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Reduction of actinides in higher oxidation states by hydroquinone-enriched humic derivatives

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Abstract

Natural humic materials are known to cause a reduction of penta- and hexavalent plutonium; however, contradicting results have been previously reported for neptunium. The goal of this study was to determine if incorporation of additional reducing centers into humic structure would yield material with enhanced reducing performance with respect to higher valent actinides, nominally, Pu(V) and Np(V). Hydroquinone-moieties were used as the redox centers. They were incorporated into humic structures using formaldehyde condensation at different monomer-to-humic ratios to obtain materials of different reducing properties. Reduction of model actinides by the hydroquinone-enriched humic materials was studied under both oxic and anoxic conditions at acidic and neutral pH values. Redox speciation of plutonium and neptunium was monitored using solvent extraction techniques and liquid scintillation counting. It was shown that both nonmodified leonardite humic acid and all the obtained derivatives were able to reduce Pu(V) quantitatively both at neutral and acidic pH and under oxic and anoxic conditions. The reduction rate increased with an increase in the degree of modification of the humic material and reached its maximum for HQ500 derivative. For neptunium, reduction was observed only under anoxic conditions at acidic pH. The hydroquinone-modified derivatives had much higher reducing performance when compared to nonmodified leonardite humic acid. The results obtained show good prospects for a use of hydroquinone-modified humic materials as reactive agents for remediation of actinide contaminated aquifers.

Keywords: Plutonium; Neptunium; Humic substances; Hydroquinone moieties; Kinetics

1. Introduction

The concept of deep underground nuclear waste repositories in geological formations is accepted in many countries as a final step in the nuclear fuel cycle. Multi-barrier systems are designed at the repository sites and are aimed at preventing radionuclide release to the environment. Materials commonly used as components of engineered barriers should have high sorption properties towards radionuclides, low hydrolytic conductivity and maintain low Eh values of aqueous solution. Among the proposed materials are bentonite clays, cements, etc. This study deals with the possible application of humic derivatives as nanosized materials for reduction and subsequent sequestration of actinides from aqueous solutions.

Natural humic substances (HS) are known to reduce Pu(V) and Pu(VI) to less soluble and, hence, less mobile Pu(IV), and even to Pu(III). Marquardt et al. [1] established the stepwise reduction of Pu(VI) to Pu(IV) and Pu(III) by HS from groundwater collected at Gorleben (Germany). According to Andre and Choppin [2], only tetravalent plutonium was found in solution after several days of equilibration with Aldrich humic acid (HA) at pH 8 and HA concentration of 10.9 mg/L. At the same time, disparate results were reported for Np(V). According to Choppin [3], Np(V) was not reduced by Aldrich HA, whereas Artinger et al. [4] observed slow reduction of Np(V) by HS of Gorleben groundwater. This contradiction could stem from different contents of quinonoid moieties in the HS studied that are responsible for their redox properties. It was hypothesized that the reducing capability of natural humic materials towards higher valence actinides could be enhanced by incorporating additional hydroquinone moieties into humic structures [5].

The goal of this research was to assess reducing performance of leonardite humic acid and its hydroquinone-enriched

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Table 1
Description and properties of humic derivatives used in this study

Sample	Description	—COOH[a] (mmol/g)	—ArOH[b] (mmol/g)	Reduction capacity (mmol/g)
CHP	Leonardite HA	4.2 ± 0.2	1.1	0.6 ± 0.1
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

[a] As determined by calcium acetate technique.

[b] Calculated as a difference between total acidity and —COOH content.

derivatives with respect to Pu(V) and Np(V). The capability of humic materials to reduce actinides in higher oxidation states offers them quite useful as components for in situ remediation technologies and in the design of permeable reactive barriers at the nuclear waste sites.

2. Experimental

2.1. Synthesis and characterization of HS

The quinonoid-enriched humic derivatives were obtained as described by Perminova et al. [5] using the reaction of formaldehyde copolycondensation between leonardite humic acid (CHP) and hydroquinone. Leonardite humic acids were isolated from commercially available potassium humate (Powhumus^{TM}) produced by Humintech Ltd., Germany. For this purpose, a known weight of potassium humate was dissolved in distilled water and centrifuged to separate and discard any insoluble mineral components. The supernatant was then acidified to pH 2 with concentrated HCl and centrifuged. The precipitate of humic acids (HA) was collected, washed with distilled water, desalted using electrodialysis, evaporated at 60 °C, and stored in a desiccator over P_2O_5. The material obtained was used for condensation with hydroquinone at different monomer-to-humic ratios: 100, 250 and 500 mg of hydroquinone per 1 g of CHP. The corresponding derivatives were designated as HQ100, HQ250 and HQ500, respectively. The degree of modification of the derivatives obtained was determined using calcium acetate and barium hydroxide techniques and the reduction capacity of the derivatives was determined using ferricyanide as oxidizing agent as described in [5]. List and properties of the derivatives obtained are given in Table 1.

2.2. Kinetics of Pu(V) and Np(V) reduction by hydroquinone-enriched humic derivatives

Pu(V) and Np(V) reduction kinetics was studied using ^{238}Pu, ^{239}Pu, ^{242}Pu and ^{237}Np. Plutonium in its pentavalent form was prepared by the procedure described in [6]. Radioactivity counting was performed using semiconductor alpha-spectrometry and liquid scintillation counting. The reduction of Pu(V) by humic derivatives at tracer level concentrations (2.3×10^{-9} M) and HS concentrations of 10 mg/L was studied by solvent extraction technique as described by Morgenstern and Choppin [7]. Pu(IV) was separated by 1-(2-thenoyl)-3,3,3-trifluoroacetone (TTA) in toluene. Pu(III) was determined using the same procedure after its oxidation to Pu(IV) by addition of small amount of $KBrO_3$. Pu(III) concentration was calculated as a difference between plutonium extracted with and without addition of $KBrO_3$ [8]. Redox speciation of Np(V) was studied using extraction with di-(2-ethylhexyl)-phosphoric acid (HDEHP, Aldrich), which extracts Np(IV) from 1 M HCl solution [7]. Experiments were carried out under both oxic (ambient atmospheric conditions) and anoxic (Ar atmosphere) conditions.

Experiments under anoxic conditions were performed in foiled plastic 50 ml vials to prevent photolysis of humic derivatives and in a glove box filled with N_2 or Ar to keep oxygen-free conditions to prevent hydroquinone fragments from oxidation by air oxygen. The ionic strength was close to zero and constant pH values of 4.5 ± 0.2 and pH 7.5 ± 0.2 were maintained without buffer solutions. The oxidation states of Pu were monitored periodically by extraction of 1.5 mL aliquots of solution.

3. Results and discussion

The properties of humic materials used in this study are listed in Table 1. The reduction capacity increased along with an increase in hydroquinone content so that the derivatives could be put in the following ascending order: CHP < HQ100 < HQ250 < HQ500.

3.1. Pu(V) reduction by humic derivatives

The kinetics of Pu(V) reduction in the presence of parent leonardite HA under oxic and anoxic conditions is shown in Fig. 1. The reduction rate under anoxic conditions was significantly higher compared to oxic conditions. Under anoxic conditions, almost complete Pu(V) reduction occurred within 3–4 h, while under atmospheric conditions, it took 120 h for complete Pu(V) reduction. Much slower reduction kinetics of Pu(V) was evidently caused by competitive interaction of redox centers of CHP with air dissolved in the test solution. To avoid the influence of oxygen, all further experiments were carried out under anoxic conditions in a glove box filled with argon gas.

The kinetics of Pu(V) reduction in the presence of different hydroquinone-enriched derivatives under anoxic conditions at pH 7.5 is shown in Fig. 2. As can be seen, complete Pu(V) reduction was observed in the presence of all derivatives. However, the rate of reduction increased along with an increase in the degree of modification of the derivative tested. It increased in the order of CHP < HQ100 ≤ HQ250 < HQ500, which corre-

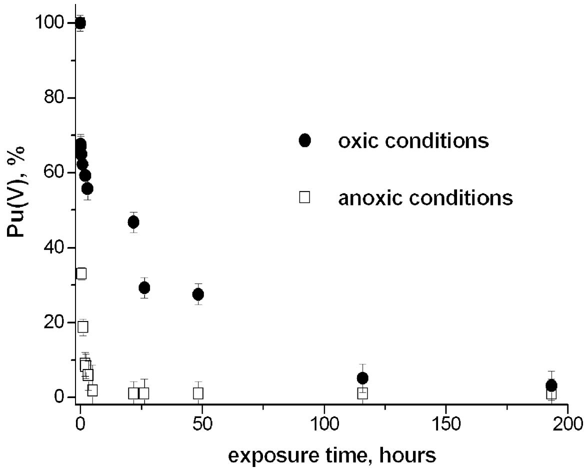

Fig. 1. Pu(V) reduction by leonardite HA (CHP) under oxic and anoxic conditions: $C_{tot}(Pu) = 7.17 \times 10^{-9}$ M, $C_{tot}(HS) = 10$ mg/L, pH 4.7 ± 0.2, $I = 0$ M.

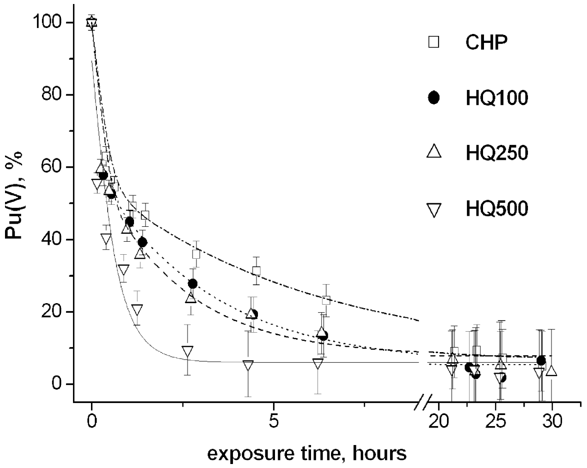

Fig. 2. Pu(V) reduction by hydroquinone-enriched humic derivatives under anoxic conditions at neutral pH (7.5 ± 0.2): $C_{tot}(Pu) = 2.3 \times 10^{-9}$ M, $C_{tot}(HS) = 10$ mg/L, $I = 0$ M.

lates with the values of reduction capacity presented in Table 1. For HQ500, equilibrium was reached within 4 h, for HQ100 and HQ250 within 12 h, and for CHP within 22 h.

At lower pH (4.5), the reduction kinetics was much faster. As can be seen in Fig. 3, equilibrium was reached within 1–2 h for all samples tested. The difference in reduction rates observed between samples is attributed to the uncertainty of radioactivity measurements. No Pu(III) formation was detected in the solution over the total exposure time.

The results obtained corroborate the findings of Andre and Choppin [2] and Marquardt et al. [1] on Pu(V) reduction by natural HS.

3.2. Np(V) reduction by humic derivatives

In contrast to Pu(V), reduction of Np(V) in the presence of the humic derivatives tested was much slower. Comparative results on Pu(V) and Np(V) reduction under anoxic conditions at pH 4.5 are presented in Table 2. At 2 h of exposure time reduction of Np(V) is negligible as compared to almost complete reduction of Pu(V). As can be seen, only partial reduction of Np(V) was taking place in the presence of CHP, HQ100and HQ250, and almost complete reduction was observed in the presence of HQ500 derivatives for 144 h of exposure time. In contrast to Pu(V), there was no reduction of Np(V) observed under oxic conditions for all humic derivatives tested. Our results corroborate well with the findings of Rao and Choppin and Artinger et al. [9,4], who observed partial reduction of Np(V) by HS from Gorleben groundwater.

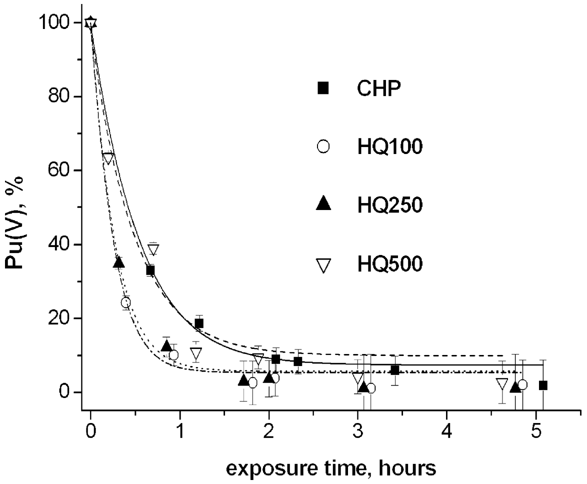

Fig. 3. Pu(V) reduction by hydroquinone-enriched derivatives under anoxic conditions at acidic pH (4.5 ± 0.2): $C_{tot}(Pu) = 2.3 \times 10^{-9}$ M, $C_{tot}(HS) = 10$ mg/L, $I = 0$ M.

Table 2
Np(V) reduction by hydroquinone-enriched HS under anoxic conditions; $C_{tot}(Np) = 1.44 \times 10^{-6}$ M, $C_{tot}(HS) = 10$ mg/L, pH 4.5 ± 0.2, $I = 0$ M

Sample	Np(V) content (percent of initial) in reaction mixture at two different exposure times	
	2 h (%)	144 h (%)
CHP	98.9 ± 2.7	67.3 ± 3.3
HQ100	96.8 ± 2.8	55.3 ± 3.6
HQ250	80.2 ± 2.7	39.6 ± 3.8
HQ500	95.7 ± 2.7	<5

The character of pH dependence found for Pu(V) and Np(V) reduction in the presence of humic derivatives tested was in agreement with that expected from the Nernst equation for hydroquinone moieties: the rate of redox reaction increased with a decrease in pH. According to Garten et al. [10], the Oak Ridge Reservation has predominantly acidic soils: the pH values vary between 4.5 and 5.7 and the average value of dissolved oxygen as determined by Liang et al. [11] did not exceed 2.36 mg/L. These conditions allow us to expect high reducing performance of hydroquinone-enriched humic derivatives both with respect to Np(V) and Pu(V). This shows good promise for the use of humic-based reagents in in situ remediation of aquifers contaminated with actinides in higher oxidation state.

4. Conclusions

Humic derivatives enriched with quinonoid moieties were shown to possess much higher reducing potential with respect to Pu(V) and Np(V) as compared to nonmodified humic material. In the case of plutonium, hydroquinone-enriched derivatives caused almost complete reduction of pentavalent plutonium in aqueous solution both under anoxic conditions and in the presence of atmospheric air. An increase in the degree of modification of hydroquinone-enriched copolymers was accompanied by an increase in reducing ability of the corresponding derivatives with respect to Pu(V). In the case of neptunium, only partial reduction was observed under anoxic conditions, and no reduction was observed under ambient atmosphere. Reduction of model actinides by HQ-derivatives was highly pH-dependent with reduction rates being higher at low pH (3.5) and much slower at higher pH (7.5). For neptunium(V), reduction was observed only at low pH values. The results obtained demonstrate a viability of the undertaken approach in producing humic materials with enhanced redox properties. This opens a way for broad application of these reactive humic materials in the practice of remediation technologies.

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