ESRF	Experiment title: Study of the influence of humic acid on the U(VI) sorption onto kaolinite	Experiment number: CH-2086			
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Report:

In the present study we investigated the influence of humic acid (HA) on the nearneighbor surrounding of U(VI) in kaolinite surface complexes. Results of the EXAFS measurements in the ternary system U(VI)-HA-kaolinite were interpreted and compared with those from literature. U(VI) was adsorbed onto kaolinite under the following conditions: [U(VI)]: $1\cdot10^{-5}$ M, [HA]: 10 mg/L, S/L ratio: 4 g kaolinite/L, pH 3–8.5, p(CO₂): $10^{-3.5}$ atm, I: 0.1 M NaClO₄. The sorption procedure is described elsewhere [1]. Uranium L_{III}-edge absorption spectra were recorded in fluorescence mode at room temperature.

Fig. 1 shows U L_{III}-edge k^3 -weighted EXAFS oscillations and their corresponding Fourier transforms (FTs, not corrected for phase shift) of the samples prepared at pH ~ 7 with and without HA. Both samples exhibit comparable EXAFS oscillations and FTs without any significant differences. The structural model for fitting the EXAFS oscillations was derived from the EXAFS investigations of the binary system U(VI)kaolinite KGa-1b [2]. The obtained structural parameters are summarized in Tab.1.

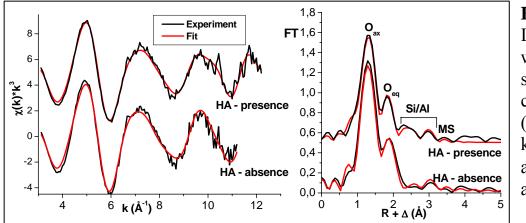


Fig.1: Uranium L_{III}-edge k³weighted EXAFS spectra (left) and corresponding FTs (right) of uranylkaolinite sample at pH \sim 7 with and without HA.

Tab.1: Structural parameters of the uranyl-kaolinite samples with and without HA.

	2 x O _{ax}		5 x O _{eq}		1 x Si ₁ /Al ₁		1x Si ₂ /Al ₂			
pH ~ 7	R (Å)	σ ² (Å ²)	R (Å)	σ ² (Å ²)	R (Å)	σ^2 (Å ²)	R (Å)	σ ² (Å ²)	ΔE	Red.
	(Å)	(A)	(Å)	(A)	(Å)	(A)	(Å)	(A)	(eV)	error
HA-presence	1.77	0.0041	2.33	0.0145	3.08	0.0030	3.29	0.0032	-13.0	0.113
HA-absence	1.77	0.0030	2.34	0.0123	3.06	0.0040	3.26	0.0042	-12.6	0.155
$\Delta \mathbf{R} \cdot + 0.02 \text{ Å}$	$\Lambda \sigma^{2}$	+0001 Å								

 ΔR : ± 0.02 A, $\Delta \sigma^{2}$: ± 0.001 A,

R: interatomic distance, σ^2 : Debye-Waller factor, ax: axial, eq: equatorial

The obtained EXAFS data are comparable for both samples, only the U-Si/Al distance is slightly reduced in the presence of HA. The values of the structural parameters obtained for the ternary system U(VI)-HA-kaolinite studied in this work are similar to those of the binary system [2]. Furthermore, they are comparable to values obtained for other systems, e.g., UO₂-silica [3], UO₂-kaolinite KGa-2 [4] and UO₂SiO₄H₂ [5]. Therefore, it could be concluded that HA has no effect on the EXAFS structural parameters in the system U(VI)-HA-kaolinite. Moreover, it seems that in spite of the presence of HA, U(VI) prefers to adsorb rather directly onto kaolinite than via HA, otherwise no U-Si/Al interactions could be detected.

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