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Np(V) reduction by humic acid: Contribution of reduced sulfur functionalities to the redox behavior of humic acid

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ABSTRACT

The role of sulfur-containing functional groups in humic acids for the Np(V) reduction in aqueous solution has been studied with the objective to specify individual processes contributing to the overall redox activity of humic substances. For this, humic acid model substances type M1-S containing different amounts of sulfur (1.9, 3.9, 6.9 wt.%) were applied. The sulfur functionalities in these humic acids are dominated by reduced-sulfur species, such as thiols, dialkylsulfides and/or disulfides. The Np(V) reduction behavior of these humic acids has been studied in comparison to that of the sulfur-free humic acid type M1 at pH 5.0, 7.0 and 9.0 under anaerobic conditions by means of batch experiments. For Np redox speciation in solution, solvent extraction and ultrafiltration were applied. In addition, redox potentials of the sample solutions were monitored. At pH 5.0, both rate and extent of Np(V) to Np(IV) reduction were found to increase with increasing sulfur content of the humic acids. At pH 7.0 and 9.0, sulfur functional groups had only a slight influence on the reduction behavior of humic acid toward Np(V). Thus, in addition to quinoid moieties and non-quinoid phenolic OH groups, generally acknowledged as main redox-active sites in humic substances, sulfur functional groups have been identified as further redox-active moieties of humic substances being active especially in the slightly acidic pH range as shown for Np(V). Due to the low sulfur content of up to 2 wt.% in natural humic substances, their contribution to the total reducing capacity is smaller than that of the other redox-active functional groups.

1. Introduction

Humic substances (fulvic acids and humic acids), organic polyelectrolytes naturally occurring in the environment, are known for their potential to influence actinide transport by forming dissolved complexes and stable colloids and by affecting redox states and sorption behavior of actinides (Artinger et al., 2000, 2002; Choppin, 1992; Kim, 1986; Silva and Nitsche, 1995). Thus, with respect to risk assessment of contaminated sites and long-term safety assessment of deep geological nuclear waste repositories the role of humic substances for the geochemical behavior of actinides has to be studied.

In general, redox processes control the chemical speciation and thus, mobility of toxic and radiotoxic metal ions in the environment. For instance, Np(V), which is dominant under oxic conditions, poorly sorbs to mineral surfaces and is therefore regarded as a rather mobile species. In contrast, Np(IV), which is prevalent under reducing conditions in deep geological environments, is regarded as much less mobile due to its strong tendency to hydrolyze even at low pH (Neck and Kim, 2001) and to sorb onto mineral surfaces. However, it is known that tetravalent actinides strongly interact with organic ligands such as humic substances forming soluble complexes or stable colloids and thus, can become mobile (e.g., Artinger et al., 2000; Evans et al., 2011; Reiller et al., 2008). For instance, the Np(IV) sorption onto kaolinite was found to be very low in the presence of humic acid especially in the near-neutral pH range which was attributed to the strong Np(IV) complexation by humic acid in solution (Schmeide and Bernhard, 2010).

In the literature, the redox activity of humic substances has been primarily ascribed to the reversible hydroquinone/quinone redox couple with semiquinone-type free radicals as significant electron donor/acceptor intermediate species (e.g., Aeschbacher et al., 2011; Cory and McKnight, 2005; Lovley et al., 1996; Scott et al., 1998). Furthermore, it is ascribed to the oxidation of phenolic OH groups to phenoxy radicals (e.g., Helburn and MacCarthy, 1994; Rocha et al., 2003; Sachs and Bernhard, 2011; Schmeide and Bernhard, 2009) with their subsequent reactions, such as coupling reactions and tautomerizations (Musso, 1967), leading to a regeneration of phenolic OH groups. The role of quinoid moieties and phenolic OH groups for the redox behavior of humic substances toward Np, Pu and U was studied in detail by various authors (e.g., Marquardt et al., 2004; Sachs and Bernhard, 2011; Schmeide and Bernhard, 2009; Shcherbina et al., 2007).

In addition to quinone-like moieties and phenolic OH groups, reduced forms of organically bound sulfur and nitrogen, present in natural organic matter, have been proposed as potential redox-active groups (Fimmen et al., 2007; Ratasuk and Nanny, 2007; Szulczewski et al., 2001).

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Depending on their origin, humic substances contain different amounts of sulfur. For instance, for soil and aquatic humic substances sulfur contents of 0.1–3.6 and 0.5–1.43 wt.%, respectively, were reported (Xia et al., 1998). For humic acids, sulfur contents ranging from 0 to 2 wt.% were described (Stevenson, 1994). The speciation of organic sulfur in natural humic substances has been determined by X-ray absorption near-edge structure (XANES) spectroscopy (e.g., Einsiedl et al., 2008; Hundal et al., 2000; Hutchison et al., 2001; Olivella et al., 2002; Schäfer et al., 2005; Solomon et al., 2003; Vairavamurthy et al., 1997; Zhao et al., 2006), X-ray photoelectron spectroscopy (XPS) (e.g., Bubert et al., 2000; Fimmen et al., 2007; Olivella et al., 2002), and pyrolysis-mass spectrometry (e.g., Olivella et al., 2002). Sulfur occurs in humic substances in various oxidation states both in reduced (thiol (S_{-1}), thiophene, sulfide, di- and polysulfide (S_0)) and oxidized (sulfoxide (S_{+2}), sulfone (S_{+4}), sulfonate (S_{+5}), ester-bonded sulfate (S_{+6})) forms. Reduced-sulfur structures (organic sulfides, di- and polysulfides) occur essentially as intramolecular bridges as opposed to the highly oxidized forms of sulfur which can only be present as end groups (Vairavamurthy et al., 1997). The proportions of the various sulfur oxidation states were found to depend on humic substance origin and the prevailing specific geochemical conditions as well as on the method used for isolation of the humic material (Hutchison et al., 2001; Xia et al., 1998). It was detected that a significant proportion of humic sulfur occurs in the reduced oxidation state. The amount of reduced organic sulfur ranged from 10% of the total sulfur in humic substances from mineral soils (Xia et al., 1998) to more than 50% in some aquatic fulvic acids (Einsiedl et al., 2008; Fimmen et al., 2007; Xia et al., 1998) and even up to 72% for a salt marsh humic acid (Vairavamurthy et al., 1997). A high content of reduced sulfur was also shown for muck humic substances with 56–62% of the total sulfur (Szulczewski et al., 2001) as well as for enhanced dissolved organic carbon and channel brine-derived fulvic acids in the Gorleben aquifer system with 69% and 61%, respectively (Schäfer et al., 2005). Reduced organic sulfur groups in humic acid were found to be stable in the pH range 3.5 to 12.4, even when exposed to O_2 for up to 44 h (Hutchison et al., 2001).

By means of XANES spectroscopy, it could be shown that a thiol/disulfide redox couple is involved in the Cr(VI) reduction by humic substances in chromium-contaminated soils analogous to the Cr(VI) reduction by simple thiol-containing compounds such as cysteine and glutathione (Szulczewski et al., 2001).

While sulfur functional groups of natural organic matter have not been studied as reducing agents toward actinides such as U, Np or Pu so far, simpler organic compounds containing sulfur in the reduced form such as various free and coordinated thiols as well as sulfide were found to reduce Np(VI) and Pu(VI) (Lavallee et al., 1973; Nash et al., 1986; Weschler et al., 1974). Thus, it is to check whether or not sulfur functional groups in humic substances act as redox-active functional units toward actinides. Such detailed investigations allow mechanistic insights into redox processes of humic substances that affect the mobility of actinides under environmentally relevant conditions.

In the present work, the role of sulfur functional groups of humic acids for their reduction capability toward Np(V) was studied for the first time. For this, humic acid model substances M1-S-1, M1-S-2 and M1-S-3 containing 1.9, 3.9, or 6.9 wt.% sulfur (Sachs et al., 2010), were applied. Their Np(V) reduction capability was studied as a function of pH under anaerobic conditions and compared to that of the respective sulfur-free synthetic humic acid (M1; (Pompe et al., 1996)). Previous studies have shown that the sorption and metal ion complexation behavior of the humic acid model substance M1 is comparable to that of natural humic acids (e.g., Pompe et al., 1996, 2000; Sachs et al., 2005; Schmeide et al., 2000, 2003). In a recent study applying the sulfur-containing humic acid model substances an involvement of reduced sulfur functionalities, such as thiol groups, in the U(VI) complexation by humic acid has been shown (Sachs et al., 2010).

2. Experimental

2.1. Humic substances

The following synthetic humic acid model substances, prepared from xylose, glycine, phenylalanine, cysteine and water (Sachs et al., 2010), were applied: M1 which contains no sulfur due to synthesis in the absence of cysteine and furthermore, M1-S-1, M1-S-2 and M1-S-3 that contain increasing amounts of sulfur (1.9, 3.9, or 6.9 wt.%) due to the use of increasing amounts of L-cysteine as precursor material (cf. Table 1).

The functional group contents of these humic acids are compiled in Table 1. The carboxyl group content, determined with the calcium acetate exchange method (Schnitzer and Khan, 1972), slightly increases from M1 to M1-S-3. The phenolic/acidic OH group content, analyzed by a radiometric method based on the derivatization of humic acid functional groups with [^{14}C]diazomethane (Bubner and Heise, 1994), is nearly the same for all humic acid samples. The elemental composition (not shown) and the functional group contents of these humic acids are comparable to those of natural humic acids. Further details to synthesis and characterization of these humic acids are given by Sachs et al. (2010).

2.2. Sample preparation

The preparation of the initial Np(V) stock solution (^{237}Np, 0.03 M Np in 1 M $HClO_4$) from NpO_2 (CEA Marcoule, France) is described by Schmeide and Bernhard (2009). The oxidation state purity of the stock solution was verified by NIR absorption spectroscopy and solvent extraction.

The samples were prepared in a glove-box (N_2 atmosphere, <20 ppm O_2) using O_2- and CO_2-free Milli-Q water (Milli-RO/Milli-Q-System, Millipore, Molsheim, France). For preparation of the various humic acid stock solutions, humic acid (25 mg) was dissolved in about 3 mL water with addition of 0.1 M CO_2-free NaOH (295 µL to 425 µL depending on humic acid) and degassed under vacuum. Then, the total volume of the humic acid solutions was increased to 10 mL by adding water. The samples for redox studies were prepared by adding 2 mL humic acid stock solution and 5 mL degassed 1 M $NaClO_4$ stock solution (p.a., Merck, Darmstadt, Germany) and filling up to 50 mL with water. The reduction experiments were started by adding 85 µL of a diluted Np(V) stock solution (2.94×10^{-3} M) to the humic acid solutions. The final Np and humic acid concentrations were 5×10^{-6} M and 100 mg/L, respectively. The ionic strength of the solutions was 0.1 M ($NaClO_4$). The pH values of the samples (pH 5.0, 7.0, 9.0) were adjusted with diluted NaOH (p.a., Merck) or $HClO_4$ (p.a., Merck) solutions, no buffers were added. During the experiments, the pH of the solutions was checked and readjusted repeatedly. All samples were stored in 50 mL centrifuge tubes (Cellstar, Greiner Bio-One, Kremsmünsterand, Austria) at room temperature. The tubes were wrapped in aluminum foil to exclude light-induced degradation processes of the organic material. The experiments were conducted over an 11-month period. The Np concentration in solution was determined by liquid scintillation

Table 1
Content of functional groups and sulfur in humic acids.

Humic acid	COOH[a]	Phenolic/acidic OH[b]	S[a]	
	(meq/g)	(meq/g)	(wt.%)	(mmol/g)
M1	1.18 ± 0.20	1.82 ± 0.01	0	0
M1-S-1	1.49 ± 0.02	2.35 ± 0.02	1.9 ± 0.1	0.6 ± 0.03
M1-S-2	1.64 ± 0.06	1.86 ± 0.02	3.9 ± 0.1	1.2 ± 0.03
M1-S-3	1.70 ± 0.14	1.88 ± 0.01	6.9 ± 0.1	2.2 ± 0.03
Hyd-Glu[c]	3.65 ± 0.14	5.8 ± 0.2	0.2 ± 0.1	0.1 ± 0.03

[a] Sachs et al. (2010).
[b] Radiometrically determined according to Bubner and Heise (1994).
[c] Sachs and Bernhard (2011).