Understanding Humic Acid / Zr(IV) Interaction – A Spectromicroscopy Approach

Jörg Rothe, Markus Plaschke, Melissa A. Denecke

Forschungszentrum Karlsruhe, Institut für Nukleare Entsorgung, P.O. Box 3640, D-76021 Karlsruhe, Germany

Abstract. Complexation of Zr(IV) by humic acid (HA) and polyacrylic acid (PAA) is investigated from the point of view of the organic ligand. STXM spectromicroscopy and C 1s-NEXAFS point to different interaction mechanisms between Zr(IV) cations and oxo/hydroxo colloids and PAA. Under conditions where the metal aquo ion is stable, strong complexes are formed. In contrast, unspecific surface coating is identified when PAA is contacted with Zr(IV) oxo/hydroxide colloids. HA exhibits similar C 1s-NEXAFS features indicating a complexation reaction.

Keywords: humic acid, metal ion complexation, Scanning Transmission X-ray Microscopy, C 1s-NEXAFS

PACS: 68.37.Yz, 61.10.Ht

INTRODUCTION

HA are dark-colored, heterogeneous biopolymers generated mainly by microbial metabolism of organic matter. They are ubiquitous in soils and natural water, possessing the ability to complex and transport trace metal ions in groundwater aquifers. HA are considered to play a significant role in the far-field transport of radionuclides, including actinide cations, following hydrolysis and oligomerization. The chemical properties and colloid stability of these inorganic particles may be altered by surface reactions with HA. As part of the assessment of HA impact on actinide transport phenomena, it is crucial to characterize both the nature of HA/actinide ion complexes and HA hetero-aggregates with actinide oxo/hydroxide colloids. In the present study, Zr(IV) acts as a chemical homologue for Pu(IV).

X-ray absorption spectroscopy and soft X-ray spectromicroscopy studies have great potential for characterizing HA interaction with trace metal ions and inorganic colloids. We apply Scanning Transmission X-ray Microscopy (STXM) to study the interaction between HA and tetravalent Zr or its hydrolysis products. PAA is chosen as an appropriate model compound to clarify the role of carboxyl groups in the HA / metal ion interaction. In our previous studies striking similarities are found in spectral trends of the C 1s-NEXAFS (Near Edge X-ray Absorption Fine Structure) signatures before and following complexation of trivalent metal ions by HA and PAA (1).

MATERIALS AND METHODS

Aqueous suspensions of purified commercial HA (Aldrich) and PAA (GPC-standard, Fluka), both 100 mg/L, were contacted with solutions of Zr(IV) (ICP standard) at different pH. Addition of metal cations to saturate HA and PAA loading capacities ([Zr(IV)] = 1.1E-3 mol/L) or acidification of HA suspensions to pH 1 induces the polymers to precipitate from solution. Resulting aggregate flocs are of ideal dimension to be probed by soft x-ray microscopy at the carbon K-edge. STXM investigations were performed at beamline X-1A (outboard STXM) at the NSLS, Brookhaven, New York (2). Here a spatial resolution better than 100 nm can be achieved. Zr(IV)-HA and -PAA aggregates are investigated sandwiched between two silicon nitride membranes in fully hydrated state. Stacks of images from selected sample regions are recorded as a function of incident photon energy E. E is varied in 1 eV steps in the range 280-283 eV, 0.1 eV for 283-292 eV, 0.5 eV for 292-300 eV, and 1 eV for 300-305 eV. C 1s-NEXAFS spectra are extracted through the analysis of the absorption signal, μ(E)*d = ln(I0(E)/I(E)), of vertical projections onto aligned image stacks. Details on wet cell sample preparation and stack data analysis can be found in Refs. (3) and (4), respectively.
RESULTS AND DISCUSSION

A typical STXM micrograph of Zr(IV)-PAA at pH 5 is shown in Fig. 1a. The C 1s-NEXAFS of Zr(IV)-PAA strongly depends on the solution pH (Fig. 2). At pH 5, we observe the spectrum of uncomplexed PAA, with a NEXAFS comparable to the Na-form (1). At pH 4.3, the decrease of the carboxyl peak and the appearance of a shoulder adjacent to the carboxyl peak (arrows) points to complex formation, as recently observed for Eu(III) and other polyvalent metal cations (5). This shoulder becomes more pronounced at pH 3. We offer the following interpretation: at pH 5, Zr(IV) hydrolysis and oxo/hydroxide formation is dominant (6). PAA is merely coating and co-precipitating with these inorganic particles; no specific metal organic interaction is discernible from the C 1s-NEXAFS. This interpretation is corroborated by Zr K-EXAFS measurements (unpublished results), giving evidence for Zr(IV) colloid formation under these conditions. Decreasing the pH leads to an increased fraction of ionic Zr(IV) which can be complexed by PAA carboxyl groups. This reaction becomes more favorable at pH 3, indicated by the stronger complexation effect in the C 1s-NEXAFS.

We previously observed that HA aggregation induced by addition of polyvalent metal cations at slightly acid pH (≤ 5.0) is always accompanied by segregation into zones with different optical densities (7). Both dense or ‘dark’ and less dense or ‘light’ zones possess characteristic C 1s-NEXAFS signatures. Similar segregation into different HA fractions induced by Zr(IV) addition is observed in the STXM image in Fig. 1b, where confined dark patches embedded into a lighter matrix of carbonaceous material are visible. The corresponding C 1s-NEXAFS signatures are compared in Fig. 3. The aromatic peak at ~285 eV and the dominant carboxyl peak at ~288.5 eV are evident. The spectrum of the light zones (I) shows a distinct peak at ~286.7 eV, generally
attributed to phenolic carbon. The spectrum of the dark zones (II) exhibits a somewhat weaker aromatic peak and a shoulder leading to the more pronounced carboxyl resonance. Spectrum III, taken from (1), was extracted from a HA precipitate observed at pH 4.3 without addition of metal cations. HA aggregates at pH 1 without added Zr(IV) exhibit a spectrum similar to signature I (not shown). Averaging the spectroscopic signal over entire aggregates at pH 4 with added Zr(IV) also yields spectrum I. We conclude that signature II obviously characterizes a minority fraction. The shoulder in II resembles the complexation feature observed for Zr(IV)-PAA at pH 3-4. II also resembles the signature of HA at pH 4.3 (III), indicating lack of strong complexation.

**CONCLUSIONS**

STXM measurements of metal cation / HA interaction phenomena point to the necessity to establish and further develop spatially resolved spectroscopy techniques to investigate inhomogeneous natural sample systems. Quantum chemical calculations of our C 1s-NEXAFS investigation are currently being performed to understand the underlying molecular processes.

**ACKNOWLEDGMENTS**

We are grateful for financial support from the Helmholtz Association of National Research Centres, Bonn, Germany within the Virtual Institute ‘Functional Properties of Aquatic Interfaces’. We acknowledge beam-time allotment by BNL/NSLS. The X-1A STXM was developed by the group of Janos Kirz and Chris Jacobsen at SUNY Stony Brook, with support from the Office of Biological and Environmental Research, U.S. DoE under contract DE-FG02-89ER60858, and the NSF under grant DBI-9605045.

**REFERENCES**