

Impact of humic acid on the uranium migration in the environment

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Abstract. Redox properties of different humic acids (HA) were determined and the stability of the oxidation state of U(VI) in presence of humic acid was studied. Applying laser-induced photoacoustic spectroscopy a qualitative spectroscopic proof for the reduction of U(VI) to U(IV) by humic acid was obtained. By column experiments it was found that humic acid influences the transport of both, U(IV) and U(VI). In presence of humic acid both redox species migrate nearly as fast as the groundwater flow. In case of U(VI) humic acid exhibits a clear mobilizing effect. There are strong indications for a similar impact on the U(IV) migration.

Introduction

The remediation of contaminated areas and facilities of the former uranium mining and milling in Saxony and Thuringia (Germany) requires profound knowledge on interaction processes of uranium in natural aquifer systems. Humic acids, ubiquitous, polyelectrolytic, organic macromolecules, are of high importance for these processes. Due to their pronounced ability for complex formation they can impact the speciation and therefore the transport of radiotoxic and toxic metal ions in the environment. In addition to that, humic acids can affect the oxidation state of metal ions because of their redox properties (e.g., Choppin 1999, Zeh et al. 1999, Schmeide and Bernhard 2005). The oxidation state stability of U(VI) in presence of lignin, wood degradation products, and humic acid was studied by Abraham (2002). It was observed, that U(VI) is reduced to U(IV) by these materials. A further characteristic of humic acids is their colloidal behavior in solution. Results of column experiments with natural sandy aquifer material and groundwater rich in humic substances demonstrated that a certain fraction of load metal ions, e.g., U(VI) (Artinger et al. 2002), migrate humic colloid-borne, controlled by kinetic processes, as fast as the groundwater flow.

Reducing conditions can occur in deep underground environments. They are expected in deep water of flooded timbered underground mines (Abraham et al. 2004). Under such conditions, redox processes mediated by wood degradation products and humic substances can induce, among other processes, the reduction of U(VI) to U(IV). Consequently, the tetravalent oxidation state can dominate the speciation and migration of uranium. Profound knowledge on the influence of humic substances on the redox speciation of uranium and on the transport of U(IV)/U(VI) is a pre-requisite for the trustworthy modeling of the uranium migration in the environment. However, the existing understanding and data base for these processes is insufficient up to now.

In order to improve the knowledge on the interaction between humic acids and uranium the redox properties of different humic acids were studied (Sachs et al. 2004 and 2005). Investigations were performed to characterize the oxidation state stability of U(VI) in presence of different humic acids on a time-scale of several weeks (Sachs 2005). In addition to that, the transport behavior of the redox couple U(IV)/U(VI) in quartz sand in presence of humic acid was studied by column experiments and compared to that of U(VI) in absence of humic acid (Mibus et al. 2005).

Experimental

Humic material

The present studies were performed using synthetic humic acid M42 (condensation product of xylose and glutamic acid) and Cat-Gly (oxidation product of catechol synthesized in presence of glycine). Synthesis and characterization of these model substances are described in detail in Sachs et al. (2004). For comparison natural humic acid from Aldrich (AHA) was applied after purification (Kim and Buckau 1988). Table 1 shows some elemental and functional properties of the humic acids used in these study in comparison to natural humic acids (Stevenson 1994). From Table 1 it becomes clear that synthetic humic acid M42 and Cat-Gly show elemental compositions close to those of AHA and other natural humic acids. Due to the use of nitrogen-containing precursors, both model substances show higher nitrogen contents than AHA. The carboxyl group content of M42 and Cat-Gly are similar to those of natural humic acids. However, due to the use of catechol as starting material, Cat-Gly show a significant higher phenolic/acidic OH group content than M42 and AHA.

Table 1. Characterization of the humic acids applied in this study.

	M42	Cat-Gly	Humic acid AHA	Natural humic acid (Stevenson 1994)
Elemental composition				
C (%)	56.1 ± 0.3	48.8 ± 0.1	58.6 ± 0.1	53.8 - 58.7
H (%) ^a	4.1 ± 0.1	2.8 ± 0.2	3.0 ± 0.1	3.2 - 6.2
N (%)	4.4 ± 0.1	5.1 ± 0.1	0.8 ± 0.1	0.8 - 4.3
S (%)	-	0.9 ± 0.1	3.8 ± 0.1	0.1 - 1.5
O (%) ^b	26.8 ± 0.3	31.1 ± 0.2	23.5 ± 0.1	32.8 - 38.3
Ash (%)	0.1	1.7	2.4	
Moisture (%)	8.4	9.5	7.9	
Functional groups				
COOH (meq/g) ^c	3.76 ± 0.09	4.16 ± 0.04	4.49 ± 0.14	1.5 - 5.7
Phenolic/acidic OH groups (meq/g) ^d	2.0 ± 0.2	6.6 ± 0.7	3.1 ± 0.1	2.1 - 5.7

^aCorrected for the water content of the humic acid. ^bThe oxygen content was calculated from the difference to 100% under consideration of the ash and moisture content. ^cDetermined by calcium acetate exchange (Schnitzer and Khan 1972). ^dRadiometrically determined (Bubner and Heise 1994).

Redox studies

The humic acids were characterized with regard to their redox properties (Sachs et al. 2004 and 2005). For that, the formal redox potentials of the humic acids were measured according to Österberg and Shirshova (1997). The Fe(III) redox capacities of the humic materials were determined at pH 3.0 and pH 9.2 according to Mack (2002) and Matthiessen (1995), respectively.

The redox stability of U(VI) in presence of synthetic humic acid Cat-Gly and natural humic acid AHA was studied at pH 6, 8, and 9 in 0.1 M NaClO₄ (Sachs et al. 2005). According to Abraham (2002), U(VI) solutions with humic acid were prepared with initial concentrations of 1·10⁻⁴ M and 0.4 g/L, respectively. The sample preparation was performed applying CO₂-free solutions under nitrogen atmosphere and exclusion of light. The pH values of the solutions were adjusted with NaOH and HClO₄ and periodically checked in order to keep the pH conditions constant. Laser-induced photoacoustic spectroscopy (LIPAS) was applied for the direct spectroscopic detection of U(IV). For that, a tunable laser system (Geipel et al. 1998) was used. The wavelength range between 600 and 675 nm was studied. In contrast to U(VI), U(IV) shows characteristic absorption bands in this range. For sample preparation, an aliquot of the sample solution was acidified with 6 M H₂SO₄ in order to precipitate the humic acid, to decompose U(IV) humate complexes, and to stabilize U(IV) in form of the sulfate complex. The humic acid precipitate was separated and the supernatant was spectroscopically studied by LIPAS.

Column experiments

Migration experiments were performed in a glove box under nitrogen atmosphere, at room temperature and exclusion of light. Columns, 250 mm in length and 50 mm in diameter, packed with quartz sand (marine fine sand from Heerlen, Netherlands, mean grain diameter 153 μm) were used.

The experiments were performed using synthetic humic acid M42. In order to allow a very precise humic acid detection in environmentally relevant concentrations, the humic acid solutions were spiked with ^{14}C -labeled synthetic humic acid M42 (Sachs et al. 2004). Both, the unlabeled and ^{14}C -labeled synthetic humic acid show comparable properties.

The transport properties of the conservative tracer were determined by tritiated water (HTO). For the study of the U(IV) migration in presence of humic acid, U(IV) was prepared by electrochemical reduction of an uranyl (^{234}U) nitrate solution. The $^{234}\text{U(IV)}$ solution was added to the ^{14}C -labeled humic acid solution. The final concentrations of uranium and humic acid in solution amounted to 50 mg/L (^{14}C : 70 kBq/L) and $1 \cdot 10^{-6} \text{ M } ^{234}\text{U}$ (64 kBq/L), respectively. The pH value was adjusted to pH 7.5 and the ionic strength was set to 0.1 M NaClO_4 . This solution was equilibrated for two hours prior to start of the experiment. A continuous pulse was applied to inject the tracer. The tracer impulse was followed by a multiple elution of the column with 0.1 M NaClO_4 (pH 7.5). Breakthrough curves of humic acid and uranium were measured by fraction analysis using liquid scintillation counting (LSC; Wallac, Perkin Elmer with α - β separation).

In order to differentiate between U(IV) and U(VI) in the initial solution and in the effluent fractions the redox speciation was determined by liquid-liquid extraction with TTA (thenoyltrifluoroacetone; Bertrand and Choppin 1982). A detailed

Table 2. Formal redox potentials (E^{0*}) and Fe(III) redox capacities determined for the studied humic materials.

Humic acid	E^{0*} (mV)	$\Delta E/\Delta \text{pH}$ (mV/pH)	Fe(III) Redox capacity (meq/g) ^a	
			pH 3.0	pH 9.2
M42	548 ± 19	-67 ± 10	6.1 ± 0.1	18.1 ± 0.6
Cat-Gly	517 ± 12	-57 ± 12	14.5 ± 1.6	36.9 ± 0.2
AHA	570 ± 9	-65 ± 1	1.2 ± 0.1	7.2 ± 1.9

^a Reaction time: ~3 weeks.

Table 3. Redox potentials (E_h) of U(VI)/U(IV) and formal redox potentials (E^{0*}) of humic acid Cat-Gly and AHA at pH 0 and pH 8.

		pH 0	pH 8
U(VI)/U(IV) (Choppin 1983)	E_h (mV)	338	-70 ± 80
Cat-Gly	E^{0*} (mV)	517 ± 12	61 ^a
AHA	E^{0*} (mV)	570 ± 9	50 ^a

^a Calculated from the pH dependence of the formal redox potential.

description of the experimental set-up and of all experimental conditions is given in (Mibus et al. 2005).

Results and discussion

Redox properties of the studied humic acids

The results of the humic acid characterization with regard to their redox properties are summarized in Table 2.

The formal redox potential of AHA agrees with those of Aldrich humic acid (578 ± 16 mV, $-(57 \pm 10)$ mV/pH) and lignin (579 ± 6 mV, $-(54 \pm 1)$ mV/pH) determined by Mack (2002). Compared to AHA, slightly lower formal redox potentials were measured for M42 and Cat-Gly.

The comparison of the Fe(III) redox capacities shows that both humic acid alike products, especially synthetic humic acid Cat-Gly, exhibit a more pronounced redox behavior towards Fe(III) ions than AHA. In previous studies it was observed that phenolic/acidic OH groups dominate the redox properties of humic acids (Sachs et al. 2004). Thus, the significant increase of the Fe(III) redox capacities of Cat-Gly compared to M42 and AHA basically can be ascribed to its higher phenolic/acidic OH group content.

Redox stability of U(VI) in presence of humic acids

The ability of humic acid to influence the oxidation state of metal ions is determined by their redox potentials. Comparing the redox potentials of U(VI)/U(IV) with the formal redox potentials of AHA and Cat-Gly (Table 3) it becomes clear that these are close together in the studied pH range. Therefore, it can be concluded that a humic acid-mediated reduction of U(VI) to U(IV) is possible.

Fig. 1 depicts the LIPAS spectra of the uranium solutions equilibrated with synthetic humic acid Cat-Gly for 52 days. The Cat-Gly samples show in their LIPAS spectra two absorption bands at about 640 and 655 nm. In contrast to that, no absorption signals were found in the spectra of the AHA solutions (not shown, Sachs 2005). Thus, it was concluded that no detectable U(IV) concentration (limit of detection 10^{-6} mol/L; Abraham 2002) was formed by an AHA-mediated U(VI) reduction.

The U(IV) aquo ion shows characteristic absorption maxima at 629.5, 649.1, and 671.7 nm (Geipel et al. 2002). These are close to those observed in the uranium solutions of the Cat-Gly samples. This is an indication for the occurrence of U(IV) in the uranium solutions of the synthetic product. Further, the spectra of the synthetic humic acid test solutions are similar to that which was obtained after equilibration of a U(VI) solution with wood degradation products. In this study the

spectroscopic evidence for the reduction of U(VI) to U(IV) by these substances was given (Abraham, 2002).

In the measured LIPAS spectra the absorption bands are shifted compared to those of the solvated U(IV) ion. Similar peak shifts were already identified for the U(IV) complexation by arsenate (645.1, 662.9 nm; Geipel et al. 2002), phosphate (645.0, 656.6, 667.0 nm; Geipel et al. 2002) and sulfate (634.6, 652.8, 670.0 nm; Sachs et al. 2005). The observed shifts of the absorption maxima can be attributed to the formation of U(IV) sulfate complexes after adding sulfuric acid for sample preparation. The deviations of the peak maxima compared to those of U(IV) in 1.2 M H₂SO₄ (Sachs et al. 2005) could be explained by an additional interaction of U(IV) by incompletely removed humic acid molecules.

It can be concluded that humic acid Cat-Gly with pronounced redox properties is able to reduce a part of the added U(VI) to U(IV). The higher Fe(III) and U(VI) redox capacities of Cat-Gly compared to AHA can be attributed to its higher phenolic/acidic OH group content. Studies are in progress in order to quantify the U(VI) redox capacities of Cat-Gly. Similar results were already obtained for the reduction of Np(V) to Np(IV) (Schmeide and Bernhard 2005) and can be expected for other actinide and metal ions.

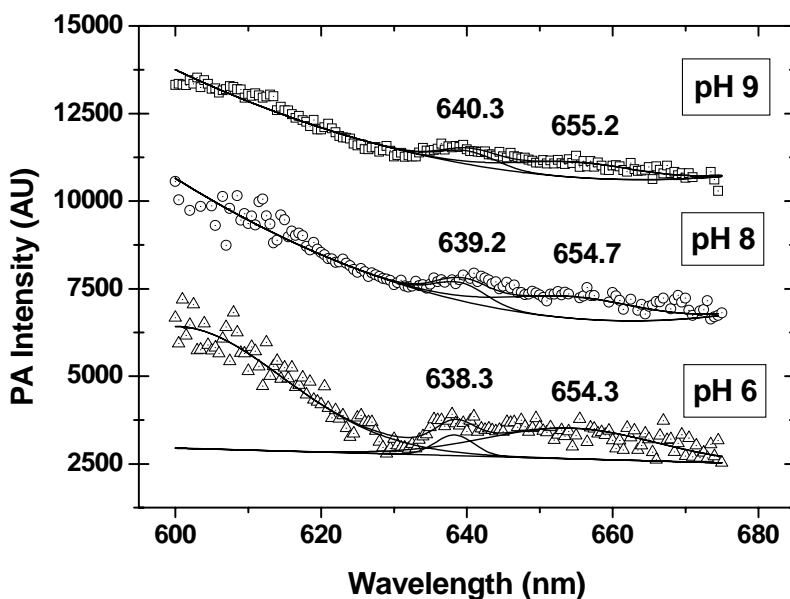


Fig. 1. LIPAS spectra of uranium solutions equilibrated with humic acid Cat-Gly at pH 6, 8, and 9. The humic acid was separated before the LIPAS measurements. The spectra are shifted along the y-axis for clarity.

Migration of U(IV)/U(VI) in presence of humic acid

The distribution of U(IV) and U(VI) in the starting solution amounts to 13 % and 84 %, respectively. The measured redox speciation was stable over the entire experiment. It was also determined in the effluent fractions. Therefore, it can be concluded that no redox processes occurred in the column.

Fig. 2 shows breakthrough curves for humic acid, U(IV) and U(VI). Retardation factors, R_f , representing the quotient of the effluent volume and the effective pore volume, as well as total recoveries of all studied species were determined. These are summarized in Table 4 in comparison to those of U(VI) in absence of humic acid (Mibus et al. 2005).

The R_f values of humic acid, U(IV), and U(VI) agree within their experimental errors. They are only somewhat higher than that of the conservative tracer HTO ($R_f = 1$). This indicates a slightly retarded transport of the studied species compared to the water flow.

Comparing the transport parameters of U(VI) in absence and presence of humic acid (Table 4) it becomes clear that the presence of humic acid significantly decreases the R_f value of U(VI). This points to an accelerated U(VI) transport in presence of humic colloids. Furthermore, the U(VI) recovery is increased in presence of humic acid, which is attributed to the formation of soluble U(VI) humate complexes. From these results it can be deduced, that the U(VI) migration in presence of humic acid is governed by a humic colloid-borne transport.

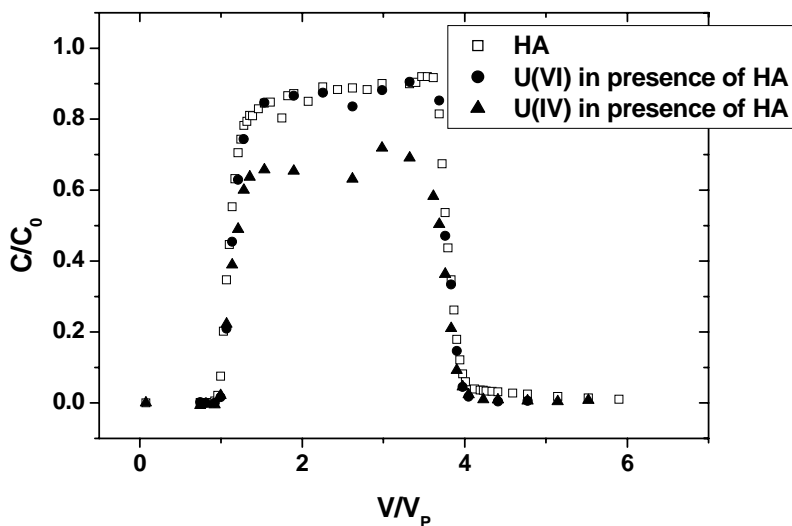


Fig. 2. Breakthrough curves of HA, U(IV), and U(VI) in the laboratory system quartz sand/0.1 M NaClO₄ at pH 7.5 ([HA]: 50 mg/L, [U]_{tot}: 1·10⁻⁶ mol/L). C: measured and C₀: initial concentration; V: effluent volume; V_p: effective pore volume.

Table 4. Retardation factors (R_f) and total eluate recoveries (R_{eluate}) of humic acid, U(IV) and U(VI) (Mibus et al. 2005).

Species	R_f	R_{eluate}
Humic acid	1.09 ± 0.02	0.90 ± 0.02
U(IV) + humic acid	1.11 ± 0.02	0.66 ± 0.05
U(VI) + humic acid	1.13 ± 0.02	0.90 ± 0.06
U(VI)	2.22 ± 0.11	0.43 ± 0.02

Although U(IV) and U(VI) are characterized by different thermodynamic properties (Choppin 1983) no significant differences were observed in their R_f values under the applied experimental conditions. However, the eluate recoveries of the studied species differ. These effects are caused by association/dissociation processes in the system U(IV)/U(VI)-humic acid-quartz sand. In spite of the higher uncertainty of the extraction data, the U(IV) recovery is lower than that of U(VI). This points to a stronger interaction of U(IV) with the quartz sand surface and thus to a more distinct immobilization. Nevertheless, there are strong indications that humic acid has not only a mobilizing effect on the U(VI) transport in the investigated system but also on the U(IV) migration due to its complexing ability.

Conclusions

The redox properties of humic acids with different functionalities were determined. Among the studied materials synthetic humic acid Cat-Gly, that is characterized by a high phenolic/acidic OH group content compared to the other humic acids used in this work, shows the most pronounced redox properties. Applying this synthetic humic acid a qualitative spectroscopic proof for the reduction of U(VI) to U(IV) by humic acid with distinct redox properties was obtained. By means of column experiments it was observed that humic acid affects the migration behavior of both U(IV) and U(VI). The column experiment shows that U(IV) and U(VI) can be transported by humic colloids. In case of U(VI) a strong transport accelerating effect of humic acid was observed.

Although the systems under investigation represent a considerable simplification of natural aquifers they are suitable to identify processes that impact the migration of uranium in the environment. The performed studies demonstrate the relevance of humic materials for the migration of uranium under oxic as well as under reducing conditions. From that, it follows the requirement to involve interaction processes between humic acids and uranium in the geochemical modeling of the migration behavior of uranium in the environment.

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