Synthesis and characterization of sulfur-containing humic acid model substances

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Introduction: Depending on their origin, humic substances contain different amounts of sulfur ranging from 0.1 to 3.6% and 0.5 to 1.43% in soil and aquatic humic substances, respectively [1]. Reduced (e.g., sulfides, disulfides, thiols, thiophenes), intermediately oxidized (e.g., sulfoxides, sulfonates) and highly oxidized (e.g., sulfates) sulfur functionalities occur in humic substances [2]. However, their importance for the metal ion complexation by humic substances is still unclear. Sulfur-containing humic acid model substances have been synthesized and characterized for the study of the influence of sulfur functionalities on the metal ion complexation by humic substances.

Experimental: The synthesis of sulfur-containing humic acids type M1-S was performed in aqueous solution based on the synthesis of humic acid type M1 [3]. Syntheses starting from xylose (2.83 M), phenylalanine (0.76 M) and varying amounts of glycine and cysteine were performed. The initial concentration of cysteine was increased from 0 to 0.83 M to obtain humic acids with different sulfur contents. In parallel, the glycine concentration was reduced for the same amount from 0.83 to 0 M, ensuring constant amino acid concentrations in the synthesis mixtures. The resulting synthetic products were characterized for their elemental composition, structure and functionality by elemental analysis, FTIR spectroscopy and potentiometric titration, respectively. First X-ray photoelectron spectroscopy (XPS) measurements of humic acid M1-S-1 were performed in comparison to L-cysteine to identify sulfur species in the synthetic product.

Results: Table 1 shows sulfur content and proton exchange capacity (PEC) of the synthesized humic acids. Both, sulfur content and PEC increases with increasing initial cysteine concentration in the reaction mixtures. However, independent of the sulfur content, all synthetic products show comparable FTIR spectra (not shown) indicating similar overall structures. No FTIR absorption bands pointing to sulfur-containing functional groups were observed in the FTIR spectra. This is attributed to the low sulfur content of the humic acids and the overlapping of IR absorption bands of sulfur functionalities with those of other structural elements of the humic acids.

Table 1. Sulfur content and proton exchange capacity (PEC) of humic acid model substances synthesized with varying cysteine concentrations.

HA	$[Cysteine]_0$ (M)	S (%)	PEC (meq/g)
M1	0	0	1.56 ± 0.13
M1-S-1	0.26	1.94 ± 0.01	1.63 ± 0.16
M1-S-2	0.57	3.94 ± 0.04	1.90 ± 0.17
M1-S-3	0.83	7.72 ± 0.05	2.71 ± 0.13

Figure 1 shows the S 2p XPS spectrum of humic acid M1-S-1. In this spectrum two components were detected indicating the occurrence of at least two different sulfur species in humic acid M1-S-1. Table 2 summarizes the S 2p binding energies of L-cysteine and humic acid M1-S-1.
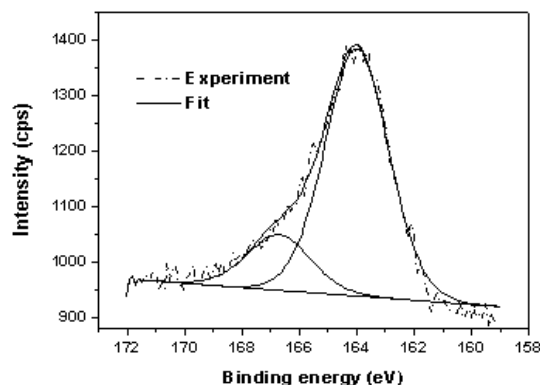

Figure 1. S 2p XPS spectrum of humic acid M1-S-1.

Table 2. S 2p binding energies of cysteine and humic acid M1-S-1 in eV. Electrostatic charging of the sample surface was corrected by setting the C 1s binding energy of M1-S-1 to 285.0 eV.

	S 2p binding energy (eV)	
L-cysteine	163.8	-
M1-S-1	164.0	166.7

Based on literature data [4] and on the binding energy of cysteine, an assignment of the binding energies of humic acid M1-S-1 to different sulfur species was performed. The XPS signal at 164.0 eV can be retained to reduced sulfur species such as thiols, dialkylsulfides and/or disulfides. About 82% of sulfur in humic acid M1-S-1 occurs in this reduced form. The binding energy at 166.7 eV is attributed to sulfoxides, representing about 18% of the sulfur species. From that it is concluded that the main part of sulfur groups in humic acid M1-S-1 occurs in reduced form which is due to the use of L-cysteine as precursor.

Further XPS measurements are performed to characterize the sulfur species in the humic acid model substances with higher sulfur content. The results will be compared to those of natural humic acids. Furthermore, the newly developed sulfur-containing humic acid model substances are used in complexation studies with uranium(VI) to determine the influence of the identified sulfur species on the uranium(VI) complexation by humic acids. The results will be used to assess the impact of sulfur-containing humic acid functionalities on the uranium(VI) complexation by humic acids in comparison to oxygen and nitrogen functionalities.

References
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