

## Speciation of oxalate at corundum colloid–solution interfaces and its effect on colloid aggregation under conditions relevant to freshwaters

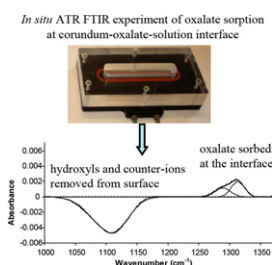
Mirella Del Nero\*, Catherine Galindo, Guillaume Bucher, Sylvia Georg, Valerie Mazan, Remi Barillon

Institut Pluridisciplinaire Hubert Curien, UMR 7178 CNRS/UDS, 23 rue du Loess, BP 28, 67037 Strasbourg Cedex 2, France

### HIGHLIGHTS

- ▶ We investigate oxalate speciation at corundum colloid–solution interfaces by ATR FTIR.
- ▶ Oxalate at trace levels is sorbed at the interface via a reaction of surface ligand exchange.
- ▶ The reaction of surface ligand exchange imparted negative charges to corundum surface.
- ▶ It induced a decrease in  $\xi$  potential resulting in aggregation of the corundum colloids.
- ▶ The results have implications for mobility of Al(hydr)oxide colloids in freshwaters.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 3 September 2012  
 Received in revised form 30 October 2012  
 Accepted 1 November 2012  
 Available online 17 November 2012

#### Keywords:

ATR FTIR spectroscopy  
 Alumina colloids  
 Corundum–solution interface  
 Oxalate  
 Surface speciation  
 Sorption  
 Surface ligand exchange  
 Zeta potential  
 Aggregation

### ABSTRACT

We address the speciation of oxalate sorbed at Al oxide colloid–oxalate–solution interfaces under conditions of freshwaters (trace levels of oxalate and of Al dissolved) and its effect on surface reactivity, surface charges and aggregation of the colloids, which is a key issue for colloidal transport of trace metals. Attenuated Total Reflectance Fourier Transform Infrared spectroscopy was used to explore *in situ* concomitant changes in surface charges and in identity of species formed at the interface during the sorption process at slightly acidic pH, for different ionic strength conditions ( $I$ : 0.001–0.1 M), or along gradual increase in oxalate concentration (1–50  $\mu\text{M}$ ) and surface coverage. Focusing on the reactions taking place at the interface provided first-time direct spectroscopic evidence that oxalate at trace levels (1–8  $\mu\text{M}$ ) is sorbed through removal of singly coordinated surface hydroxyls and direct bonding of oxalate on surface Al(III), imparting negative charges to the surface. Comprehensive understanding of corundum aggregation behavior as related to oxalate surface speciation was achieved by complementing the spectroscopic information with the changes in zeta potential and in size of alumina aggregates recorded during the sorption of oxalate in alumina suspension. An important finding was that the reaction of surface ligand exchange operating at trace levels of oxalate had a huge effect of decreasing  $\xi$  and promoting colloid aggregation. These results stress that oxalate, even when existing at low concentrations in natural waters, affects dramatically the transport of trace metals by natural Al-(oxi)hydr)oxide colloids by controlling the surface reactivity, surface charges and mobility of the colloids.

© 2012 Elsevier B.V. All rights reserved.

### 1. Introduction

Oxalate is a dicarboxylic acid anion that is present in solutions of soil and in freshwaters at concentrations in the ranges  $10^{-4}$  to  $10^{-3}$  M and  $10^{-5}$  to  $10^{-6}$  M, respectively [1]. Oxalate is

\* Corresponding author. Tel.: +33 3 88 10 64 08; fax: +33 3 88 10 64 31.  
 E-mail address: [mireille.delnero@iphc.cnrs.fr](mailto:mireille.delnero@iphc.cnrs.fr) (M. Del Nero).

involved in many reactions that govern the availability of metals in soil, including reactions of formation of bidentate chelates with dissolved metals [2] and a range of sorption reactions taking place on the surface of soil minerals such as metal (hydr)oxides. The speciation of oxalate in metal (hydr)oxide–oxalate solution systems has been the subject of intensive research, including molecular-level research studies using spectroscopy [3–11]. For example, it has been shown that oxalate participates in the formation of inner-sphere surface complex (ISSC) of oxalate on the surface of Al-(hydr)oxides [5,7,8], promoting dissolution of the oxide and release of Al in solution [5,7], and in the formation of surface–oxalate–metal complexes onto Fe-(hydr)oxides [11]. The speciation studies have focused mainly on systems with high concentrations of oxalate in order to identify coupled reactions of adsorption and dissolution, which is of significance for the issue of the transfer of Fe and Al between the different compartments of the soil. In freshwater systems, oxalate is present in trace amounts and it cannot influence significantly the extent of dissolution of metal (hydr)oxides. Oxalate has however a strong impact on the transport of trace metals by metal (hydr)oxide particles of colloidal size, which are ubiquitous in the freshwater system. For example, sorbing oxalate is expected to influence both the metal sorption capacity and the mobility of natural Al-(hydr)oxide colloids, due to its ability to bind as an ISSC on the surface of Al (hydr)oxides, which modifies the chemistry, reactivity, charge and potential of the oxide surface. Depending on their surface charge and potential, colloids are transported with freshwaters as dispersed particles or they are possibly immobilized as large aggregates. Thus, surface reactivity and aggregation of colloids as related to the surface speciation of oxalate is a key issue for the colloidal transport of trace metals in freshwater. While several spectroscopic studies on identity of species existing in Al (oxihydr)oxide–oxalate–solution systems at high oxalate concentration (1–25 mM) have been published, a molecular-level description of the interactions occurring at the interface between Al (hydr)oxide colloids and solutions with concentrations of oxalate relevant to freshwaters is missing, as well as knowledge of the surface charges imparted by the interactions. Such knowledge is critically needed to achieve comprehensive understanding of the effect of oxalate sorption on colloid aggregation.

Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR FTIR) is amongst the rare technique enabling to analyze *in situ* sorbed species existing in solid–solution systems [12]. Regarding Al (oxihydr)oxides and oxalate, FTIR data available in the literature concern batch sorption samples at high oxalate concentrations ( $\geq 1$  mM) analyzed as wet pastes [5,7,8]. The speciation analyses provided information on the speciation of oxalate in the whole systems studied (with complicated background subtraction procedures being necessary to extract the IR signals for adsorbed oxalate, e.g., in ref. [8]), and on the interrelationships existing between the oxalate adsorption and the surface dissolution, for conditions representative of organic-rich soils. The studies indicated the existence of two types of oxalate species in the pastes, with relative contributions of species depending on oxalate surface coverage. One type of species was described as hydrated oxalate sorbed weakly to the surface via H-bonds. The other type of species was proposed to exist as an ISSC of oxalate or a mixture between the ISSC and solution species consisting of a combination of several Al(III)–oxalate complexes generated in high concentrations due to ligand-enhanced dissolution of solid and release of  $\text{Al}^{3+}$  ions (up to 25 mM in ref. [8]). Spectroscopic studies designed to probe *in situ* and specifically the interface between colloids and oxalate solutions are now required for identifying the adsorption reactions of oxalate occurring at the interface and for elucidating their effect on surface charge development, for low concentrations of oxalate and dissolved aluminum that are relevant to freshwaters. One of most appropriate approach is applying ATR

FTIR spectroscopy to analysis of the interface between the solution and a thin layer of colloids (deposited on the ATR crystal), which allows monitoring of reactions at the interface, identifying *in situ* interfacial species, and obtaining clear information on the relation between the sorption reactions and the charges imparted to the surface. The approach merges important needs in sorption studies, e.g., increased sensitivity of ATR FTIR spectroscopy for adsorbed species and monitoring of the evolution of the interface during the process of sorption. It was applied recently, for instance, to follow the growth of Al-phosphate precipitates at corundum–solution interfaces during the processes of sorption of phosphate ions and dissolution of the solid [13], to studying surface speciation during adsorption of trace levels of uranyl at corundum-phosphate solution interface [14] or hematite–solution interface [15], or to monitoring surface excess concentration of counter-ions during surface titration experiments [16].

In this paper, we address the sorption reactions and surface speciation of oxalate at the corundum colloid–acidic solution interface, and their effect on the aggregation behavior of the colloids, by means of *in situ* ATR FTIR spectroscopy and more conventional and complementary measurements, i.e., electrophoretic mobility (EM) and size distribution profile (SDP) measurements. Corundum is of interest because it is a model substrate representative of Al-(oxihydr)oxides that is widely used to study the sorption behavior of anions [7,8,13,14,17]. The first important point to us was substantiating the identity of the surface species and their effect on surface charges by ATR FTIR investigations of the corundum–solution interface, during the phenomena of oxalate adsorption and solid dissolution, to obtain clear information on (evolving) structures/charges existing at the interface, not in the whole system containing several aqueous oxalate species. A second point was exploring the interface during the uptake of oxalate from the trace levels to the low concentration level (1–50  $\mu\text{M}$ ), and for low concentrations of dissolved Al ( $\leq 50 \mu\text{M}$ ), which is important for the transferability of the spectroscopic results to the freshwater system. To these ends, we recorded the IR spectra of the interface between oxalate solutions at acidic pH ( $4.6 \pm 0.1$ ) and a well-characterized layer of corundum particles of colloidal size. The layer was deposited on the ATR crystal prior to the experiment using a procedure that warranted the characteristics, stability and repeatability of the deposits [18], and hence a high sensitivity and reproducibility of IR measurements for interfacial species. *In situ* monitoring of the dynamic of interfacial species, including sorbed oxalate, surface hydroxyls and surface counter-ions, was conducted to explore concomitant changes in surface speciation and in surface charges along the process of oxalate sorption, for different conditions (*I*:  $10^{-3}$  to  $10^{-1}$  M  $\text{NaClO}_4$  or  $\text{NaCl}$ ), or along a gradual increase in oxalate concentration (1–50  $\mu\text{M}$ ) and surface coverage (1.3–6  $\mu\text{mol m}^{-2}$ ). Comprehensive understanding of the aggregation behavior of corundum as related to the surface speciation of oxalate was achieved by complementing the spectroscopic information with changes in zeta potential and in size of alumina aggregates (as determined from *on line* measurements of the EM and SDP of alumina, respectively) during experiments of oxalate sorption in alumina–solution suspensions. The results presented here have important implications for the surface reactivity, surface charge behavior and mobility of oxide colloids in the freshwater system.

## 2. Experimental

The alumina colloids (corundum) used in this study were Alfa Aesar's  $\alpha\text{-Al}_2\text{O}_3$  crystallites (chemical purity: 99.95%, surface area: 7.6  $\text{m}^2/\text{g}$ ), with a particle size of  $380 \pm 20$  nm and a high value of iso-electric point of 8.2 [13]. Solutions were prepared using reagent

Download English Version:

<https://daneshyari.com/en/article/593864>

Download Persian Version:

<https://daneshyari.com/article/593864>

[Daneshyari.com](https://daneshyari.com)