Forschungszentrum Dresden Rossendorf

Experiment Report Form

The double page inside this form is to be filled in for each experiment at the Rossendorf Beamline (ROBL). This double-page report will be reduced to a one page, A4 format, to be published in the Bi-Annual Report of the beamline. The report may also be published on the Web-pages of the FZD. If necessary, you may ask for an appropriate delay between report submission and publication.

Should you wish to make more general comments on the experiment, enclose these on a separate sheet, and send both the Report and comments to the ROBL team.

Published papers

All users must give proper credit to ROBL staff members and the ESRF facilities used for achieving the results being published. Further, users are obliged to send to ROBL the complete reference and abstract of papers published in peer-reviewed media.

Deadlines for submission of Experimental Report

Reports shall be submitted not later than 6 month after the experiment.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the reference number of the proposal / experiment to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.
- bear in mind that the double-page report will be reduced to 71% of its original size, A4 format. A type-face such as ”Times” or ”Arial” , 14 points, with a 1.5 line spacing between lines for the text produces a report which can be read easily.

Note that requests for further beam time must always be accompanied by a report on previous measurements.

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ROBL-CRG	**Experiment title:** EXAFS investigation of the effects of humic acid on uranyl adsorption on goethite	**Experiment number**: 20-01-689
Beamline: BM 20	**Date of experiment**: from: 25.07.2009 to: 28.07.2009	**Date of report**: 01.06.2010
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Report:

Humic substance (HS) is a group of organic nanocolloids found in diverse environments. HS affects the buffering and barring capacity of the environments against the inputs of toxic metal ions such as heavy metals and radionuclides[1]. Although the effects of HS on metal adsorption are now recognized, our understanding on the underlying mechanisms is far from satisfactory. Depending on solution conditions, the type of a adsorbing metal and the magnitude of HS loading on a surface, the adsorption of metal is enhanced, diminished or virtually unaffected, which have never been explained clearly. This is partly due to the lack of the molecular-scale information on a metal/HS/mineral ternary system. In this study uranyl (UO_2^{2+}) adsorption on goethite was studied by EXAFS spectroscopy both in the absence and presence of humic acid (HA) in order to extract the structural information on dominant species.

Sorption of UO_2^{2+} on synthesized goethite particles with and without purified Aldrich HA (PAHA) was studied by both macroscopic batch adsorption experiments and molecular-level EXAFS measurements. All samples were prepared in Ar or N_2 atmosphere to exclude CO_2. The adsorption experiments were performed with 1 g/L goethite suspension as a function of pH, salt concentration and PAHA concentrations. The total concentrations of UO_2^{2+} and PAHA were 50 μM and 50 mg/L, respectively. The salt concentration was adjusted with 1 M $NaClO_4$ to 0.1 or 0.01 M. The U L_{III} EXAFS measurements were performed with 5 g/L goethite suspension at pH 4 and 0.1 M $NaClO_4$, where the UO_2^{2+} sorption was enhanced in the presence of PAHA. As reference UO_2^{2+}/HA and UO_2^{2+}/goethite binary samples were measured as well. For the UO_2^{2+}/gothite binary and the UO_2^{2+}/

PAHA/ goethite ternary samples, the total UO_2^{2+} concentration was 200 μM UO_2^{2+}, which resulted in similar surface loading of UO_2^{2+} on goethite. The concentration of PAHA in the latter samples was varied from 20 to 500 mg/L. The UO_2^{2+}/PAHA binary sample was prepared with 500 mg/L PAHA and 400μM UO_2^{2+}. The obtained EXAFS spectra were analyzed by the iterative target transformation factor analysis (ITTFA)[2] to determine the number of different UO_2^{2+} species and their structural characteristics as a function of the HA loading.

The adsorption of UO_2^{2+} on goethite was increased by PAHA at pH < 5.5 and diminished at pH > 6. The former can be explained by the formation of ternary complexes among UO_2^{2+}, PAHA and goethite and the latter by the binding of UO_2^{2+} to PAHA in aqueous phase. From the EXAFS radial distribution function (RDF) of UO_2^{2+} adsorbed on goehite without PAHA in Figure 1, there were distinct contribtions both at 3 and 3.5 Å (without phase-shift correction), suggesting the formation of both edge-sharing and corner-sharing bidentate coordination of UO_2^{2+} to iron octahedra[3]. The comparison of EXAFS RDF of the binary and ternary samples at pH 4 (Figure 2) showed a systematic variation in the elemental arrangements around adsorbed UO_2^{2+} ions. The ITTFA analysis further revealed that the variation is a mixture of HA- and goethite-like contributions (Figure 2 (a)) and that the latter dominated even at relatively high PAHA loading (Figure 2 (b)). This strongly suggests that the formation of the PAHA/UO_2^{2+}/goethite Type-A ternary complex is responsible for the observed enhancement of UO_2^{2+} adsorption in the presence of PAHA.

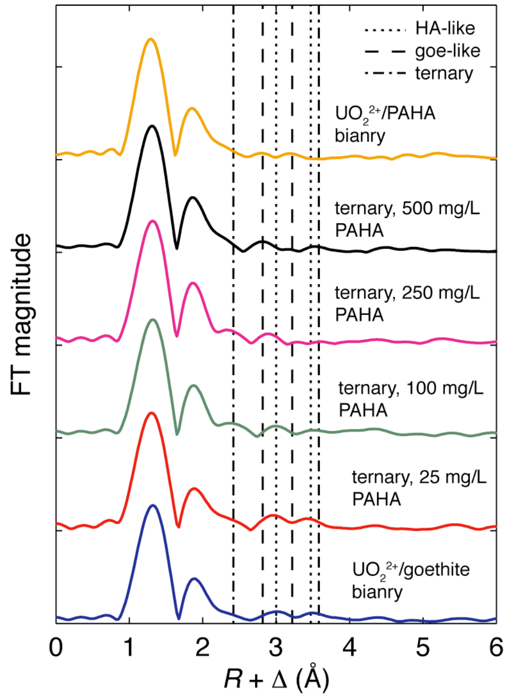

Figure 1. EXAFS radial distribution function (RDF) of UO_2^{2+} adsorbed on goethite in the presence of PAHA (the UO_2^{2+}/PAHA/goethite ternary samples). For comparison, the RDF of the UO_2^{2+}/ goethite and UO_2^{2+}/PAHA binary samples are included.

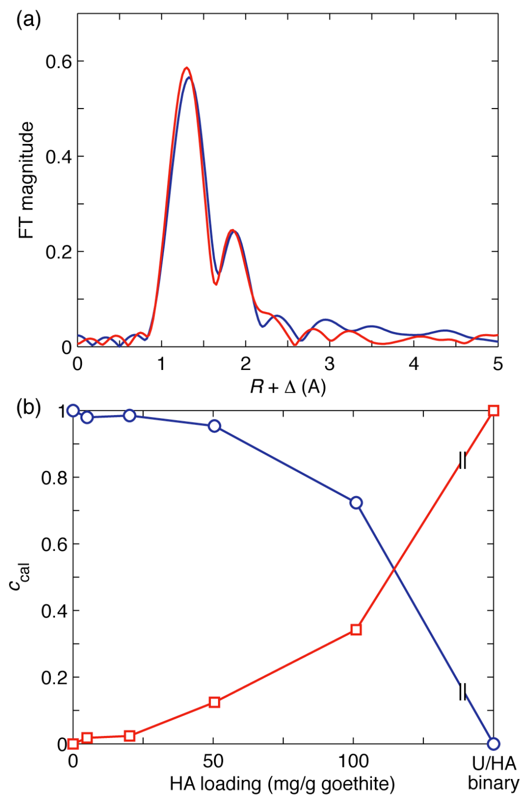

Figure 2. Extracted goethite- and HA-like RDF (a) and their contributions (a) from the ternary EXAFS spectra by ITTFA.

Literature cited

1. Saito, T., et al., *Environ. Sci. Technol.* **2005**, *39*, 4886-4893.
2. Rossberg, A., et al., *Anal. Bioanal. Chem.* **2003**, *376*, 631-638.
3. Sherman, D. M., et al., *Geochim. Cosmochim. Acta* **2008**, *72*, 298-310.