set. The calculated results will be compared with experimental data on HA adsorption onto goethite that show the effects of the pH, ionic strength, and HA loading on the adsorption [13]. Further, the differences in the adsorption of HA in comparison to FA adsorption are interpreted based on the model findings.

2. Experiments

2.1. HA adsorption experiment

The experimental data on HA adsorption onto goethite have been published elsewhere [13]. Humic acid (HA) was prepared from the B-horizon of a forest soil from the Netherlands (Tongbersven) following the IHSS (International Humic Substance Society) procedures. The purified HA material contains 54% carbon. The weight-average molar mass (M_m) of the HA is 13.2 kDa (Table 1), which was measured using size exclusion chromatography (TSK 3000) in combination with TOC measurements [38]. The charging behavior has been determined previously with acid–base titration in KNO_3 solution [6]. The goethite preparation has been described by Hiemstra et al. [34]. The specific surface area of goethite measured with the BET-N_2 method is 94 m^2/g. The surface charge has been determined with acid–base titrations in $NaNO_3$ solution [24]. The pristine point of zero charge (PZC) of this goethite material is pH 9.3 (Table 2). Adsorption of HA onto goethite was measured with batch experiments. Three salt levels were studied: 0.002, 0.01, and 0.10 M $NaNO_3$. The initial HA concentrations were 150, 300, and 450 mg/L HA. Acid or base solution (HNO_3 and NaOH) was added to adjust the pH to values in the range 3–11. The final concentration of goethite was 1.0 g/L. After being shaken for 3 days at 20 °C, the suspensions were centrifuged at 18,000*g* for 30 min. A subsample of the supernatant was acidified to pH 3–4 and the concentration of dissolved organic C in the supernatant was measured with a TOC analyzer. The final pH was measured in the supernatant.

Table 1
NICA-Donnan model parameters for HA[a]

Ligand	Q_{max} (mol/kg)	N_{max} (mol/mol)	m	p	$\log \tilde{K}_H$	n_H	b	M_m (kg/mol)
Carboxylic	2.40	31.65	0.49	0.61	2.49	0.81	0.31	13.2
Phenolic	2.39	31.52	0.26	0.41	8.60	0.63		

[a] Q_{max}, m, and $\log \tilde{K}_H$ have been derived by fitting the NICA-Donnan model to the acid–base titration data of the Tongbersven HA [32]. n_H has been taken from the generic parameter set for HA [32]. p is calculated with $p = m/n_H$.

Table 2
Basic properties and model parameters of goethite

Specific surface area (m^2/g)	PZC	Site density ($/nm^2$)[a]		Capacitance (F/m^2)	
		$–Fe_1OH^{-0.5}$	$–Fe_3O^{-0.5}$	C_1	C_2
94	9.3	3.45	2.7	0.83	0.74[b]

[a] The site densities have been determined by [34].

[b] The capacitance of the second Stern layer (C_2) has been fitted by [39]. Capacitance of the first Stern layer (C_1) is fitted in this work.

2.2. FA adsorption experiment

The original data on FA adsorption have been published in a previous paper [6]. The FA (Strichen) used was prepared from the Bs-horizon of a peat soil from Scotland (carbon content 43%, molar mass 0.683 kDa). Goethite material was prepared in a way similar to that used in the HA experiment, with the same BET-N_2 surface area of 94 m^2/g and PZC of pH 9.2. Adsorption of FA onto goethite was measured with batch experiments similar to those for HA adsorption, with initial FA concentrations of 75, 150, and 300 mg/L and goethite concentration of 5.0 g/L in 0.015 and 0.1 M $NaNO_3$ at pH 3–11.

3. Modeling

In this work, the LCD model is extended and applied to describe adsorption of HA onto goethite. The basic concept of the LCD model has been formulated by Filius et al. [20,23] and Weng et al. [24] and the model has recently been improved and used to describe FA adsorption onto goethite [37]. For a detailed model description, we refer to the previous paper [37]. Here, a summary of the essence of this model approach will be given, with special attention to the changes/extensions made in this application. A list of symbols used can be found at the end of the paper.

The LCD framework consists of four modules: NICA-Donnan, NICA-LD, CD-MUSIC, and ADAPT.