Environmental Science & Technology

Article

pubs.acs.org/est

Nonreversible Immobilization of Water-Borne Plutonium onto Self-Assembled Adlayers of Silanized Humic Materials

Natalia S. Shcherbina,[†,‡] Stepan S. Kalmykov,[†] Leonid A. Karpiouk,[†,§] Sergey A. Ponomarenko,[†,∥] Kirk Hatfield,[⊥] Richard Haire,[#] and Irina V. Perminova[†,*]

[†]Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory 1-3, Moscow 119991, Russia

[‡]Department of Nuclear Energy and Safety, Paul Scherrer Institute (PSI), Villigen, 5232, Switzerland

[§]Bochvar High-Technology Research Institute of Inorganic Materials of the State Atomic Energy Corporation ROSATOM, Rogova Str. 5a, Moscow 123098, Russia

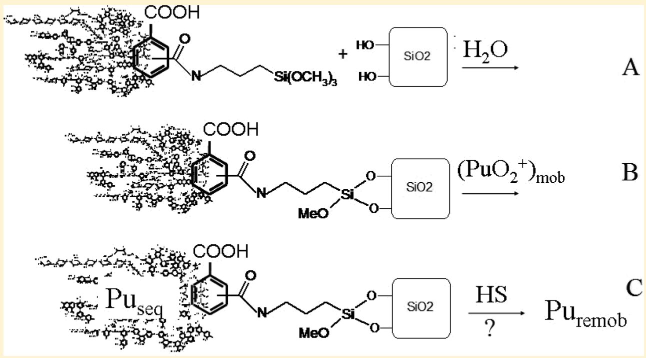
[∥]Enikolopov Institute of Synthetic Polymeric Materials, RAS, Profsoyuznaya Str. 70, Moscow 117393, Russia

[⊥]Engineering School of Sustainable Infrastructure and Environment, University of Florida, Gainesville, Florida 32611, United States

[#]Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States

Ⓢ *Supporting Information*

ABSTRACT: The objective was to study plutonium partitioning between immobile and mobile humic materials at the water−solid interfaces. Immobilization of the humic materials on solid supports was performed in situ using self-adhesive silanized humic derivatives. The presence of the humic adlayers on solid supports was shown to significantly enhance Pu sorption and its retention under both steady state and dynamic conditions. While plutonium may exist in multiple oxidations states plus colloidal forms, the major thrust in this work was to study the behavior of most mobile − the PuO_2^+ form in dilute solutions. The values of the plutonium partition coefficients (K_d) between water and humics-coated silica gels after 10 days exposure reached 1.6×10^4 L·kg^{-1} at pH 7.5 under anaerobic conditions with a total plutonium concentration of 1.2×10^{-8} M exceeding those for the uncoated SiO_2 (6.3×10^2 L·kg^{-1}). Column tests showed substantial sequestration of water-borne plutonium (up to 73%) on the humics-coated silica gels. Remobilization experiments conducted under batch conditions at different pH values (3.5, 4.5, 7.5) showed that no more than 3% of the sequestered Pu was remobilized from the humics-coated silica gels by treatment with dissolved humic materials at environmentally relevant pH of 7.5. Consequently, silanized humic materialas can be seen as both molecular probes and as potent candidate materials for scavenging mobile Pu from an aqueous phase.



INTRODUCTION

The continuing problems encountered with nuclear reactors at the Fukushima-1 Nuclear Power Plant in Japan, which were damaged by the disastrous earthquake and tsunami in 2011, have renewed the public's and scientific concerns with respect to radioactive pollution, and plutonium contamination.[1,2] In contrast to Chernobyl, only minute amounts of Pu were found in Japan.[1,2] Still, release of plutonium into aquatic environments is particularly dangerous given the mobility of high-valent species of plutonium (i.e., plutonoyl ions (PuO_2^+). The migration of plutonium, as well as other actinides, can be facilitated by mobile colloids consisted of natural organic matter (e.g., humic materials) or retarded by immobile phases.[3−7]

The colloid-facilitated transport of actinides has attracted considerable attention following the pioneering work of McCarthy and Zachara.[8] And since then extensive evidence finds for colloid facilitated mobilization of actinides, both in field studies[9,10] and in laboratory experiments.[5,11,12] On the other hand, a retarded transport of actinides in porous media, such as soils and sediments, has been reported as well.[13−15] The direct correlations between accumulation of Pu and the content of total organic carbon (TOC) in soils and sediments were observed.[17,18] It was also reported that the migration rate of Pu can be reduced substantially with an increase in the soil's organic content.[16,19]

These above cited studies have motivated numerous investigations regarding the impact of humic substances (HS) on actinide transport in aquatic systems and soils.[15,20−22] HS comprise of 50−80% of natural organic matter (NOM),[23] and their molecular structures include reducing and complexing units, which provide for both redox and complexing

Received: October 17, 2013
Revised: January 20, 2014
Accepted: January 24, 2014
Published: January 24, 2014

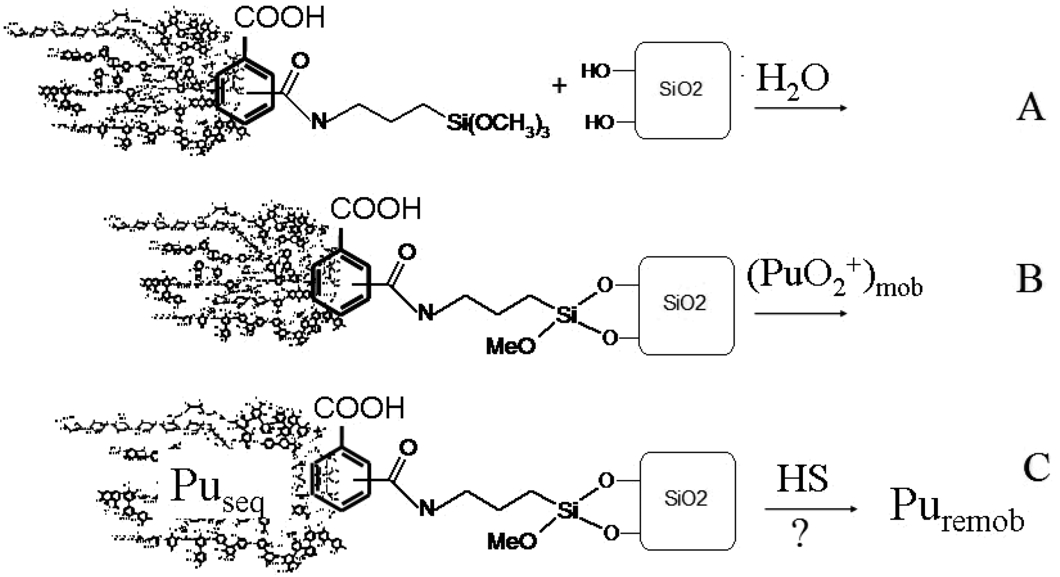


Figure 1. Schematic representation of humic coating immobilization onto silica gel by self-assembly of mineral-adhesive silanized HS (A) followed by Pu(V) sequestration onto immobilized organic coatings (B) and its remobilization in the presence of mobile humic substances (HS) (C). $(PuO_2^+)_{mob}$ designates mobile water-borne plutonium: Pu_{seq} stands for plutonium sorbed onto humic adlayers; and Pu_{remob} stands for plutonium remobilized by mobile HS.

interactions with plutonium and other actinides.[15,20,24] Comparable interactions with plutonium are characteristic of bacterial exopolymers as recently reported in the literature.[25,26] Given that these humic materials occur throughout the environment both in mobile colloidal and immobile organo-inorganic states they can be considered as important matricies for manipulating and controlling actinide migration.

We have focused on exploring plutonium interactions with mobile and immobile humic materials which were specifically modified to acquire adhesive properties with solid materials. Previously, we have reported that Pu(V) was efficiently sequestered by humic adlayers formed due to self-assembly of the silanized HS at water−solid interfaces using experimental batch conditions.[28,29] Those findings hold promise for using humic coatings for scavenging water-borne actinides in higher valence states. Thus, the specific objectives of these studies were first, to estimate plutonium partitioning onto humic adlayers under dynamic conditions, and second, to estimate the remobilization potential of the scavenged plutonium by mobile humic materials. These issues are of primary concern for practical applications of humic coatings for preventing or retarding migration of water-borne plutonium and other actinides.

To achieve the above objectives, we used the mineral-adhesive humic derivatives developed in our research group,[30,31] to prepare the HS-coated, solid supports. The corresponding derivatives are prepared by reacting carboxyl groups of humic polyanions with amino groups of 3-aminopropyltrimethoxysilane (APTS). The specific feature of these silanized derivatives is their ability to dissolve in water and then to attach to hydroxyl-carrying surfaces via Si−O−Si or Si−O−M bonds producing humic adlayers at the water−solid interface as schematically shown in Figure 1A. Covalent bonding is of particular importance as it precludes the facile mobilization of a humic adlayer and any contaminant bound to it. This makes the silanized humic derivatives perfect surface probes for self-assembly of humic adlayers on surfaces of oxidized silicon substrates (e.g., silica gel) aimed at mimicking geochemical interfaces in natural soil- or sediment- systems. The self-assembled humic adlayers were then used to explore Pu(V) sequestration under laboratory conditions, and to determine the potential for remobilization via mobile organic matter. The corresponding experimental scheme is shown in Figure 1B,C.

EXPERIMENTAL SECTION

Materials and Chemicals. All reagents used in the experiments were of analytical grade. KOH and HCl were used for humic materials isolation, and KH2PO4 and Na2HPO4·12H2O were used to prepare 0.03 M buffer solution. Silica-gel 60 (Merck) with a specific surface area of 540 m2/g was used as a solid support for immobilization of the humic derivatives. Silica gels have specific surface area comparable to those of clay minerals which are major carriers of organic adlayers in the subsurface. The sufficiently similar surface properties justify the use of silica gel as a surrogate for subsurface media. Leonardite humic acid was isolated from commercially available potassium humate (Powhumus) produced by Humintech Ltd., Germany, by acidifying solution of potassium humate to pH 2 and dialyzing the resulting precipitate of humic acids. The isolated humic acid was designated CHP and used for synthesis of silanized humic derivatives with different degrees of modification as described in our previous publications.[30,31] Modification protocol and characteristics of the silanized derivatives are given in the Supporting Information (SI).

Immobilization of the Silanized Humic Materials on Silica Gels. To incorporate the silanized humic materials on silica gel, a 100 mL solution of the respective CHP derivative at a concentration of 5 $g \cdot L^{-1}$ was added to 1 g of silica gel in a 0.028 M phosphate buffer at pH 6.8 and then shaken for 48 h until sorption equilibrium was reached. Decreases in humic derivative concentration were monitored by measuring its UV-absorbance at 254 nm. The silica-gel was then centrifuged and washed repeatedly with distilled water. The product obtained was then dried in a vacuum desiccator over P_2O_5 for 48 h and labeled CHP-APTS-X-SiO_2 (where X stands for a value of modification degree: 20, 50, or 100). The content of humic material in the resultant products was calculated from the measured loss of CHP-APTS-X in solution. The contents of carboxyl groups in the same products were determined using calcium acetate technique as described elsewhere.[32]

Stock Solutions of Pu(V). The Pu(IV) solution was purchased from RIAR (Dimitrovgrad, Russia) as an isotopic mixture of Pu-238 (1.14%), Pu-239 (12.47%) and Pu-242 (86.39%) (% refers to activity distribution). Stock solutions of Pu(V) were prepared from the Pu(IV) solution as described elsewhere.[33] In brief, Pu(IV) was first oxidized to Pu(VI) and then reduced to Pu(V) under controlled conditions using chemical redox reactions. The Pu(V) was separated from the residual Pu(IV) and Pu(VI) using solvent extraction as described by Morgenstern and Choppin.[34] For our purpose, an aliquot of the Pu(V) solution (50 μL) was diluted with Milli-Q water (1.5 mL), acidified with 3.3 M HCl (0.6 mL) and mixed with 1 mL of 6.7% di-(2-ethylhexyl)-phosphoric acid (HDEHP) in toluene. By measuring the activity in the water and organic phases using liquid scintillation counting (LSC, TriCarb2700TR, Canberra Ind., Australia), the conversion of Pu(IV) to Pu(V) was determined to be 85%. The final concentration of Pu(V) stock solution was 1.26×10^{-6} M at pH 5.

Solutions of Humic Material. A known weight of dry humic material was dissolved in a few drops of concentrated NaOH, diluted with 50 mL of Milli-Q water, and then neutralized with $HClO_4$. Concentration of the humic material in the stock solution was 270 mg·L^{-1}.

Experiments on Pu(V) Interactions with the Mobile Humic Solutes. All experiments on Pu(V) interactions with the dissolved humic materials were carried out in a glovebox flushed with high-purity Ar gas to remove oxygen and CO_2. This was done to exclude competitive interactions of Pu with carbonates in the model system. The sample vials were wrapped with aluminum foil to prevent any photolysis of the humic materials due to exposure to daylight. Work solutions were prepared by spiking 40 mL of deionized water with stock solutions of Pu(V) (70 μL) and humic materials (1.5 mL) to yield final concentrations of 2.26×10^{-9} M and 10 mg·L^{-1} for Pu and HS, respectively. Next, the pH was adjusted to 7.5 with either $HClO_4$ or NaOH. The Pu(V) concentrations were monitored by sampling the work solutions at selected time intervals and analyzed by a solvent extraction technique[34] as desribed in SI.

Kinetic and Sorption Experiments on Pu(V) Partitioning to Humics-Coated Silica-Gels. All experiments were carried out in a glovebox flushed with high-purity Ar gas to remove oxygen and CO_2. For kinetic studies, a known weight of the humics-coated silica gel (7 mg) was introduced into the plastic tube, added with 20 mL of deoxygenated Milli-Q water, and spiked with 200 μL aliquot of the Pu(V) stock solution to acquire a total plutonium concentration of 1.2×10^{-8} M. The pH was then adjusted to 7.5 using $HClO_4$ or CO_2-free NaOH solutions. The tubes were then sealed, shaken, and kept in the dark in the glovebox over 10 days). The solutions were periodically sampled for determining plutonium concentrations using LCS. Data obtained were used for calculating K_d according to the equation:

$$K_d = \frac{C_0(\mathrm{Pu}) - [\mathrm{Pu}]_{\mathrm{sol}}}{[\mathrm{Pu}]_{\mathrm{sol}}} \cdot \frac{V}{m} \tag{1}$$

where C_0(Pu) is the total concentration of Pu, $[\mathrm{Pu}]_{\mathrm{sol}}$ is the residual concentration of Pu in the solution, V/m is the volume to mass ratio (L·kg^{-1}). The measured value of the K_d coefficient was used to calculate the K_{OC}—the partition coefficient normalized to the organic carbon content (OC) in the humics-coated silica gel ($K_{OC,}$ L·kg^{-1}).

For the sorption experiments, a known weight of the humics-coated silica gel (17.5 mg) was added to 50 mL of deionized Milli-Q water and spiked with different amounts of Pu(V) stock solutions. The pH of these solutions was adjusted to 7.5. In these experiments, the Pu concentration varied from 5.15×10^{-9} to 5.10×10^{-8} M with a constant ratio of solid to liquid of 0.35 g·L^{-1}. After 10 days for establishing equilibrium, the vials were centrifuged, and the Pu concentrations in the solution were measured using LSC. Uncoated silica gel was used as a reference material in the control experiments. Sorption data were then fitted to the Langmuir isotherm:

$$Q = Q_{\max} \cdot \frac{K \cdot [\mathrm{Pu}]_{\mathrm{sol}}}{[\mathrm{Pu}]_{\mathrm{sol}} \cdot K + 1} \tag{2}$$

where K and $Q_{\max}$ are the values of adsorption constant (L·mol^{-1}) and maximum sorption of Pu(V) on the solid phase (mol·kg^{-1}), respectively; $[\mathrm{Pu}]_{\mathrm{sol}}$ is the equilibrium plutonium concentration in the solution (mol·L^{-1}).

Flow-Through Column Experiments on Pu(V) Sequestration by Immobile Humic Materials. Flow-through experiments were conducted using a chromatography system composed of a LC pump (Abimed), glass column (1.5 cm i.d. and 10 cm length) packed with silica-gel, an UV detector (Abimed) and a fractional collector (Abimed) were employed. Deionized water was used as a mobile phase at a linear flow rate of 0.1 mL·min^{-1}. The Darcy flow through the water-saturated silica gel was 0.8 m·day^{-1}, the average pore water velocity was 1.9 m·day^{-1}. Porosity of the silica gel was 0.43. Its bulk density was 0.43 g·cm^{-3}. The void volume of the column was 8.5 mL as determined from the breakthrough curve of HTO (1×10^{-9} M tritium). The latter was injected into the column as a pulse of 0.5 mL. Fractions of 1 mL were collected and analyzed by LSC to determine the tritium elution profile. Then 0.5 mL of the solution of PuO_2^+ with a concentration of 1.03×10^{-8} M at pH 7.5 was injected into the same column. As in case of tritium, fractions of 1 mL were collected. They were analyzed by the extraction- LSC technique to determine the plutonium elution profile. Then, the solution of the CHP-APTS-100 derivative at a concentration of 1.54 g·L^{-1} was eluted through this silica-gel column for 24 h until the UV absorbance of the column effluent reached a plateau. The eluent was then switched to deionized water and eluted for 24 h to remove any weakly bound humic derivative from the column. And finally, 0.5 mL of the same solution of PuO_2^+ with a concentration of 1.03×10^{-8} M was injected into the column treated with CHP-APTS-100. This Pu(V) solution was then eluted as described above from the column using deionized water as an eluent.

Plutonium Remobilization Experiments. The remobilization experiments were conducted in the glovebox flushed by Ar free of CO_2. Uncoated SiO_2 and CHP-APTS-100-SiO_2 were used for this purpose. They were first loaded with Pu using sorption experiments at three different pH as described in the SI. Then each solid phase was centrifuged and suspended in 20 mL of humic material solution with a pH being identical to the initial experimental solutions (3.5, 4.5, or 7.5). Humic-material solutions contained 10 mg·L^{-1} of CHP or CHP-APTS-100 derivative. The amount of remobilized Pu was determined by sampling the solutions at the specific time intervals (by taking 1.5 mL aliquots) and measuring the Pu content using LSC. The initial amounts of Pu bound to SiO_2 and to the humics-modified silica gels were calculated during the sorption experiments and accounted for 7.6×10^{-7} and 8.4×10^{-4} $mol \cdot kg^{-1}$, respectively. The fraction of desorbed Pu was calculated by eq 3:

$$Pu_{desorb} = \frac{I_{sol}}{I_{tot}} \cdot \frac{20}{1.5} \cdot 100\% \qquad (3)$$

where Pu_{desorb} is the fraction of remobilized plutonium, I_{sol} is the counting rate of the sampled solution aliquot, I_{tot} is the counting rate of Pu-loaded solid phase. Twenty (mL) is the total volume of the experimental solution, 1.5 (mL) is a size of the sampled solution aliquot.

■ RESULTS AND DISCUSSION

Plutonium Interactions with Mobile Humic Materials. We have conducted kinetic experiments on Pu interactions with the humic solutes using the parental humic material CHP and the silanized humic derivative CHP-APTS-100. Resultant kinetic curves are shown in Figure 2.

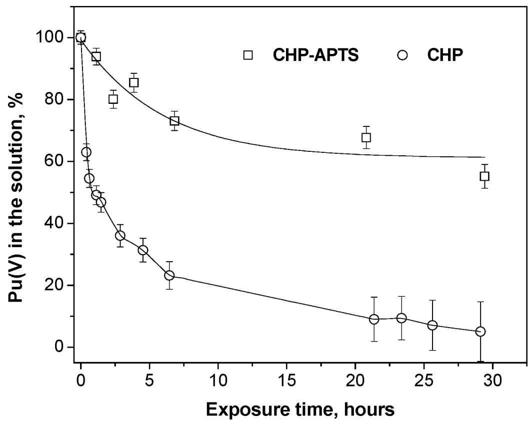


Figure 2. Removal kinetics of Pu(V) in the presence of the parental leonardite HS (CHP) and its alkoxysilanized derivative (CHP-APTS-100) in an Ar atmosphere at pH 7.5 [$C_{tot}(HS) = 10\ mg \cdot L^{-1}$, $C_0(Pu) = 2.26 \times 10^{-9}$ M].

A decrease in Pu(V) content in the solution can be seen with both the parental HS and its silanized derivative. However, the latter is characterized by a slower kinetics and smaller degree of removal as compared to the parental HS. The observed reduction of Pu(V) via natural humic materials corroborates well with the corresponding literature data[14,25] and our previous results.[29] At the same time, the lower performance of the silanized HS reflects the important role of carboxyl groups and complexation with respect to Pu(V) redox interactions with the humic materials.[20,21] The modification of the HS decreases their ability to form complexes with PuO_2^+, which then results in the decline of their reducing capacity. Similar observations were reported for redox-sensitive actinides.[3,9,20,21]

To confirm that the observed reduction of Pu(V) resulted from complexation with the electron-donating HS rather than from disproportionation to Pu(IV) and Pu(VI), the stability of Pu(V) in the absence of humic materials was monitored in the blank experiments. The latter study revealed that $Pu(V)O_2^+$ was stable for a month in the neutral pH conditions (data are not shown). In addition, there was no plutonium sorption as observed on the vial walls in the solutions of the both humic materials studied. These results indicated that plutonium(V) partitioning to the mobile humic materials was accompanied by complexation and followed by reduction to a lower valence state.

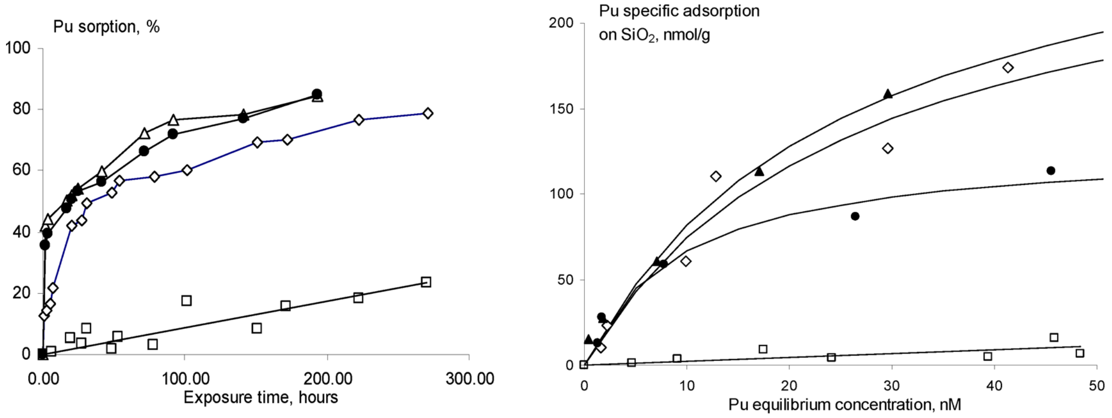
Plutonium(V) Partitioning to the Immobile Humic Materials. To study the interactions of waterborne plutonium with immobile humic coatings in aquatic environments, we designed batch experiments where the silica gels were coated with the humic adlayers formed by self-assembly of silanized humic derivatives, which possessed different degrees of modification (20, 50, and 100%). Anaerobic conditions were used in our tests to provide favorable conditions for reducing Pu(V) by humic materials as shown in our previous publication.[29] Anaerobic conditions are not uncommon in aquifers, sediments, and gleyic soils. Corresponding kinetic curves and sorption isotherms of Pu(V) on the humics-coated silica gels are shown in Figure 3A and B, respectively.

Removal kinetics of Pu from the test solutions was rather slow and approached steady state by the tenth day of exposure (Figure 3A). For this reason, data from the 10th day of exposure were used for calculating K_d and K_{oc} values for the humics-coated silica gels (Table 1). It can be seen that Pu(V) had stronger sorption affinities for the humics-coated silica gels as compared to the uncoated SiO_2. All isotherms were of the Langmuir type (Figure 3B). Fitted sorption parameters as well as the characteristics of the humics-coated silica gels (the content of bound humic materials per weight of silica gel (m_{HS}) and the amount of residual carboxylic groups (COOH) in the humics-coated silica gels) were summarized in Table 1.

The silica gel modified with the humic derivative having the lowest degree of modification (CHP-APTS-20) had the highest affinity for Pu(V). The corresponding value of the sorption constant was $1.1 \times 10^5\ L \cdot kg^{-1}$. However, maximum sorption was a factor of 2 lower ($1.3\ mol \cdot kg^{-1}$) compared to the more modified derivatives ($2.7-2.9\ mol \cdot kg^{-1}$). This finding is understood as the magnitude of the sorption constant is determined by the strength of the binding centers inherent in the adsorbent, whereas the maximum sorption is determined by the total quantity of the binding centers available in the adsorbent. From Table 1, the CHP-APTS-20-SiO_2 possesses the lowest content of humics (143 mg), but the highest content of carboxyl groups with the strongest Pu(V) binding affinity. In contrast, the lowest number of carboxyl groups ($0.09\ mmol \cdot kg^{-1}$) are found for the CHP-APTS-100-SiO_2 where measured mass of HS and organic carbon are the highest. Thus, the highest binding affinity for Pu(V) occurs on CHP-APTS-20-SiO_2, whereas the greatest amount of Pu sorption exists with the CHP-APTS-100-SiO2.

In general, the plutonium K_d values found for the HS-modified silica gels fell within the range of $1.1-1.6 \times 10^4\ L \cdot kg^{-1}$, which agreed well with the estimates of K_d values reported for batch experiments on soil and sediment particles; the latter were on the order of $10^4\ L \cdot kg^{-1}$.[14,35] The corresponding K_{OC} values ranged from 1.2 to $4.4 \times 10^5\ L \cdot kg^{-1}$, well within the range of partition coefficients reported for organic-rich geosorbents.[35,36]

Given these results we concluded that HS derivatives possessing the highest degree of modification were the most suited for removal of Pu. Hence, the following dynamic



A

B

Figure 3. Kinetic curves (A) and sorption isotherms (B) of Pu(V) on the humics-coated silica-gels at pH 7.5 (Ar atmosphere): the circles (●) designate the data points for CHP-APTS-20-SiO_2; the triangles (▲) indicate CHP-APTS-50-SiO_2; the diamonds (◊) indicate CHP-APTS-100-SiO_2; and the squares (☐) indicate uncoated SiO_2. Solid to liquid ratio was 0.35 g·L^{-1}. Pu(V) concentration in the kinetics experiments was 1,14 × 10^{-8} M. The solid lines in sorption isotherms show the best Langmuir-fits to the experimental data.

Table 1. Characteristics of Humics-Coated Silica Gels and Their Sorption Parameters with Respect to Pu(V)[a]

sample	m_{HS}, g/kg SiO_2	COOH, mol/kg	K_d, L·kg^{-1}	K_{OC}, L·kg^{-1}	Q_{max}, mol·kg^{-1}	K, L·kg^{-1}	R^2
CHP-APTS-20-SiO_2	143	0.23 ± 0.01	1.6 × 10^4	4.4 × 10^5	1.3 × 10^{-4}	1.1 × 10^5	0.972
CHP-APTS-50-SiO_2	155	0.10 ± 0.01	1.5 × 10^4	3.3 × 10^5	2.9 × 10^{-4}	3.8 × 10^4	0.987
CHP-APTS-100-SiO_2	210	0.09 ± 0.01	1.1 × 10^4	1.2 × 10^5	2.7 × 10^{-4}	3.8 × 10^4	0.986

[a] K_d for the uncoated silica gel determined after 10 days of exposure was 6.3 × 10^2 L·kg^{-1}.

experiments on Pu(V) sequestration were conducted using the CHP-APTS-100 derivative.

Partitioning of Pu(V) to Immobile Humic Coatings under Dynamic Conditions. To investigate partitioning of Pu(V) to immobile humic coatings under dynamic conditions, the column tests were conducted using silica gel possessing attached humic adlayers. For this purpose, the column was packed with silica gel and washed until saturation with a solution of CHP-APTS-100. Next, pulse loads of Pu(V) solutions were injected into the column packed with silica gel before and after treatment with this humic derivative. Corresponding breakthrough curves for Pu(V) are shown in Figure 4.

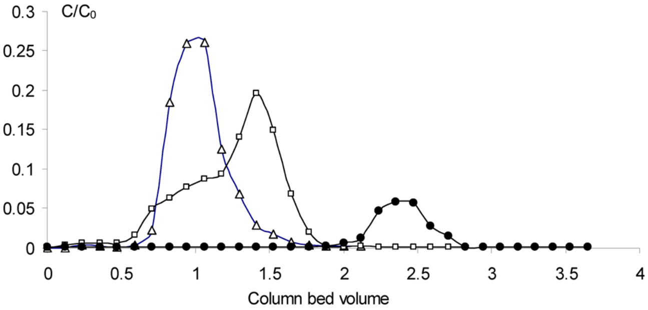


Figure 4. Breakthrough curves of HTO (passive tracer, Δ) and Pu before (☐) and after (●) treatment of the silica gel column with a solution of CHP-APTS-100 derivative: the injected volume of the PuO_2^+ solution was 0.5 mL, PuO_2^+ concentration was 1.03 × 10^{-8} M, pH 7.5, ambient atmosphere (pCO_2 = 3.5), the flow rate 0.1 mL·min^{-1} [column i.d. = 1.5 cm, length = 10 cm], void volume of the column 8.5 mL.

Pu breakthrough on the uncoated silica gel followed at 10.4 mL which corresponds to retardation factor of 1.2. This value is much less than it would be expected from the equilibrium K_d value of plutonium(V) on the uncoated silica gel of 6.3 × 10^2 L kg^{-1} given in Table 1. Still, it is rather consistent with the very low K_d values of about 0.5−1 L kg^{-1} which can be estimated from Figure 3A for the exposure times on the order of hours, or exactly the time frame relevant for these column experiments. It should be noted that 100% of the applied Pu(V) has exited the untreated column, whereas only 27% of the injected Pu has exited the column treated with the silanized humics.

Inhomogenous humic adlayers could compromise the retention of Pu and explain the partial breakthrough of Pu (27%) from the treated column. This might be well expected given possible flow-distortions, packing imperfections, and limited accessibility of inner pores of silica gel for the humic derivatives. At the same time, the 73% of the applied plutonium were retained on the humics-treated column demonstrating high affinity of Pu(V) to immobile humics.

Remobilization of Pu(V) from the Humic Coatings via Mobile Humic Materials. To address the possible remobilization of the sequestered plutonium from the humic coatings, ternary systems were designed using the humics-coated silica gels loaded with Pu and employing solutions of parental and silanized humic materials (CHP and CHP-APTS-100) as a mobile phase. The uncoated silica gel and humic-coated silica gel contained 7.6 × 10^{-7} and 8.4 × 10^{-4} mol Pu·kg^{-1}, respectively. The concentration of dissolved humic materials in solution was 10 mg·L^{-1}. The results for the Pu released at three different pH values are presented in Figure 5.

In the range of neutral pH values relevant to environmental aqueous systems, remobilization of Pu from the organic-coated

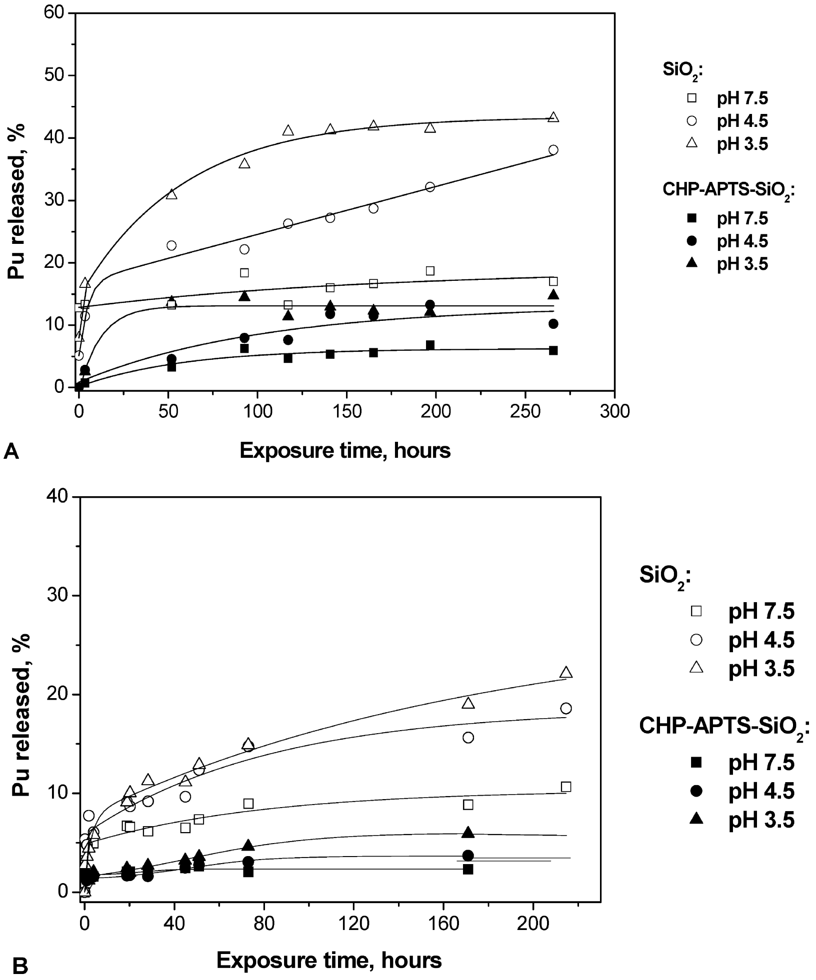


Figure 5. Kinetics of Pu release from uncoated and humics-coated silica-gels (CHP-APTS-100-SiO$_2$) in aqueous solutions of parental HS (CHP) (A) and of the alkoxysilanized derivative (CHP-APTS-100) (B) [C_{tot}(HS) = 10 mg·L^{-1}, Ar atmosphere].

silica-gels did not exceed 3% in the presence of dissolved CHP-APTS-100 and 5% - in the presence of CHP. Much higher Pu remobilization values were observed with more acidic conditions, which is in line with literature data for lower K_d values of Pu in more acidic solutions.[14,37] A use of a silanized derivative CHP-APTS-100 having a low carboxylic content as the mobile component promoted less Pu release into the solution as compared to the parental humic material – CHP.

These results indicate that the sequestered Pu is firmly hold by the humics-modified surfaces even in the presence of mobile humic solutes in solution. This might be a consequence of Pu(V) redox transformation (disproportionation/reduction) induced by the humic coatings followed by the formation of surface complexes of Pu(IV) with humics on the modified silica gel surfaces with possible contribution of polymerized forms of Pu(IV) oxides. The latter have extremely low solublity and are highly adhesive to many solid surfaces.[38,39]

The studies conducted here have shown silanized humics proved to be a useful molecular tool in probing surface reactions of Pu(V) at the water–solid interface. They can be easily attached to nonmobile substrates (i.e., clays, sand, etc.) providing "adhesive" sites for probing the immobilization of the actinides. Using this approach, we have confirmed that mobile PuO_2^+ exhibits high partitioning with immobile humic coatings and shows a low remobilization potential when exposed to mobile humic materials. This may explain an environmental process of enhanced accumulation of Pu in organic-rich geosorbents (e.g., soils, sediments) observed by different researchers.[16,19] Moreover, the presence of a silanized humic material on a solid support promoted Pu(V) adsorption. This allows us to conclude that the silanized humic derivatives studied here can be considered as both molecular probes and potent candidate materials for scavenging mobile Pu from an aqueous phase. They can efficiently intercept and retain Pu in an immobilized state by formation of surface complexes on the humic coatings. A use of powerful spectroscopic techniques such as EXAFS and TEM for investigation of the Pu distribution over humic coatings is needed to make more realistic forecasts with respect to the fate of the sequestered plutonium on humic coatings, which is our next immediate goal.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Preparation protocol of the silanized humic derivatives with different modification degree is provided including Table S1 with characteristics of the derivatives. A solvent extraction technique used for determination of Pu(V) in the work solutions and preparation of the Pu-loaded materials used for remobilization experiments are described. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Phone/fax: +7 (495) 9395546; e-mail: iperm@org.chem.msu.ru.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We dedicate this effort to Richard G. Haire in honor of his receiving the ACS 2013 Glenn T. Seaborg Award in nuclear chemistry.

This work was supported by joint research program of US DOE and Russian Academy of Sciences (project RUC2-20006 MO-04), Russian Foundation for Basic Research (11-03-12177-OFI-M-2011), NATO-CLG (grant ESP.EAP.CLG 983197), and Russian State Contract 16.740.11.0183.

REFERENCES

(1) Schneider, S.; Walther, C.; Bister, S.; Schauer, V.; Christl, M.; Synal, H.-A.; Shozugawa, K.; Steinhauser, G. Plutonium release from Fukushima Daiichi fosters the need for more detailed investigations. *Nat. Sci. Rep.* **2013**, *3*, 2988 DOI: 10.1038/srep02988.

(2) Zheng, J.; Tagami, K.; Uchida, S. Release of plutonium isotopes into the environment from the Fukushima Daiichi nuclear power plant accident: What is known and what needs to be known. *Environ. Sci. Technol.* **2013**, *47* (17), 9584−9595.

(3) Degueldre, C. Identification and speciation of actinides in the environment. In *The Chemistry of Actinide and Transuranium Elements*; Morss, L. R., Edelstein, N. M., Fuger, J., Eds.; Springer: Dordrecht, The Netherlands, 2010; Chapter 27, Vol. *5*, pp 3013−3085.

(4) Kersting, A. B.; Efurd, D. W.; Finnegan, D. L.; Rokop, D. J.; Smith, D. K.; Thompson, J. L. Migration of plutonium in ground water at the Nevada test site. *Nature* **1999**, *397*, 56−59.

(5) Kim, J. I.; Delakowitz, B.; Zeh, P.; Klotz, D.; Lazik, D. A column experiment for the study of colloidal radionuclide migration in Gorleben aquifer systems. *Radiochim. Acta* **1994**, *66/67*, 165−171.

(6) Novikov, A. P.; Kalmykov, S. N.; Utsunomiya, S.; Ewing, R.; Horreard, F.; Merkulov, A.; Clark, S. B.; Tkachev, V. V.; Myasoedov, B. F. Colloid transport of plutonium in far-field of the Mayak Production Association, Russia. *Science* **2006**, *314*, 638−641.

(7) Zhao, P.; Zavarin, M.; Leif, R.; Powell, B. A.; Singleton, M.; Lindvall, R.; Kersting, A. Mobilization of actinides by dissolved organic compounds at the Nevada test site. *Appl. Geochem.* **2011**, *26*, 208−218.

(8) McCarthy, J. F.; Zachara, J. M. Subsurface transport of contaminants: Binding to mobile and immobile phases in groundwater. *Environ. Sci. Technol.* **1989**, *23*, 496−504.

(9) Kaplan, D. I.; Powell, B. A.; Demirkanli, D. I.; Fjeld, R. A.; Molz, F. J.; Serkiz, S. M.; Coates, J. T. Influence of oxidation states on plutonium mobility during long-term transport through an unsaturated subsurface environment. *Environ. Sci. Technol.* **2004**, *38*, 5053−5058.

(10) Kersting, A. B.; Reirnus, P. W. Colloid-facilitated transport of low-solubility radionuclides: A field, experimental, and modeling investigation. In *US DOE Technical Report UCRL-ID-149688*; 2003.

(11) Artinger, R.; Marquardt, C. M.; Kim, J. I. Humic colloid-borne Np migration: Influence of the oxidation state. *Radiochim. Acta* **2000**, *88*, 609−612.

(12) Xu, D.; Wang, X. K.; Chen, C. L.; Zhou, X.; Tan, X. L. Influence of soil humic acid and fulvic acid on sorption of Thorium(IV) on MX-80 bentonite. *Radiochim. Acta* **2006**, *94*, 429−434.

(13) Loyland Asbury, S. M.; Lamont, S. P.; Clark, S. B. Plutonium partitioning to colloidal and particulate matter in an acidic, sandy sediment: Implications for remediation alternatives and plutonium migration. *Environ. Sci. Technol.* **2001**, *35*, 2295−2300.

(14) Mahara, Y.; Matsuzuru, H. Mobile and immobile plutonium in a groundwater environment. *Water Res.* **1989**, *23*, 43−50.

(15) Moulin, V. Complexation of radionuclides with humic substances. In *Use of Humic Substances to Remediate Polluted Environments: From Theory to Practice*, NATO Science Series: IV: Earth and Environmental Sciences; Perminova, I. V., Hatfield, K., Hertkorn, N., Eds.; Springer: Dordrecht, The Netherlands, 2005; Vol. *52*, 155−174.

(16) Novikov, A. P.; Pavlotskaya, F. I.; Goryachenkova, T. A. Radionuclide content in water and bottom sediments of some storage basins at Mayak. *Radiochemistry* **1998**, *40*, 468−476.

(17) Iwata, H.; Sakamaki, K.; Yasuda, K.; Ohnuki, T.; Utsunomiya, S. Fate of plutonium derived from the atomic bomb detonated at Nagasaki, Japan. Abstract for Migration conference, Beijing, 2011.

(18) Pavlotskaya, F. I. Specific behavior of microquantities of matter in natural processes: A case of artificial radionuclides. *Geochem. J.* **2002**, *40*, 260−266.

(19) Bunzl, K.; Kracke, W.; Agapkina, G. I.; Tikhomirov, A.; Shcheglov, A. I. Association of Chernobyl-derived Pu-239−241, Sr-90 and Cs-137 with different molecular-size fractions of organic-matter in the soil solution of grass land soils. *Radiat. Environ. Biophys.* **1998**, *37* (3), 195−200.

(20) Andre, C.; Choppin, G. R. Reduction of Pu(V) by humic acids. *Radiochim. Acta* **2000**, *88*, 613−616.

(21) Reiller, P. Prognosticating the humic complexation for redox sensitive actinides through analogy, using the charge neutralization model. *Radiochim. Acta* **2005**, *93*, 43−55.

(22) Santschi, P. H.; Roberts, K. A.; Guo, L. Organic nature of colloidal actinides transported in surface water environments. *Environ. Sci. Technol.* **2002**, *36*, 3711−3719.

(23) Thurman, E. M. *Organic Geochemistry of Natural Waters*; Martinus Nijhof/Dr. W. Junk Publishers: Dordrecht, The Netherlands, 1985.

(24) Seibert, A.; Mausel, A.; Marquardt, C. M.; Keller, H.; Krayz, J. V.; Trautmann, N. Complexation behaviour of neptunium with humic acids. *Radiochim. Acta* **2001**, *89*, 505−510.

(25) Roberts, K. A.; Santschi, P. H.; Honeyman, B. D. Pu(V) reduction and enhancement of particle-water partitioning by exopolymeric substances. *Radiochim. Acta* **2008**, *96*, 739−745.

(26) Xu, C.; Santschi, P. H.; Zhong, J. Y.; Hatcher, P. G.; Francis, A. J.; Dodge, C. J.; Roberts, K. A.; Hung, C. C.; Honeyman, B. D. Colloidal cutin-like substances cross-linked to siderophore decomposition products mobilizing plutonium from contaminated soils. *Environ. Sci. Technol.* **2008**, *42*, 8211−8217.

(27) Xu, C.; Zhang, S. J.; Chuang, C. Y.; Miller, E. J.; Schwehr, K. A.; Santschi, P. H. Chemical composition and relative hydrophobicity of microbial exopolymeric substances (EPS) isolated by anion exchange chromatography and their actinide-binding affinities. *Mar. Chem.* **2011**, *126*, 27−36.

(28) Perminova, I. V.; Karpiouk, L. A.; Shcherbina, N. S.; Ponomarenko, S. A.; Kalmykov, S. N.; Hatfield, K. Preparation and use of humic derivatives covalently bound to silica-gel for Np(V) and Pu(V) sequestration. *J. Alloys Compd.* **2007**, *444*−*445*, 512−517.

(29) Shcherbina, N. S.; Kalmykov, S. N.; Perminova, I. V.; Kovalenko, A. N. Reduction of actinides in higher oxidation states by hydroquinone-enriched humic derivatives. *J. Alloys Compd.* **2007**, *444*−*445*, 518−521.

(30) Karpiouk, L. A.; Ponomarenko, S. A.; Mourran, A.; Bochkariov, D.; Muzafarov, A. M.; Hatfield, K.; Perminova, I. V. Self assembly of alkoxysilanized humic substances into multidomain adlayers at water-solid interface: Linking surface morphology to molecular structures of adsorbate. *Soft Matter* **2012**, *8*, 2452−2459.

(31) Perminova, I. V.; Karpiouk, L. A.; Ponomarenko, S. A.; Konstantinov, A. I.; Hertkorn, N.; Hatfield, K. Controlling aqueous sorption of humic substances on silica gel by directed alkoxysilyl-derivatization of their functionalities. *Colloids Surf., A* **2012**, *396*, 224−232.

(32) Swift, R. S. Organic matter characterization. In *Methods of Soil Analysis. Part 3. Chemical Methods*; Soil Science Society of America and American Society of Agronomy, 1996; pp 1036−1041.

(33) Saito, A.; Choppin, G. R. Separation of actinides in different oxidation states from neutral solutions by solvent extraction. *Anal. Chem.* **1983**, *55*, 2454−2457.

(34) Morgenstern, C.; Choppin, G. R. Kinetics of the oxidation of Pu(IV) by manganese dioxide. *Radiochim. Acta* **2002**, *90*, 69−74.

(35) *Understanding Variation in Partition Coefficient, K_d, Values*, EPA 402-R-99-004B; Office of Radiation and Indoor Air, Office of Solid Waste and Emergency Response, EPA [and] Office of Environmental Restoration, U.S. DOE: Washington, DC, 1999; Vol. II.

(36) Glover, P. A.; Miner, F. J.; Polzer,W. O. Plutonium and Americium behavior in the soil/water environment. I. Sorption of Plutonium and Americium by soils. In *Proceedings of Actinide-Sediment Reactions Working Meeting*, Seattle, Washington, BNWL-2117; Battelle Pacific Northwest Laboratories: Richland, WA, 1976; pp 225−254.

(37) Nelson, D. M.; Penrose, W. R.; Karttuen, J. O.; Mehlhaff, P. Effects of dissolved organic carbon on the adsorption properties of plutonium in natural water. *Environ. Sci. Technol.* **1985**, *19*, 127−131.

(38) Clark, D. L.; Hecker, S. S.; Jarvinen, G. D.; Neu, M. P. Plutonium. In *The Chemistry of Actinide and Transuranium Elements*; Morss, L. R., Edelstein, N. M., Fuger, J., Eds.; Springer: Dordrecht, The Netherlands, 2010; Chapter 7, Vol. 2, pp 813−1264.

(39) Haire, R. G.; Haschke, J. M. Plutonium oxide systems and related corrosion products. *MRS Bull.* **2001**, *26*, 689−696.