Redox and Complexation Interactions of Neptunium(V) with Quinonoid-Enriched Humic Derivatives

NATALIA S. SHCHERBINA,*,†,‡
IRINA V. PERMINOVA,†
STEPAN N. KALMYKOV,†
ANTON N. KOVALENKO,†
RICHARD G. HAIRE,§ AND
ALEXANDER P. NOVIKOV‡

Department of Chemistry, Lomonosov Moscow State University, 119992 Moscow, Russia, Vernadsky Institute of Geochemistry and Analytical Chemistry, RAS, 119991 Moscow, Russia, Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

Actinides in their higher valence states (e.g., MO_2^+ and MO_2^{2+}, where M can be Np, Pu, etc) possess a higher potential for migration and in turn pose a substantial environmental threat. To minimize this potential for migration, reducing them to lower oxidation states (e.g., their tetravalent state) can be an attractive and efficient remedial process. These lower oxidation states are often much less soluble in natural aqueous media and are, therefore, less mobile in the environment. The research presented here focuses on assessing the performance of quinonoid-enriched humic derivatives with regards to complexing and/or reducing Np(V) present in solution. These "designer" humics are essentially derived reducing agents that can serve as reactive components of a novel humic-based remediation technology. The derivatives are obtained by incorporating different quinonoid-moieties into leonardite humic acids. Five quinonoid-derivatives are tested in this work and all five prove more effective as reducing agents for selected actinides than the parent leonardite humic acid, and the hydroquinone derivatives are better than the catechol derivatives. The reduction kinetics and the Np(V) species formed with the different derivatives are studied via a batch mode using near-infrared (NIR)-spectroscopy. Np(V) reduction by the humic derivatives under anoxic conditions at 293 K and at pH 4.7 obeys first-order kinetics. Rate constants range from 1.70×10^{-6} (parent humic acid) to $1.06 \times 10^{-5} \, sec^{-1}$ (derivative with maximum hydroquinone content). Stability constants for Np(V)–humic complexes calculated from spectroscopic data produce corresponding $Log\beta$ values of 2.3 for parent humic acid and values ranging from 2.5 to 3.2 at pH 4.7 and from 3.3 to 3.7 at pH 7.4 for humic derivatives. Maximum constants are observed for hydroquinone-enriched derivatives. It is concluded that among the humic derivatives tested, the hydroquinone-enriched

ones are the most useful for addressing remedial needs of actinide-contaminated aquifers.

Introduction

Actinides in their higher valence states (e.g., MO_2^+ and MO_2^{2+}, where M can be Np, Pu, or other actinide) pose a substantial threat to the environment due to their higher solubilities, potential for migration, and radio-toxicity (1−5). In this regard, neptunium is of special concern given the stability of Np(V) and long half-life of 2.14×10^6 years for its most common isotope, ^{237}Np (1). The interactions of actinides with natural materials are important facets affecting their migration, release and overall control within the environment (4, 5). Changing the oxidation state of actinides is one means of altering their release and migration. For example, simple reduction to the tetravalent state reduces the mobility of actinides in higher valence state (e.g., Np(V, VI), Pu(V, VI), U(VI)) by decreasing solubility and increasing sorption to other matrices (1−4).

In this regard, of particular importance are interactions of actinides with humic substances (HS), which are naturally occurring polyelectrolytes with inherent redox properties (6−13). HS can facilitate actinide transport by forming soluble complexes and stable colloids (14). Conversely, HS can form stable coatings on immobile mineral surfaces where they can then intercept and retain dissolved or complexed actinides (15). It has been reported that HS can reduce actinides, and in turn, alter their speciation, solubility, and sorption properties (11, 16). In this way, HS could be used to control actinide migration.

The redox properties of humic materials are the result of reversible redox transformations of quinonoid moieties inherent within humic structures (16, 17). Reductions of Cr-(VI) to Cr(III) and Mn(IV) to Mn(II) by natural HS were reported (18, 19). According to Maes et al. (20), TcO_4^- was reduced to Tc(IV) during one week by dissolved boom clay HS. The TcO_4^- reduction was observed at almost neutral pH (8.3) and under highly reducing conditions with the electrode potential (E_h) ranging from −270 to −320 mV. XANES (X-ray absorption near edge structure) spectroscopic studies confirmed the formation of HS−Tc(IV) species in the presence of different Fe-containing reducing surfaces and at neutral pH (7.0−8.7) (21).

At the same time, data on the interactions of HS with actinides, particularly with regards to Np(V) reduction, would appear rather limited. Experimental results on Np(VI), Pu-(VI), and Pu(V) reduction by natural HS were reported by Nash et al. (11) and by Andre and Choppin (22). The latter authors established a slow reduction of Pu(V) with Aldrich HA in the absence of light at pH 7. The reduction was concentration dependent; the rate increased significantly when the system was exposed to daylight. Choppin (23) did not observe Np(V) reduction in the presence of HS. In contrast, Artinger et al. (24) reported a slow rate of Np(V) reduction by dissolved organic matter (DOM) isolated from Gorleben groundwater (Germany). The reduction occurred at pH 7.6 under reducing conditions ($E_h = −150$ mV). Kim and Zeh (25, 26) also reported Np(V) and U(VI) reduction by Gorleben groundwater, containing 65.6 and 19.2 mg C/L of humic and fulvic acids, respectively. According to their observations, the reduction of Np(V) occurred first through the complexation with HA and FA, followed by reduction to Np(IV). Sakamoto et al. (27) also demonstrated that the presence of HS strongly influenced Np(V) migration through

* Corresponding author phone/fax: (+7-495) 9393220; e-mail: sher@radio.chem.msu.ru.
† Lomonosov Moscow State University.
‡ Vernadsky Institute of Geochemistry and Analytical Chemistry.
§ Oak Ridge National Laboratory.

laboratory sandy soil and granite columns due to formation of Np(IV)−humic complexes.

These findings suggest HS could be used to remediate actinide contaminated sites if the redox properties of natural humics could be enhanced via chemical modification. The humic derivatives would function as reactive agents in a comprehensive site remediation strategy designed to decrease actinide mobility by reducing species to the tetravalent state. The level of site remediation would depend partly on the actinide of concern, the redox properties of the humic derivative, site geochemistry, and the requirements of long-term stewardship.

The objective of this work was to test the redox performance of humic derivatives enriched with quinonoid moieties with respect to the Np(V) reduction. Quinonoid moieties were incorporated into leonardite humic acids using a polycondensation technique as described in our previous publication (28). NIR spectroscopy was used to study reactions kinetics. The conditional stability constants for the Np(V)−HS complexes were calculated using a charge-neutralization model (8).

Materials and Methods

All Reagents employed here were of analytical grade and used without further purification. The (2-ethylhexyl)-phosphate (HDEHP) (Merck-Schuchardt, Germany) was of 99% purity and the 1-(2-Thenoyl)-3,3,3-trifluoroacetone (TTA) was purchased from Lancaster (UK). All experiments were conducted using deionized, "MilliQ" water (Ω = 18MOhm).

^{237}Np Stock Solution, NpO_2^+ in 1 M HNO_3, was obtained from RIAR (Dimitrovgrad, Russia). The ^{233}Pa daughter was separated from the parent ^{237}Np by solvent extraction using 1-(2-thenoyl)-3,3,3-trifluoroacetone (TTA) in toluene as described in ref 29. The radiochemical purity of the ^{237}Np solution was determined using an alpha-spectrometer equipped with Si-surface barrier detector (model 7401, Canberra Ind.). The final concentration of the ^{237}Np in the stock solution was 1.4×10^{-2} M as determined by liquid scintillation counting (LSC, TriCarb2700TR, Canberra Ind.).

Leonardite Humic Acid (CHP) and Its Quinonoid-Enriched Derivatives were prepared as described in our previous publication (28). In brief, the parent humic material, leonardite humic acid, was isolated from commercial potassium humate (Powhumus, Humintech Ltd, Germany) and the purified HA was modified using polycondensation techniques (28). Three different types of CHP derivatives enriched with hydroquinone (HQ) and catechol (CT) moieties were generated.

Hydroquinone enriched derivatives were synthesized using formaldehyde condensation of CHP with HQ and radical condensation of CHP with p-benzoquinone (BQ). CT-enriched derivatives were created using formaldehyde condensation (28). The derivatives were synthesized at monomer to CHP ratios of 100, 250, and 500 mg per gram of CHP. The five derivatives, modified with HQ, CT, and BQ, were designated as HQ100, HQ250, HQ500, CT500, and BQ500. The content of functional groups and redox capacity of the derivatives are given in Table 1.

Stock solutions of the humic derivatives (13.5 g/L) were prepared by dissolving a known mass of a dry sample in a small volume of concentrated NaOH, and then adjusting to the desired volume with deionized water. These stock solutions were prepared in a glove box under an anoxic and carbonate free atmosphere (N_2) and stored in the dark at +4 °C to avoid oxidation and/or photolysis of humic derivative.

Kinetic Studies were conducted in a nitrogen atmosphere (99.9% purity) in a glove box. The experimental arrangement for studying pH dependence employed Np(V) and HS

TABLE 1. Functional Groups Content and Redox Capacity of the Humic Derivatives Used (27)

sample	description	−COOH[a], mmol/g	−ArOH[b], mmol/g	redox capacity[c], mmol/g
CHP	Leonardite HA	4.2 ± 0.2	1.1	0.6 ± 0.1
	copolymers of CHP with hydroquinone			
HQ100	HQ:CHP ratio of 100:1000 mg	4.3 ± 0.3	4.0	1.2 ± 0.2
HQ250	HQ:CHP ratio of 250:1000 mg	3.6 ± 0.1	4.4	2.9 ± 0.1
HQ500	HQ:CHP ratio of 500:1000 mg	3.1 ± 0.2	4.3	4.0 ± 0.1
	copolymers of CHP with catechol			
CT500	CT:CHP ratio of 500:1000 mg	3.6 ± 0.8	4.6	2.9 ± 0.4
	copolymers of CHP with p-benzoquinone			
BQ500	BQ:CHP ratio of 500:1000 mg	3.9 ± 0.1	4.1	2.0 ± 0.1

[a] Determined by calcium acetate method (30). [b] Calculated as a difference between total acidity and −COOH content (30). [c] Cetermined as described in ref 31 using ferricyanide as an oxidant.
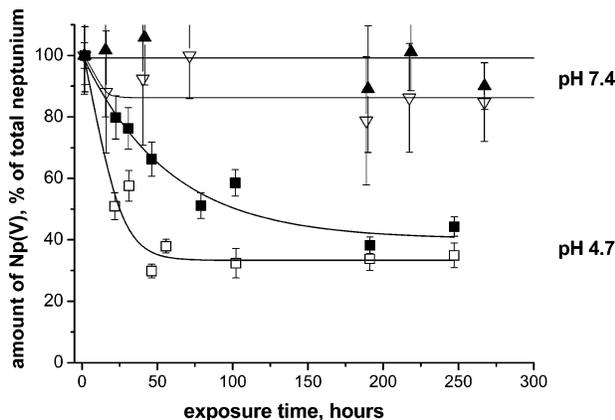
concentrations of 3.5×10^{-5} M and 250 mg/L respectively, and pH values of 4.7 and 7.4. A slightly different set up was used for comparative studies of reducing performance among the different humic derivatives. They employed Np(V) and HS concentrations of $6.6 \cdot 10^{-5}$ M and 500 mg/L, respectively, at pH 4.7. Deionized water was used as a solvent without electrolytes.

Working solutions were prepared by adding aliquots of the Np(V) and HS solutions into 22 mL scintillation vials, adjusting them to the desired pH, diluting with deionized water, and then transferring resulting solutions into plastic cuvettes (PS, Sarstedt, Ltd & Co, Germany) having a one cm path length. The cuvettes were covered with plastic tops, sealed with Parafilm, and kept in the glove box during the entire exposure time of 400 h except when they were removed for the NIR analyses.

NIR Absorption Spectroscopy of Np(V) in the presence of the quinonoid-enriched humic derivatives was conducted using a UV/vis/NIR-spectrophotometer (Cary-50, Varian,). The absorption spectra of the Np(V)−HS solutions were measured from 950 to 1030 nm. Given the high concentrations (250−500 mg/L) of the strongly absorbing HS, all spectra were recorded versus solutions having the same HS concentrations and at the pH, used in the experimental solutions.

The spectra of the aqueous NpO_2^+ ion and of Np(V)−S complexes showed absorbance maxima at 981.5 and 987 nm, respectively (see Supporting Information Figure S1). The molar extinction coefficient of the NpO_2^+ ion was calculated from optical densities of neptunyl-solutions from 2.52×10^{-5} to 1.39×10^{-4} M and it was determined to be 377.7 L·mol^{-1}·cm^{-1}. This value is close to the 395 L·mol^{-1}·cm^{-1} value reported in the literature (32, 33). The observed difference may be due to differences in pH conditions. A determination of the molar extinction coefficient of Np(V)−humic complexes was not feasible in our study, as all humic materials used (including the parent leonardite HA) reduced Np(V). As a result, the value of 222.4 L·mol^{-1}·cm^{-1} was used as determined by Kim and Sekine (8).

NIR Spectra were processed using Peak Fit (Version 4) software. The program performs a deconvolution of the spectra into two components as shown in Figure S1 (Supporting Information), which correspond to the free NpO_2^+ species and the neptunium bound to the humic derivative. The amount of residual Np(V) in the presence of quinonoid-enriched humic derivatives was calculated to be the sum of complexed and freely dissolved Np(V) ions.

FIGURE 1. Kinetics of Np(V) reduction by humic derivatives under anoxic conditions at different pH: filled symbols, BQ500; open symbols, HQ250; $C_0(^{237}Np) = 3.8 \times 10^{-5}$ M, $C_0(HS) = 250$ mg/L.

Results and Discussion

Np(V) Reduction Kinetics with Quinonoid-Enriched Humic Derivatives. Kinetics is a crucial issue for redox interactions. In this study, to quantify kinetics of neptunium reduction, the experiments were conducted under anoxic conditions that were optimal for the synthesized derivatives (see Figure 1S from the Supporting Information). The influence of pH on the reduction of Np(V) by two different humic derivatives is shown in Figure 1.
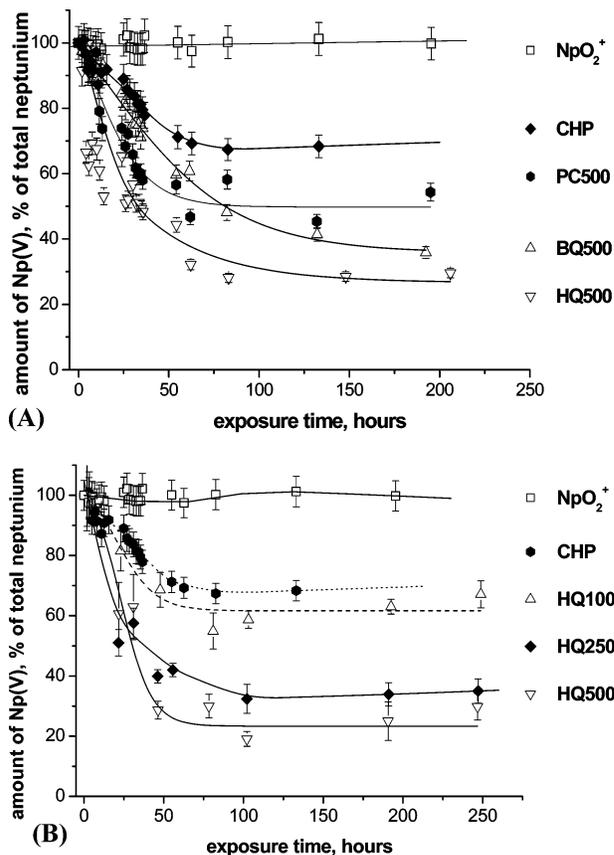
Reduction was not observed at pH 7.4, but did occur at pH 4.7. This is consistent with the Nernst equation that predicts an increase in reducing potential of hydroquinone with a decrease in pH. Hence, further experiments were conducted at pH 4.7 under anoxic conditions. The kinetic experiments were conducted with all five quinonoid-enriched humic derivatives used in this study. Results for f humic derivatives with different quinonoid moieties (hydroquinone, catechol, benzoquinone) and different HA to monomer ratios are shown in Figures 2A and B, respectively.

In the absence of HS, the NpO_2^+ reduction was not observed. The addition of parent leonardite HA to the Np(V) solution, up to Np(V):HS molar ratio of 1:50 (as calculated from CHP carboxylic acidity value of 4.2 mmol/g, see Table 1), induced a 30% reduction of the Np(V). At the same time, the addition of modified humic acids induced a more rapid and complete reduction. Maximum of Np(V) reduction, as monitored by NIR-spectroscopy under steady-state conditions, was observed with the HQ500; a derivative representing the greatest degree of modification.

First-order rate constants for Np(V) reduction by the quinonoid-enriched derivatives were evaluated by fitting a linear rate equation to data from Figure 2. Corresponding model fits for these data are shown in Figure S3 (Supporting Information). In general, high correlation coefficients were obtained assuming the first-order model for every experiment (Table 2). Rate constants, k's (sec^{-1}) for each derivative together with % residual Np(V) remaining at the end of each experiment are listed in Table 2.

The fastest reduction was observed for the derivatives obtained using formaldehyde condensation with hydroquinone-HQ500. The reduction rate for HQ250 was almost the same as that for CT500 and BQ500, which are also samples with higher degrees of modification. HQ500 and HQ250 induced not only the fastest, but also the most complete reduction—note 30% residual Np(V) from (Table 2), whereas for CT500 and BQ500, values were 50 and 40%, respectively.

These data corroborate values of redox capacity of the humic derivatives measured by ferricyanide reduction

(A)

(B)

FIGURE 2. Reduction of Np(V) by humic derivatives under anoxic conditions and pH 4.7, $C_0(Np) = 5.4 \times 10^{-5}$ M, $C_0(HS) = 500$ mg/L, Np(V):HS ratio = 1:40. A, Effect of quinonoid monomer nature incorporated into humic structure; B, Effect of different parent HA-to-monomer ratio for HQ enriched derivatives.
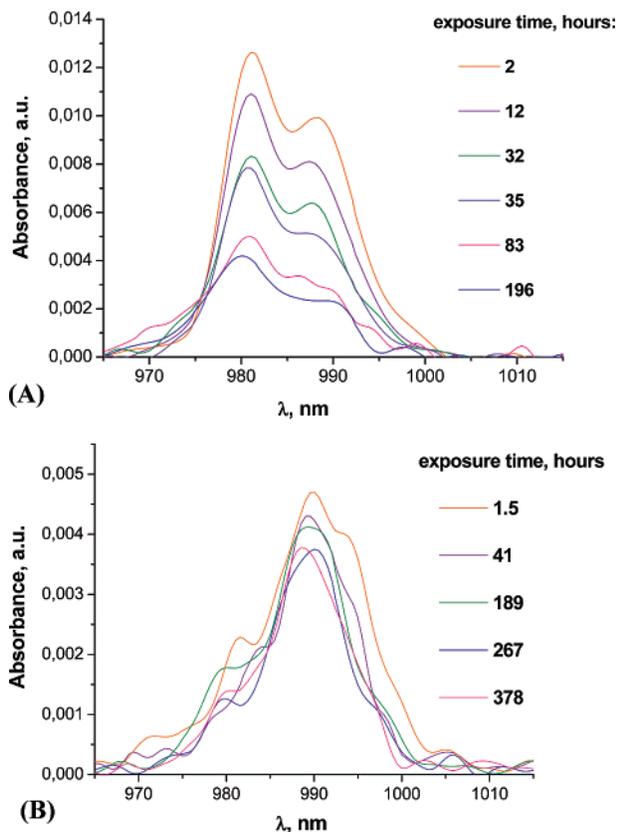
TABLE 2. Reduction of Np(V) by Different Humic Derivatives Under Anoxic Conditions and pH 4.7, $C_0(NpO_2^+) = 5.4 \times 10^{-5}$ M, $C_0(HS) = 500$ mg/L

sample	residual Np(V) after equilibration, %	first-order rate constant, sec^{-1}	regression coefficient, r
NpO_2^+	99 ± 1		
CHP	69 ± 1	1.70×10^{-6}	0.964
HQ100[a]	55 ± 3	2.00×10^{-6}	0.977
HQ250	28 ± 3	3.98×10^{-6}	0.982
HQ500	29 ± 2	10.5×10^{-6}	0.931
BQ500	42 ± 4	2.45×10^{-6}	0.974
CT500	50 ± 4	4.07×10^{-6}	0.988

[a] $C_0(NpO_2^+) = 1.98 \times 10^{-5}$ M, $C_0(HS) = 250$ mg/L.

(Table 1). Slower reduction rates were observed with the hydroquinone derivatives obtained via radical polymerization with 1,4-benzoquinone, as compared to formaldehyde-condensation products, which could be explained by conjugation of aromatic rings in the structure of BQ500. This stabilizes intermediate semiquinone moieties; and as a result, decreases the rate of Np(V) reduction. At the same time, the aromatic rings in the formaldehyde derivatives (HQ500 and CT500) were bound to the humic backbone via methylene-bridges, which would hinder semiquinone stabilization.

Complexation of Np(V) with Quinonoid-Enriched Humic Derivatives. Together with reduction kinetics, the complexation of Np(V) with quinonoid-enriched humic derivatives was studied using NIR-spectroscopy. Dynamic changes in the Np(V) spectra after reacting with HQ250 at two different

FIGURE 3. Dynamics of NIR absorption spectra of Np(V) in the presence of HQ250 under anoxic conditions. A, $C_0(^{237}Np) = 5.4 \times 10^{-5}$ M and $C_0(HS) = 500$ mg/L pH 4.7; B, $C_0(^{237}Np) = 3.8 \times 10^{-5}$ M and $C_0(HS) = 250$ mg/L, pH 7.4.

TABLE 3. Derived Stability Constants for Np(V)-humic Complexes at pH 4.7 and 7.4

sample	Logβ (pH 4.7)[a]	Logβ (pH 4.7)[b]	Logβ (pH 7.4)[b]
CHP	2.26 ± 0.16		
HQ100		2.77 ± 0.18	3.47 ± 0.48
HQ250	2.89 ± 0.11	3.32 ± 0.21	3.62 ± 0.39
HQ500	2.87 ± 0.14	2.23 ± 0.63	3.32 ± 0.34
BQ500	2.63 ± 0.03	2.79 ± 0.20	3.57 ± 0.35
CT500	2.50 ± 0.48	2.57 ± 0.05	3.26 ± 0.57
Aldrich HA *(32)*			3.59 ± 0.17
Aldrich HA *(8, 34)*		2.28 ± 0.06 (pH 6)	3.70 ± 0.04

[a] $C(NpO_2^+)_0 = 5.37 \times 10^{-5}$ M, $C(HS) = 500$ mg/L. [b] $C(NpO_2^+)_0 = 1.98 \times 10^{-5}$, $C(HS) = 250$ mg/L.

conditional binding constant is defined by the following equation:

$$\beta = \frac{[NpO_2^+HS]}{[NpO_2^+]_f \cdot [HS]_f} \qquad (3)$$

where $[NpO_2^+HS]$ is the equilibrium concentration of NpO_2^+ bound to HS, $[NpO_2^+]_f$ is the equilibrium concentration of the free metal ion, and $[HS]_f$ is the equilibrium concentration of free proton-exchange sites (mol/L). The latter can be found from the carboxyl content in the humic derivative (see Table 1). Given the large excess of the total HS over NpO_2^+ concentrations used in the experiments, $[HS]_f$ can be set to equal $C_0(HS)$. In this case, the dimensional units of the calculated constant are L/mol.

The molar extinction coefficient of NpO_2^+ was measured by varying the neptunium concentration from 2.52×10^{-5} to 1.39×10^{-4} M. The value of 377.7 L·mol^{-1}cm^{-1} determined here was close to 395 L·mol^{-1}cm^{-1} reported by Kim and Saine *(8)*. We could not apply a similar technique to determine molar extinction coefficient of $NpO_2(HS)$ species: in our studies, the Np(V) was reduced by both the modified and the nonmodified humic materials. Hence, for the Np(V)−humic complexes, we used molar extinction coefficient value of 222.4 reported by Kim and Sekine *(8)*. Values of the conditional stability constants derived for the different conditions (pH's and Np:HS ratios) were summarized in Table 3.

As can be seen from the Table 3, logβ values for all quinonoid-enriched derivatives were half-an-order of magnitude larger than that of the parent HS for the same conditions, and did not differ substantially from each other with the highest value seen with HQ-derivatives (2.87 and 2.89) and the lowest value for CT500 (2.5). The stability constants increased slightly with pH and were very similar to those reported by Sachs and Bernhard *(32)* and by Seibert et al. *(34)*. For their complexation studies, these authors used the same metal:HS ratios.

Based on changes in absorption spectra (see Figure 3), we speculated that the reduction of Np(V) at pH 4.5 occurred through its complexation with humic derivatives. This is consistent with general tendency that lower redox states are more stable at lower pH values and they produce stronger complexes with HS *(35)*. The best solution for immobilization of the Np(IV)−humic complexes would be a use of alkoxysilylated humic derivatives able to form covalent bonds with mineral surfaces as it was shown in our recent publication *(35)*. In this case, Np(V) would be reduced to more stable Np(IV)−humic complex and further immobilized onto the granular support.

Environmental Implications. The results obtained in this study suggest opportunities may exist for the future development of humics-based remediation technologies for actinide-contaminated sites. However, to employ these approaches, some requirements need to be met regarding

pH's are illustrated in Figure 3. Similar results were obtained with the other derivatives, and corresponding spectra were given in the Supporting Information (Figures S3−S6). The absorbance spectra of Np(V) in the presence of humic derivatives were represented by overlapping peaks of the free NpO_2^+ and of its complexed species (NpO_2−HS) with absorbance maxima at 981.5 and 987 nm, respectively. The contribution of these peaks to the overall spectrum changed substantially with exposure time. At pH 4.7, the absorbance of Np(V)−humic complexes decreased rapidly with exposure time. A similar but slower trend, was observed for the noncomplexed Np(V) species. This was indicative of an overall decrease in Np(V) concentrations upon exposure to derivatives and increases in Np(IV). At pH 7.4, reduction of Np(V) was not observed.

After the system reached equilibrium (e.g., no further changes in spectrum were observed), the distribution of neptunium(V) between free and complexed species was used to calculate stability constants for NpO_2^+−HS complexes. For these calculations, the charge neutralization model *(8)* was used to equate the amount of bound metal cations to a number of protons exchanged. This resulted in the following equation:

$$NpO_2^+ + nHS \leftrightarrow NpO_2(HS)_n \qquad (2)$$

where $NpO_2(HS)_n$ is the Np(V)−HS complex. This model assumed that the amount of complexed metal ions depended on solution pH and ionic strength, as well as on the nature of humic materials. Therefore, only conditional stability constants could be calculated from data obtained at the two values of pH and for the three Np to HS ratios as it was done in our studies. In case of $n = 1$ for a given reaction, the

the contaminated site conditions and the type of humic derivatives to be deployed. Regarding the choice of humic derivatives, a preference should be given to the hydroquinone-modified derivatives with a monomer content not less than 250 mg per g of parent humic material (e.g., the leonardite HA). Concentration of the humic material in the remedial solution should be at least 250 mg/L, preferably, 500 mg/L. Deployment of the humic derivatives under these conditions can attenuate the Np(V) concentration to 30%. This scenario is consistent with the data of Reiller (35), who speculated the possibility for Np(V) reduction under reducing conditions (Eh ≤ 100 mV/SHE) for HS concentrations higher than 100 mg/L. Np(IV) is less mobile given its much lower solubility and greater tendency to sorb on other matrices than does Np(V). Complexation of Np(IV) with HS could make it more susceptible to sorption onto Fe-containing surfaces as compared to neptunyl-ion. This could be used to enhance performance of Fe(0)-barriers. To solve the problem of neptunium(IV) migration bound to humic complexes, the best approach would be to use quinonoid-enriched humic derivatives with incorporated alkoxysilyl-moieties (36). These derivatives will produce a covalently bound coating on the mineral support to provide a potential for in-situ installation of a permeable reactive barrier (PRB).

Another promising application for the quinonoid-enriched humic derivatives would be to use them as auxiliary agents—redox mediators—for facilitating microbial redox reactions at actinide contaminated sites. In this case, the derivatives could be used at much lower concentrations. Furthermore, the association of Np with HS would provide a better substrate for microbes compared to freely dissolved NpO_2^+ species.

With regard to required contaminated site conditions, the highest performance for humic-based technology would be expected under anoxic and acidic or slightly acidic conditions (e.g., pH < 5). These conditions can be met, for example, at areas 1 and 3 of the Field Research Center of the Oak Ridge National Laboratory, U.S. DOE (37), where high concentrations of uranium (mg/L) and technetium are found. Groundwater is normally acidic or slightly acidic (pH varies between 5 and 6.5), dissolved oxygen concentration is about 2 ppm, and E_h values range as high as 100−400 (at the reactive barrier sites) and lower than −250 mV (in deep groundwater). These conditions are considered appropriate for effective use of humic derivatives to lower the valence states of actinides and, in turn, reduce their mobility.

For actinide contaminated sites with oxygenated groundwaters and pHs close to neutral, such as the Siberian Chemical Industrial Complex, Russia (SCIC) (38), and another highly contaminated Russian site, the Production Association "Mayak", in Western Ural (39), the proposed humic-based technology may not be effective for lowering mobility of neptunium, but it will be for immobilizing Pu(V). This conclusion follows from the results of our findings on the efficient reduction and immobilization of Pu(V) by quinonoid-enriched humic derivatives (36, 40) under much broader range of conditions as compared to neptunium(V): Pu(V) was reduced both in the presence and absence of oxygen and at slightly acidic and neutral pHs.

The in situ experiments for the derived humic derivatives are foreseen as components of bioremediation. A use of alkoxysilylated derivatives enriched with quinones is foreseen for testing humic curtain−permeable reactive barrier (PRB) technology based on a use of humic redox surfactants. In general, the experimental results obtained here provide positive evidence for the potential value of designer humics for aiding immobilization of hazardous actinides. The findings of this work show that the properties of chemically modified humic materials can be manipulated efficiently and in a reproducible manner. This technique affords new opportunities for the wide application of these naturally abundant materials that are currently not being tapped for critically needed remedial purposes.

Supporting Information Available

Kinetic curves for Np(V) reduction by the quinonoid-enriched humic derivatives under oxic and anoxic conditions are shown in Figure 1S. Short explanation of solvent extraction technique usage is given. A typical Np(V) NIR spectrum in the presence of humic derivatives and its deconvolution into peaks representing NpO_2^+ and Np−humic complexes is shown in Figure 2S. The Figure 3S illustrates first-order model fits to experimental kinetic data showing the reduction of Np(V) by different HS. A series of NIR spectra are provided that demonstrate the real time dynamics of Np(V) absorption spectra when exposed to quinonoid-enriched humic derivatives (Figures 4S−7S). This material is available free of charge via the Internet at http://pubs.acs.org.

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