XPS study of humic acid/kaolinite interaction

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Previous studies showed that the presence of HA influences the adsorption of U(VI) onto the clay mineral kaolinite [1]. To understand the effect of HA on U(VI) sorption, it is worthwhile to study how HA interacts with the clay surface. XPS is a powerful tool for qualitative and quantitative surface analysis [2].

EXPERIMENTAL. Solutions of 10 mg/L synthetic HA of type M42 [3] in 0.1 M $NaClO_4$ were contacted with kaolinite KGa-1b (Source Clays Repository) at pH 4.0 and 7.5, respectively. 94% of HA was adsorbed at pH 4.0 corresponding to 2.4 mg HA/g kaolinite (sample HA_4.0). At pH 7.5, the HA uptake by kaolinite was 45% corresponding to 1.2 mg/g (sample HA_7.5). An additional sample (R11/04KS) resulted from the synthesis of HA in the presence of kaolinite as described in [4]. The uptake of humic substances by kaolinite was 9 mg/g. Kaolinite powder without any treatment was measured as reference.

For XPS measurements, the dry powders were pressed into indium foil without further treatment. XPS spectra were excited by Mg Kα radiation (1253.6 eV). The analyzer pass energy was 50 eV. The vacuum during the measurements was $2 \cdot 10^{-8}$ mbar. The electrostatic charging of the sample surface was corrected by setting the C1s binding energy to 285.0 eV.

RESULTS. The elements C, O, Al, Si, and minor amounts of Na were detected in the overview spectra of all HA samples. The binding energies and relative intensities of the XPS lines of C, O, Al, and Si were determined from twenty sweeps of each line. Sample HA_7.5 was measured twice. The O1s, Si2s, Al2s, Si2p, and Al2p binding energies of the HA/kaolinite samples agree within the experimental uncertainty of ±0.1 eV with each other and with those of the untreated kaolinite sample (see Table 1).

The following conclusions can be drawn from the relative intensities given in Table 2:

1) Relatively small amounts of adsorbed hydrocarbons, i.e., approximately 1 atom% C, were detected at the untreated kaolinite surface. Although the HA uptake by kaolinite varied by a factor of eight (9 mg/g – 1.2 mg/g), the C1s/Al2p intensity ratio is nearly constant and does not show any correlation with the HA loading. The surface of the HA/kaolinite samples contains only approximately 5 atom% C. This leads to the important conclusion that the surface of the clay particles is not covered by a homogenous HA layer. Part of the HA must be distributed between the particles. This implies that in the ternary system U/kaolinite/HA U(VI) can interact with significant parts of the kaolinite surface that are not covered by HA.

2) All HA/kaolinite samples show the same surface composition with respect to Si, Al, and O as the untreated kaolinite. The chemical composition of the kaolinite surface was not altered by HA adsorption or during HA synthesis.

3) The experimental intensity ratios Si2p/Al2p and O1s/Al2p agree with the theoretical values that were calculated according to the chemical composition of kaolinite, i.e., $\{Al_2[Si_2O_5(OH)_4]\}$.

4) After sputtering sample HA_7.5 10 min with Ar^+ ions, the C1s/Al2p intensity ratio decreased from 0.47 to 0.18 (Table 2). This means that a significant amount of carbon, i.e., approximately 60%, could be removed by Ar^+ sputtering from the surface of the clay particles. However, the C1s/Al2p intensity ratio after sputtering was nearly twice that of the untreated kaolinite surface. This indicates that the remaining HA may not be bound to the kaolinite surface but could be located between the clay particles (*cf* first conclusion).

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REFERENCES

[1] A. Křepelová et al., Report **FZR-419**, 50 (2005).
[2] D. Briggs et al., Surface Analysis by Auger and X-ray Photoelectron Spectroscopy, IM Publications, West Sussex (2003).
[3] S. Sachs et al., Report **FZR-399** (2004).
[4] S. Sachs et al., Report **FZR-419**, 49 (2005).

Tab. 1: Binding energies E_b of O1s, Si2s, Al2s, Si2p, and Al2p XPS lines in eV. E_b(C1s) = 285.0 eV. Error ±0.1 eV.

Sample	O1s	Si2s	Al2s	Si2p	Al2p
HA_4.0	531.9	153.6	119.0	102.6	74.3
HA_7.5	532.0	153.8	119.1	102.7	74.4
HA_7.5	531.9	153.7	119.0	102.6	74.3
HA_7.5[a]	531.8	153.5	119.4	102.5	74.6
R11/04KS	532.0	153.7	119.0	102.7	74.3
KGa-1b[b]	532.2	153.9	119.3	102.9	74.6

a) after 10 min Ar^+ sputtering (4000 V, 10 – 15 μA)
b) untreated kaolinite.

Tab. 2: Relative XPS line intensities and uptake of humic substances by kaolinite. Error ±5 %.

Sample	mg/g	C1s/Al2p	Si2p/Al2p	O1s/Al2p
HA_4.0	2.4	0.61	1.60	20.6
HA_7.5	1.2	0.45	1.55	20.0
HA_7.5	1.2	0.47	1.62	20.1
HA_7.5[a]	-	0.18	1.48	16.6
R11/04KS	9.0	0.52	1.59	20.0
KGa-1b[b]	-	0.10	1.54	19.6
Calculated[c]	-	0	1.52	22.7

a) and b) see Table 1; c) $\{Al_2[Si_2O_5(OH)_4]\}$.